A PHYSICO-CHEMICAL INVESTIGATION OF REFRACTORY HARD METALS

Thesis
Submitted in Partial Fulfilment of
the Requirements for the Degree
of
DOCTOR OF PHILOSOPHY
of Rhodes University
by
HAMISH IAN PHILIP
September 1972.

DECLARATION OF ORIGINALITY

I hereby declare that this thesis is my own work and that it has not been submitted for any other degree at any other University.

H. I. PHILIP.

ACKNOWLEDGEMENT/........

ACKNOWLEDGEMENT

I wish to express my sincere thanks to Professor L. Glasser of Rhodes University, under whose guidance and direction this investigation was carried out; to Mr. C. Phillpotts of Rhodes University for his assistance and our many helpful discussions; to Messrs. J. Murray and G. Randell of the technical staff of the Chemistry Department of Rhodes University for their assistance with the apparatus; to the National Institute for Metallurgy for their generous bursary and financial assistance in acquiring the apparatus; to Dr. J. van Wyk of ISCOR for performing the neutron activation analyses; to Messrs. Grahamstown Potteries who supplied refractory materials; to Dr. R. Kieffer for his assistance and VN samples; to Dr. R. Caveney of the Diamond Research Laboratories for the pressing of the hot-pressed samples; and to my parents for their encouragement and assistance in compiling this work.

ABSTRACT/.......

ABSTRACT

In this investigation, the resistivity of vanadium nitride at elevated temperatures has been measured using a resistance bridge based on the Dauphinée/Mooser (1955) chopper system.

In general, an almost linear increase of resistivity with temperature was observed for VN, but at certain temperatures, deviations from linearity (anomalies) were observed, these have been classified into three types.

Attempts have been made to correlate the anomalous behaviour and temperature coefficients of resistivity with the ambient atmospheres and with the impurities, (especially oxygen), stoichiometry and density of this material.

Oxygen and excess nitrogen appear to be electron donors in their effects on VN and result in a decrease in the slope of resistivity vs temperature curves.

Oxygen and/........

Oxygen and excess nitrogen also appear to increase the overall resistivity due to an increase in defect concentration.

No effects due to the ambient atmosphere have been observed in the case of hot-pressed samples. Indicating that reaction can only occur if the reacting gases can reach the interior of the samples.

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(I) INTRODUCTION

I (i) REFRACTORY HARD METALS

Refractory hard metals are a group of ionic chemical compounds which are formed by combination of nitrogen, oxygen or carbon with transition metals of the 4th, 5th, or 6th groups. These compounds are characterized by extreme hardness, high melting point, metallic lustre and an electrical conductivity approaching that of the transition metals. This latter has led to the theory that their conduction mechanism is similar to that of the transition metals although, under certain circumstances, they show semiconducting behaviour.

I (ii) ELECTRICAL PROPERTIES OF CRYSTALLINE SOLIDS

(1) Theories of Conduction and Metallic Conductors

A number of theories have been proposed in attempts to explain all facets of the conduction mechanism. However all such theories are only approximations to the truth and each has its inherent limitations.

(a) Free Electron Theory

The Free Electron theory is based on the argument that orbital overlap occurs when atoms are brought together to form a crystal, then orbital overlap being so extensive that the quantization scheme, in which each electron is associated with a given atom, breaks down for the valence electrons, leaving these valence electrons, the so-called conduction electrons, free to move as if they were a gas about the crystal, whose structure is defined by the fixed positive ion cores of the atoms (Ziman 1964). The mutual repulsion between electrons is ignored and the field due to the positive ions is assumed uniform throughout the crystal.

The kinetic energy of a free electron is given by:

$$\begin{aligned} E-V &= \tfrac{1}{2}mv^2 \\ &= p^2/2m \end{aligned}$$

where p is the momentum and m is the mass of the electron, p being related to the de Broglie wavelength λ by the relation:

$$p = h/\lambda$$

Now, defining a wave number k by:

$$k = 2\pi/\lambda,$$

it follows that:

$$k = \frac{2\pi}{h}p$$

Hence:

$$E-V = \frac{h^2k^2}{8\pi^2m}$$

i.e. the energy/..........

i.e. the energy is a quadratic function of the wave number, k. Thus the E-k curve for a free electron will be parabolic, Fig 1.

Conduction is explained as being due to the acceleration of the electrons towards the positive pole, the current being limited by electron-ion and electron-phonon collisions, a phonon being a quantum of the lattice vibration energy, and being proportional to the applied voltage according to Ohm's law:

The current density $j = ne^2\tau E/m = ne\mu E$

where τ = relaxation time

E = applied field

m = electronic mass

μ = mobility = $e\tau/m$

Now if $j = \sigma e$

it follows that: $\sigma = ne\mu$

where n = no. of charge carriers per unit volume

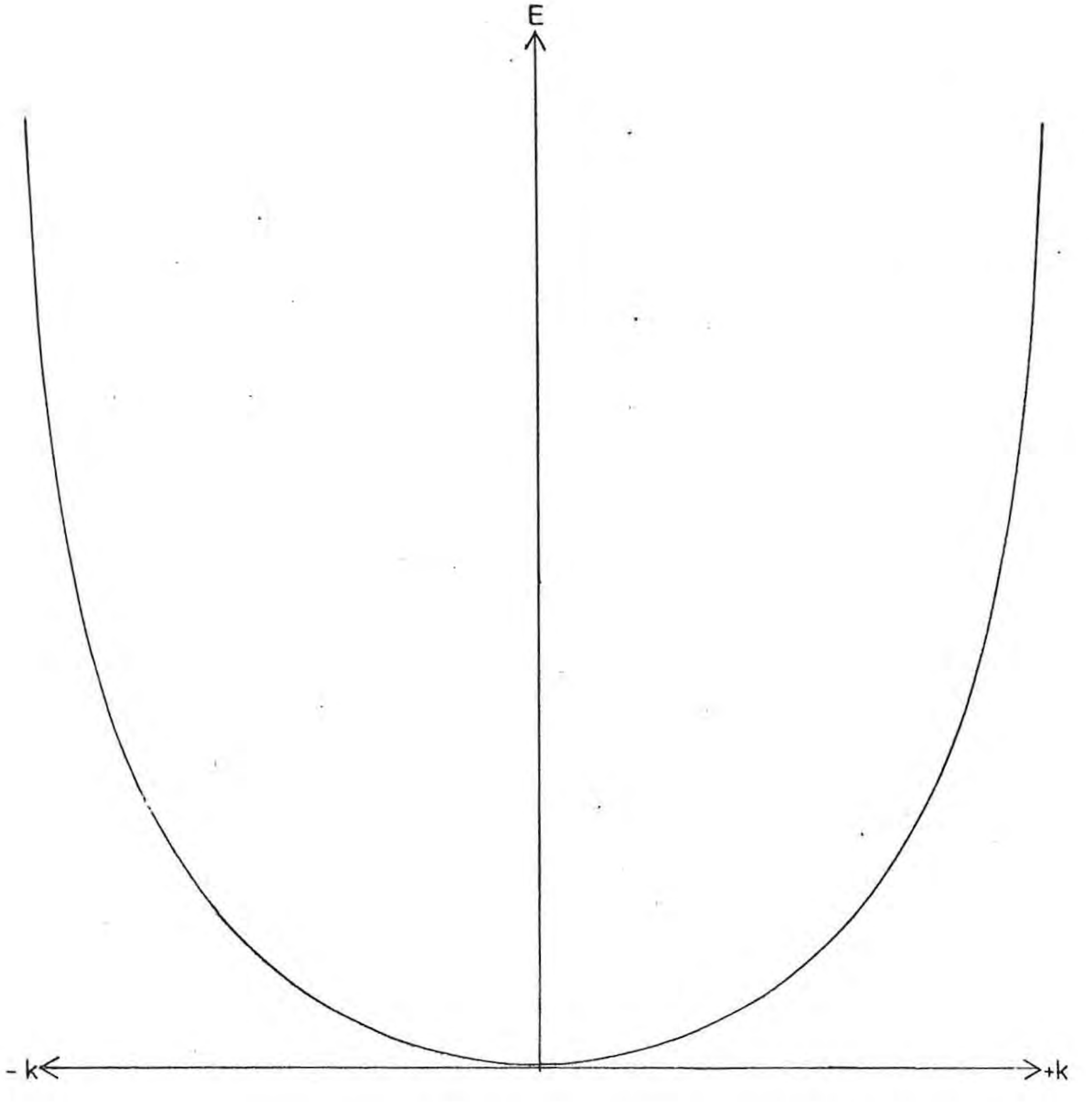
e = electronic charge

Now, defining the current I by the relation:

$$I = -nev$$

where v is the average drift velocity, it can be shown that I should be proportional to the temperature because v, is limited by collisions between the electrons and lattice phonons. The number of phonons is proportional to the temperature and thus the probability of scattering

is proportional/......



FREE ELECTRON PARABOLA.

(FIG 1)

is proportional to temperature (Kittel 1968). From this it may be seen that the current, and hence the conductivity, is proportional to $(\text{temperature})^{-1}$. The free electron density in a metal changes little with increasing temperature (n is independent of T) if the core electrons are not thermally excitable, thus its conductivity decreases due to the increased scattering, i.e. μ decreases as T increases.

This theory cannot explain why some materials are conductors, while others are semiconductors or insulators.

(b) Zone/Band Theory

The potential field inside a crystal is in fact not spatially uniform, but varies in a periodic manner through the crystal according to the translational periodicity of the ion cores. Bloch (1928) has shown that the energy spectrum of an electron in a periodic crystal may be divided into allowed and forbidden zones, Fig 2.

When the parabola representing the energy of a free electron, as a function of k, is compared with the energy spectrum of an electron in a periodic field, it

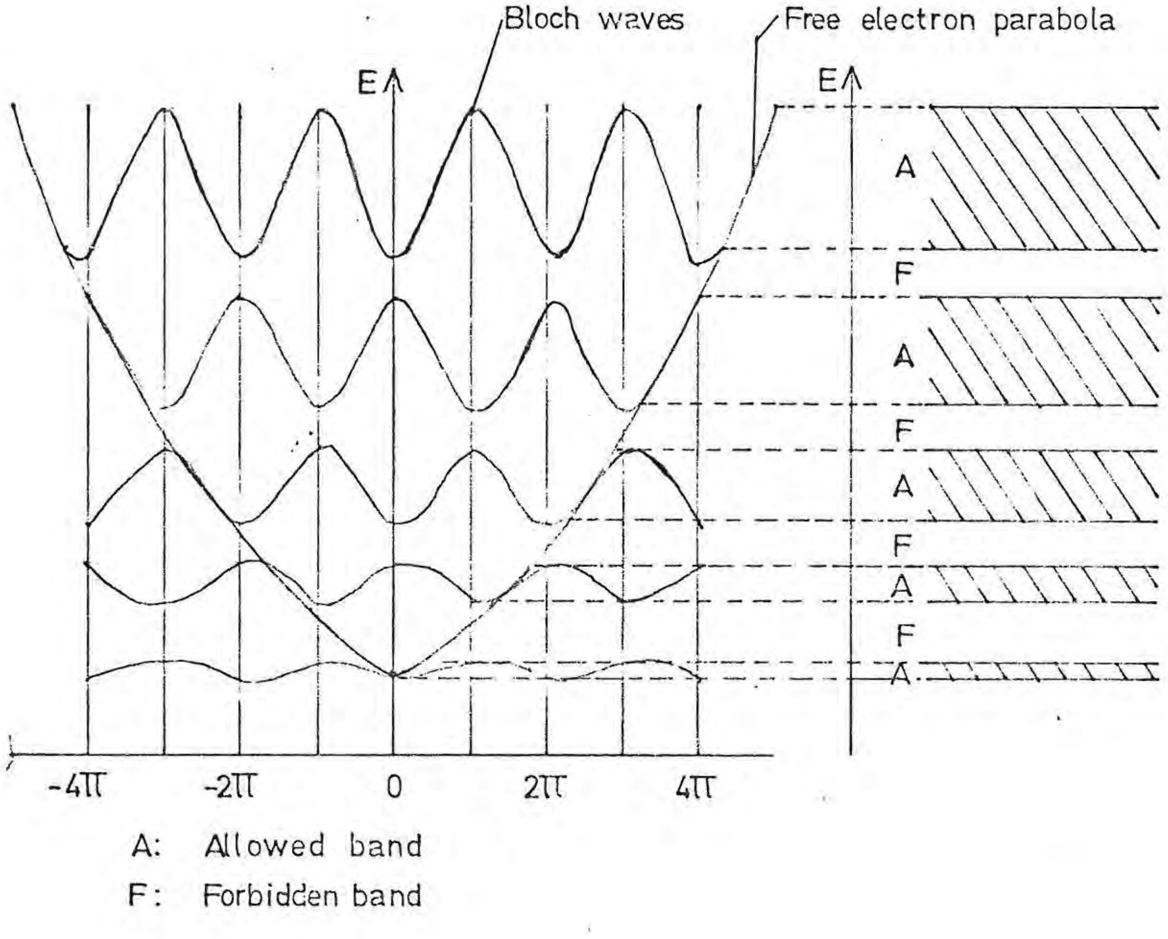

Bloch waves
Free electron parabola
E
E
A
F
A
F
A
F
A
F
A
-4π
-2π
0
2π
4π
A: Allowed band
F: Forbidden band

Fig 2

may be shown, defining a wave number:

$$k = 2\pi/\lambda \text{ .... } (1)$$

that discontinuities will occur in the free electron parabola for values of k given by:

$$k = n\pi/a \text{ .... } (2)$$

where n ±1, ±2, ±3, ...

and a is the lattice spacing, Fig 2. Combining (1) and (2) leads to the result:

$$n\lambda = 2a \text{ .... } (3)$$

which corresponds to the Bragg condition for the diffraction of X-rays or electrons for the glancing angle $\Theta = 90^\circ$, and follows directly from the wave nature of electrons. (2) may be written as follows:

$$k[uvw] = \pi/d(hkl) \text{ .... } (4)$$

where d(hkl) is the spacing of planes (hkl) normal to the direction uvw of movement of the electrons. Equation (4), which determines the discontinuities in the energy spectrum of the electron, may be interpreted to mean total reflection of electron waves by planes normal to their direction of motion, or as Bragg reflections by other crystallographic planes so that such waves cannot be propagated through the crystal - they are forbidden.

We may define a reciprocal lattice as follows: A reciprocal lattice is a lattice whose primitive vectors a^*_1, a^*_2, a^*_3 defining the unit cell, are defined by:

$a^*_i . a_j = 1$ if $i = j$/......

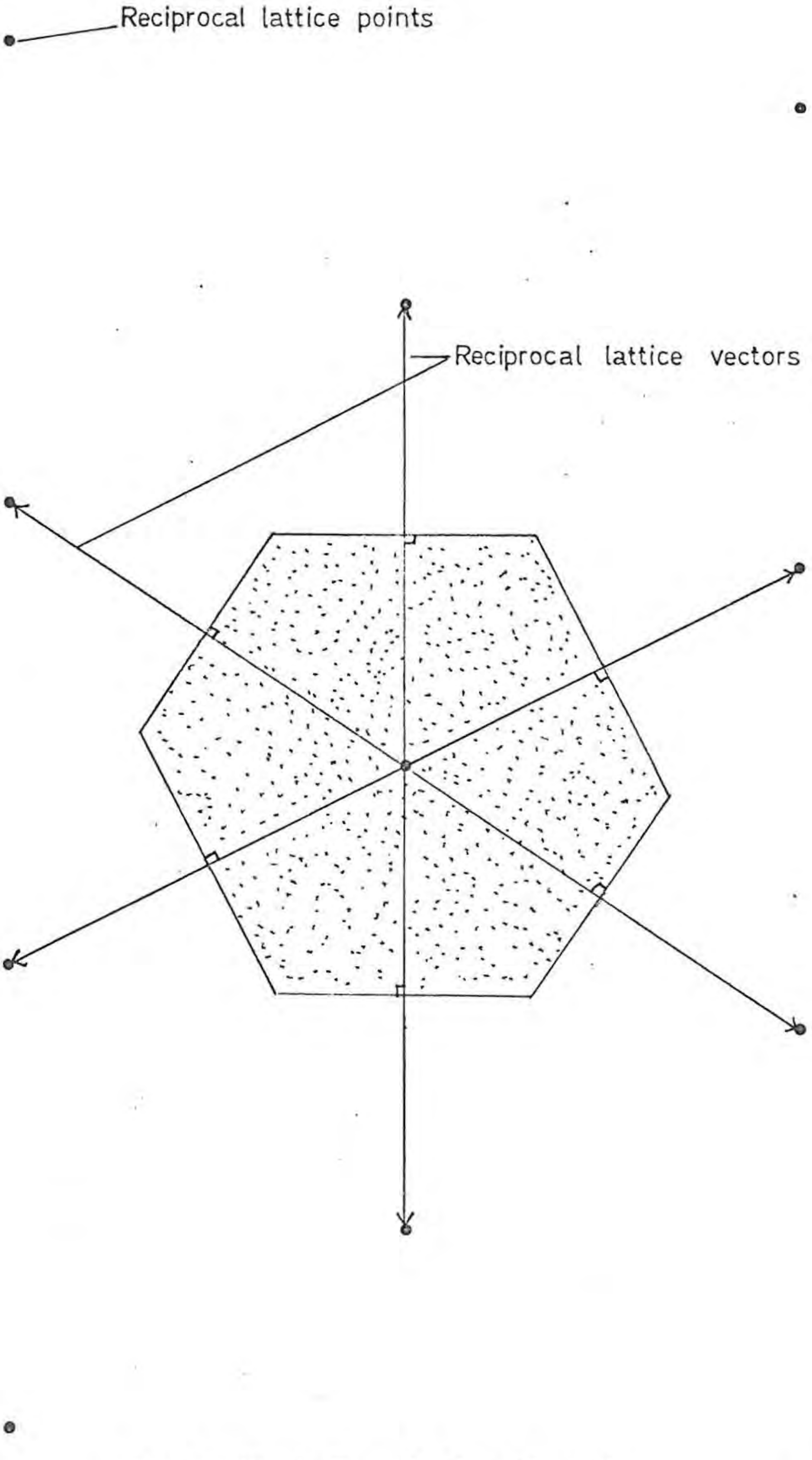
$$a^*_i . a_j = 1 \text{ if } i = j$$

$$a^*_i . a_j = 0 \text{ if } i \neq j$$

where a_1, a_2, a_3 are the primitive vectors of a crystal lattice. (Cusack, 1958).

If we now imagine a number of straight lines joining the nucleus of a metal atom with those of its nearest and next-to-nearest neighbours, then we may define an atomic polyhedron or Wigner-Seitz (primitive) unit cell by planes which bisect these lines perpendicularly. (Dekker 1958). Similarly, we may construct a Wigner-Seitz cell in reciprocal space, Fig 3 (Kittel 1968), and the Wigner-Seitz cell of the reciprocal lattice corresponds to the first Brillouin zone, in k space of the crystal. It may be shown that the planes which most strongly reflect the electron waves are those which go to define the first Brillouin zone of the crystal lattice. Another, more closely spaced, set of planes is required to reflect electrons lying in the second Brillouin zone etc. It can be shown that the energy spectrum is continuous inside the first Brillouin zone, but there is an energy gap on crossing a zone boundary, i.e. the energy spectrum shows gaps, and the electronic energy levels fall into bands whose limits are defined by the zone boundaries.

The E-k curve shows energy discontinuities at



First Brillouin Zone In Two Dimensions

Fig 3

the zone boundaries, thus different E-k curves arise for different directions in k space for complicated, i.e. non-spherical, zone shapes. This results in the discontinuities in the E-k curves occurring at different energies and at different k values, in different directions in k space.

While the zone shapes are determined by the crystal lattice type, the shapes of the E-k curves, the widths of the allowed and forbidden energy bands and their degree of overlap are determined by the nature of the atoms and by their separation.

The energy contour enclosing the occupied states is called the Fermi surface, as it lies at the Fermi energy, which is the maximum energy available to the electrons at 0 K, or the energy at which exactly half the states are occupied at some higher temperature.

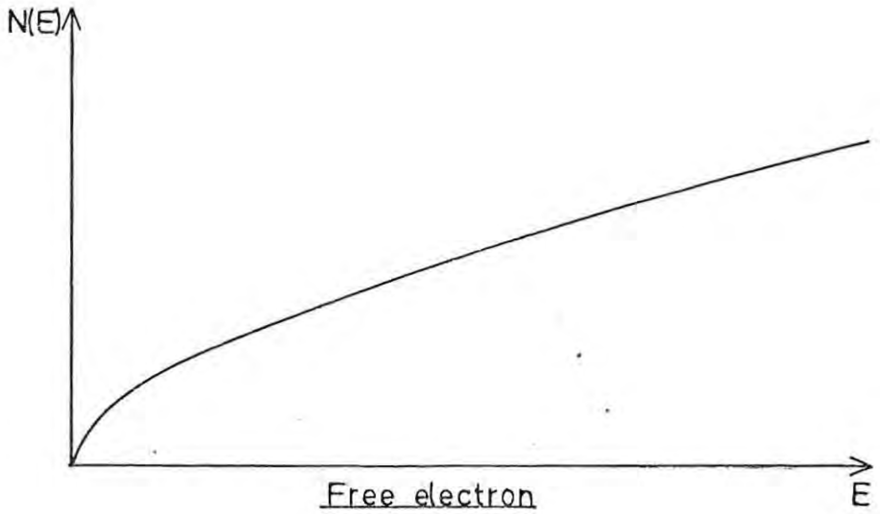
If the bands overlap, then the quantum states at the bottom of the second band are at a lower energy than those at the top of the first band, thus it is impossible to completely fill one band without partially filling another, thus the upper bands of such crystals will be only partially filled, if there are sufficient electrons available to fill the isolated lower band.

When bands/........

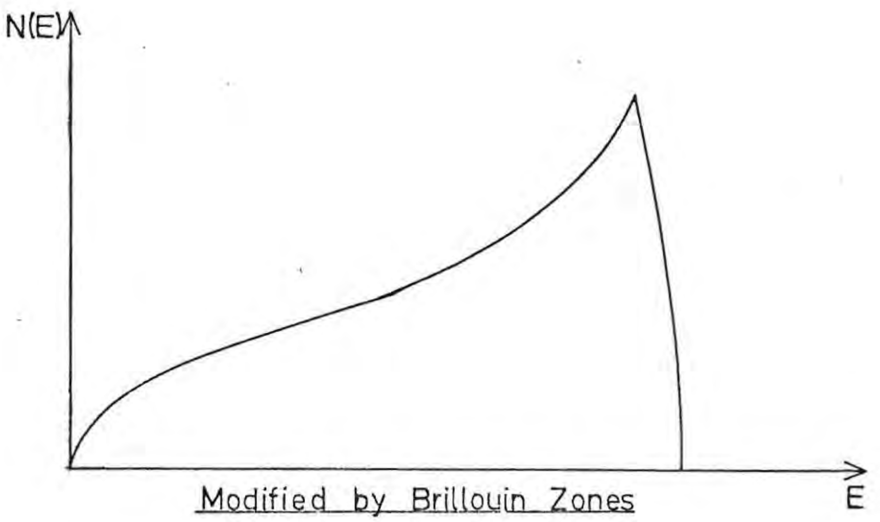
When bands are only partially filled, or when band overlap occurs, electrons lying near the Fermi energy will be able to move from one quantum state to another under the influence of an applied electric field, and the crystal will be a conductor. If however the first band is completely filled, and the bands do not overlap, then electrons will not be able to move into adjacent quantum states; those lying near the top of the band cannot be excited to states outside the allowed band, as these are forbidden, thus such a crystal will be an insulator, or semiconductor if the forbidden gap is not too large, and can be bridged at the temperature of operation.

The number of quantum states per unit energy interval in each zone is denoted dN/dE or N(E)/dE and is termed the density of states per unit energy interval. The density of states N(E) may be shown to increase as $E^{\frac{1}{2}}$, and therefore a plot of N(E) against E will be parabolic for free electrons but will be modified by the Brillouin zones in an actual crystal, being parabolic for low electron energies, but falling to zero as the zone boundary is reached. In the case of two overlapping zones, then, overlap of the N(E) against E curve also occurs, Fig 4, the resultant curve being obtained by superposition of the individual curves. It is possible to deduce how the available states are occupied by electrons in a

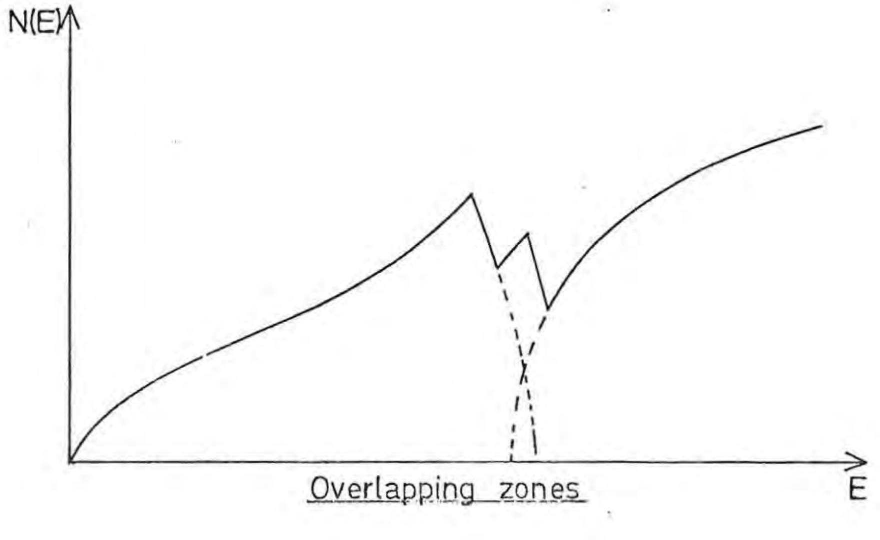
Curves Of N(E) vs. E



Free electron



Modified by Brillouin Zones



Overlapping zones

Fig 4

crystal at a particular temperature by examination of the density of states function, as the density of states that are occupied, N(E), is related to S(E), the density of available states. The distribution of the electrons among the available states is given by the Fermi distribution function applicable to a degenerate system obeying the Pauli exclusion principle:

$$N(E)dE = f(E)S(E)dE = \frac{S(E)dE}{e^{(E-Eo)/kT}+1}$$

where f(E) = Fermi function

E = energy of allowed state

Eo= Fermi energy.

The value of f(E) gives the fraction of levels at a given energy E, which are occupied when the system is in thermal equilibrium.

(c) Resonating Valence Bond Theory

Pauling (1938, 1947, 1948) has assumed that the metallic bond is very similar to the covalent bond, i.e. that some of the outermost electrons of metal atoms form electron pair bonds with neighbouring atoms but, since the number of electron pairs available is usually smaller than the number of nearest neighbours, it is assumed that resonance of electron pairs between the available positions occurs.

Pauling has postulated that the length of a bond is a measure of its strength and therefore of the number of electron pairs which resonate among the available positions in the lattice. He has shown that the valence of the metal increases from 1 to 5.78 in the series K, Ca, Sc, Ti, V, and Cr, remains constant at 5.78 for Mn, Fe, Co and Ni, and begins to fall with Cu. Since only one s and three p orbitals are available, these large bond orders suggest that at least some of the d orbitals must participate in bonding. Pauling also postulates that not all the d orbitals participate in bonding, those remaining being termed the atomic orbitals; the 4th, 5th, and 6th groups of the periodic table which are best suited for the formation of refractory hard metals have unoccupied atomic d orbitals.

Pauling (1949) has shown the existence of Brillouin zones to be compatible with the resonating valence bond theory; by a consideration of the resonance of electron pairs among all the available positions in the crystal, an approximation to the wave function for a metal may be obtained. Thus if each atom in the metal has coordination number n, then there will be $\frac{1}{2}nN$ available positions for N atoms and the $\frac{1}{2}nN$ electron pair wave functions will constitute an energy band which will be split into Brillouin zones as a result of the lattice periodicity.

This approach has been used by Eastman et al (1950) in their discussion of bonding in the sulphides of thorium and uranium, these workers proposing that the stability of these compounds and their abnormally short bond lengths are due to the availability of d electrons which may be used to form metallic bonds, US, U_2S_3 and ThS each having two d electrons per metal atom which are involved in metallic bonding.

Holt (1960) in an investigation of "dangling" bonds in III-V compounds uses a similar approach, proposing that the bonds on the III and V element faces are made up by resonance of tetrahedral orbitals, although this theory was challenged by Gatos (1961) who claimed that it did not fit the experimental results. This approach is also used by Robertson and Rapp (1969) in their study of niobium oxides. They propose that two of the five outer electrons of each Nb atom in NbO form resonating bonds with the 2p electrons of the surrounding O atoms, and conclude that considerable overlap occurs between the non-bonding electrons of the Nb ions.

Criteria for good metallic Conduction

According to Weisskopf (1943) the following

conditions are/........

conditions are required for good electrical conduction in a solid metal:

(1) The atoms should be monovalent, in order that the zones be not completely filled.

(2) The atoms should be massive, in order to reduce the amplitude of thermal vibrations and their scattering effect on the charge carriers.

(3) The metal should be hard. The harder the metal, the lower the amplitude of the atomic vibrations for a given energy.

I (iii) SEMICONDUCTORS, INSULATORS AND METALLIC CONDUCTORS

(a) Summary

In a crystal composed of N unit cells, 2N energy states are available in each allowed band; thus, if the primitive unit cell contains an odd number of electrons, it is not possible to fill all of the allowed energy states and the crystal must be a conductor. On the other hand, if the primitive unit cell contains an even number of electrons, then it will be a conductor only if the valence and conduction bands overlap, i.e. if there is no forbidden band between valence and conduction bands.

(b) Semiconductors/........

(b) Semiconductors

If the forbidden energy gap in a non-conductor is small, then some of the electrons lying near the top of the valence band may gain sufficient thermal energy to bridge the forbidden gap, and transfer to empty states in the conduction band. Since such electrons are able to contribute to the conductivity, the crystal becomes a semiconductor, such a material being called an intrinsic semiconductor. The density of conduction electrons will increase with increasing temperature in such a crystal so that its conductivity will increase with temperature.

Extrinsic semiconduction may arise as a result of imperfections, such as impurity atoms in the crystal, which have the effect of introducing further discrete energy levels in the forbidden gap. For example, we may consider germanium and silicon which are quadrivalent, and whose crystal structures are the same. If substitutional impurity atoms with five or more valence electrons enter the crystal, they are said to donate excess electrons to the crystal, as only four of their electrons are used in bond formation. The energy of these so called donor states is slightly lower than that of the bottom of the conduction band. If the impurity atoms have three or less valence electrons, however, they can then accept electrons, and the energy of these acceptor states is usually slightly greater than that of the top of the valence band, Fig 5. These impurity atoms usually occupy fixed sites in the crystal, therefore their quantum states in the energy band are localised. The energy level of the donor state depends on the energy required to remove the excess electrons from the impurity atom. If the electrons from an impurity level are more easily excited into the conduction band than those from the filled valence band, there will be a larger number of electrons in the conduction band than there are vacancies (holes) in the valence band, in which case the majority carriers will be electrons and the semiconductor will be n-type. If, however, electrons from the valence band are more easily excited into acceptor levels than into the conduction band, then there will be more vacancies in the valence band (holes) than electrons in the conduction band, in which case the semiconductor will be p-type.

If electron-donating impurities are included in an n-type semiconductor, electrons will be donated into the conduction band and conductivity will increase, but will be decreased in a p-type semiconductor. Conversely, electron-withdrawing impurities will reduce the conduction in an n-type semiconductor, but will increase it in a p-type semiconductor.

(c) <u>Insulators</u>/.......

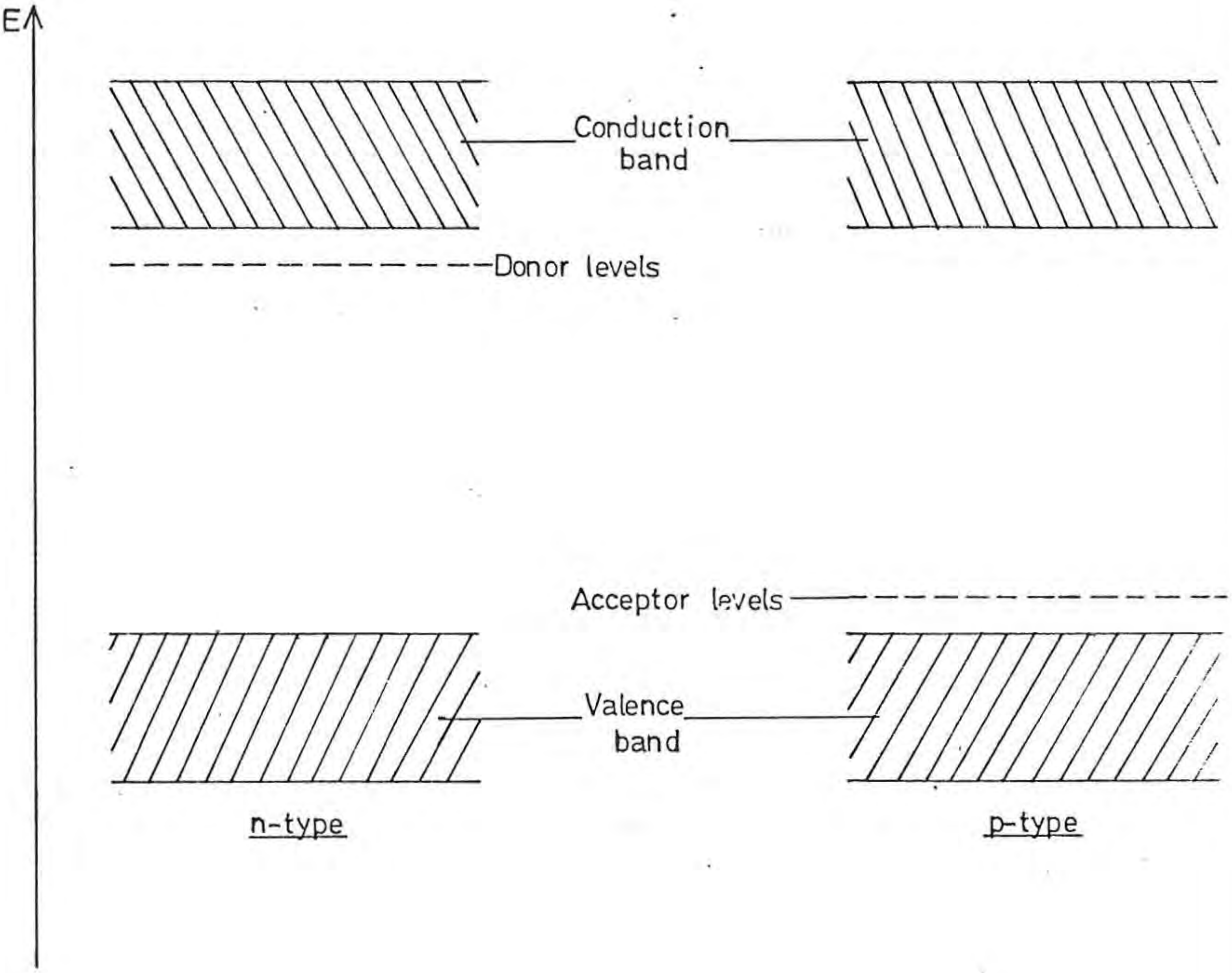

E
Conduction band
Donor levels
Acceptor levels
Valence band
n-type
p-type

Fig 5

(c) Insulators

If the valence and conduction bands are separated by a large forbidden energy gap then the electrons cannot attain sufficient thermal energy to bridge the gap, and the crystal is an insulator. Insulating crystals might conduct by migration of ions or vacancies through the crystal, however.

(d) Metallic Conductors (Structure)

The metallic bond may be regarded as an unsaturated non-directional covalent bond. This results in most, but by no means all, metals assuming the cubic or hexagonal close-packed, or body-centred cubic structures.

The electronic structures of the atoms must be considered in order to determine which crystal structure is assumed. Pauling (1949) considered the electrons of each individual atom, proposing that bonding is due to resonating electron-pair bonds, but this approach is unable to explain ferromagnetism without resorting to non-integral valencies for some of the atoms.

The transition metals form metallic bonds regardless of the number of atoms per primitive unit cell,

and their/.......

and their conductivity may be explained by zone overlap.

Copper, silver and gold have full d-shells, while nickel, platinum and palladium have almost full d shells. These d shells produce a mutual repulsion between adjacent atoms which is, however, non-directional, thus these metals assume a close-packed structure. The lighter elements scandium, titanium and vanadium, have only partially filled d shells, which can participate in bonding. In the case of vanadium, for example, all the electrons in the 3d half-shell have parallel spins, but, since the 3d orbitals of vanadium overlap, the energy of the crystal is lowered if the spins of the electrons in the overlapping orbitals are anti-parallel but this arrangement is not possible in a close-packed structure as all the atoms must be identical. However, it is possible in the body-centred structure, which is assumed by vanadium, and in which each vanadium atom is surrounded by eight nearest neighbours with opposite spins (Azaroff 1960).

(e) Bonding and the Band Theory

The band model may also be arrived at from a consideration of the covalent bond.

Considering only/........

Considering only the electrons involved in bond formation, the formation of a covalent bond results in a splitting of the energy levels into two equal groups, one of which is raised in energy, while the other is lowered in energy as described in molecular orbital theory; these are termed repulsive and attractive states respectively.

When atoms combine to form a molecule or crystal, the total number of quantum states with a particular quantum number remains unaltered, thus the total number of quantum states of any one kind in the crystal is equal to the total number of atoms present. The energies of all these states are different (Pauli exclusion principle) because of interactions, but the individual differences are too small to be detected, thus these energy levels are assumed to form continuous energy bands.

The group of higher energy states is called the antibonding or conduction band, while the lower energy band is termed the valence or bonding band. These bands are generally separated by forbidden regions which result from quantization of the electronic energy levels. The energies of these levels can only correspond to values lying within each allowed energy band. For electronic conduction to occur, an electron must gain energy and

transfer from/........

transfer from a filled quantum state to an unfilled state; thus an assemblage of atoms will exhibit metallic behaviour (electronic conduction) only when there are fewer electrons per atom than there are states per atom (resulting in an unfilled band) or when there is overlap between upper and lower bands, leaving no energy gap.

I (iv) THE HALL EFFECT

The conductivity, σ, of a semiconductor is related to the mobility, μ, of the charge carriers by the equation:

$$\sigma = ne\mu$$

where n is the carrier density
and e is the charge on the carrier (Cusack 1958).
The mobility is the average drift velocity per unit electric field, which is dependent upon the nature of the charge carriers (electrons or holes), and on the scattering due to inhomogeneities in the crystal.

The mobility of the charge carriers may be determined with the aid of the Hall effect. The Hall effect is that phenomenon in which, if a current is passed in one direction along a conductor, and a magnetic field is applied at right angles to the current direction, then a voltage normal to both the current and magnetic field directions is produced, the so called Hall voltage, whose sign and magnitude depends on the nature and mobility of the charge carriers, Fig 6.

The Hall coefficient R is determined by the carrier density n:

$$R = \frac{1}{ne}$$

where e is the charge of the carrier whose sign determines the sign of the Hall constant. The Hall coefficient is also related to the current I and applied magnetic field H by the relation:

$$V_H = \frac{RHI}{t}$$

where V_H is the Hall voltage and t is the sample thickness.

The Hall drift mobility u_H may be determined by the relation:

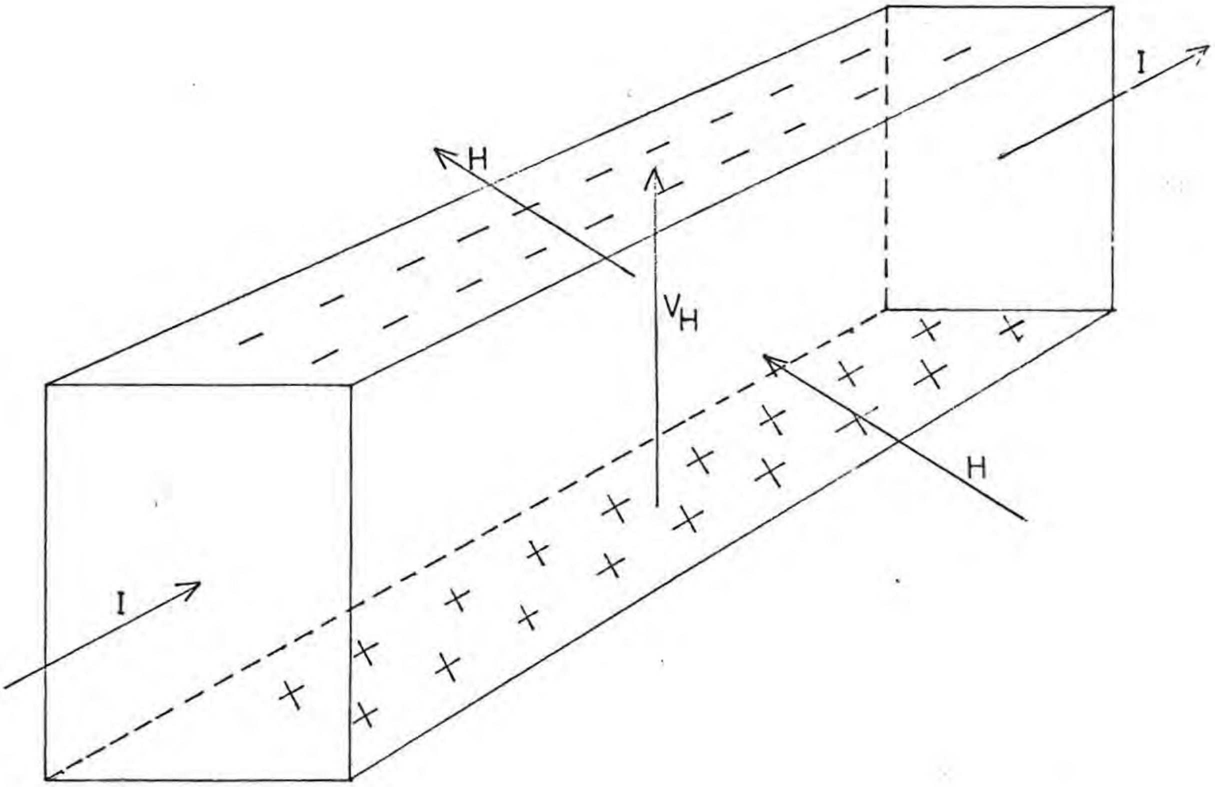
$$\mu_H = \frac{V_H t}{HI} \sigma$$

the charge carrier density from:

$$n = \frac{HI}{V_H t e}$$

while the sign of the charge carriers may be determined from the sign of R. By convention, R is taken as negative for negative carriers.

I (v) THERMOELECTRIC/........



I=Current

H=Magnetic field

V_H=Hall voltage

Hall effect for negative carriers

Fig 6

I (v) THERMOELECTRIC POWER

Thermoelectric effects may be simply explained in terms of the free electron theory (Cusack 1958).

The enthalpy of a conductor depends on the kinetic energy of the electron gas, which varies from metal to metal, i.e. the enthalpy of a given number of electrons will be different for two different metals at the same temperature. If a given number of electrons cross a junction between two metals under the influence of an applied emf, then a certain amount of heat will be absorbed or liberated due to the differing enthalpies of the electrons on either side of the junction, thus explaining the Peltier effect and its reversibility.

Alternatively, if one end of a metal rod is heated, electrons will be driven from the cold to the hot end, setting up an emf by virtue of the alteration in the charge distribution. If a second rod of a different metal is placed in contact with the first, so as to complete an electric circuit, there will be a net emf in the loop, i.e. a Seebeck effect.

If we define $E_{AB}(T1,T2)$ as the symbol for the emf of a couple made of metals A and B with junctions at

temperatures T1/........

temperatures T1 and T2, then it can be shown that:

(i) E_{AB} depends on T1 and T2 and not on the way in which the temperature is distributed along the conductors. (Law of Magnus).

(ii) $E_{AB}(T2,T1) = E_{AB}(T2,T3) + E_{AB}(T3,T1)$ (Law of Successive Temperatures).

(iii) $E_{AC}(T2,T1) = E_{AB}(T2,T1) + E_{BC}(T2,T1)$ (Law of Intermediate Metals).

Absolute Thermoelectric Power

A phenomenon which is useful in determining absolute thermoelectric power is the Thomson effect, which is the name given to the evolution or absorption of heat when a current flows along an homogenous wire in which there is a temperature gradient. The Thomson coefficient, σ_T, is equal to the heat absorbed when unit charge rises one degree in temperature (Cusack 1958).

According to Koerber (1962) the absolute thermoelectric power of a metal may be determined by placing it in series with a superconductor which has zero thermoelectric power at some very low temperature, Tc. In this way, all the thermoelectric effects will be due to the conductor alone. The value of the absolute thermoelectric power may then be determined at a temperature

T by applying the relation:

$$S = \int_{T_0}^{T} \frac{\sigma_T}{T} \, dT \quad \ldots\ldots\ldots\ldots(1)$$

where S is absolute thermoelectric power.
Now, if σ_T is proportional to temperature (and thermoelectric measurements here reported suggest that this is in fact the case for this material, since S is proportional to T), equation (1) reduces to:

$$S = \sigma_T \quad \ldots\ldots\ldots\ldots(2)$$

Once the absolute thermoelectric power has been measured for any standard metal, e.g. lead, any other absolute thermoelectric power S, may be determined by measuring the thermoelectric power of a junction between the standard and the unknown at any given temperature, and subtracting the contribution due to the standard.

If, in the measurement of absolute thermoelectric power, the hot junction becomes positive, and the cold junction negative, then the thermoelectric power is given a negative sign, and negative charge carriers are involved, the opposite polarity being observed for positive charge carriers (Putley 1960).

Jorgensen and Bartlett (1969) have determined the mobilities and numbers of charge carriers in a semi-

conducter ($LiNbO_3$)/........

conductor ($LiNbO_3$) by the relations:

$$\sigma = ne\mu \quad \ldots\ldots\ldots\ldots(3)$$

and

$$S = -\frac{k}{e}\left[2-\ln n+\frac{3}{2}\ln T+\ln\left\{\frac{2(2\ m^{*}k)^{3/2}}{h^3}\right\}\right]\ldots\ldots\ldots\ldots(4)$$

where S is thermoelectric power in μVK^{-1}

k is Boltzmann's constant

m^{*} is effective electron mass (assumed equal to that of free electrons)

h is Planck's constant

e is the electronic charge.

In this way, the sign, mobility and number (density) of current carriers may be determined by measuring absolute thermoelectric power of a semiconductor.

In the case of a metallic conductor (Clark 1968), then:

$$S = -\frac{\pi^2k^2T}{3e} \quad \frac{1}{\sigma(E)} \quad \frac{d\sigma(E)}{dE} \quad {}_{E_0}$$

where $\sigma_{(E)}$ is the corductivity of a metal with Fermi level at E.

If scattering is only produced by lattice vibrations, then the above relation reduces to:

$$S = -\frac{\pi^2k^2T}{eE_0}$$

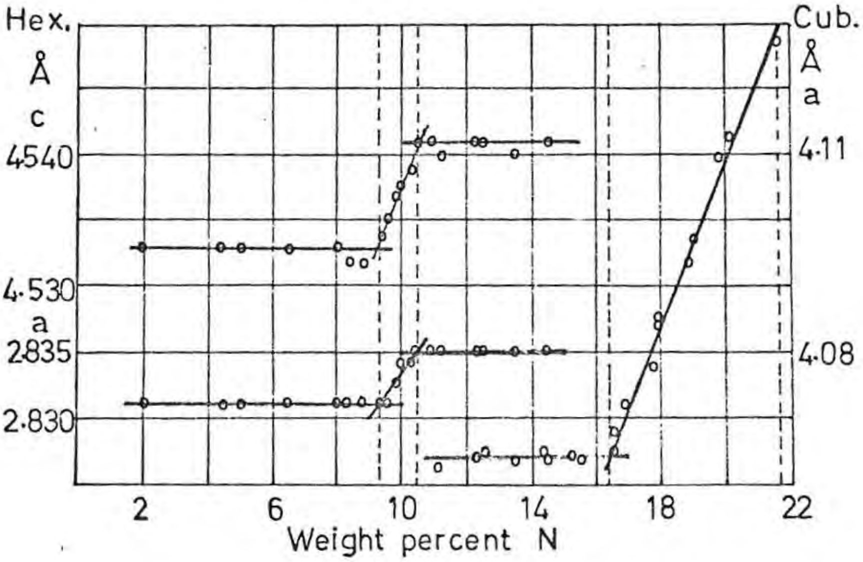
(II) PROPERTIES OF REFRACTORY HARD METALS

II (i) DEFINITION OF THE CLASS OF REFRACTORY HARD METALS

According to Schwarzkopf and Kieffer (1953), the refractory hard metals are a group of inorganic compounds of transition metals with H, B, C, N, having high melting points and metallic properties, most of these compounds having a positive temperature coefficient of resistance.

They do not exhibit a well defined stoichiometric composition however, the case of vanadium nitride being typical. The system vanadium nitrogen probably exists over a wide homogeniety range (Schwarzkopf and Kieffer 1953), two phases having been reported by Hahn (1949), the face centred cubic phase with approximate composition VN, and the hexagonal phase with approximate composition V_3N, Fig 7. A third phase, V_2N has been reported by Kiessling (1954) and its preparation by Brauer (1965).

II (ii) CRYSTAL/.......



Lattice Constant vs Nitrogen Content

Of Vanadium Nitride

From Hahn (1949)

Fig 7

II (ii) CRYSTAL STRUCTURES

Hägg (1930, 1931) began the study of the crystal structures of these compounds by the investigation of the available X-ray data, and postulated that the structures of these phases are determined by the radius ratio of the non-metal:metal atoms. When this is less than 0.59, then the structure can be described as a simple metal lattice, with the non-metal atoms placed into the interstices of these lattices. Hägg observed that the metal atoms form a cubic or hexagonal close-packed structure, in which the small hydrogen or boron atoms tend to occupy tetrahedral interstices with coordination number 4 (e.g. the system Zr-H, which may have the composition Zr_4H (cubic), Zr_2H (hex.), ZrH (cubic), while the larger carbon and nitrogen atoms prefer the octahedral sites with coordination number 6 (e.g. the system Ta-C, which exists in the homogeneity range Ta_2C (hex.) and TaC (cubic)). Phases having these structures were termed simple structures, but complicated structures result when the radius ratio exceeds 0.59; many of these complicated structures, nevertheless exhibit metallic properties.

In the case of radius ratios which are close to 0.59, simple structures are observed with a low non-metal atom concentration but with higher concentrations,

more complicated/........

more complicated structures are observed. The formation of complicated structures was regarded as resulting from an increase in lattice parameter with an increase in the non-metal concentration, i.e. although the radius of the metal atom remains constant, the increase in lattice parameter which results on increasing the non-metal concentration is considered due to an effective increase in the radius of the non-metal atom with increasing concentration, causing a deviation from the critical radius ratio 0.59, thus resulting in complicated structures. Analysis of these structures led to the conclusion that refractory hard metals could only form when the lattice dimensions permitted contact between the non-metal atoms and the surrounding metal atoms, resulting in the concept of a lower limit to the permissible radius ratio. It can be shown by geometrical considerations that, for the occupation of octahedral interstices, this lower radius ratio is 0.41, with the non-metal atoms at all times tending to attain the highest possible coordination number. According to Hägg, the metal atoms in these compounds are no longer in the close-packed structure, although their arrangement is still the same as in the parent metal, but the metal atoms are now in contact with non-metal atoms, instead of with other metal atoms, and the existence of the critical radius ratio is due to limitations on the extent to which the metal

lattice may/........

lattice may expand. However, as Rundle (1948) has indicated, the metal lattice in refractory hard metals is very seldom of the same crystal structure as the parent metal (see Table 1). Investigations on the borides by Ehrlich (1949), and on metal-carbon-boron systems by Glaser (1952), have shown that not all refractory hard compounds form simple structures as proposed by Hägg, Schwarzkopf (1950) having reported no less than eight different structures among the borides, of which only the hexagonal diborides and the related structures of Mo_2B_5 and WB_5 can be considered to be simple. The crystal structure in fact appears to depend on the atomic structure of the parent metal and the number of available valence electrons.

II (iii) ELECTRONIC STRUCTURE

The interatomic binding forces rather than the crystal structure should be taken into account when the metallic character of the refractory hard metals is considered. When a curve of atomic radius against atomic number of transition metals is compared, the 4th, 5th and 6th group metals are found to lie on falling portions of the curve; these metals also show high para- or even ferromagnetic behaviour and relatively low electrical conductivity. The free atoms of these metals are found

TABLE 1

Comparison of Interstitial Nitrides and Parent Metals

Parent Metal	Structure of Parent Metal	Lattice Constants of Metal Å	Nitride (Schwarzkopf and Kieffer)	Structure of Nitride (S & K)	Radius Ratio (S & K)	Lattice Constant of Nitride (S & K) Å
Ti	HCP	a=2.950 c=4.686	TiN	FCC	0.48	4.23
Zr	HCP	a=3.232 c=5.147	ZrN	FCC	0.44	4.56
V	BCC	3.04	VN	FCC	0.53	4.13
			V_3N	HEX	0.53	a=2.83 c=4.54
Nb	BCC	3.30	NbN	FCC	0.49	4.39
Ta	BCC	3.30	Ta_2N	HEX	0.49	a=3.05 c=4.95
Cr	BCC	2.88	CrN	FCC	0.56	4.14
			Cr_2N	HEX	0.56	a=4.80 c=4.47
Mo	BCC	3.15	MoN	HEX	0.51	a=2.86 c=2.80
			Mo_2N	FCC	0.51	4.16
W	BCC	3.16	$W_2N(\beta)$	FCC	0.51	4.12
			$W_2N(\gamma)$	CUB	0.51	4.13
Th	FCC	5.05	ThN	FCC	0.39	5.20
U	FCC	3.47	UN	FCC	0.47	4.88
			UN_2	FCC	0.47	5.31
			U_2N_3	BCC	0.47	10.68

to have incomplete d-shells with lower principal quantum numbers than the highest occupied s-shell. Comparing the refractory hard phases, it is observed that simple structures result when the sum of the electrons in the outermost s-shell and incomplete d-shell is four or five, while complex structures arise in the case of Cr, Mo and W, whose sum of s and d electrons is six (Schwarzkopf and Kieffer, 1953).

Two different theories, the band theory and the resonating valence bond theory, have been employed in an attempt to elucidate the electronic structures of the refractory hard metals.

(1) The Theory of Ubbelohde

Ubbelohde (1931), whose theory corresponded to the band theory, proposed that when hydrogen was dissolved in transition metals such as Pd, Ta and Ti, then the hydrogen was in the metallic state, i.e. it exists as H^+ ions with free electrons. In support of this theory it was noted that Pd had 0.55 holes per atom in the d-band, and that when 55 atom percent of hydrogen was absorbed by the Pd, the magnetic moment of the Pd was lowered and it became diamagnetic, i.e. when the concentration was sufficient to fill all the holes in the d-band with electrons from the hydrogen. Also, the high solubility of hydrogen in Pd could be reduced by alloying the metal with silver, in which case the electrons from the silver would fill the holes in the Pd. Ubbelohde suggested that the tendency of the transition metals to form refractory hard compounds was due to the ability of the metal to absorb electrons from the non-metal, into holes in the d-bands; thus the structures of the hard metals were interpreted by assuming that the metal is an electron acceptor.

As the ionisation potentials of carbon and nitrogen are similar to those of hydrogen, this theory has been extended to cover other refractory hard phases as well, since the energy relations would not preclude ionisation of carbon and nitrogen.

In support of this theory, Seith and Kubaschewski (1935) have demonstrated the electrolytic migration of carbon in γ-iron, suggesting that the carbon is in fact in an ionised state.

The hardness of these phases is considered to be due to the presence of non-metal atoms between the close-packed metal atoms, which severely restrict slip processes during plastic deformation, increasing the

hardness above/..........

hardness above that of the pure metal.

(2) The Theory of Rundle

The theory of Rundle (1948), which corresponds to the resonating valence bond theory of Pauling, applies only to the monocarbides, mononitrides and monoxides of transition metals and postulates that the formation of phases of the NaCl type involves a rearrangement of the metal lattice, providing octahedral interstices which become available for occupation by non-metal atoms. Rundle observed that the formation of refractory compounds involved a lengthening in the metal-metal (M-M) bond distance, i.e. a weakening in the M-M bond due to the withdrawal of electrons which are utilised in the formation of metal-non-metal bonds. The high melting points of these compounds in spite of the weakening of the M-M bonds, suggests considerable strength in the metal-non-metal bonds and Rundle has suggested that the hardness and brittleness of these compounds is due to the formation of directional metal-non-metal bonds which would have the octahedral configuration in NaCl type compounds.

Rundle and Sturdivant (1947) in their examination of tetramethyl platinum and other electron deficient compounds, based their interpretation of the structure on the concepts of half bonds, i.e. bonds that are formed by one of the non-metal orbitals and an electron pair from the metal atom which resonate between two transition metal orbitals, thus forming two bonds. (a) In this way the three 2p orbitals of the non-metal could form six directed half bonds, three electrons being required in the formation of metal-non-metal bonds, or: (b) The s and a p orbital could hybridise and the two hybridised sp orbitals together with the two remaining p orbitals, could participate in bonding - necessitating the formation of electron-pair bonds by two of these orbitals and the other four forming half bonds, all six bonds being made equivalent by resonance. In this case, 4 electrons would be required to form metal-non-metal bonds.

In fact, the bond distances (Schwarzkopf and Kieffer 1953) determined by X-ray diffraction agree with (a) in some cases and in other cases with (b), depending on the electronegativity of the atoms involved and the number of electrons available.

This theory is applicable to transition metals only, as these are the only metals whose number of bond orbitals is greater than that of C, N or O.

According to/........

According to Rundle, the metallic properties of these compounds is due to bond resonance, in analogy with Pauling's resonating valence bond theory for the metals.

This theory does not involve a net transfer of electrons from the non-metal to the metal, but the metal remains metallic and donates its electrons to the formation of bonds, thus it may rather be considered as a transfer of electrons from the metal to the non-metal phase and back donation of electrons from non-metal to metal.

(3) Recent Work

Houska (1965), in the investigation of the Ti-N system discusses his results in terms of the theory of Ubbelohde, concluding that the most stable configuration would be $TiN_{0.67}$, since in Ti metal there are four d electrons and the N would donate three p electrons to the band, becoming a positive nitride ion, and it was assumed that maximum cohesion would occur in this type of compound for a transition metal with close to six d electrons.

The results of Jaffee and Campbell (1949) in their study of Ti, appear to conflict with the extension

of Ubbelohde's/........

of Ubbelohde's theory to include oxygen and nitrogen, as these workers found that while oxygen or nitrogen concentrations of up to one atomic percent in Ti increased the resistivity of Ti linearly from 48 to 50 micro-ohm cm at 25.6°C, hydrogen at a similar concentration had no effect, suggesting that oxygen and nitrogen in a crystal do not behave in the same manner as does hydrogen. This could be due to the additional 2s and 2p electrons of nitrogen or oxygen being made available for the formation of metallic bonds, whereas there are insufficient electrons available to the hydrogen atom.

The results of Piper (1964), in the study of several transition metal carbides and nitrides appear to support Rundle's theory. Piper has proposed that the electronic band structures of compounds such as NbC, ZrN and TaC are determined by the valence electron concentration (VEC). He has proposed that as the VEC is increased above 8, then the additional electrons start to form a new energy band. This leads to the result that the density of states increases from zero at a VEC of 8, reaching a maximum near 9.

Denker (1964) in an investigation of TiO, concludes that the hardness of TiC is due to an almost full bonding band, while in TiN and TiO, additional

electrons go/.........

electrons go into antibonding levels and these are therefore not as hard as TiC and have lower melting points. This theory is in agreement with that of Rundle, both the metal and non-metal donating electrons to form bonds. This is also supported by the results of Ern and Swittendick (1965) in their study of TiC, TiN and TiO, in which they conclude that the metal-non-metal interaction decreases in the series TiC-TiN-TiO, while the metal-metal 3d interaction is strong in all three compounds. Denker (1968), in a later paper, has proposed that the high conductivity and high temperature stability of hard metals is due to a mixture of covalent and metallic bonding. He suggests that maximum temperature stability is achieved in compounds with a crystal structure in which nearly all the bonding orbitals are occupied and all the antibonding orbitals are vacant. This leads to the assumption that maximum stability occurs for a VEC of between 8 and 9, supporting the results of Piper.

Recently, Ramqvist (1968a) has correlated the hardness of group 4b carbides with certain other properties and found that the lattice parameter is very sensitive to, and is lowered by, dissolved gases, conflicting with the theories of Rundle and of Hägg, who proposed an increase in lattice parameter with the inclusion of impurities. The hardness of these compounds is found to increase with increasing carbon content and with the presence of dissolved gases, supporting the theory of Denker (1968) who predicted an increase in bond strength with increasing carbon content on the basis that the VEC tends to 8, which is the most stable configuration, as the carbon content is increased. In extending the study of carbides to the group 5B carbides, Ramqvist (1968b) showed that the hardness of V-C phases increases with increasing carbon content, as in the case of 4b carbides, but the hardness of the Ta and Nb-C phases decreased suggesting some differences in band overlap for the latter two metals. An increase in resistivity together with a decrease in lattice parameter was observed with decreasing carbon content of the group 5b cubic carbides. From an electron spectroscopic study of the transition metal carbides, nitrides and oxides, Ramqvist et al (1969a) concluded that electronic charge is transferred from the metal to the non-metal atom (conflicting with Ubbelohde's theory), resulting in the metal having fewer d electrons in the hard metal than in the pure metal. Ramqvist et al (1969b) also suggest that the charge transfer decreases in the order TiC-TiN-TiO. Ramqvist (1969c) concluded that the carbides of the 4th, 5th and 6th group transition metals have a low density of states at the Fermi level, but there is no gap between the valence and conduction bands, and they are therefore good electrical conductors, but not as good as the parent metals.

(III) THE PREPARATION/.......

(III) THE PREPARATION AND ANALYSIS OF VANADIUM NITRIDE

III (i) THE PREPARATION OF VANADIUM NITRIDE

Suitable methods for preparing oxygen-free VN were investigated. So far as possible these methods involved starting with, or preparing, oxygen-free reagents, and necessitated developments beyond the techniques of other workers.

In an attempt to obtain approximately stoichiometric $V_{1.0}N_{1.0}$, the VN was prepared and sintered at about 1100°C, this being about the most suitable temperature for the preparation of stoichiometric VN, according to the observations of Epelbaum and Ormont (1947) in their investigation of the V-N system.

A number of methods are available for the preparation of vanadium nitride:

(a) By heating vanadium or its oxides or carbides in nitrogen and hydrogen, or in ammonia.

This method was used by Duwez and Odell (1950),

and by/........

and by Agte and Moers (1931), who heated vanadium metal powder in nitrogen/hydrogen mixtures, while Kiessling (1954) used ammonia as the gas. This method was not employed in the present project, as pure vanadium metal powder was not readily available, and because Hoy (1963) has shown that there are difficulties in nitriding the metal fully.

A similar method was employed by Shomate and Kelley (1949), who heated vanadium carbide in a nitrogen and hydrogen mixture, and by Friedrich and Sittig (1925) who heated the oxide with carbon in the presence of nitrogen, but obtained a product containing 0.5% SiO_2. Satoh (1938) prepared vanadium nitride by heating vanadium oxide in ammonia, but also obtained a product containing SiO_2 (2%).

These latter methods have not been employed in the present project, as they appear likely to result in oxygen- or carbon-containing products.

(b) Thermal decomposition of ammonium vanadate in ammonia.

The decomposition of NH_4VO_3 in NH_3 was investigated by Epelbaum and Brager (1940), who used it as a method for preparing VN. This method was also used in work reported in a later paper by Epelbaum and

Ormont (1947),/........

Ormont (1947), and was used extensively by Hahn (1949), Hoy (1963) and King (1963).

For the preparation of VN, NH_4VO_3 is heated in NH_3 at about 1100°C for 8 to 48 hours. Although convenient, this method was not used extensively in the present project as the resulting product usually contains oxygen.

Author		Approximate Reported Oxygen Content
Hoy	(1963)	4%
Hardy and Hulm	(1954)	2%
Epelbaum and Ormont	(1947)	0.4%

(c) Van Arkel (1925) vapour phase decomposition of vanadium halides on an incandescent filament.

In this method, which has been employed by Moers (1931), by Campbell and co-workers (1949) and which has been extensively investigated by Pollard and Fowles (1952), for a number of refractory hard metals, a tungsten or molybdenum filament is heated to about 1500°C in a mixture of nitrogen and hydrogen containing VCl_4, which results in crystals of VN being deposited on the filament according to the stoichiometric equation:

$$2VCl_4 + N_2 + 4H_2 \rightarrow 2VN + 8HCl.$$

This method/.......

This method was investigated in the present project, but was found to be unsuitable, as it is not convenient for the preparation of large quantities of VN, and it is difficult to obtain oxygen-free VCl_4. On the other hand, it would be useful for the preparation of single crystals of VN, and has been so used (Campbell and co-workers, 1949).

(d) Decomposition of vanadium halides in ammonia or nitrogen/hydrogen mixtures.

Funk and Böhland (1964) used this method to prepare VN by heating ammonium fluorovanadate in ammonia to 600°C for 1 hour.

This was investigated in the present project.

Preparation of Vanadium Nitride in the Present Project

(a) $$V_2O_3 \text{ or } VX \xrightarrow[\Delta]{NH_4HF_2} (NH_4)_3VF_6 \xrightarrow[\Delta]{NH_3} VN$$

$(NH_4)_3VF_6$ was prepared by the method of Sturm and Sheridan (1963) in which V_2O_3 and NH_4HF_2 were heated to 250°C for about 30 minutes, in a graphite crucible in air. The product was recrystallized from water in order to remove any carbonaceous impurities. This product was then placed in a porcelain boat, contained in a silica

tube, and/........

tube, and heated to 640°C in NH_3 for one hour in a tube furnace, and then allowed to cool in the NH_3 stream. The "d spacings" from the X-ray powder pattern for this compound were found to agree closely with those calculated for VN and with the ASTM Powder Data Index values, but the purity of the VN was not checked by vanadium analysis at this stage. The purity of the ammonium hexafluorovanadate was suspect, however, and was investigated using X-ray powder methods. The "d spacings" obtained for this compound did not agree with those given in the "A.S.T.M." index, suggesting that it was in fact not $(NH_4)_3VF_6$, but the true nature of the compound was not determined. Other methods of preparation of $(NH_4)_3VF_6$ were then investigated, and that due to Haendler, Johnson and Crockett (1958) was attempted. In this method, vanadium bromide dissolved in methanol is added to an excess of a methanolic solution of NH_4HF_2 from which $(NH_4)_3VF_6$ precipitates. An X-ray powder photograph of the resulting product was found to agree with the "A.S.T.M." data for $(NH_4)_3VF_6$, and a vanadium analysis on this material gave a value (22.7%) very close to the theoretical (23.3%). A further sample of VN was then prepared by heating this compound in NH_3, as detailed before, using AE & CI "refrigeration grade" NH_3, in order to produce VN. However, a vanadium analysis on this product gave a very low result, suggesting that it was in fact V_2O_3 rather than VN. It was then concluded that the ammonia used in the preparation of the VN was excessively contaminated with O_2, and methods of preparation which did not involve its use were investigated.

(b) $$V_2O_5 \xrightarrow{S_2Cl_2} VCl_3 \xrightarrow[\Delta]{H_2} VH \xrightarrow[\Delta]{N_2} VN$$

V_2O_5 was prepared from "B.D.H. Analar" ammonium metavanadate (containing not less than 98.5% NH_4VO_3) by heating to 450°C overnight, in air, which should afford complete conversion to V_2O_5 according to the results of Taniguchi and Ingraham (1964). The V_2O_5 was then converted to VCl_3, using the method of Brauer (1965), by refluxing overnight (about 14 hours) under anhydrous conditions with "B.D.H. S_2Cl_2", with continuous stirring at about 130 - 140°C.

At first, an attempt was made to purify the VCl_3 by converting it to VCl_4, distilling the VCl_4, and then converting back to VCl_3. The VCl_3 was converted to VCl_4 by heating in an inclined pyrex tube, through which chlorine was passed. The chlorine was generated by oxidation of hydrochloric acid with potassium permanganate in the apparatus as described by Sweeney (1917), and was purified and dried by passing through potassium permanganate solution followed by H_2SO_4. The VCl_4 was collected in a pear-shaped flask contained in an ice bath. The VCl_4

was then/........

was then distilled under chlorine, the fraction boiling between 170 and 185°C being collected. This purified VCl_4 was converted back to VCl_3 by heating under dry hydrogen at about 165°C for two days, according to the method of Simons and Powell (1945). The VCl_3 thus obtained was found to result in a product which contained oxygen, and this purification was abandoned.

During later preparations, the crude VCl_3 was purified by extracting with carbon disulphide overnight in a "Soxhlet" extractor, in order to remove sulphurous impurities. The excess carbon disulphide was then removed by keeping the VCl_3 under vacuum in a desicator for 2-3 hours.

The VCl_3 was then placed in an unglazed, hard porcelain boat contained in a non-porous "Dimulit" (Mullite) furnace work-tube (manufactured by "Rosenthal" of Germany); this tube was fitted with Quickfit joints held in place by hard vacuum wax. The inlet and outlet tubes were of glass in order to exclude oxygen. The system was first flushed with high purity nitrogen, which had been passed over copper turnings heated to about 375°C, in order to remove any traces of oxygen. The VCl_3 was then slowly heated to about 900°C in a current of hydrogen, purified by passing through a palladium thimble, with a flow rate of about 10 l/h. The VCl_3 was kept at this temperature for approximately 22 hours, after which time no further HCl or H_2S was evolved, and by which time the VCl_3 had been converted to vanadium or vanadium hydride (Brauer 1965). The furnace temperature was then raised to approximately 1100°C for 21 hours while high-purity nitrogen, first passed over heated copper turnings, was passed through the tube at a flow rate of about 15 l/h, thus converting the vanadium or vanadium hydride to VN. The product was then allowed to cool to room temperature in the nitrogen stream and, upon removal from the tube it was observed to be brown in colour with a violet lustre. Sometimes, gold coloured particles were observed in this product.

(c) Ready prepared vanadium nitride.

A number of samples of vanadium nitride which had been prepared by the direct nitridation of vanadium metal wire were kindly supplied to us by Dr. R. Kieffer of the Technical Institute Vienna.

These samples were employed in the later runs, and in the preparation of dense (hot-pressed) samples.

III (ii) THE ANALYSIS/.......

III (ii) THE ANALYSIS OF VANADIUM NITRIDE

(1) Review of Analysis Methods

A number of methods have been employed in the determination of the composition of vanadium nitride.

(a) X-Ray Crystallographic Analysis

X-ray powder methods have been used by several authors in order to determine the composition of VN, although this is rather a crude technique for accurate analysis.

Shomate and Kelley (1949) used this method in order to determine the purity of VN, while Epelbaum and Brager (1940, 1946) have determined the relationship between lattice parameters and oxygen content of the VN-VO system. Hahn (1949) has investigated the relationship between the stoichiometry and lattice parameter of the V-N system.

This method was used in the present project in order to obtain a rough estimate of the purity of VN.

(b) Nitrogen Analysis

Three general/.........

Three general "wet chemical" methods are available for nitrogen analysis, viz. Dumas, Kjeldahl and vacuum fusion analysis.

Although the Dumas method was considered unsuitable by Epelbaum and Ormont (1948) it has been employed by Hahn (1949), and has recently been described in modified form by Parker, Healy and Henderson (1968). The Kjeldahl method, which has been employed by Epelbaum and Ormont (1947) and by Hoy (1963), was found to give unsatisfactory results in the case of VN by Hoy (1963), Healy and Parker (1970), and Parker, Healy and Henderson (1968), probably on account of difficulties in dissolution of the material, (Bollman and Mortimore 1971). Vacuum fusion analysis is complicated by the fact that it is not suited to metals which form carbides e.g. Ti and V (Gocken and Tomkins 1962) and the complex apparatus was not available in the present investigation. Of these three methods, the Dumas method, (as described by Parker, Healy and Henderson 1968), appeared most suitable for the determination of N, and was employed in the later stages of the investigation.

Another method, which does not appear to have been used in the analysis of N in VN before, is neutron activation analysis. However this is at best only 1% accurate in the determination of major components, e.g. N in VN.

(c) Vanadium Analysis/........

(c) Vanadium Analysis

Two general methods are available for analysis; i.e. gravimetric and titrimetric.

In the gravimetric method, the VN is calcined, in a stream of oxygen, to V_2O_5, which is weighed. This method was used by Friedrich and Sittig (1925), Satoh (1938), Epelbaum and Ormont (1947), and by Hahn (1949), but was not used in the present investigation as it is not suitable for determinations on small amounts of VN due to the possibility of decomposition of the V_2O_5 at elevated temperatures (Taniguchi and Ingraham 1964).

In the titrimetric method, the vanadium is oxidised to $V^{(V)}$ and titrated to $V^{(IV)}$ with ferrous solutions. This method has been employed in the determination of the vanadium content of steels for "British Chemical Standards", and was also the method used by Hoy (1963).

In the second method, the vanadium is reduced to $V^{(IV)}$ and titrated to $V^{(V)}$ with $KMnO_4$. This method was that employed by Satoh (1938) and as a control by Hahn (1949). This method is suggested by Scott (1939) and by Vogel (1961).

(d) Oxygen Analysis

With the exception of Hardy and Hulm (1954), who employed vacuum fusion analysis (which was not used in this investigation for reasons detailed in (b)), most previous authors appear to have determined oxygen by difference. This necessitates both an accurate vanadium and an accurate nitrogen determination. Attempts have been made however, to observe the effects of oxygen content directly by ultraviolet reflectance and by infrared absorption spectrophotometry. Neutron activation analysis appears to be a promising method for the determination of oxygen as this is only a minor constituent of the VN.

(2) Analysis Methods Used in the Present Project

(a) Vanadium Analysis

(i) In the first method employed, the V in VN was oxidised to $V^{(V)}$ with HNO_3 and H_2SO_4, and titrated with ferrous solutions.

About 35 mg of VN was weighed out and dissolved by heating in a mixture of 10 ml concentrated nitric acid, and 5 ml concentrated sulphuric acid, the heating

being continued/........

being continued until brown nitrous fumes were no longer evolved. This treatment also converted the vanadium to the $V^{(V)}$ state. The acid solution (A) was diluted to about 200 ml, 3 ml of 85% phosphoric acid were added and the vanadium was titrated potentiometrically using a Pt/W electrode couple, against standard 0.1M ferrous ammonium sulphate. This method gave low results, considered to be due to incomplete oxidation of the vanadium.

(ii) The vanadium in VN was oxidised with $KMnO_4$ and titrated with ferrous solutions.

In an attempt to oxidise the vanadium completely to $V^{(V)}$, the acid solution (A), prepared as detailed in (i), was diluted to about 200 ml, and sufficient 0.01M $KMnO_4$ solution was added to impart a faint pink colour to the solution, about 0.5 ml of the $KMnO_4$ solution being required. Phosphoric acid (3 ml) was added to the solution, which was then titrated with the standard 0.1M ferrous solution. Two separate end-points were obtained, the first being due to the excess permanganate, and the second being due to the vanadium, difference between the two end-points giving the vanadium content. This method gave an apparent vanadium content which depended on the excess of permanganate which was used.

(iii) Procedure (ii) was repeated using 0.1M ceric sulphate in place of the permanganate. This method gave good results in some cases, but in others, no end-point was obtained at all, possibly as a result of poisoning of the electrode system. This method was later greatly improved by carefully cleaning the electrodes with chromic acid after each titration, and gave results reproducible to within about 0.5%

(iv) The procedure detailed by Welcher (1958) was attempted.

The vanadium in VN was reduced to $V^{(IV)}$ and titrated with an excess of E.D.T.A., which was then back titrated with $Mn^{(II)}$ solution.

The acidic solution (A) prepared as in (i) was diluted to about 100 ml and boiled, until blue in colour, with about 1.5 g of sodium sulphite in order to reduce the vanadium to $V^{(IV)}$. A small excess of standard 0.1M E.D.T.A. was added to the solution, which was then neutralised with ammonium hydroxide, and acidified to about pH 3 with acetic acid. The solution was then heated to boiling and diluted to about 250 ml with cold water, after which about 0.1g of ascorbic acid was added. This solution was rendered ammoniacal and back-titrated potentiometrically with the Pt/W electrode system, against 0.01M manganese (II) sulphate, using Eriochrome Black T as indicator in some cases, in addition to the potentiometric end-point detection.

(v) The vanadium in VN was reduced with excess ferrous sulphate which was then back-titrated with $K_2Cr_2O_7$.

The acid solution (A) prepared as in (i) was diluted to about 200 ml and an excess (15 ml) of 0.1 M standard ferrous ammonium sulphate was added. 5 drops of 1% diphenylamine sulphate indicator was then added and the excess ferrous ion back-titrated with standard 0.1 N potassium dichromate. The results, using this method were in close agreement with those using method (iii), with none of the disadvantages introduced by the electrodes.

(b) Oxygen Analysis

The oxygen contents of several samples were determined by ISCOR, using neutron activation analysis, with a precision of about 10% of the total oxygen present.

(c) Nitrogen Analysis

(i) Several of the samples were sent to Harwell for determination of their nitrogen content by neutron activation analysis, a precision of about 5% of the total nitrogen content being claimed.

(ii) The nitrogen content of a number of the later samples was determined using a modified Dumas technique, described by Parker, Healy and Henderson (1968).

About 20 mg of VN was placed into a porcelain boat together with about 1 g of CuO. The boat was then introduced into a silica tube sealed at the one end (which contained sodium bicarbonate) and which was connected to a nitrometer, via a tube containing heated copper gauze. After flushing the system with CO_2, generated by heating the $NaHCO_3$, the portion of the tube containing the boat was heated to 800°C in a furnace for about 5 minutes after which the temperature was raised to 1000°C until nitrogen evolution ceased. CO_2 was passed through the system throughout, and nitrogen evolution ceased after about 30 minutes.

IV (i) DISCUSSION OF/........

IV (i) DISCUSSION OF RESISTIVITY AND HALL EFFECT MEASURING TECHNIQUES

High sensitivity and reliability were required for the measuring system with which the electrical measurements were to be made on the VN. The criteria for the choice of a suitable measuring system are discussed critically below.

Requirements of the Measuring System

According to Dauphinée and Mooser (1955), apparatus for the measurement of Hall coefficients and resistivity should have the following characteristics:

(i) It should be quick and easy to set up.

(ii) It should be easy to handle, not demanding long-term stability, and should only have to be balanced once for each reading.

(iii) The measuring range should be wide, and cover resistances from 10^{-3} to 10^{5} ohms, the Hall coefficients from 10^{-4} to 10^{5} cm^{3} $coulomb^{-1}$.

(iv) Measurements should not be affected by thermal emfs.

(v) At balance, no current should flow in the potential leads, which would result in errors due to contact resistances.

(1) Measuring Techniques

These may be divided into three main groups:

(a) D.C. methods.

(b) A.C. methods.

(c) Chopper methods.

(a) D.C. Methods

These are usually of great sensitivity and are of several different types, which may broadly be divided into two groups, i.e. potentiometric and bridge methods.

(i) Potentiometric Methods

These are the methods usually employed in determining accurate resistivity values (Lark-Horowitz and Johnson, 1959).

Basically, these methods consist in measuring the voltage across the sample, while a known current is flowing. This may involve two probes only, Fig 8, but suffers from the disadvantage that contact resistances are also included in the total resistance measured, as a voltage due to current flow across the sample-contact junction will also be measured and in the case of low resistance samples, this may lead to serious errors, e.g. the contact resistance may be of the order of 10^{-1} ohms, while the sample resistance may only be about 10^{-3} ohms. However in the case of high resistance samples, this method has been used successfully, e.g. by Robertson and Rapp (1969) in measuring the resistivity of NbO (about 50 ohm cm). A better method, and one which does not include appreciable effects due to contact resistances, is the four-probe method, Fig 9, using two probes to complete the circuit for the current, another two to measure the voltage drop across the sample. If the voltage is measured using a potentiometer, neglible current will be drawn from the potential probes and thus no voltage other than that due to the sample resistance should be observed. This method was used to good effect by Hoy (1963) in determining the resistivity of VN.

(ii) Bridge Methods

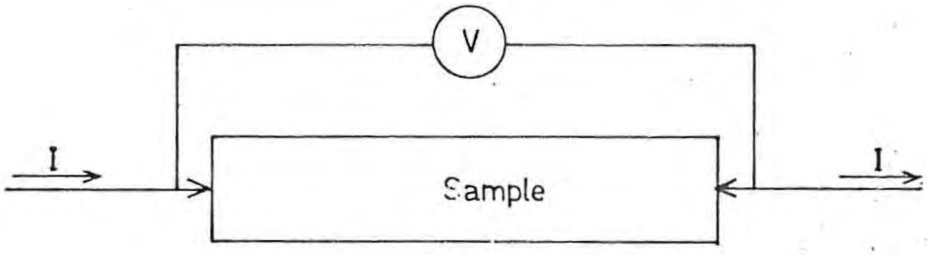
These are used to measure differences in resistances, and to compare resistances, and are of two basic types:

(a) Those employing a Wheatstone type bridge, and

(b) those employing a Kelvin Double bridge.

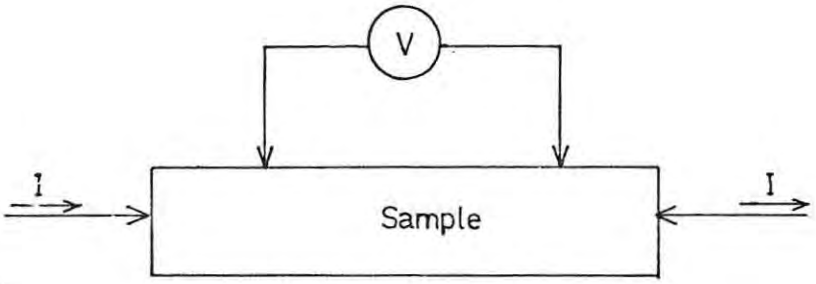
(a) In the Wheatstone bridge circuit, Fig 10, an unknown resistance Rx is directly compared with a known resistance

Rs. This/........



Two probe method

Fig 8



Four probe method

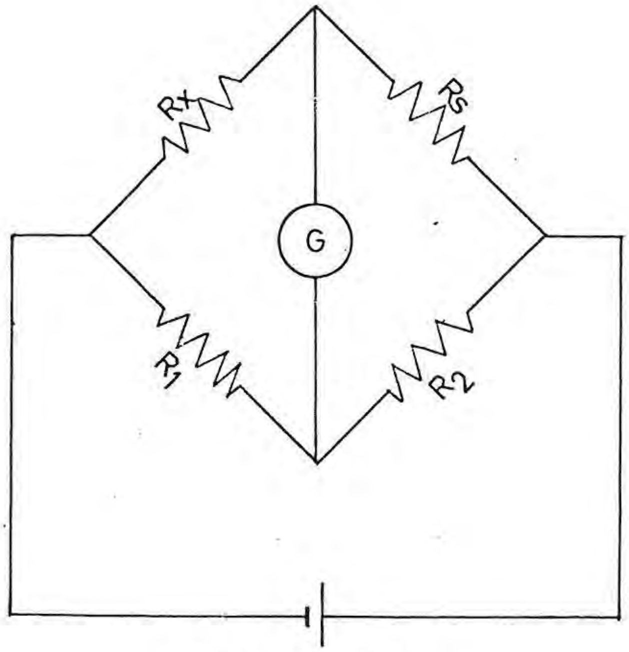
Fig 9

Rs. This circuit suffers from the same serious disadvantage for small resistances, that contact resistances in Rx, (which is a two-probe resistance) are also included in the resistance which is measured.
(b) For the measurement of low resistance samples, the Kelvin Double bridge, Fig 11, is usually employed. Errors due to switch, lead and contact resistances are virtually eliminated in this bridge, as the sample has four probes.

When taking measurements using d.c. methods it is necessary to make multiple balances, i.e. separate measurements with both current directions, and with both magnetic field directions, in the case of Hall effect measurements, in order to eliminate stray emfs. In the case of the Kelvin Double bridge, the various resistors R1, R2, R3, and R4, Fig 11, must be varied alternately, and the balance point approached by a series of approximations, this being rather a lengthly procedure which renders rapid measurement with this type of bridge difficult.

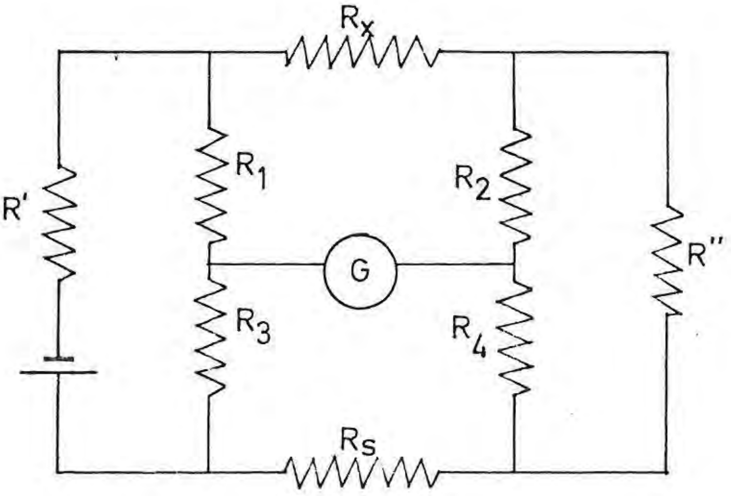
In some cases, the thermal emfs may be considerably larger than the emfs to be measured, and several ingenious methods have been employed in attempts to eliminate these. The most common remedy is the

application of/.......



Wheatstone Bridge

Fig 10



Kelvin Double Bridge

Fig 11

application of a "bucking" voltage, this method having been employed at a relatively early stage by Smith (1910), who used an auxiliary potentiometer to counteract misalignment and thermoelectric emfs, while determining the Hall coefficients of metals. Other methods usually involve the reduction of temperature gradients across the sample so far as possible, liquid baths (Tufte and Ewald 1961) and copper plates, in thermal (but not electrical) contact with the sample (Sanford et al, 1961) having been used for this purpose. These methods however cannot easily be employed when taking measurements at high temperatures.

(b) A.C. Methods

A.C. methods are applicable to both potentiometer- and bridge-type circuits.

The main advantage of a.c. methods is the elimination of thermal and other stray d.c. emfs, thus only a single balance need be made for each measurement, and no bucking circuits are required.

The rapid alternation of the sample current is roughly equivalent to taking d.c. measurements with both current directions, and in this way, stray thermal and

contact emfs/.......

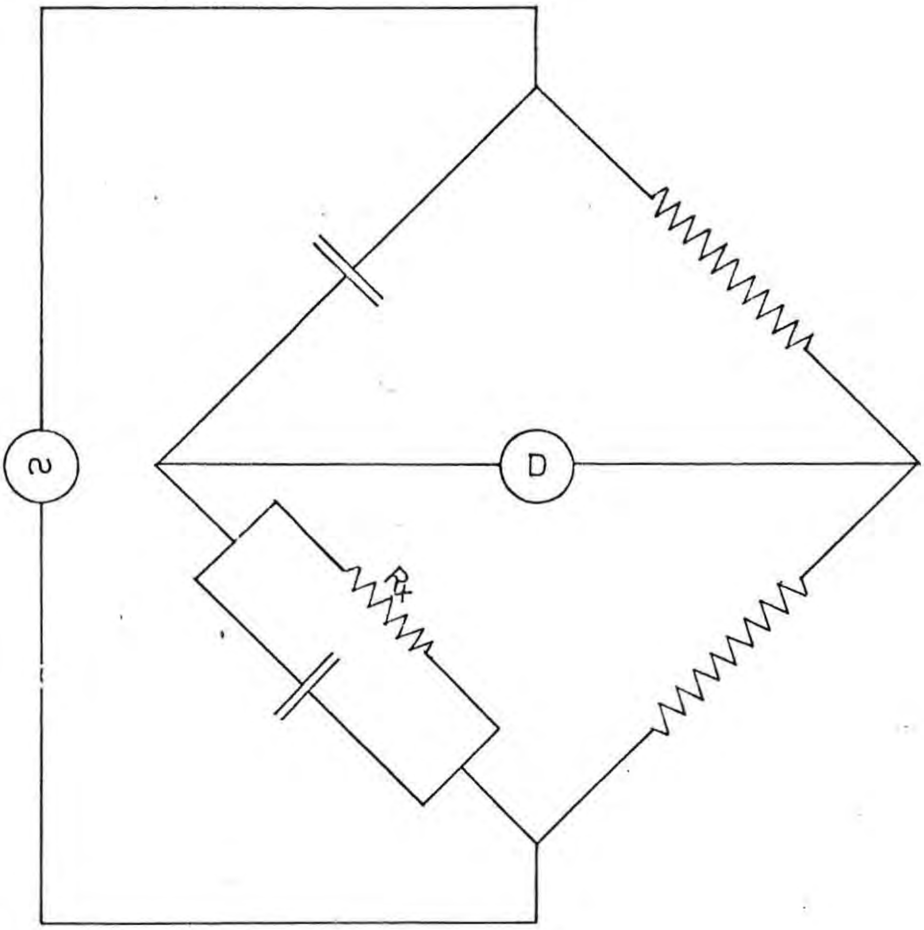
contact emfs may be eliminated. Thus, by introducing blocking capacitors into the circuit, which will pass a.c., but not d.c., the effects of even relatively large thermal emfs may be eliminated.

Conventional d.c. potentiometers may be used with a.c. sample currents, but a.c.-sensitive detectors, such as oscilloscopes or headphones, must be employed in place of the galvanometer. This method has been employed by Donoghue and Eatherly (1951) using a modified d.c. potentiometer with a.c. sample current, and a peaked a.c. amplifier and oscilloscope as detector.

Conventional d.c. bridges such as the Wheatstone or Kelvin Double bridge may also be used with an a.c. power supply and oscilloscope as detector, and a.c. bridges, such as the Schering bridge, Fig 12, in which capacitative elements in addition to the usual resistive elements are included, may also be employed. This type of bridge has the advantage that effects due to sample capacitance which may render the use of a d.c. type bridge difficult, due to phase shifts, may be eliminated.

A number of disadvantages are inherent in a.c. methods, especially if a high sensitivity is desired.
(i) The apparatus is usually complicated, and difficult

to set/.......



Schering Bridge

Fig 12

to set up, as high stability a.c. power supplies and a.c. amplifiers must be used, e.g. Lavine (1958).

(ii) Shielding of all components is essential, as these circuits are very sensitive to stray a.c. electric and magnetic fields, and inadequate shielding will result in a pick up of these fields, usually due to a.c. mains, which would result in the production of spurious "beat" frequencies. These "beats", or the stray a.c. fields themselves may be amplified by the high gain amplifiers used in such circuits, unless the amplifiers are tuned to reject all such frequencies. This implies long term stability in the amplifiers, which is very difficult to achieve.

(iii) If relatively high a.c. frequencies are used, then capacitative effects may introduce phase shifts which will render balancing of the circuits very difficult or impossible. These capacitances usually arise between the circuit and its surroundings, such as shielding, bench tops etc., and are very difficult to eliminate.

These effects together reduce the available sensitivity of a.c., as opposed to d.c. methods.

(c) Chopper Methods

Chopper methods involve bridge circuits, i.e.

comparison of/........

comparison of resistances, and are a combination of a.c. and d.c. techniques.

The chopper method, first described by Dauphinée and Mooser (1955), combines the merits of the rejection of stray d.c. signals by a.c. techniques with the detection sensitivity of the d.c. technique.

Choppers (motor driven switches) are used to convert a d.c. current into a square wave a.c. current, which then passes through the sample and standard resistor in series. Further choppers are used to rectify the voltages appearing across the sample and standard, while the difference (zero at the null balance) is measured using a conventional d.c. galvanometer circuit.

This type of circuit has a number of advantages, combining the best features of a.c. and d.c. methods.
(i) As the sample current is alternating, stray d.c. voltages are cancelled out, and capacitors can be interposed in the potential leads to block such emfs. This also eliminates the necessity for bucking voltages, or elimination of all temperature gradients across the sample, (although these must be kept to a minimum).
(ii) As the output voltage is d.c., a simple and sensitive d.c. galvanometer may be used as detector,

eliminating the/........

eliminating the necessity for unstable, high-gain amplifiers.

(iii) The apparatus is simple to set up, requiring no extended warming-up period or elaborate setting of controls.

(iv) Elaborate shielding is not essential, as the chopper frequency may be chosen in order to reduce beat frequencies produced by stray a.c. fields. Some shielding between components is, however, desirable.

(v) At the relatively low chopper frequencies employed in this system, capacitative effects in the circuit are negligible and may be ignored.

(vi) The sensitivity of the apparatus may be made as high as that of d.c. equipment, as it is mainly limited by the sensitivity of the detection system, in this case, a d.c. galvanometer. Thus resistances as small as 10^{-3} ohms and Hall coefficients of 10^{-2} cm^3/coulomb may be determined to a precision of about 1%.

(vii) Practically no current flows in the potential leads at balance, i.e. it is a four-probe method, thus effects due to contact resistances are virtually eliminated.

This method was chosen for use in the present project on account of these advantages.

A number of disadvantages are also inherent in the method however:

(i) Unless very high quality choppers, with (preferably) solid gold contacts are employed, then the choppers themselves will be likely to give rise to spurious voltages.

(ii) The choppers must be motor driven, as the magnetic field developed by magnetically driven choppers is likely to give rise to spurious voltages. As the choppers are motor driven, difficulties are encountered in keeping the chopper frequency constant, which is most important if the choppers are to reject stray a.c. fields.

(iii) The chopper units themselves are extremely sensitive to a.c. magnetic fields which give rise to stray emfs when they are "rectified" by the choppers.

(iv) The sensitive d.c. galvanometer circuit is sensitive to thermal emfs which must be eliminated by means of a bucking voltage from a "thermal compensator".

Most of the above disadvantages can be minimised however, by careful attention to the design and building of the circuit, and use of only the highest quality components available.

(2) Contacts and Sample Designs

(a) Contact Arrangements

(i) Standard Four Probe

In this probe arrangement (Lark-Horowitz and Johnson 1959), Fig 9, two current contacts are applied to the sample as close to the ends as possible. Two potential probes are then placed in contact with the sides of the sample, sufficiently far removed from the current contacts to avoid fringing or end effects. The current contacts usually have a relatively large surface area in order to ensure good contact, while the potential probes are as small as possible, in order that their separation may be determined accurately, so that they do not disturb the fields within the sample.

When taking measurements by this method, it is necessary to determine the cross section of the sample accurately, in addition to the probe separation. The resistivity of samples with a uniform cross section between the potential probes is given by:

$\rho = \frac{Va}{Il}$ .... Potentiometer method

or $\rho = \frac{Ra}{l}$ .... Bridge method

Where V is voltage across probes

I is sample current

R is resistance between probes

a is cross sectional area

l is probe separation.

In this/.......

In this method however, it is difficult to determine the resistivity of samples which do not have a uniform cross section. In such samples, the resistivity is usually determined by comparison with the measured resistivity of known samples with the same dimensions, this method having been employed by Hoy (1963).

(ii) Spreading Resistance Measurement

In this method, Fig 13, two contacts are employed, one of large area and low contact resistance, the other a whisker of much smaller area. The resistance measured will be dependent mainly on the resistance at the point contact, the resistivity being determined from:

$\rho = 2DR$ .... (Lark-Horowitz and Johnson 1959)

where D is diameter of the contact

R is the measured resistance.

Although useful in the determination of the resistivity of surface layers, it suffers from the drawback that it is very difficult to determine the actual area of contact, and it also suffers from the other problems associated with two probe methods.

(iii) Four Point/.......

(iii) Four Point Probe Method

In this method, Fig 14, all of the current and potential contacts are point probes which are usually held in a special holder with their points in contact with the surface of the sample. Two contacts carry the current, the other two being potential probes. The separation of the probes must be smaller than the smallest dimension of the sample, and they must not be placed too close to the edge of the sample.

The conductivity of the sample is given by:

$$\sigma = \frac{1}{2\pi V}\left(\frac{1}{S_1} + \frac{1}{S_3} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}\right) \ldots\ldots \text{ (Lark-Horowitz and Johnson)}$$

where S is probe separation

V is measured voltage.

The disadvantages of this system are due to the small probe separations, which are difficult to measure, and small measured voltages. In low conductivity samples the possibility of carrier injection may cause trouble. This method has nevertheless been used by Kruger and Moser (1967) in their study of the carbide, phosphide and sulphide of plutonium, these workers reporting that the high conductivity of these samples prevented carrier injection.

(iv) The van/........

(iv) The van der Pauw Method

In this method, Fig 15, (van der Pauw, 1958), the resistivity and Hall coefficient of samples of arbitrary shape may be measured, using a four probe technique, four point probes being applied to the edge of the sample. The sample may in fact be of almost any shape, provided that it is uniform in thickness, and that no isolated holes are present. This has the advantage that only the sample thickness need be measured and not any other dimensions, or the probe separations. For convenience of preparation, a disc shaped sample is used.

Numbering successive contacts 1, 2, 3 and 4, at arbitrary positions around the circumference of the sample, and defining the resistance R12,34 as the voltage V4-V3 between contacts 3 and 4 per unit current through contacts 1 and 2, and defining the resistance R23,41 similarly, it may be shown that (van der Pauw, 1958):

$$\exp(-\pi R12,34\ d/\rho) + \exp(-\pi R23,41\ d/\rho) = 1 \ \ldots\ldots \ (A)$$

Where ρ is resistivity

and d is sample thickness

Equation (A) has a solution of the form:

$$\rho = \frac{\pi d}{\ln 2} \frac{(R12,34 + R23,41)}{2} f\left(\frac{R12,34}{R23,41}\right) \ \ldots\ldots \ (B)$$

where f is a function of the ratio R12,34/R23,41 and

satisfies the/........

satisfies the relation:

$$\frac{R12,34 - R23,41}{R12,34 + R23,41} = \frac{f}{\ln 2} \operatorname{arccosh} \frac{\exp(\ln 2/f)}{2} \quad \ldots\ldots \text{(C)}$$

which cannot be solved for explicitly for f.
If R12,34 and R23,41 are almost equal, then f can be approximated by the equation:

$$f = 1 - \left(\frac{R12,34 - R23,41}{R12,34 + R23,41}\right)^2 \frac{\ln 2}{2} \quad \ldots\ldots \text{(D)}$$

However if R12,34/R23,41 is greater than 2, then (D) does not provide a very close approximation, thus (C) must be solved directly.

In the present project, (C) was solved for R12,34/R23,41 by generating decreasing values of f, in small steps, and computing the corresponding values of R12,34/R23,41 using an ICT 130_ computer programmed in "Manchester Autocode". Values of f, and the corresponding values of R12,34/R23,41 were printed out, for values of R12,34/R23,41 between 1 and 104, and values of f from 1.00000 to 0.40000, in steps of 0.00005. The values so obtained were in agreement with the graphical solution presented by van der Pauw (1958).

The Hall coefficient, Rh, may be obtained from the equation:

$$R_h = \frac{d}{B} \Delta R24,13$$

where Δ R24,13/........

where $\Delta R_{24,13}$ is the change in $R_{24,13}$ produced by applying the magnetic field B.

The van der Pauw method may be used either in a potentiometer circuit, in which case the potential across contacts 3 and 4 would be measured with a known current flowing through 1 and 2, or it may be used in a four-probe bridge circuit, in which case the resistance $R_{12,34}$ would be measured directly.

A number of disadvantages are inherent in this method, as all the contacts are point contacts:

(i) There exists the possibility of carrier injection; but in the case of VN, which has a relatively low resistivity, this effect should be negligible

(ii) In the case of the preliminary tests on a nickel sample, heating at the points of contact was observed. However, in the case of VN, this did not occur, as a lower sample current was required than in the case of nickel, in order to produce a measurable potential across the sample.

(iii) The theory requires true point contacts which are not possible in practice, but exceptionally large

contact areas/........

contact areas are necessary before appreciable errors would arise. van der Pauw (1958) presents an error analysis.

(iv) Reasonable results are only obtained if the contacts are approximately evenly spaced out otherwise the voltages generated are very small. Thus the method is not suitable for measurements on long thin samples.

(b) <u>Types of Contact</u>

In order to facilitate measurements on low resistance samples, it is necessary that the contact resistances be kept as low as possible. Although the four probe method will eliminate most of the problems associated with high contact resistances, the measuring circuit must still draw some current through the potential probes, especially when in an unbalanced condition, and this results in difficulty in obtaining a balance.

If high contact resistances are present at the current contacts, then Joule heating may occur at the contact points, leading to temperature gradients across the sample and possible contamination at the contact points.

A number of methods are available for the reduction of contact resistances; as follows:

(i) Metal Foil Contacts

These have been employed by Bevan and Anderson (1948) and by Hoy (1963), who used strips of gold leaf held in contact with the sample. Although this gives a good contact, due to the large surface area of contact, there are a number of disadvantages, viz. the current path will not be uniform near the ends of the sample, especially if it is relatively thick, and foil contacts do not behave as point contacts, thus it is difficult to determine their separation. Nevertheless, this type of contact is suitable as a current contact, provided that it is not too close to the potential probes, and has been employed in this way in the present project.

(ii) Spot Welded Contacts

These have been employed by a number of workers, e.g. Schindler and Gillespie (1963) on Nb/Zr alloys and Heckman (1967) on cerium hydride. The former workers were however dealing with a metal alloy, onto which probes could be welded without causing thermal decomposition, which would probably occur in the case of VN before its melting point (over 2000^{o}C). Heckman applied contacts to an ingot of cerium metal before hydriding, which would be difficult in the case of VN, as nitriding of a

vanadium ingot/........

vanadium ingot would be extremely difficult and, in any case, VN was not prepared by the direct nitridation of vanadium metal in the present project.

(iii) Plated Contacts

These may be employed at relatively high temperatures, and are formed by evaporating metal contacts onto the samples. A few VN samples were treated in this way, by evaporating silver onto selected points on the sample in vacuo, however this did not appear to improve the contact greatly, and could lead to contamination of the samples.

(iv) Soldered Contacts

A number of workers have employed soldered contacts, using indium or gallium alloy solders, e.g. Tufte and Ewald (1961) in their measurements on grey tin. However, these workers conducted measurements below 300°K, at which temperature contamination due to diffusion of the solder was unlikely. At high temperatures such diffusion could easily occur, and although high temperature solders have been described by Harman (1960), all attempts to make such alloys adhere to VN were unsuccessful.

(v) Bridge Samples/........

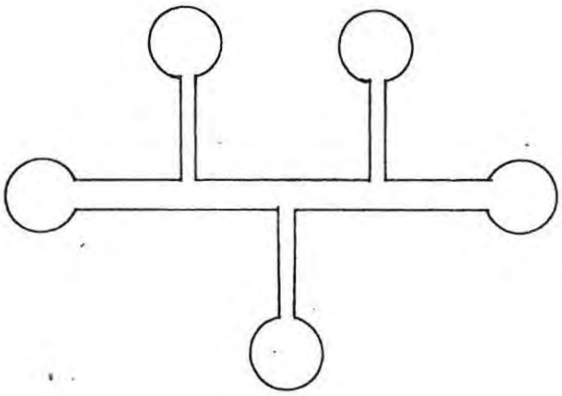
(v) Bridge Samples

These are cut with large contact areas in order to minimise contact resistances, Fig 16, in such a way as not to disturb the geometry of the current flow through the sample. However, it would be extremely difficult to cut VN into bridge shapes on account of its extreme brittleness, although sand blasting might be suitable.

(vi) Pressure Contacts

Pressure contacts are favoured at elevated temperatures, as they can be constructed from inert metals which will not lead to contamination of the samples. Also, by spring-loading such contacts, movement of the sample due to thermal expansion will not result in breakage of the contacts. Such contacts have been used extensively in the present investigation, but suffer from the disadvantage that they often result in excessively high contact resistances whose effects are, of course, considerably reduced by the method of measurement.

IV (ii) EXPERIMENTAL/........



Bridge-Type Sample

Fig 16

IV (ii) EXPERIMENTAL

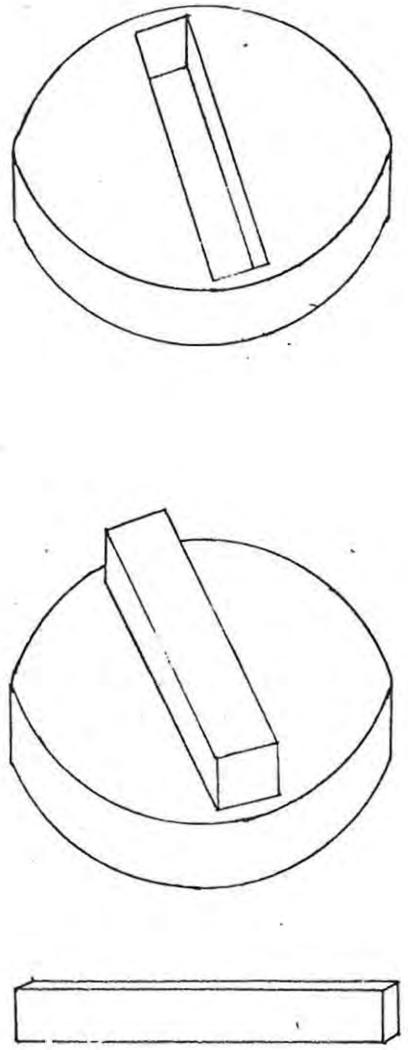
(1) Sample Pressing and Sintering

(a) Rectangular Samples

Rectangular samples, approximately 45mm x 8mm x 1mm were used in the initial measurements. These were pressed in a circular die, 50mm in diameter with suitable inserts, manufactured by G. Haslam and Co. of Johannesburg, Fig 17.

The samples were pressed from dry VN powder at room temperature, the die being subjected to vibration before pressing, in order to obtain a uniform thickness of VN in the die. The sample was then pressed in an hydraulic press at a pressure of about 3.8×10^3kg cm^{-2} for two minutes. Upon removal from the die, the sample was found to be very fragile, and unsuitable for insertion into the conductivity cell. In an attempt to improve the mechanical properties of the samples, they were sintered in ammonia for 24 hours at 1000°C. After this period they were still fragile, necessitating further sintering in ammonia for 24 hours at 1000°C. After the second sintering, the sample had excellent mechanical properties and resembled fine porcelain in texture, and hardness.

Later samples/........



Inserts of die for pressing rectangular samples

Fig 17

Later samples were sintered by heating to 1100°C in ammonia for 48 hours, the temperature being raised to this value over a period of about 18 hours in order to avoid thermal shock. The samples were then allowed to cool to room temperature, over a period of about 12 hours, in the stream of ammonia. After this sintering process the mechanical properties of the samples were usually very good. Some of the samples curled slightly during the sintering, however, rendering measurement impossible.

(b) Disc Samples

In the later measurements, based on the van der Pauw (1958) equations, disc samples were used. These were approximately 13mm in diameter and 0.2-0.7mm thick, and were pressed at room temperature in a "Paul Weber" KBr disc die. It was found necessary to "skim" and polish the faces and sides of the die in order to prevent the VN from sticking to it during the pressing, and to avoid breaking the samples upon removal from the die. The samples were pressed at about 9 x 10^3 kg cm^{-2} for 1 minute in an hydraulic press. The samples thus prepared had fairly good mechanical properties and measurements could be made on the unsintered samples, but their electrical properties were found to be very erratic, necessitating sintering.

These samples/........

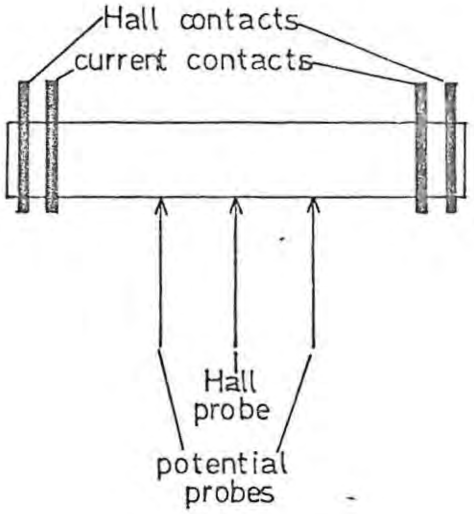
These samples were sintered at 1100°C for 48 hours in high purity nitrogen, first passed over heated copper turnings in order to remove residual oxygen. The furnace temperature was raised to 1100°C over about 12 hours, and the furnace was allowed to cool over a similar period in order to avoid damage to the samples due to thermal shock. A few of these samples curled slightly during sintering, but not to the same extent as did the rectangular samples.

(2) The Conductivity Cell

(a) For Rectangular Samples

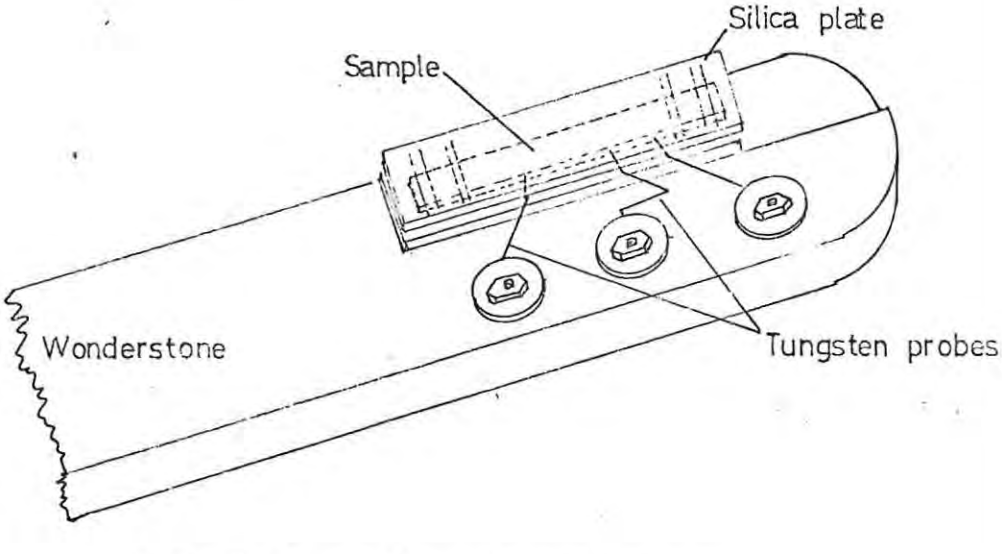
A sample holder, which was a combination of the designs of Bevan et al (1948), Butler (1960), and Brooker et al (1957), was constructed for measuring conductivity and Hall coefficient on rectangular samples. The layout of the point probes and current contacts is similar to that given by Lark-Horowitz and Johnson (1959) Fig 18.

The cell, Fig 19, was fitted with a chromel/alumel thermocouple in the base, directly underneath the sample. This had the disadvantage of being ferromagnetic. The current and end Hall probes were of platinum foil, while the potential probes were of stainless



Layout of contacts

Fig 18



Conductivity cell for rectangular samples

Fig 19

steel wire which had the necessary "springiness" at elevated temperatures. Platinum wires were used in connecting the sample contacts to the external circuit and the contact mounting screws were of stainless steel. The cell was mounted on a base of Wonderstone, which was first cut to size and shape, (allowance being made for the contraction upon firing) while holes were drilled for the various wires and screws, after which it was embedded in talc, and fired in air at 1160°C for 12 hours, the temperature being raised to this value over about 14 hours and cooled over about 12 hours in order to prevent cracking and distortion. During the firing process, the colour of the Wonderstone changed from grey to pink, and its hardness increased until it was about the same as that of glass. The potential probes were held directly onto the base by means of stainless steel screws and were clamped between stainless steel washers, while the sample was clamped between an upper silica plate and a lower Wonderstone plate.

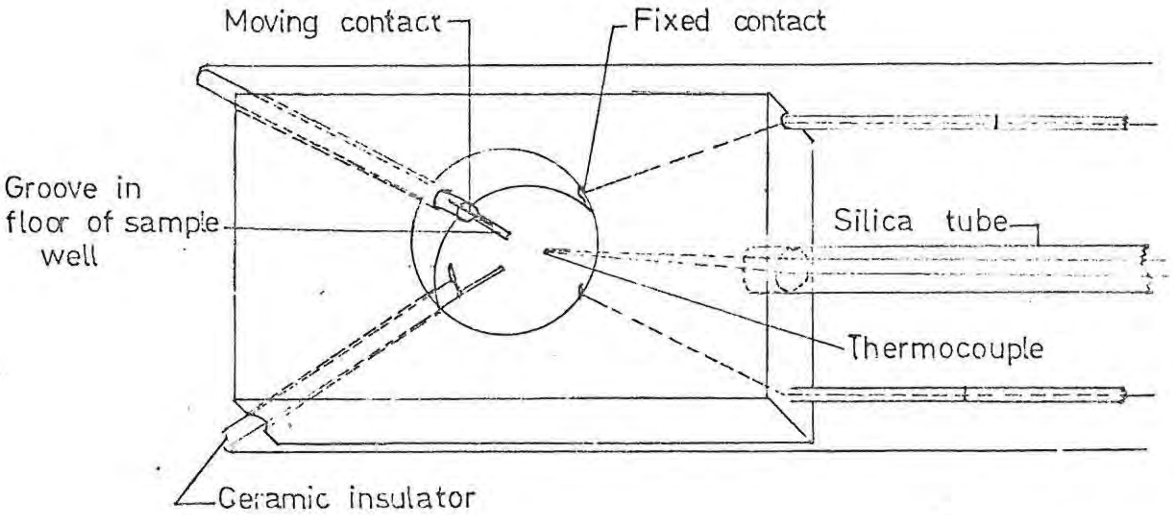
These materials were chosen for the construction of the cell as they were unreactive (platinum, Wonderstone, silica) or only slightly reactive under the system conditions (stainless steel). They were also relatively unaffected by high temperatures, had a low coefficient of expansion and were not ferromagnetic.

In order to arrive at this final design, several modifications were made to the original design, which had a base of asbestos cement, brass fixing screws and tungsten probes, these materials being replaced in successive designs, as they proved too susceptible to oxidation and repeated heating and cooling.

Difficulty was encountered in making good probe-to-sample contact with this cell design, and a perfectly flat sample was also required; these were difficult to prepare, as bending of the samples usually occurred during sintering. Therefore a new method of measurement, the van der Pauw (1958) method was investigated.

(b) A new conductivity cell, which was used to take measurements by the van der Pauw (1958) method, was constructed, Fig 20, in order to hold 13mm diameter samples with four instead of seven probes.

The design for this cell was based on that of Germann and Rogers (1966), but the brass was replaced by Wonderstone, steel coil springs were used in place of flat springs to tension the contacts; the springs were attached to the probes by means of long connecting wires. This cell of Wonderstone was rectangular, with a circular well about 15mm in diameter and 4mm deep in the centre of



van der Pauw Conductivity Cell

Fig 20

the base. This was also fitted with a platinum/platinum-13%rhodium thermocouple, which replaced the earlier ferromagnetic chromel/alumel thermocouple. The thermocouple was situated immediately below the well.

The cell was fitted onto the end of a silica tube of 6.3mm outside diameter, which served as a holder for the thermocouple leads, and which was held into the base by means of powerful springs attached to the ends of the fixed contact connecting wires.

The cell was fitted with two fixed and two moving contacts, of non ferromagnetic chromel thermocouple wire, the moving contacts being held in contact with the sample by means of springs (situated in the part of the cell maintained at room temperature) which were connected to the probes by means of stainless steel wires. The moving contacts were fitted into ceramic insulating tubes which were a sliding fit in holes drilled into the base of the cell.

In the earlier designs of the cell the connecting wires and probes were of stainless steel, which was later replaced by platinum which proved too brittle, then by nichrome which was unsuitable because it was ferromagnetic, and finally by chromel which is

not ferromagnetic/........

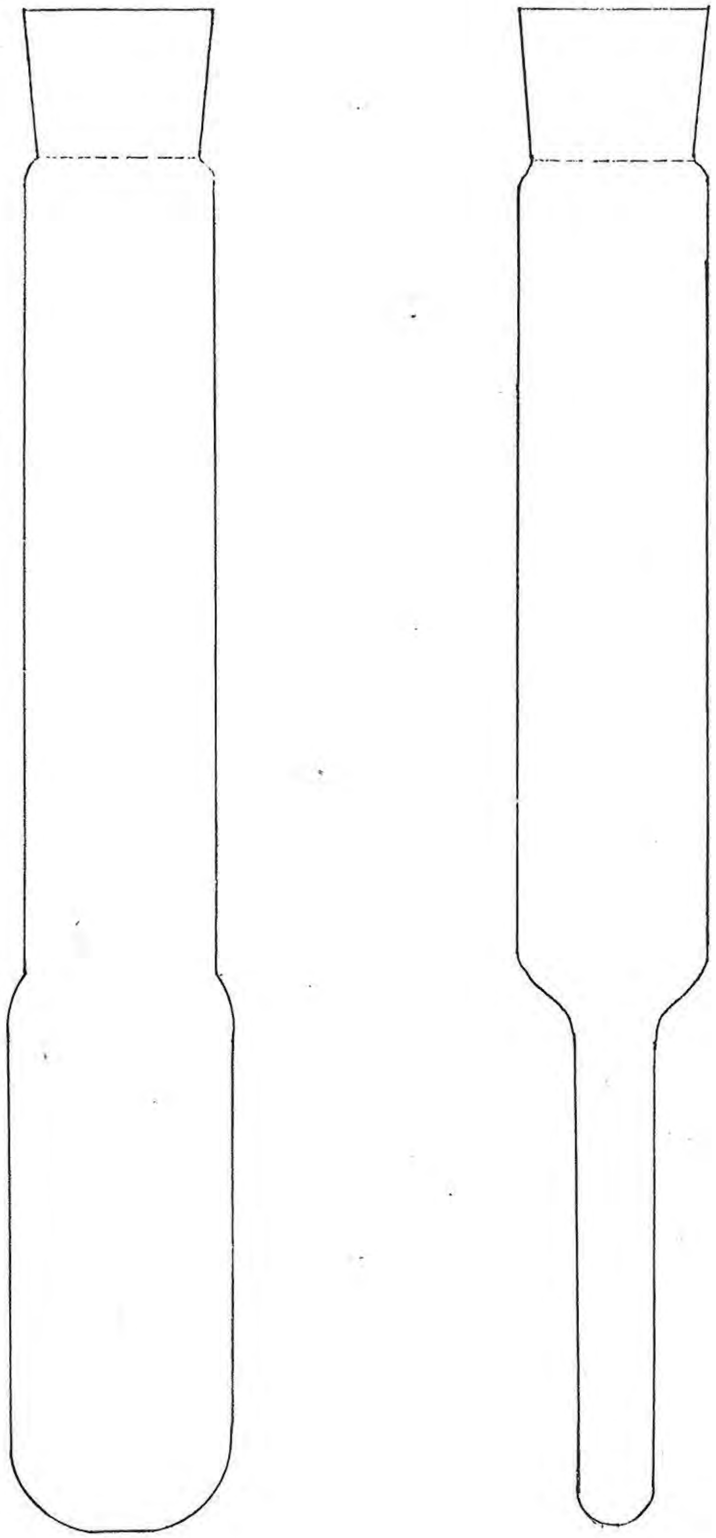
not ferromagnetic and was entirely satisfactory.

Most of the later runs were performed using the cell in its final form.

(3) The Furnace Tube

A furnace tube of silica was constructed, Fig 21, by the National Institute for Metallurgy in Johannesburg. This was provided with a B34 "Quickfit" socket at its open end, in order to facilitate the connection of gas supplies and connecting wires, also permitting insertion and removal of the conductivity cell. This tube had a 34mm inside diameter along most of its length, but was flattened at the end, having an internal cross section of 11 x 40mm in order to permit its insertion between the magnet poles which had to have a relatively small gap, in order to ensure an intense, uniform field.

A furnace to heat the furnace tube was constructed in the form of a miniature tube furnace of rectangular cross section, Fig 22, constructed of flat porcelain plates provided with open tubular element holders, into which a coiled heating element was placed. This type of furnace replaced an earlier design, in

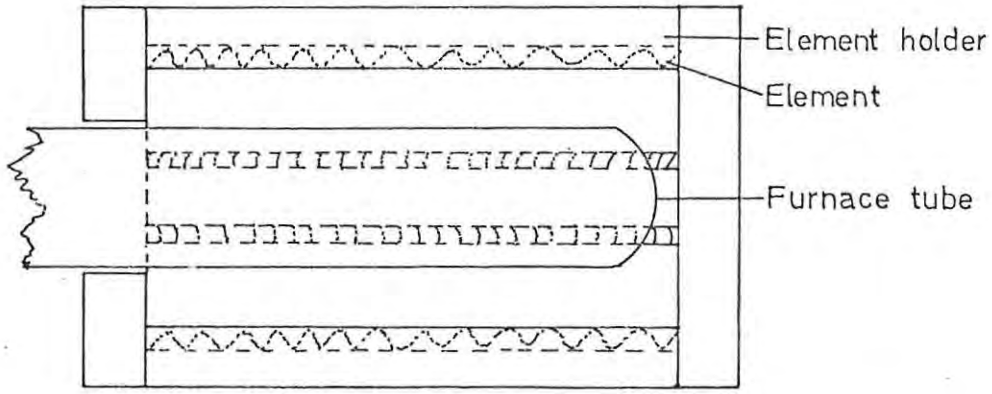


Top

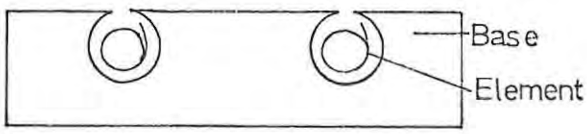
Side

Furnace Tube

Fig 21



Heater



Element holder

Furnace

Fig 22

which the heater was integral with the tube and had the following advantages over this design:

(i) Coiled heating elements were less likely to develop short circuits through expansion, as they were run in separate tubes.

(ii) The windings could easily be replaced, as no cement was used in the construction of the furnace.

(iii) If short circuiting of the wires were to occur, then no damage to the furnace tube would result.

(4) The Furnace Controller

Good temperature control and stability was required for the furnace that was used to heat the sample during measurements, and this necessitated the use of a furnace controller.

A commercially available temperature controller, Eurotherm "PID-SCR", was used.

This operated by means of a thyristor-controlled output, in order to give "stepless" control. The a.c. furnace current, however, was found to produce galvanometer deflections in the measuring circuit, making it necessary to rectify the output of this controller.

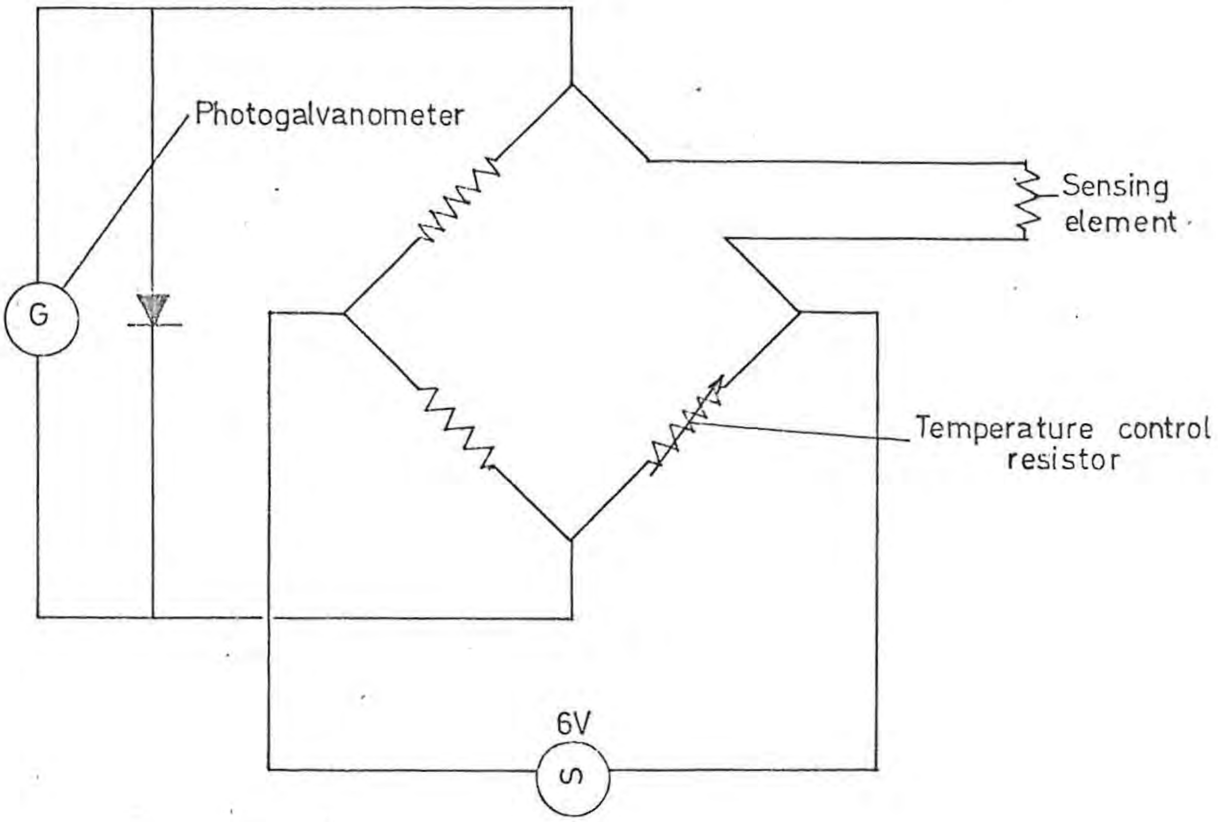
A choke-input/........

A choke-input rectifier constructed for this purpose was capable of handling the furnace current of approximately 5 amps. This rectifier employed a bridge rectifier circuit, obtained from Hamrad of Cape Town. The sensitivity of this controller necessitated considerable lagging of the furnace with asbestos and glass wool in order to maintain a steady temperature at elevated temperatures. The controller employed a platinum/platinum-10%rhodium thermocouple as sensing element, which was placed in the furnace as close to the windings as possible.

This circuit replaced earlier temperature control units which were used in the earlier measurements.

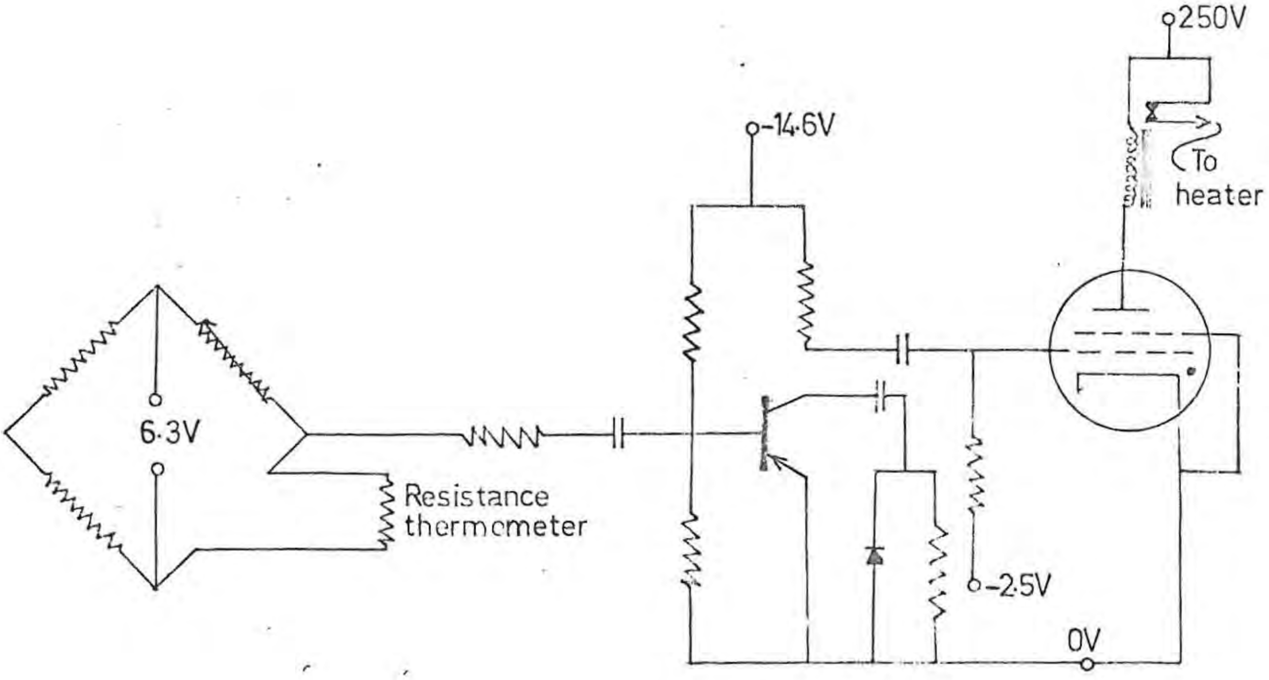
The first controller, Fig 23, employed a galvanometer amplifier to trigger the furnace current, the galvanometer being operated by a bridge circuit, one arm of which was arranged as a temperature-sensitive resistor, close to the furnace windings; failure of the photoresistors within the galvanometer circuit resulted in this method being abandoned.

A second furnace controller based on the design of Tomizuka and Zimmerman (1959) was used later, Fig 24. This circuit employed a platinum resistance thermometer in one arm of an a.c. resistance bridge, the output of



Temperature Control Bridge

Fig 23



Temperature Controller

Fig 24

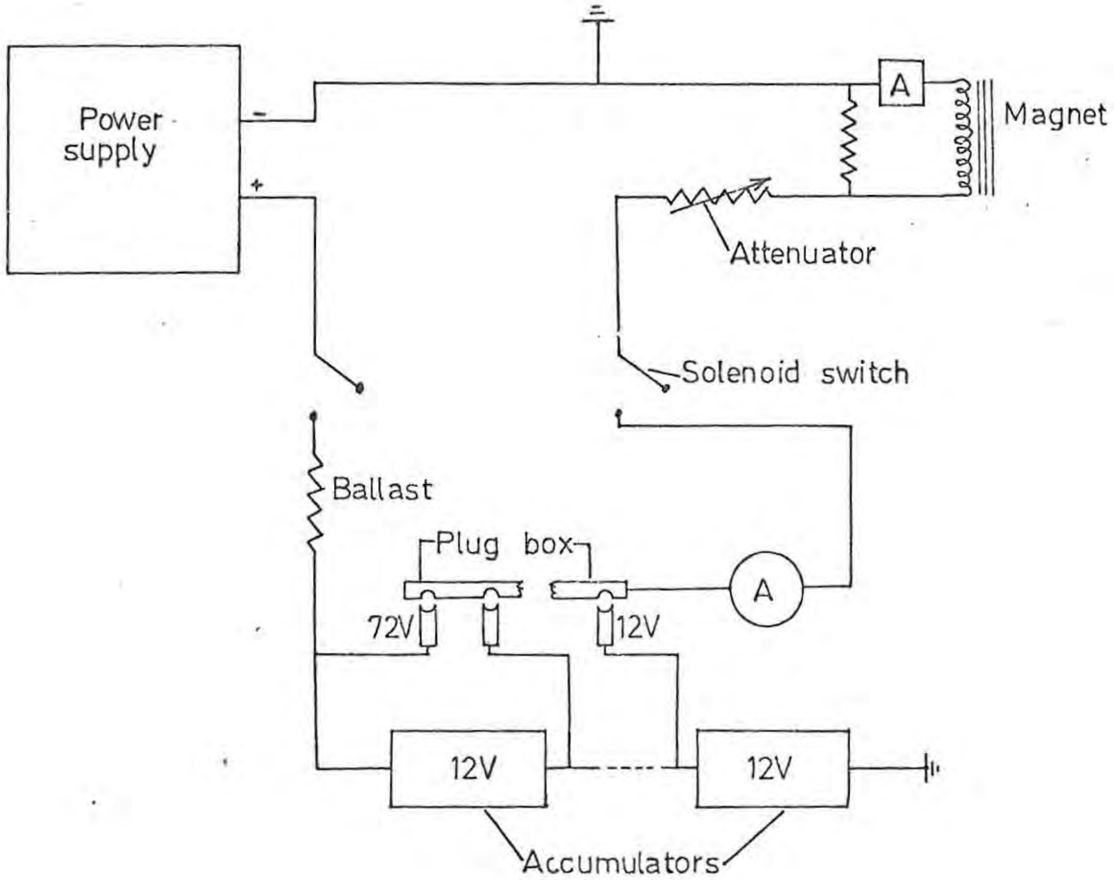
which was amplified and used to switch the furnace current; control was not very good with this instrument.

(5) The Magnet Circuit

In order to supply the magnet with power, a source of very steady d.c. was required in order to prevent fluctuations in the magnetic field.

The most convenient source of steady d.c. was found to be accumulators, after attempts to stabilise a d.c. power supply adequately had failed. A battery of 12 volt accumulators was used with a total voltage of 72 volts. These accumulators were charged by means of an S.T.C. power supply with a suitable water-cooled resistor in series; they were only charged when not in use, however, as the magnetic field from the transformer of the power supply affected the stability of the measuring circuit.

The current to the magnet was switched by means of motor car starter solenoids which were operated by means of push buttons and a relay system, Fig 25; a large knife switch was provided in series with the solenoids in order to interrupt the current should they fail.



Magnet power supply

Fig 25

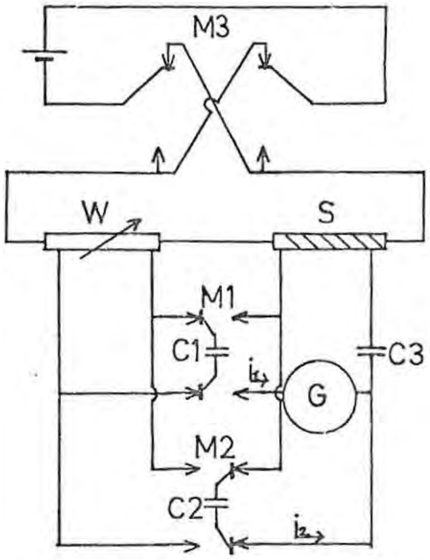
(6) The Electrical Circuit

The Dauphinée-Mooser (1955) chopper system was employed in the electrical measurements.

The design of this circuit is derived from that of the basic measuring circuit, Fig 26. The mode of operation of the circuit is as follows:
When capacitor C1 is connected to W (standard resistor), it charges up to the voltage Vw^+. C1 is then switched to the sample S by means of the chopper M3, when C1 either charges or discharges through galvanometer G until it has the voltage $-Vs^-$. This process is repeated about 30 times each second, and the result of any difference between Vw^+ and $-Vs^-$ is a pulsating direct current, i_1, through the galvanometer circuit, similarly a current, i_2, is produced by the chopper unit M2 if $Vw^- \neq -Vs^-$, i_1 and i_2 are 180° out of phase with each other. If there are no stray emfs in W or the sample, and if the forward and reverse currents are equal, then $Vw^+ = -Vw^-$, and $Vs^+ = -Vs^-$. Any difference, $\Delta V_1 = Vw^+ - (-Vs^-) = Vw^+ + Vs^-$, giving rise to current i_1 is accompanied by a corresponding difference, $\Delta V_2 = Vw^- + Vs^+ = -(Vw^+ + Vs^-) = -\Delta V_1$, giving rise to current i_2.

The pulsating currents i_1 and i_2 give rise to

a square/........



M1,M2,M3 Chopper units

Basic Measuring Circuit
(Dauphinee and Mooser 1955)

Fig 26

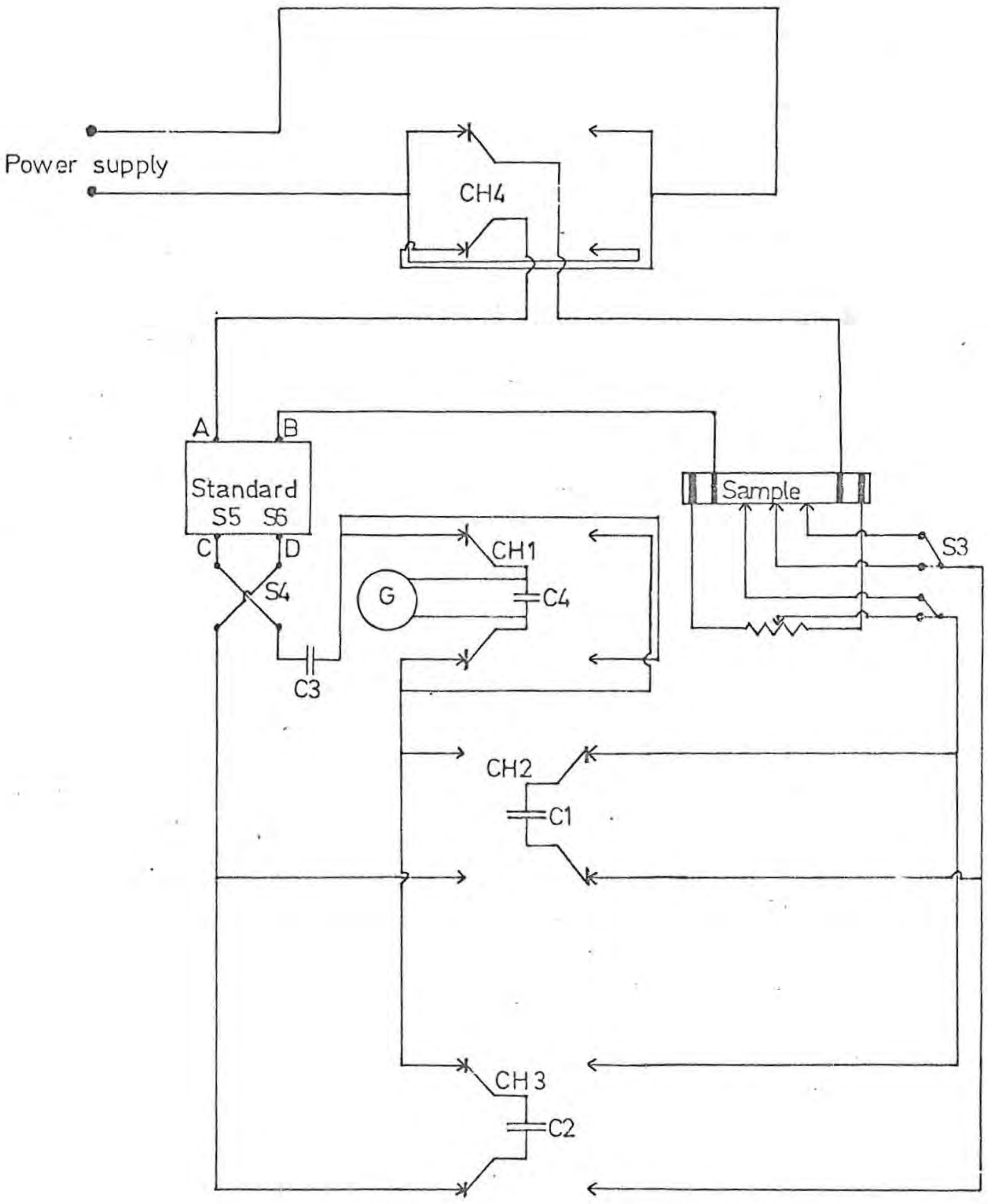
a square wave alternating current $i_1 + i_2$ which flows through the blocking capacitor C3, and the balance point where $\Delta V_1 = \Delta V_2 = 0$ and therefore $i_1 = i_2 = 0$ is shown by a null galvanometer reading. Thermal emfs, arising in W or S, are essentially direct currents, and are blocked by capacitor C3 and thus do not affect the null reading of the galvanometer.

The circuit eventually arrived at was similar to that described by Dauphinée and Preston-Thomas (1958), which is similar to the basic circuit, Fig 26, but employs a fourth chopper unit in the detector circuit in order to obtain full-wave instead of half-wave d.c. through the galvanometer, thus increasing the stability and sensitivity of the circuit, Fig 27.

Construction of Potentiometer Frame

The frame for the case of the potentiometer was made of angled aluminium which was covered with aluminium sheeting. The various components inside the case were separated by perforated aluminium shelves in order to reduce electrical interference between components and allow air circulation throughout the case, the latter being facilitated by means of a fan on the end of the chopper drive shaft. Air circulation was required in

order to/........



Bridge Circuit

Fig 27

order to maintain all of the components of the circuit at uniform temperature, and thus reduce thermal emfs.

External circuits were connected to the potentiometer by means of binding posts mounted on the outside of the case, the circuits usually being connected to these by means of "banana" plugs.

Choppers

The choppers, designed according to the specifications of Dauphinée and Woods (1955), were manufactured by Guildline Instruments of Canada, and were double-pole double-throw units driven at about 30 Hz in order to reduce 50 Hz a.c. pick up. The choppers were provided with wiping action contacts, of gold in order to prevent oxidation.

The chopper units were connected to the rest of the circuit by means of twelve-pin "Belling-Lee" plugs, in order to facilitate their rapid removal from the unit for cleaning and adjustment. The current-chopper CH4 was "make-before-break" in order to prevent sparking at the contacts and stray back-emfs, while the voltage-choppers CH1, CH2 and CH3 were all "break-before-make", in order to prevent short circuiting of the capacitors.

The Chopper/........

The Chopper Drive

The choppers were driven from a Carter 1/20 H.P. constant speed single-phase induction motor which needed to be mounted outside the case of the potentiometer in order to reduce the otherwise serious problem of a.c. magnetic pick up. This motor was connected to the choppers by means of a speedometer flexible drive cable with suitable pulleys and a rubber "O" ring drive-belt between the end of the speedometer drive and the chopper units. The diameters of these pulleys were chosen such that the chopper frequency did not give low frequency "beats" with the 50 c/s mains frequency. This also necessitated a constant chopper frequency which was provided by using this relatively powerful electric motor, whose speed was independent of the light chopper load.

Decade Resistors

The decade resistors used in the circuit were made by General Radio Co. and were divided into two sections, one for high resistance measurements, above 10 ohms, and the other for low resistance measurements. The high resistance decades consisted of a single decade box with decades of from 10 ohm to 10^5 ohm steps, while the low resistance decades consisted of three separate decade units with 0.01 ohm, 0.10 ohm and 1.00 ohm steps respectively, which were interconnected by copper wire about 2.5mm in diameter in order to reduce stray resistances to a minimum.

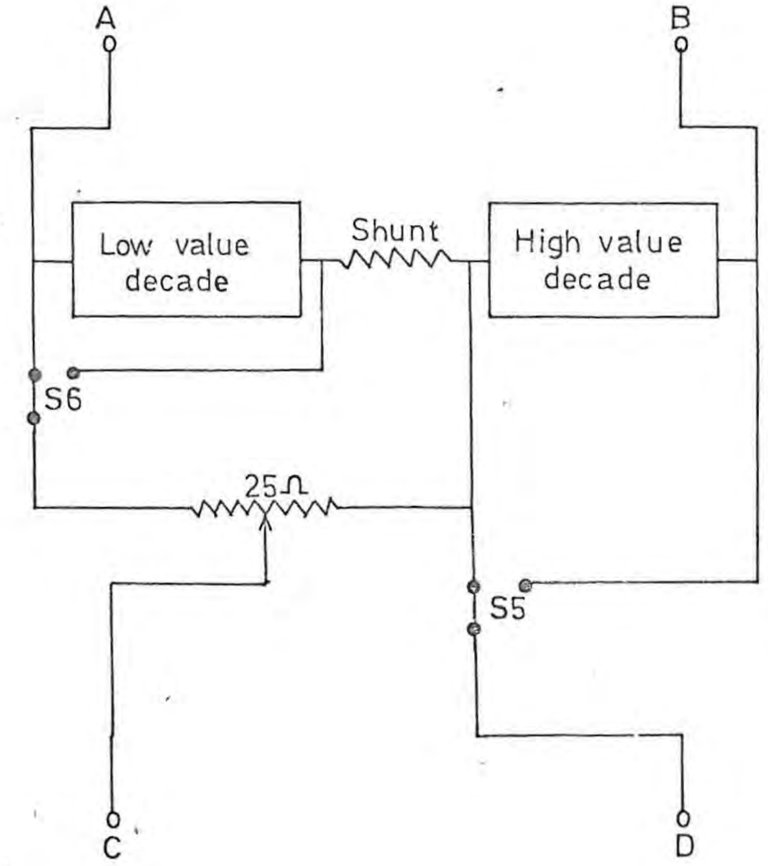
A 0.001111 ohm shunt, manufactured by Guildline, was included in the low resistance section in order to facilitate measurements in the 10^{-5} to 10^{-3} ohm range.

A low contact resistance switch (Pye), S6, was provided in the low decade section in order to switch the shunt only, or the shunt plus low resistance decades into the circuit.

A "Beckman" ten-turn, 25 ohm Helipot was included in the low resistance circuit, Fig 28, in order to obtain any fraction of the total resistance, 1 part in 3 000 being the limit of resolution of the Helipot, due to its wire winding.

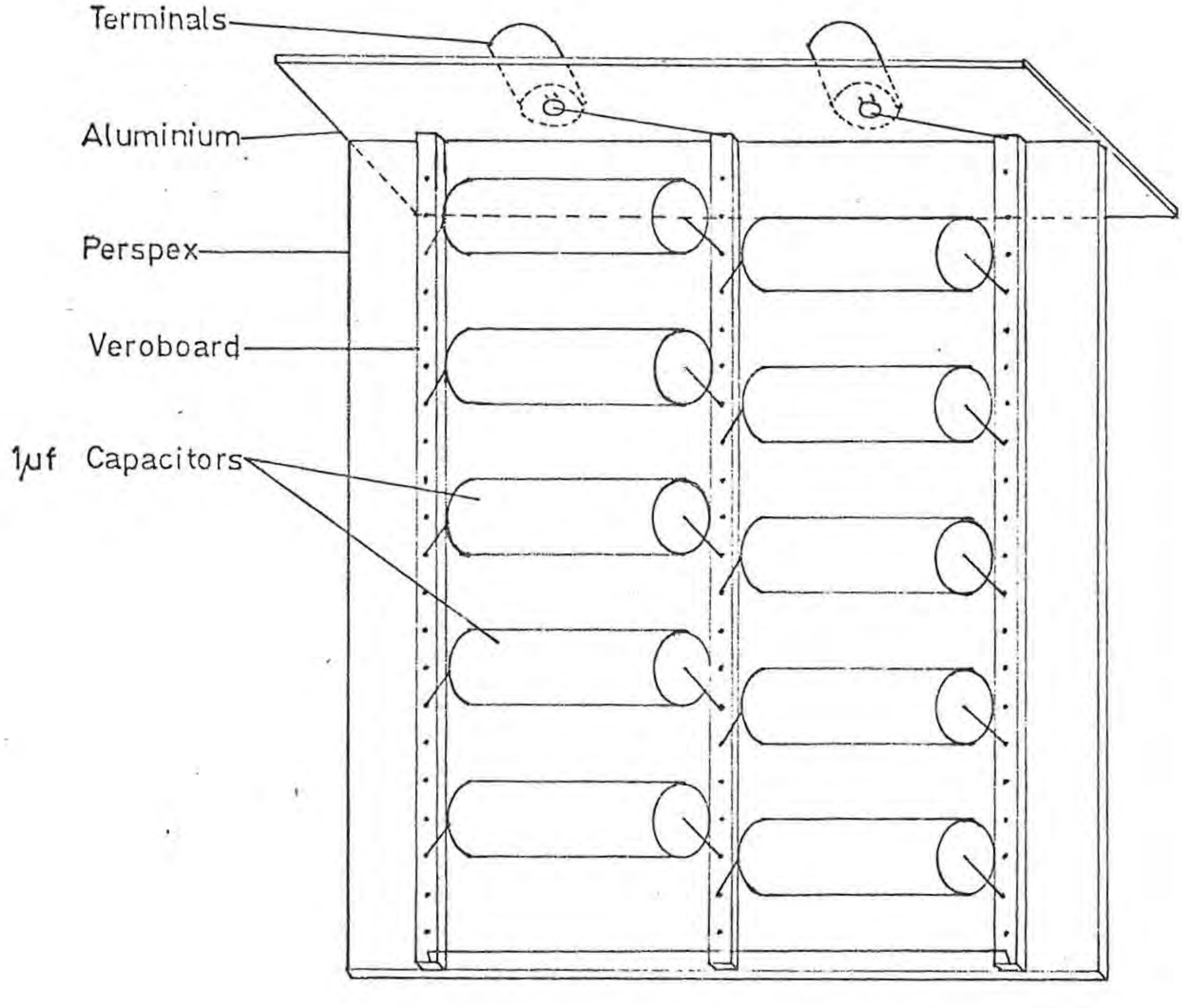
Capacitors

These were constructed by mounting a number of one micro-farad mylar capacitors onto thin strips of "Veroboard" which were cemented onto sheets of perspex with epoxy resin adhesive, Fig 29, perspex being used



Standard Resistance.

Fig 28



Capacitors

Fig 29

as it has an extremely high resistivity. One micro-farad capacitors were used in the construction of the capacitor banks, as these were relatively inexpensive and readily available.

Galvanometer

A "Tinsley" M.S. 245E galvanometer and photocell galvanometer amplifier with a sensitivity of about 200mm uV^{-1} was used as a null detector. The sensitivity of this set-up could be varied by means of a feedback control on the amplifier, and by means of a resistance-ratio circuit on the input to the amplifier, this being combined with a thermal compensator to "back-off" any stray d.c. emfs in the galvanometer circuit. The galvanometer was shunted by a 10^5 ohm resistor in order to introduce some damping, and thus improve stability.

Single strand copper wire, insulated from a surrounding grounded shield, was used in connecting up the galvanometer circuit in order to reduce thermal emfs and a c. pick up.

Both the amplifier and galvanometer were mounted on a heavy stone slab resting on cork blocks on top of a sand box in order to eliminate mechanical vibration.

The transformer/........

The transformer for the low voltage stabilised power supply to the galvanometer and amplifier was mounted on the opposite side of the sand box to the potentiometer in order to reduce a.c. pick up.

D.C. Power Supply

The d.c. supply for the potentiometer was obtained from a Philips PE 4802 constant voltage power supply, capable of delivering 15 volts at 6 amps, this being in excess of the current actually used. The choppers were protected by a 75 ohm wire-wound ballast resistor and 250 mA fuse in order to prevent short-circuiting of the power supply while both sets of contacts were closed. A reversing switch was also provided in the input in order to reverse the sign of the incoming d.c. supply, if necessary.

This power supply was mounted several metres from the potentiometer in order to avoid magnetic pick up from its transformers.

Switches

All switches used in this instrument were Pye "Precision Instrument" switches, chosen on account of their low contact potentials and resistances.

Switch Number	Type	Application
S1	D.P.D.T.	Reversal of Capacitors C1 and C2 with respect to choppers CH2 and CH3 in order to eliminate the effects of polarisation of the capacitors
S2	D.P.D.T.	
S3	D.P.D.T.	Selection of Hall or conductivity probes on sample. Later used to reverse potential appearing across potential probes of sample
S4	D.P.D.T.	Reversal of voltage appearing across standard resistance
S5	S.P.D.T.	Selection of high resistance or low resistance decade ranges
S6	S.P.D.T.	Selection of 0.001111 ohm shunt alone, or together with low value decade resistances.

(7) Testing of/.......

(7) Testing of Electrical Measuring Equipment

Capacitors

The 160 V 1 micro-farad mylar capacitors which were intended for use in the potentiometer circuit were carefully tested.

The dissipation factor was measured using a General Radio capacitance bridge, and was found to be about 5.7×10^{-4} at 30 c/s, when compared with a high quality General Radio polystyrene capacitor of the same capacitance.

Polarisation was measured by charging the capacitor followed by short-circuiting it momentarily, the residual voltage being measured using a "Lemouzy" vacuum tube voltmeter (10^{12} ohm impedance). Upon charging to about 70 V and short-circuiting, the residual voltage was found to be about 0.025 V, thus showing negligible polarisation.

The resistance of the capacitor was measured by placing it in series with a 10^{12} ohm resistor and 2 V accumulator, the voltage across the capacitor and resistor then being measured with the vacuum tube voltmeter, in this way, the resistance was found to be at least 10^{14} ohms, showing that there would be negligible loss due to leakage across the capacitor.

Capacitor Bases

The resistance of "Veroboard" and perspex were measured using the same technique as that used in measuring that of the capacitors.

In this way, the resistance between two copper strips, 4 cm apart on a sheet of "Veroboard" 30 cm long was found to be about 1.4×10^{11} ohms, this being much less than that of the capacitors.

The resistance between two strips of conductive paint 4 cm apart and 30 cm long on a perspex sheet 1.5mm thick however, was found to be about 1.5×10^{14} ohms, making it suitable as a base for the mounting of the capacitors.

Potentiometer

The potentiometer was tested and standardised by using standard four-terminal resistances in place of the sample. In this way, the low resistance decade

circuit was/........

circuit was found to have a stray resistance of about 3×10^{-3} ohms, probably due to the connecting wires and soldered terminals. This resistance was carefully determined and included in the decade value when taking measurements in this range. This was not included in the resistance of the 0.001111 ohm shunt however as this could be isolated from the rest of the circuit when necessary.

Fluctuations in the galvanometer readings leading to poor reproducibility were then investigated.

The chopper frequency was found to fluctuate appreciably but this was remedied by replacing the rubber band drive belt with a heavy rubber "O" ring and employing a more powerful electric motor than that supplied with the choppers. The frequency of the choppers was then carefully adjusted by means of layers of P.V.C. tape around the driving pulleys in order to obtain a frequency at which the galvanometer fluctuations were minimised. This did not eliminate the galvanometer fluctuations however.

The make-break ratios of the various chopper units were investigated, and it was observed that the closed time of the potential choppers overlapped that of

the current/........

the current choppers, resulting in pick-up of stray transients from the latter. Only a slight improvement was observed, however, on reducing the closed time of the potential choppers.

The effects of stray a.c. magnetic fields upon the system was investigated. The main sources of such fields were found to be the chopper drive motor, galvanometer transformer, d.c. power supply transformers and the power supply to the sample furnace. These sources of interference were all reduced however, by placing the units at distances of at least 1 metre from the chopper units, which resulted in a reduction in the galvanometer fluctuations of about 90%, and permitted measurements limited only by the resolution of the Helipot, which was about 3×10^{-7} ohms on the lowest resistance range. Negligible drift was observed with the circuit in this form, provided that the galvanometer was allowed to stabilise overnight before taking readings.

(8) Experimental Procedure

In making resistivity and Hall coefficient measurements, the dimensions of the sintered VN samples were measured, using a travelling microscope. These measurements were later used in obtaining absolute

resistivity values./........

resistivity values. The samples were then inserted into the conductivity cell and the electrical pressure contacts applied to the samples, the individual contacts each being checked by means of a "multimeter" in order to avoid excessively high contact resistances, although these are not important from the measurement point of view in the four-probe method.

The conductivity cell was then placed into the furnace tube which was in turn held between the poles of the magnet and the whole system was flushed with the carrier gas (usually high-purity nitrogen) for at least 12 hours, a flow rate of about 50 ml/min being used through the furnace tube of volume 1 000 ml.

The resistance of the sample across the potential probes was then measured at room temperature, for both input current directions, the average of the two readings being taken as the true value, this room temperature measurement being made at the start of each run. Both current directions were employed in order to eliminate errors arising from slight drifts in the galvanometer circuit which would cause the null point to be offset to some extent from the galvanometer zero. The effective resistance across the Hall probes was measured similarly, for both magnetic field directions, and this

resistance, together/........

resistance, together with the magnetic field strength was used in the calculation of the Hall coefficient.

The temperature of the sample was then raised in 50-75 degree steps and allowed to equilibrate at each temperature, 25-30 minutes being required for this; the resistance and Hall coefficient were obtained at each temperature as detailed above. The maximum temperature which was reached was usually between 700 and 800°C, after which the sample was cooled in steps, further measurements being made during cooling. The sample was finally allowed to cool to room temperature in the carrier gas stream, and the new room temperature resistance again measured.

In several of the later runs, the sample was first heated to the maximum temperature and kept at this for about one hour, in order to condition it, before commencing readings - first decreasing, and then raising the temperature in steps, until the maximum temperature was finally reached again, after which the sample was allowed to cool, and the new room temperature resistance again measured.

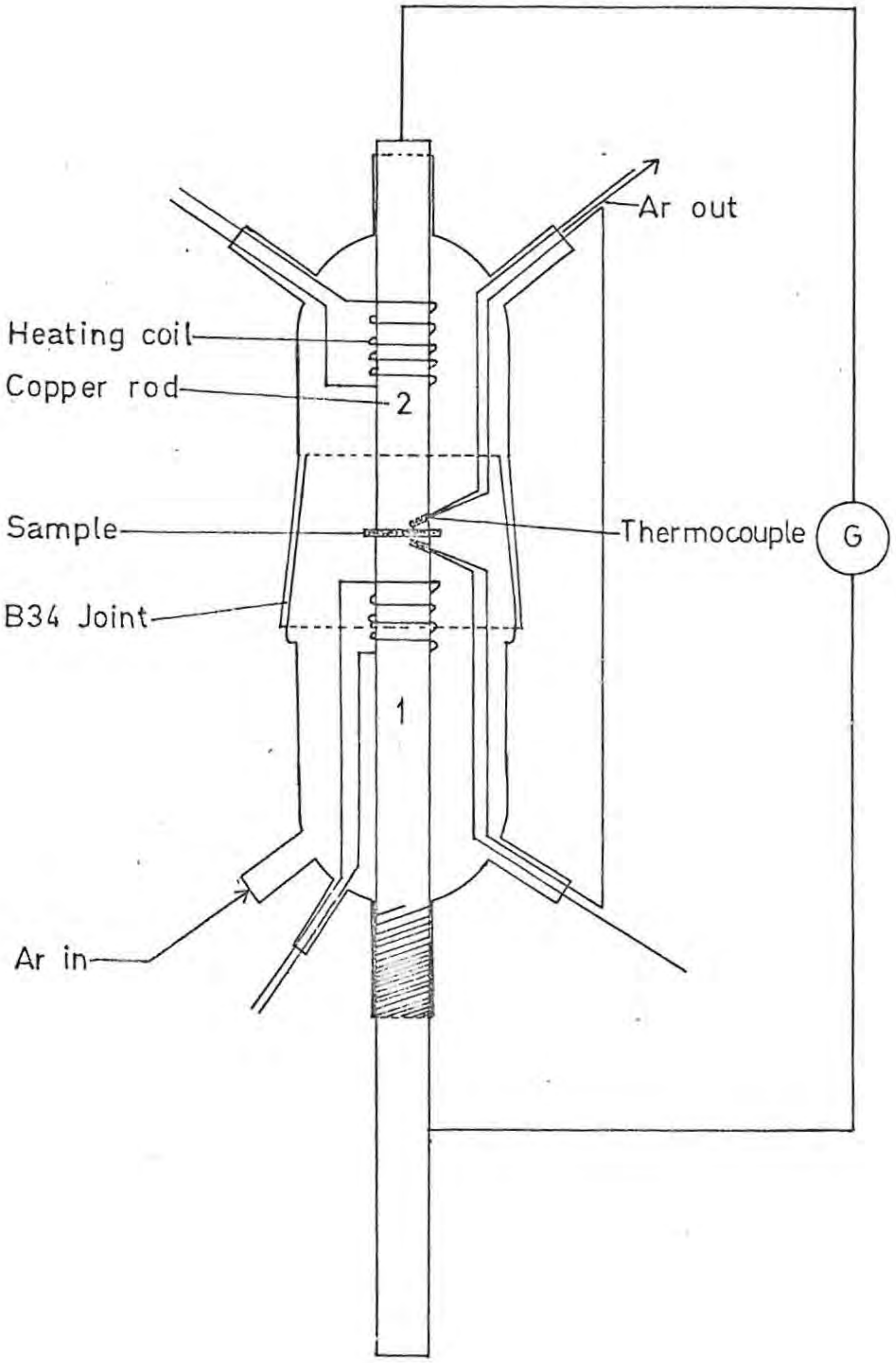
(9) Thermoelectric/........

(9) Thermoelectric Power Measurements

Thermoelectrical power measurements were made on VN samples in order to ascertain the sign and mobility of the charge carriers.

In the apparatus used, Fig 30, the sample was held between two copper rods which were both provided with heating elements and which were each controlled by a separate variable auto-transformer. The heating coils were insulated from the rods by means of asbestos paper. The ends of the rods were inside a glass envelope which was provided with a large "Quickfit" joint in order to enable the rods to be separated when inserting or removing the sample. The lower copper rod was glued into the glass envelope, while the upper rod was a sliding fit, being provided with a "stop" in order to prevent it from falling out of the envelope completely. The weight of the upper rod was sufficient to hold the sample firmly in place. The glass envelope was provided with inlet and outlet tubes which carried leads for the heating coils and thermocouples and enabled nitrogen or argon to be passed through the cell while taking measurements.

The copper rods were fitted with glass-insulated, copper/constantan, differential thermocouples near their



Apparatus For Thermoelectric Power Determination

Fig 30

ends, in order to measure the temperature difference across the sample, and also the mean sample temperature. Both the thermocouple and heater leads were insulated with a number of short glass tubes, enabling them to move freely.

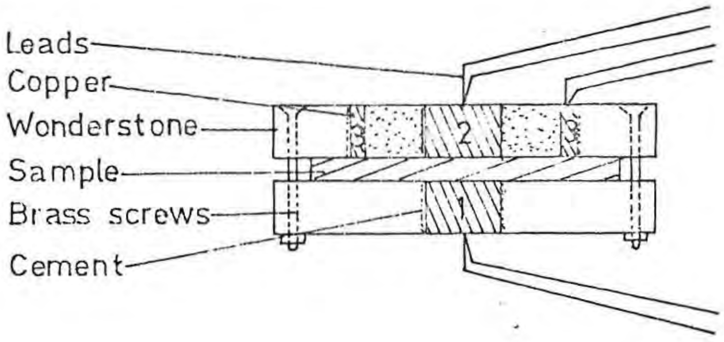
When measurements were made using this apparatus, the temperature of the two rods were adjusted so as to obtain a relatively small temperature difference (about 15^{o}) between them, while the mean temperature of the sample could be varied between about $20^{o}C$ and $200^{o}C$. The heating elements were calibrated separately beforehand so that a desired temperature, and temperature difference, could be readily attained.

(10) Surface Conduction Measurements

A number of surface conduction measurements, as opposed to bulk conduction measurements, were made on VN samples at temperatures of about $400^{o}C$, in order to determine the effect of oxidation and reduction on surface conductivity.

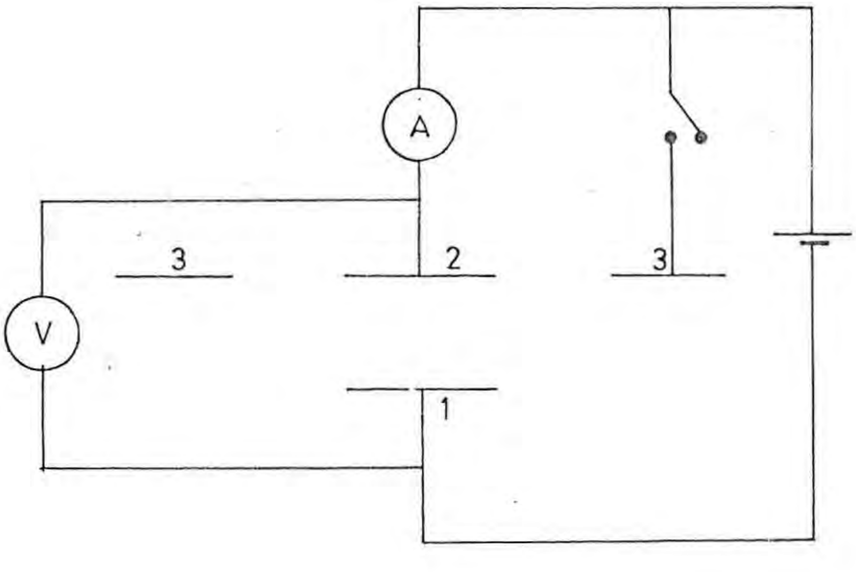
A special conductivity cell, Fig 31, was used for this purpose. The one side of the cell was fitted with a plain cylindrical electrode (1), the other side being fitted with a similar cylindrical electrode (2), surrounded by an annular guard electrode (3), the two cylindrical electrodes being opposite each other. These electrodes, which were made of copper, were held into a Wonderstone base by means of "Alundum (305)" refractory cement. The two halves of the cell were held together by means of brass screws and nuts, the sample being clamped between the two sets of electrodes together with a chromel/alumel thermocouple, used to monitor the cell temperature. The cell was enclosed in a glass envelope which was closed at one end, the other end being provided with a large "Quickfit" joint in order to exclude air from the sample while permitting its insertion into and removal from the envelope. Provision was also made for the introduction of various gases into the tube while taking measurements. This tube was placed inside a tube furnace whose temperature could be regulated by means of an "Electrothermal" energy regulator.

In the electrical circuit used, Fig 32, an ammeter was placed in series with the cylindrical electrode (2), which was surrounded by the guard ring, and the positive terminal of the d.c. supply. The negative terminal of the supply was connected to the other cylindrical electrode (1), while a switch was connected between the positive terminal of the supply



Surface Conductivity Cell

Fig 31



Electrical Circuit

Fig 32

and the guard electrode (3). A "Scalamp" galvanometer was connected across the two cylindrical electrodes in order to measure the potential difference across the sample, and thus obtain an estimate of the bulk conductivity.

When making measurements with this cell, the sample tube was first flushed with the carrier gas for about 3 hours, after which the furnace temperature was raised and allowed to come into temperature equilibrium, about 10 hours being required. Surface conduction measurements were then made on the sample in both oxidising and reducing atmospheres.

In order to determine the surface conduction, the current through the ammeter was first recorded with the switch to the guard ring open, the switch was then closed and the current again recorded, the difference between the two readings being due to, and being a measure of, the current flowing through the guard ring, and therefore of surface conduction.

(11) Hot-Pressed Samples

In order to obtain dense, non-porous VN samples with low interparticle resistances, a number of samples were hot-pressed.

Several samples were hot-pressed by the Diamond Research Laboratories in Johannesburg.

The VN powder which was employed for the pressing of these samples was that obtained from Dr. Kieffer and was pressed at 1500°C for 5 minutes in resistively heated graphite dies. This procedure resulted in the production of suitably dense samples of from 1 t 3 mm thick, depending on the quantity of VN powder used.

(12) Density Determinations

The density of the pressed VN was determined by measuring the volume of a weighed quantity of the material.

The mass of about 1 g of VN fragments was determined to ± 0.2 mg. These fragments were then introduced into a microburette containing a known volume of dibutyl phthalate, which had been evacuated in order to remove any dissolved air. After introduction of the VN, the burette was again evacuated in order to remove any air bubbles adhering to the VN particles, and the volume of the dibutyl phthalate plus the VN was then determined, the differences between the first and second volumes giving the volume of the VN.

(V) RESULTS

(1) RESISTIVITY MEASUREMENTS

In the normal four-probe technique, determination of absolute resistivities requires measurement of the dimensions of the sample and of the separation of the potential probes on the sample surface. Using a travelling microscope, these dimensions could be determined to about 0.004 cm, representing an accuracy of about 4% for the thickness of the sample, (a micrometer was not used in these measurements as these samples were very fragile). The resistivity is then obtained from:-

$$\rho = \frac{Ra}{\ell}$$

where R = resistivity measured between probes

ℓ = probe separation

a = cross-sectional area

When using the van der Pauw (1958) method, however, only the sample thickness (d) is required, and was measured to within 2% using a micrometer. The resistances $R_{12,34}$ and $R_{23,41}$ across two sets of adjacent contacts were measured and substituted into the equation:-

$$\exp(-\pi R_{12,34}\, d/\rho) + \exp(-\pi R_{23,41}\, d/\rho) = 1$$

which has/........

which has a solution of the form:-

$$\rho = \frac{\pi d}{\ln 2} \left(\frac{R_{12,34} + R_{23,41}}{2} \right) f \left(\frac{R_{12,34}}{R_{23,41}} \right)$$

In order to check the van der Pauw method, the resistivities of a number of differently shaped brass and bronze samples were measured, employing both methods for each sample. Results were very consistent by both methods, but the van der Pauw values were lower by a factor of 1.045 when checked against the four-probe method; therefore, to correct for this discrepancy and obtain resistivities appropriate to the established method, the readings obtained in all of the later runs were multiplied by this factor. No reason for the discrepancy could be found, either on checking the equations and method, or on communicating with Dr. van der Pauw himself, but the correction procedure described renders the results consistent with the standard four-probe procedure.

The absolute resistivities, at room temperature, of VN were found to average about 270 micro-ohm cm for cold-pressed samples, and about 101 micro-ohm cm for hot-pressed samples. The average resistivities recorded in the present investigation are of the same order as those reported by other workers, but no resistivities as low as those of Samsonov and Verkhoglyadova (1962)

or of/........

or of Agte and Moers (1931) have been recorded, as shown in the table following:-

Author	Resistivity/micro-ohm cm
Samsonov and Verkhoglyadova (1962)	85
Agte and Moers (1931)	86
Present investigation Hot-pressed samples	101
Hoy (1963)	100
Friedrich and Sittig (1925)	200
Present investigation Cold-pressed samples	270
Epelbaum and Ormont (1947)	332

(2) OHM'S LAW

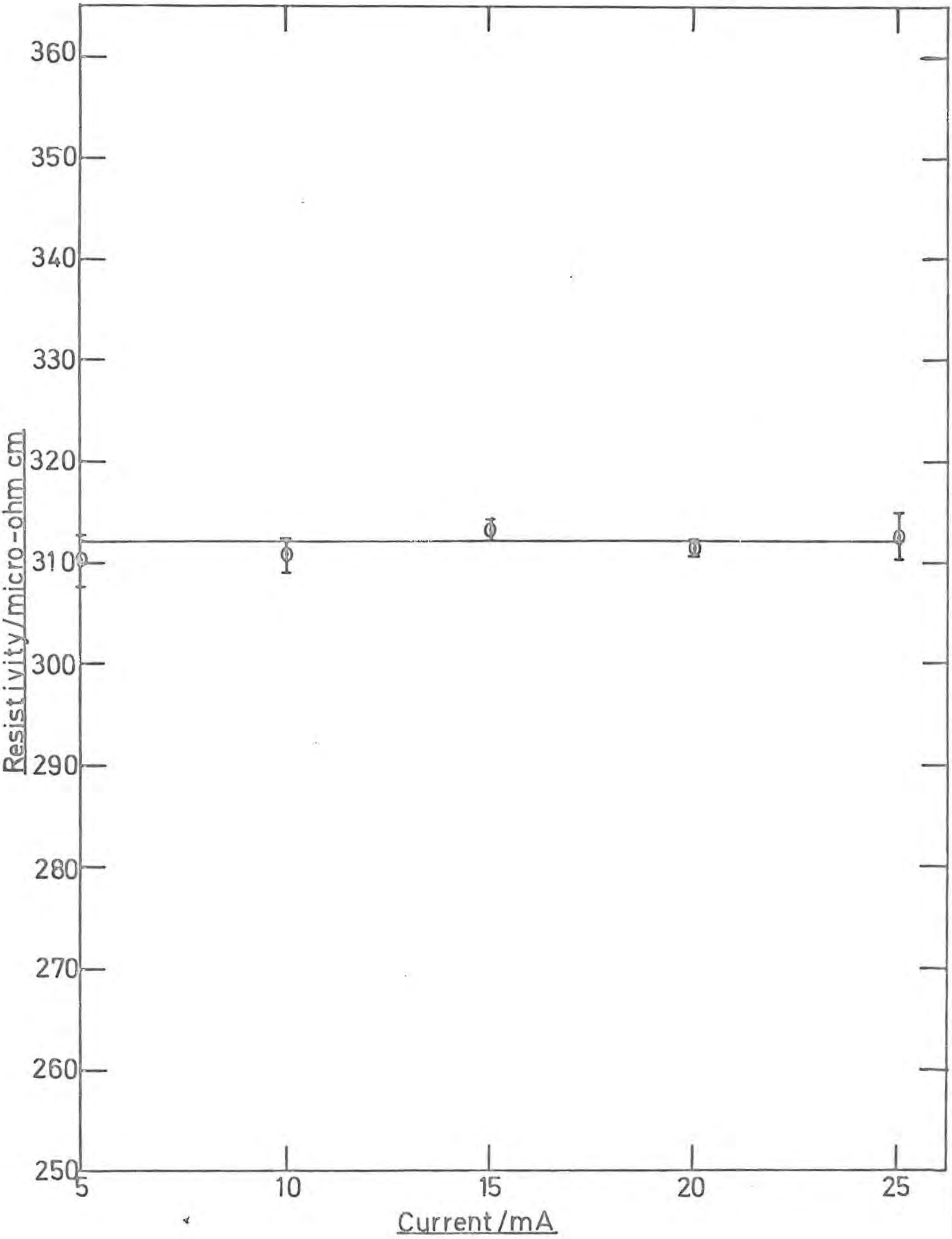
In order to verify that VN was, in fact, an ohmic conductor with the contact system and conditions used, resistivity measurements were made on a VN sample at 31°C using currents of between 5 and 25 mA, and forward and reverse current directions, as most of the measurements were made in this current range. The resistivities observed in this way, Run 16.1, were found to be independent of current, the values ranging from 310.1 to 313.3 micro-ohm cm. This variation in resistivity lay at the limit of detection of the bridge, which was

about 2.5/........

RUN 16.1

VN(XXVI) A

Atmosphere: High purity nitrogen.



about 2.5 micro-ohm cm at that stage of the investigation.

(3) RESISTANCE/TEMPERATURE BEHAVIOUR

The resistance/temperature behaviour of a number of VN samples was investigated in both reducing and oxidising atmospheres, see Table 2.

The resistivities of the samples were measured both while heating and while cooling the samples. No variation in the measured resistivity was observed, at room temperature, upon adjusting the positions of the contacts on the surface of the samples. In general, the heating and cooling curves for the hot-pressed samples were identical, but slight differences in the two curves were usually observed in the case of cold-pressed samples, probably as a result of the effects of gases which were absorbed from the ambient atmospheres at elevated temperatures, or slight annealing effects.

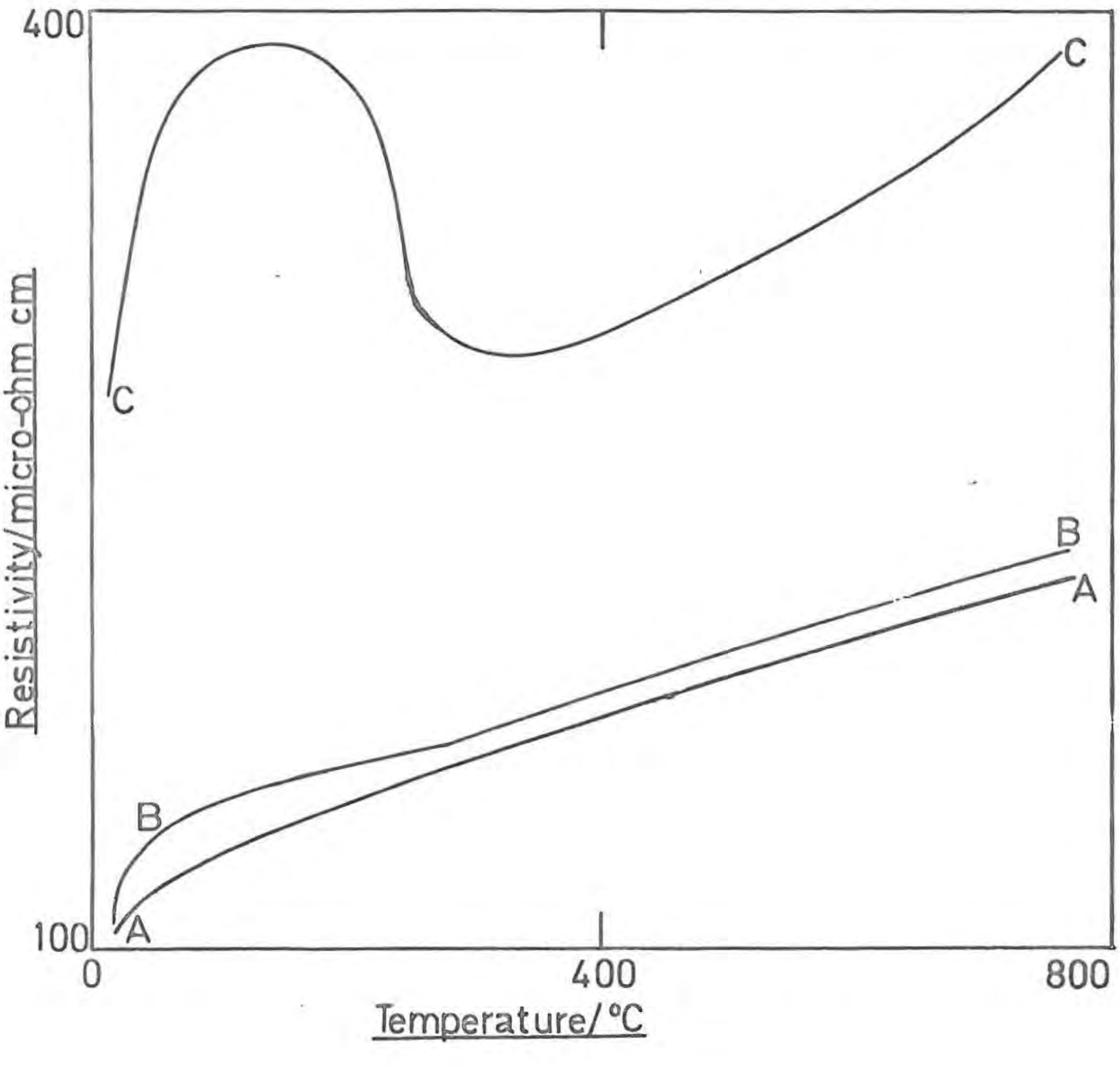
In general, metallic behaviour was observed, i.e. the resistivity increased with increasing temperature, temperature coefficients of resistivity of from 0.12-0.40 micro-ohm cm K^{-1} (at 500°C) being observed for cold-pressed samples, and from 0.060-0.072 micro-ohm cm K^{-1} (at 500°C) for hot-pressed samples.

TABLE 2

SUMMARY OF RESISTANCE VS TEMPERATURE BEHAVIOUR OF VANADIUM NITRIDE

Run No.	Sample No.	Prepared From:-	Pressing Conditions	Type of Anomaly	Temperature at which Anomaly observed /°C	Slope at 100°C		Slope at 500°C	
						$\frac{d\rho}{dT}$ / micro-ohm cm K^{-1} x 10^{-1}	$\frac{1}{\rho}\frac{d\rho}{dT}$ / K^{-1} x 10^{-3}	$\frac{d\rho}{dT}$ / micro-ohm cm K^{-1} x 10^{-1}	$\frac{1}{\rho}\frac{d\rho}{dT}$ / K^{-1} x 10^{-4}
5	VN(XXII)1	NH_4VO_3 & NH_3	Cold	A	100	3.20	1.34	2.40	7,14
19	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.90	0.83	1.30	4.57
20	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.92	0.87	1.30	4.76
21	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.87	0.80	1.29	4.52
22	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	2.00	0.82	1.22	4.15
31	VNBH1	[*]V & N_2	Hot	A	100	0.85	0.76	0.72	5.05
38	VNAH1	[*]V & N_2	Hot	A	100	0.73	0.72	0.66	5.16
23	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	B	100–350	–	–	1.09	2,62
35	VNBH2	[*]V & N_2	Hot	B	25–400	–	–	0.60	4,74
36	VNBH3	[*]V & N_2	Hot	B	25–400	–	–	0.69	4,87
34	VNAC1	[*]V & N_2	Cold	C	125	10.17	2.99	1.21	3.71
37	VNAC2	[*]V & N_2	Cold	C	160	3.48	1.12	1.51	4.34
39	VNAC3	[*]V & N_2	Cold	C	215	4.91	1.58	1,00	2.93
18	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	1.33	5.34
25	VN(XXVI)B1	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	4.00	6,86
27	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	2.13	6,63
28	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	1.78	6.08
32	VNBH1	[*]V & N_2	Hot	None	–	–	–	7.14	5.06
33	VNBH1	[*]V & N_2	Hot	None	–	–	–	6.92	5.15

[*] Supplied to us by Dr. R. Kieffer.



Types Of Anomalous Behaviour In VN

Fig 33

Several different types of anomalous behaviour (deviations from metallic behaviour), for both hot- and cold-pressed samples were observed in plots of resistivity vs temperature, all below about 400°C. Three types, which are somewhat arbitrary groupings of anomalies, have been distinguished. A graphical summary of the conclusions appears in Fig 33.

(a) Type A Anomalies

In the anomalies of type A, the curve of resistivity vs temperature has a relatively high slope at low temperatures (below about 120°C), this slope then decreases over a range of about 50° reaching a constant slope between 150 and 200°C. In Run 19 for example, the slope below 100°C is 0.19 micro-ohm cm K^{-1}, while above about 170°C it is 0.13 micro-ohm cm K^{-1}.

This type of behaviour was observed in seven runs, cycled between 25 and 700°C, on two cold- and two hot-pressed samples.

(b) Type B Anomalies

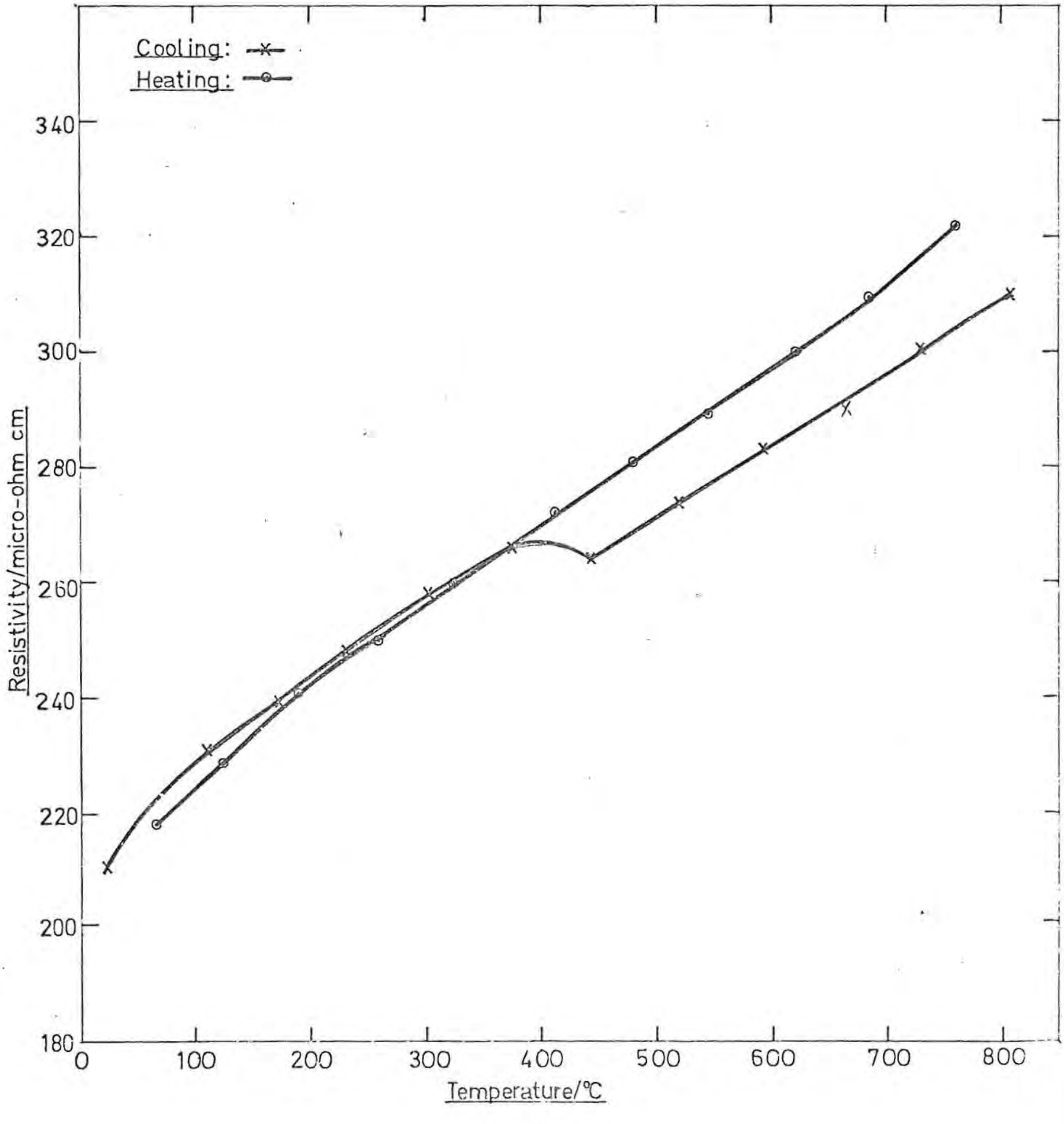
In the case of type B anomalies, the slope of the resistivity vs temperature curve has a large value at

low temperatures/........

RUN 19

VN(XXVI)A

Atmosphere:High purity nitrogen



low temperatures, but gradually decreases over a temperature range of about 300°. Between 350 and 400°C, the slope again increases to a constant value which is maintained up to the highest temperatures reached.

This type of behaviour was observed in 3 runs, on one cold- and two hot-pressed samples.

(c) Type C Anomalies

In anomalies of type C, the curve of resistivity vs temperature had a very high slope at low temperatures, about 0.5 micro-ohm cm K^{-1} being typical. The curve reached a maximum at between 100 and 250°C and then fell to a minimum at about 300°C, above which temperature a monotonic, slightly super-linear rise in resistivity up to the maximum temperatures reached was observed.

This type of behaviour was observed in 3 runs on 3 cold-pressed samples, prepared by the direct nitriding of vanadium metal, but was not observed on hot-pressed samples, or on cold-pressed samples prepared from VCl_3.

(4) EFFECTS OF/........

(4) EFFECTS OF PREPARATIVE AND PRESSING CONDITIONS ON RESISTANCE/TEMPERATURE BEHAVIOUR

The preparative conditions and the pressing conditions appeared to modify the anomalous behaviour of the VN samples. Thus type A anomalies appeared under all preparative and sintering conditions, and were observed in the case of cold-pressed samples prepared by heating NH_4VO_3 in NH_3 (Run 5), in samples prepared from VCl_3 (Runs 19-22), and were also observed in the case of samples prepared by hot-pressing VN prepared by direct nitriding of vanadium metal (Runs 31 and 38).

Anomalies of type B were observed in both hot-pressed VN (Runs 35 and 36) which was made from VN prepared by direct nitriding of vanadium, and in a sample prepared by cold-pressing and sintering VN prepared from VCl_3 (Run 23).

Anomalies of type C were only observed in cold-pressed samples of VN prepared by nitridation of vanadium metal (Runs 34, 37 and 39).

A number of VN samples showed no anomalous behaviour, and here again both hot- and cold-pressed VN samples, prepared from both VCl_3 and vanadium metal, were involved (Runs 18, 25, 27, 28, 32 and 33). It appears that only the anomalous behaviour of type C depends upon the preparation and pressing conditions of the samples, while those of type A and B are independent of the method of preparation or of pressing of the samples.

It was observed that samples which were hot-pressed showed a much lower resistivity (about 100 micro-ohm cm) than those that had been cold-pressed (about 270 micro-ohm cm), this is probably on account of the greater density of the former, which is from 97-100% of the X-ray crystal density, while that of the latter is only about 72-75% of the theoretical. The higher resistivity of the low density cold-pressed samples can probably be attributed to the effects due to interparticle resistances which would be expected to be very much higher than those of dense, hot-pressed, samples.

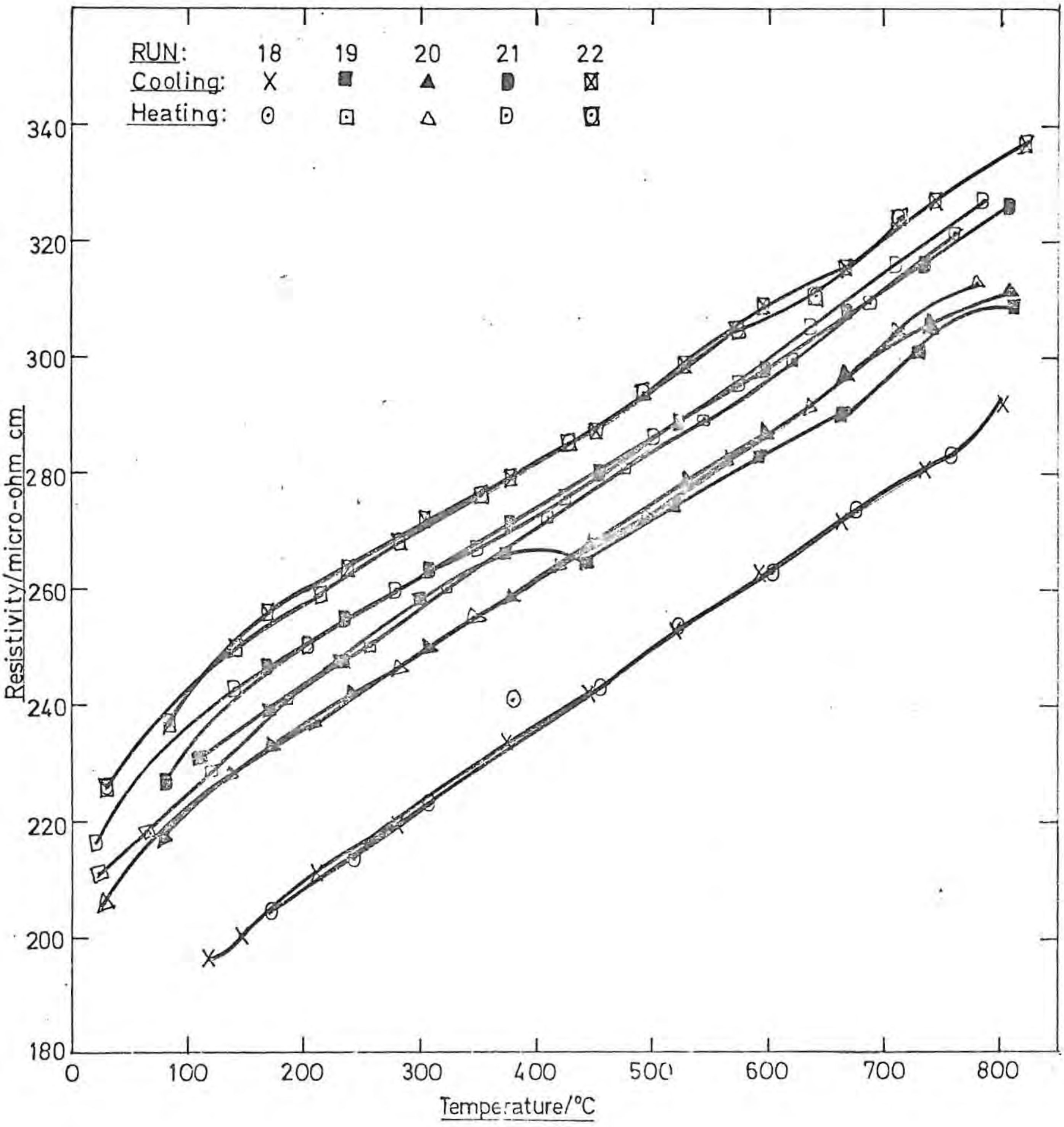
(5) REPETITIVE RUNS ON THE SAME SAMPLE

A series of runs (18-22) was conducted on a single cold-pressed VN sample in order to determine the effects of successive heating and cooling cycles on the one sample. This sample was prepared from VCl_3, by reducing in hydrogen followed by nitridation with high purity nitrogen. It was cold-pressed and then sintered

RUNS 18–22

VN(XXVI)A

Atmosphere: High purity nitrogen



at 1100°C in a high purity nitrogen atmosphere. This series of runs was conducted in an atmosphere of high purity nitrogen which was first passed over copper turnings heated to 375°C (in order to remove any residual oxygen). During this series of runs it was observed that in all, except Run 20, the resistivity of the sample was increased, the room temperature resistivity increasing by 18.5% during 5 runs, showing a mean increase of 3.7% per run.

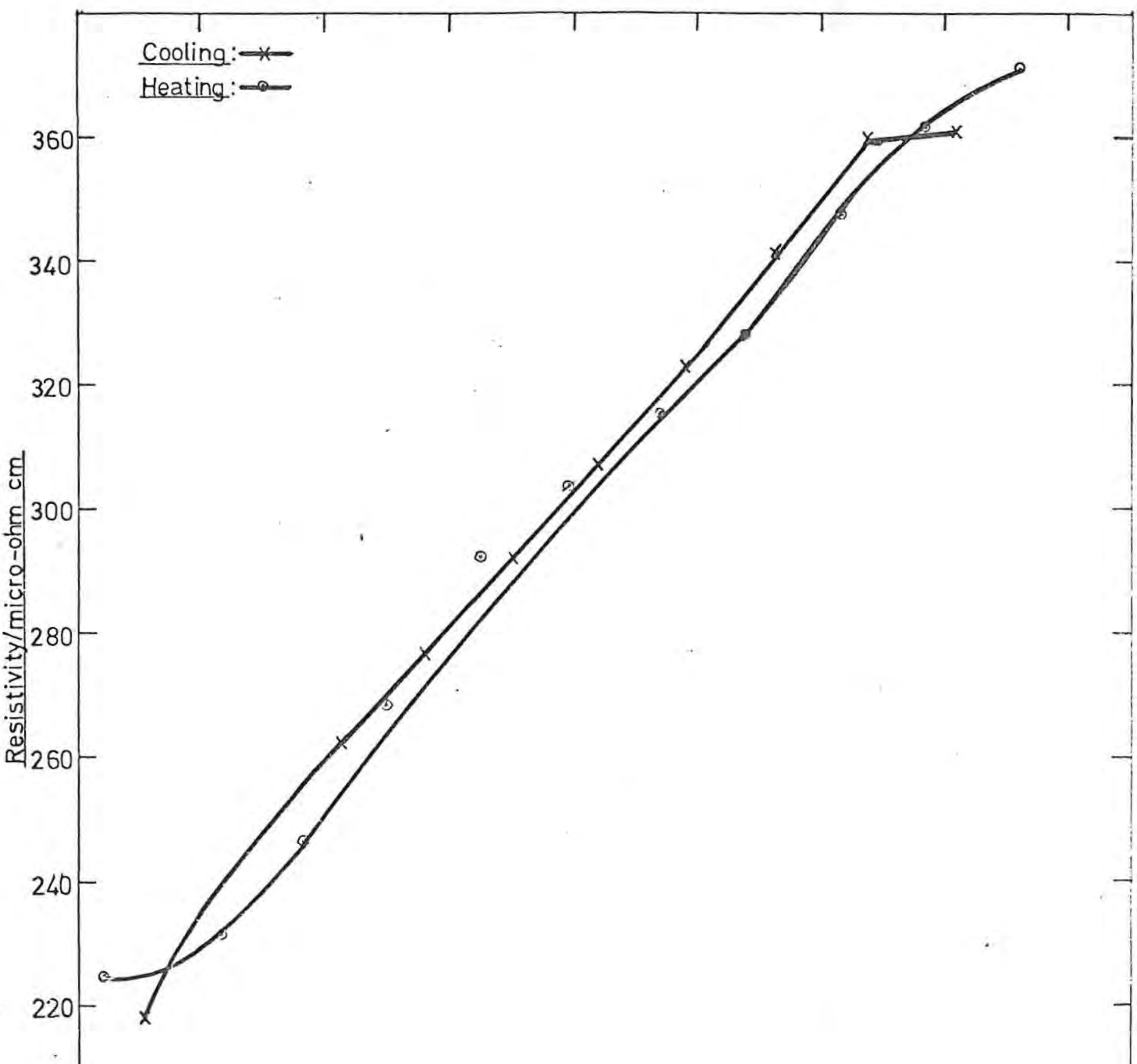
It was observed that, in the case of cold-pressed samples, the overall resistivity increased when run in a nitrogen plus about 10 ppm oxygen atmosphere, as observed in Runs 18-22, whereas it increased to a very much smaller extent or even decreased, when the samples were run in a reducing atmosphere, as in Runs 27 and 28, which were conducted in a nitrogen + 8% hydrogen atmosphere, and in which the room temperature resistivity was observed to fall by about 12%.

In the case of hot-pressed samples, the room temperature resistivity was observed to fall slightly on a first run in a nitrogen atmosphere, a fall in resistivity of 2.5% being observed in Runs 31 and 32 on the same sample. However, this is probably due to some annealing effect, as later measurements showed that the ambient atmosphere had negligible effect on the resistivity behaviour

RUN 27

VN(XXVI)B

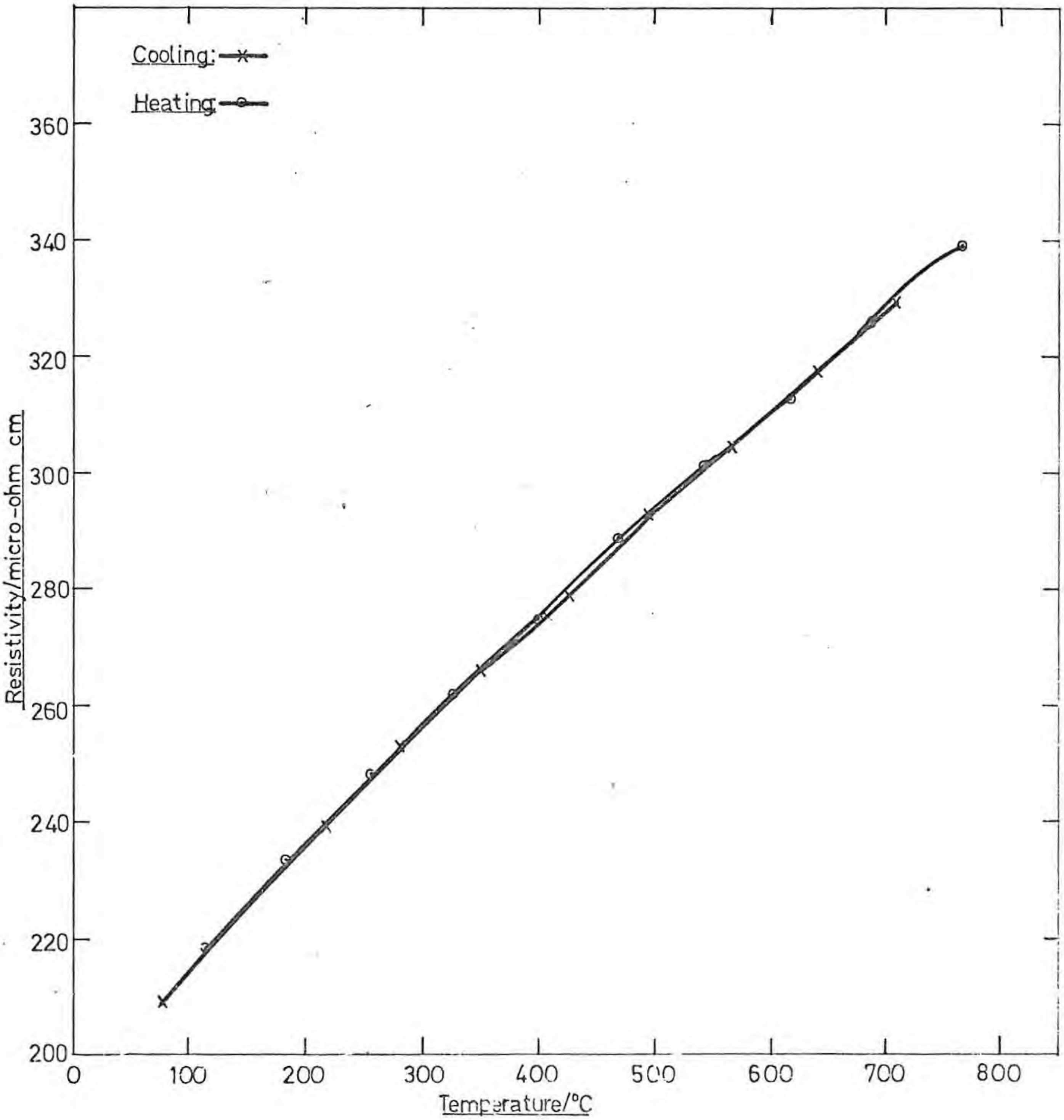
Atmosphere: Nitrogen/8%Hydrogen



RUN 28

VN(XXVI)B

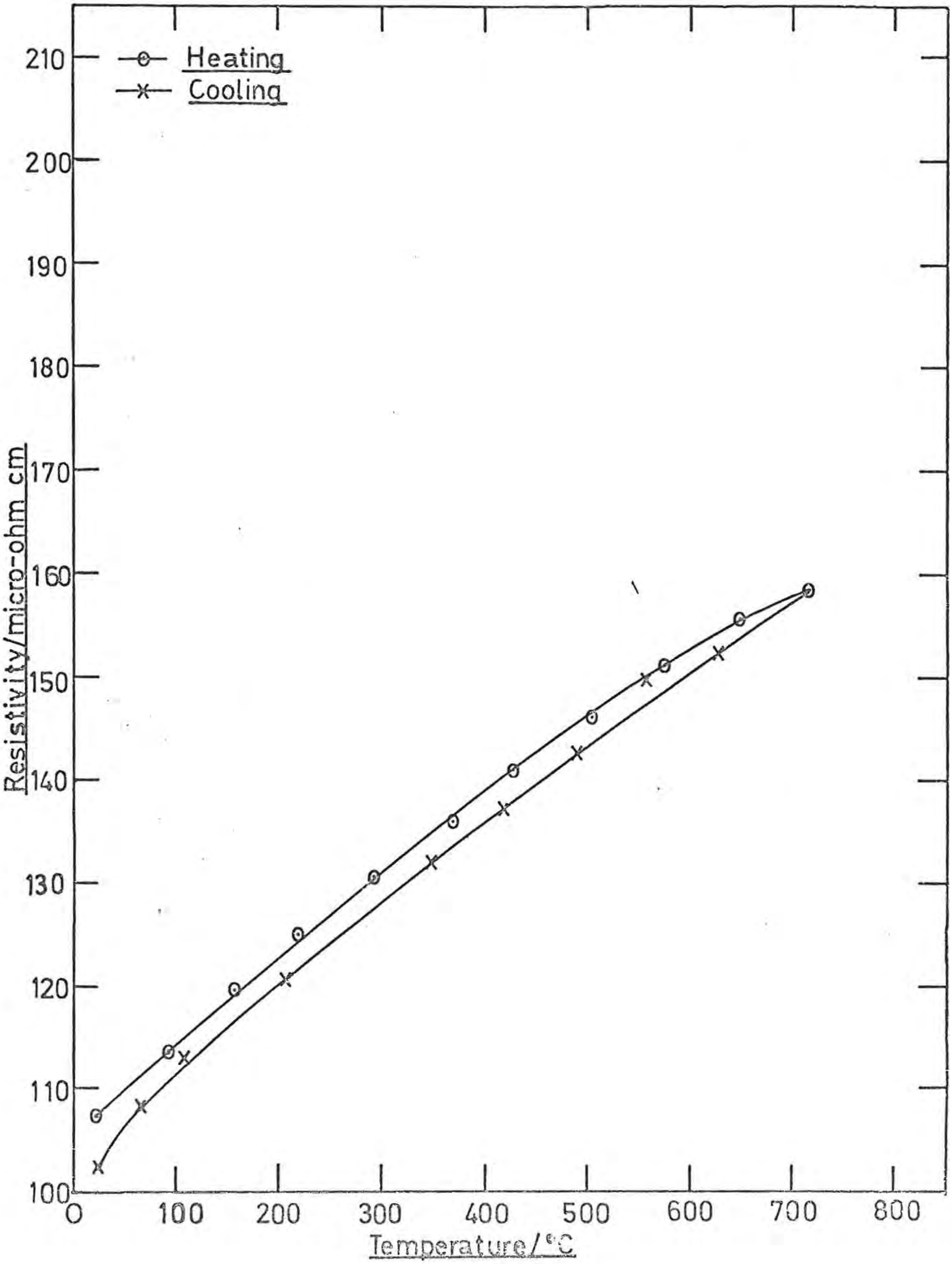
Atmosphere: Nitrogen/8% Hydrogen



RUN 31

Hot Pressed VN(B)

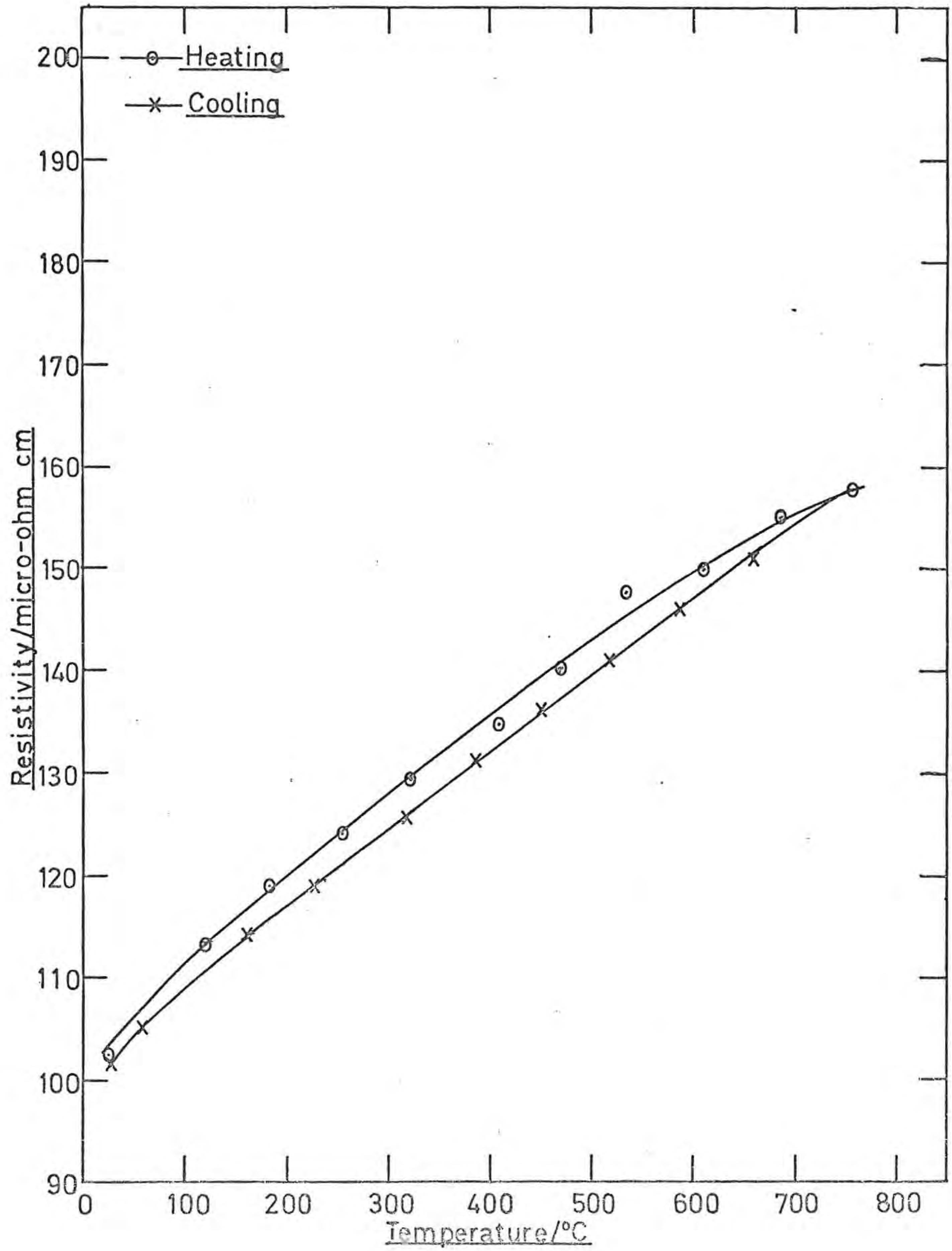
Atmosphere: High purity nitrogen



RUN 32

Hot Pressed VN(B)

Atmosphere:High purity nitrogen



of these samples.

Despite the observation that the overall resistivity of the sample used in Runs 18 to 22 showed an increase, the slope of the curve of resistivity vs temperature in Run 22 was found to have decreased by about 10% from that observed in Run 18; later runs, in general, exhibited a slightly smaller slope than earlier ones. In Runs 27 and 28, in nitrogen and hydrogen mixtures the slope of resistivity vs temperature also decreased by about 23%, the two curves appearing to converge to the same resistivity at about 163 K. In Runs 31 and 32, on hot-pressed VN, the slope of the resistivity vs temperature curve was also observed to decrease slightly, but this was probably due to the slight difference in overall resistivity, since $\left(\frac{1}{\rho}\frac{d\rho}{dT}\right)_{500^{\circ}C}$ was substantially the same, at 5.05×10^{-4} K^{-1} and 5.06×10^{-4} K^{-1}, for Runs 31 and 32 respectively.

(6) SINTERING CONDITIONS

In an attempt to produce dense samples, cold-pressed compacts were sintered at $1100^{\circ}C$ for about 48 hours. However this resulted in low density samples, of density of the order of 70-75% of the X-ray crystal density. A number of samples were sintered at $1300^{\circ}C$ instead of $1100^{\circ}C$, but, again, their density was only

about 75%/........

TABLE 3

DENSITIES OF VN SAMPLES

Preparative Conditions	Pressing Conditions	Sintering Temperature /°C	Density/ gml^{-1}	Percentage of X-ray crystal density
VCl_3 & (N_2+H_2)	Cold	1100	4.4±0.4	72±6
VCl_3 & (N_2+H_2)	Cold	1300	4.6±0.4	75±6
V & N_2	Cold	1100	4.7±0.3	77±5
V & N_2	Hot	-	6.15±0.23	100.0±3.8

about 75% of the theoretical, and their room temperature resistivity was high, being about 250 micro-ohm cm. These samples were severely cracked and distorted and could not be employed in high-temperature restitivity measurements. See Table 3.

(7) HOT-PRESSED SAMPLES

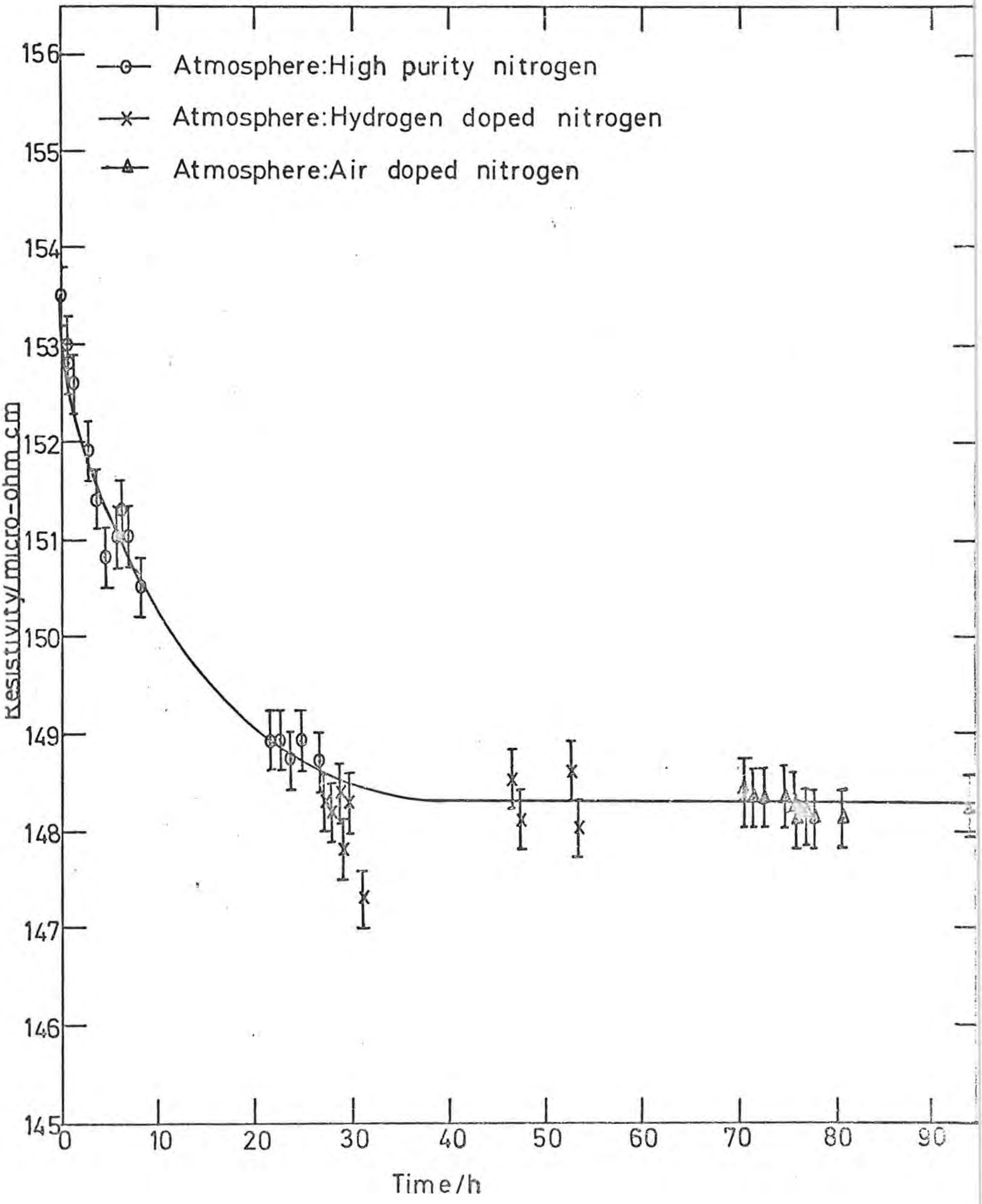
In order to prepare samples with densities close to the X-ray crystal density, a number of samples were hot-pressed. The VN powder, prepared by the direct nitridation of vanadium metal, was supplied to us by Dr. R. Kieffer. The samples were pressed at 50 kilobars at 1500°C for 5 minutes in graphite dies. The density of these samples was found to be from 97-100% of the X-ray crystal density.

These samples had a lower resistivity than had the cold-pressed samples, and were not affected by the ambient atmosphere during high temperature resistivity measurements, (Run 32.1). In their anomalous resistance/temperature behaviour, they behaved similarly to the cold-pressed samples which were pressed from VN prepared from VCl_3. The hot-pressed material, however, displayed different anomalous behaviour to cold-pressed samples from the same batch of VN, so that the mode of

pressing has/........

RUN 32·1

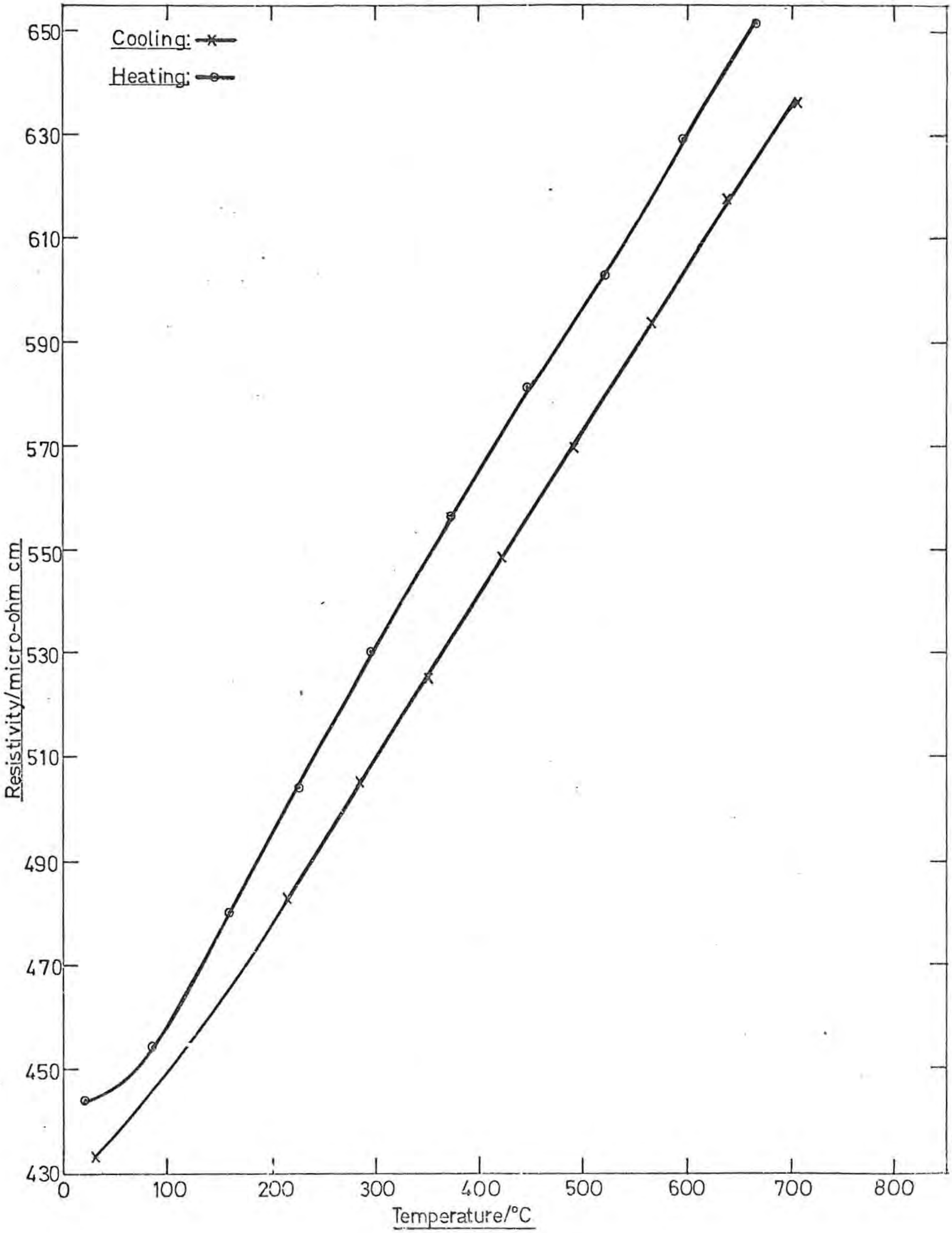
Hot Pressed VN(B)



RUN 25

VN(XXVI)B

Atmosphere: High purity nitrogen



pressing has a significant effect on the form of the anomalies.

Hot-pressed VN samples from two different batches of similarly prepared VN exhibited very similar overall resistance/temperature behaviour (cf. Runs 31 and 38), whereas the behaviour of cold-pressed samples, even from the same batch of VN, showed very different behaviour (cf. Runs 25 and 27).

The hot-pressed samples required a longer annealing time than cold-pressed samples, the resistance at 700°C of the hot-pressed samples falling continuously for about 30 hours before becoming constant, whereas that of the cold-pressed samples reached equilibrium after about 3 hours.

(8) RESISTIVITY AS A FUNCTION OF TIME

In order to examine the effects of impurities, of the ambient atmosphere, and especially of the effects of oxygen on the resistance behaviour of VN samples, a number of cold-pressed VN samples were maintained at elevated temperatures (700-720°C) for extended periods and "doped" with oxygen, which was introduced into the carrier gas stream by injecting air at intervals, or they were

maintained in/........

TABLE 4

SUMMARY OF RESISTANCE VS TIME BEHAVIOUR OF VANADIUM NITRIDE

Run No.	Sample No.	Prepared From:-	Pressing Conditions	Temperature of Run /^{o}C	Atmosphere.	Increase in Resistivity with Time	
						$d\rho/dt$ micro-ohm cm min^{-1} x 10^{-2}	$1/\rho$ $(d\rho/dt)$ min^{-1} x 10^{-4}
22.1	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	715	N_2	2.34	0.72
22.2	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	713	N_2/Air	4.53	1.34
22.3	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	715	N_2/Air	9.73	2.69
22.4	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	712	N_2/Air	5.91	1.53
23.1	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	712	N_2	3.58	0.87
23.2	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	712	N_2/Air	15.30	3.56
28.1	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	712	$N_2/8\%H_2$	-0.56	-0.17
28.2	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	713	$N_2/8\%H_2$	0.36	0.11
29.1	VN(XXVI)B3	VCl_3 & (N_2+H_2)	Cold	716	$N_2/8\%H_2$	0.60	0.07
34.1	VNACl	V & N_2	Cold	700	N_2	1.22	0.40
34.1	VNACl	V & N_2	Cold	700	N_2/Air	1.75	0.55
34.1	VNACl	V & N_2	Cold	700	$N_2/30\%H_2$	-0.12	-0.04
32.1	VNBHl	V & N_2	Hot	700	N_2/Air $N_2/30\%H_2$	0	0

maintained in a reducing atmosphere containing from 8 to 30% hydrogen, see Table 4.

In the case of Run 22.1 (in a high purity nitrogen atmosphere), for example, the increase of resistivity with time $\left(\frac{1}{\rho}\frac{d\rho}{dt}\right)$ was observed to be 7.20×10^{-5} min^{-1}, while that in Run 23.1, also in a nitrogen atmosphere, was observed to be 8.67×10^{-5} min^{-1}. This increase in resistivity suggests that some change in the composition of the VN, such as nitridation, is occurring; the possibility of oxidation also arises here, as the purification method will not have removed all traces of oxygen from the gas. In order to check this result, a number of samples were maintained at elevated temperatures in a nitrogen atmosphere while slugs of air were injected into the carrier gas stream at intervals. The rate of increase in resistivity observed in 5 such runs, $\left(\frac{1}{\rho}\frac{d\rho}{dt}\right)$ had a mean value of 1.93×10^{-4} min^{-1}, while that of three samples run in a high purity nitrogen atmosphere was observed to be 6.61×10^{-5} min^{-1}, i.e. the samples run in a nitrogen/oxygen atmosphere showed a greater increase of resistivity with time than those samples run in pure nitrogen. Other VN samples were maintained at elevated temperatures in nitrogen atmospheres to which from 8 to 30% of hydrogen was added. These samples showed a much smaller increase or, in some

cases, even/........

cases, even a decrease in resistivity with time. The average increase in resistivity with time $\left(\frac{1}{\rho}\frac{d\rho}{dt}\right)$ determined during 4 runs on 3 samples was observed to be -7×10^{-7} min^{-1}, i.e. an overall decrease of resistivity with time was observed.

Hot-pressed samples, on the other hand, did not appear to be affected by the nature of the ambient atmosphere after an initial annealing process (Run 34.1).

(9) RESULTS OF CHEMICAL ANALYSES

Several samples, sintered, unsintered, and hot-pressed, were analysed for their oxygen content by neutron activation analysis by ISCOR, see Table 5.

Neutron activation analysis enables a direct determination of oxygen to an accuracy of about 0.2%, which compares favourably with that determined by difference, the precision of the oxygen determinations by difference in the present project being 0.4-0.5%. However the accuracy appears to be only about 1.0 to 1.5%, when the results determined by difference are compared with those obtained by neutron activation analysis.

In order to examine the effect of successive heating and cooling cycles on these samples, different

TABLE 5

SAMPLE ANALYSES

Sample and Nature	V	N N.A.A	N Dumas	O N.A.A	O Difference
Weight Percent Theory for VN	78	22	22	0	0
VN(XXVI) Unsintered, prepared from VCl_3 and N_2, H_2	74.6 ±0.2	-	-	2.41 ±0.24	-
VN(XXVI)B Sintered, prepared from VCl_3 and N_2, H_2	-	17.6 ±0.2	-	1.50 ±0.15	-
VN/XXVI)B Sintered, prepared from VCl_3 and N_2,H_2 used in Runs 28, 28.1 and 28.2 under N_2/6%H_2	-	17.7 ±0.7	-	2.12 ±0.23	-
VN(XXVI)B Sintered, prepared from VCl_3 and N_2, H_2 used in Run 25 under high purity N_2	-	17.2 ±0.4	-	-	-
VN(XXVI)A Sintered, prepared from VCl_3 and N_2.H_2 used in Runs 18-22 under high purity nitrogen	73.1 ±1.5	-	-	-	-
VN(A) Hot-pressed, prepared from V and N_2, not used in measurement	79.5 ±0.2	-	20.6 ±0.2	0.81 ±0.8	0 - 0.4
VN(A) Hot-pressed, prepared from V and N_2, used in Run 38 under high purity nitrogen	79.4 ±0.2	-	20.6 ±0.3	1.25 ±0.12	0 - 0.5
VN(A) Sintered, cold-pressed, prepared from V and N_2, not used in measurement	77.9 ±0.3	-	21.1 ±0.2	1.98 ±0.20	0.5 - 1.5
VN(A) Sintered, cold-pressed, prepared from V and N_2, used in Runs 34 and 34.1	77.7 ±0.2	-	21.2 ±0.3	3.50 ±0.35	0.6 - 1.6
VN(A) Unpressed, prepared from V and N_2	79.4 ±0.2	-	20.6 ±0.2	0.15 ±0.02	0 - 0.4
VN(B) Unpressed, prepared from V and N_2	79.4 ±0.2	-	20.6 ±0.2	0.10 ±0.01	0 - 0.4
VN(B) Hot-pressed, prepared from V and N_2, not used in measurement	79.4 ±0.2	-	20.6 ±0.2	0.75 ±0.08	0 - 0.4

N.A.A is neutron activation analysis.

samples from the same sintered batch, or parts of the same hot-pressed sample (and, therefore, presumably of the same initial composition), were analysed both before and after subjection to the measuring process.

From these analyses, it was observed that, although the sample used in Runs 28.1 and 28.2 (run in nitrogen and 8% hydrogen) showed a decrease in resistivity upon heating in a reducing atmosphere, the oxygen content of this sample was actually higher, at 2.12±0.23%, than that of another sample from the same batch, with an oxygen content of 1.5±0.2%, which had not been subjected to the measuring process (Table 5), but this variation in oxygen content lies at the limit of accuracy of the analytical method.

Although the oxygen content of the samples was found to be higher than expected in samples prepared from VCl_3, probably because it was not completely removed from the V_2O_5 in converting to VCl_3, the vanadium content was found to be rather low, about 75±2% V (analytical accuracy being ± 2%) being typical, while the theoretical percentage of V in V_1N_1 (allowing for the oxygen) is 80%. This suggests other impurities besides oxygen.

In the samples prepared by nitridation of vanadium, the vanadium content was found to be

approximately 79.4%/........

approximately 79.4%, while the nitrogen content was found to be approximately 20.6%, corresponding to a V:N ratio of 1.00 to 0.94, close to the stoichiometric ratio. These figures suggest that little impurity is present in this VN; however oxygen contents of from 1 to 3% have been observed in these samples, cold-pressed samples exhibiting a higher oxygen content than hot-pressed samples. The sum of the vanadium, nitrogen and oxygen contents of some of the samples is found to be greater than 100%, suggesting some inaccuracy in the vanadium or nitrogen determinations, and showing that little reliance can be placed on oxygen determination by difference.

Several of the samples prepared from VCl_3 were analysed spectrographically by the National Institute for Metallurgy, for impurities other than oxygen, but the total of such impurities e.g. SiO_2, appears to be less than 0.5%. Several of these samples were also analysed for nitrogen by neutron activation analysis at Harwell but these values were also very low and appeared to be independent of the previous treatment of the samples, values of about 17% N being observed. The low nitrogen content suggests a nitrogen deficient compound, $V_{1.00}N_{0.86}$; however, some doubt as to the accuracy of the nitrogen determination by activation analysis exists, as the impurity concentrations determined by difference for this material were found to be about 6%

by weight, which seems unlikely in view of the spectrographic results.

(10) THERMOELECTRIC POWER DETERMINATIONS

Thermoelectric power measurements were made on several VN samples, using copper electrodes and maintaining a temperature difference of about 15° across the sample in order to obtain a measure of the differential, rather than of the integral, thermoelectric power.

The thermoelectric power, however, was found to have very poor reproducibility on comparing the heating and cooling curves, and all that could be deduced from this was that VN was apparently n-type, with the hot-pressed VN, and that prepared from VCl_3, being slightly more n-type than the cold-pressed VN prepared by nitridation of vanadium metal. The absolute thermoelectric power was about 3 micro-volts K^{-1}.

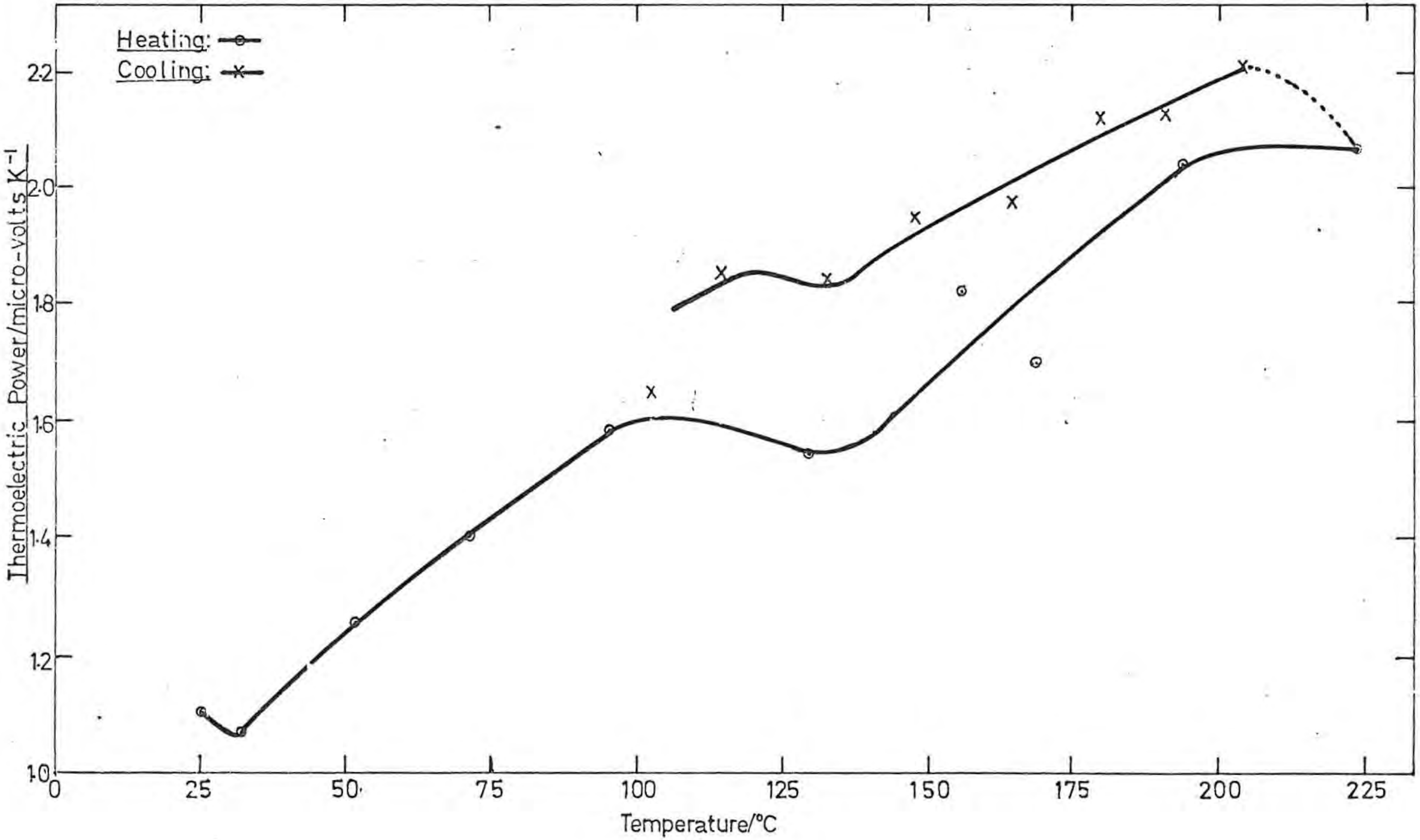
(11) SURFACE CONDUCTION

No significant results were obtained in attempts to measure the surface conduction of VN, as the contact-to-sample resistances were very much greater (10 to 100 times) than the overall sample resistances themselves. In order

RUN T/P1

VN(XXVII)A

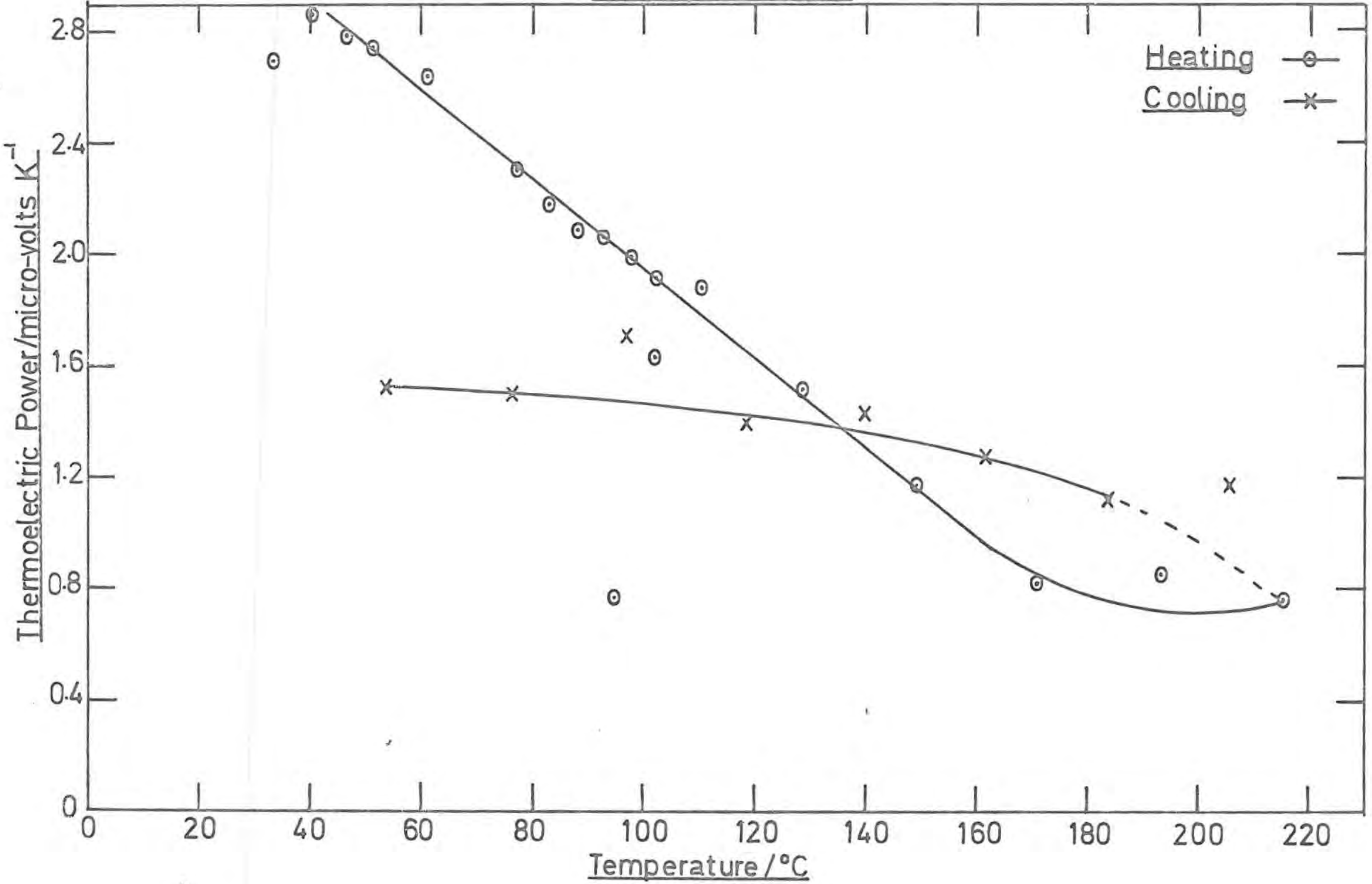
Atmosphere: Argon



RUN T/P2

Cold Pressed VN(A)

Atmosphere: Argon



to obtain reasonable results for this, it would be necessar to employ a four-probe rather than the two-probe technique which was used in the attempts.

(12) HALL EFFECT MEASUREMENTS

In an attempt to determine the sign and mobility of the charge carriers, serious and extensive attempts (which are not fully delineated here) were made to determine values of the Hall Coefficient for VN. This was found to be less than 2×10^{-5} cm^3 C^{-1}, about the limit of detection of the bridge using the available magnetic field strength of about 5000 gauss. Typical values of the Hall Coefficient for metals are of this order, e.g. that for copper is 15.5×10^{-5} cm^3 C^{-1} (Cusack 1958). The value of the Hall Coefficient here observed for VN was much lower than the value of -0.45 cm^3 C^{-1} reported for this compound by Samsonov and Verkhoglyadova (1962).

(VI) DISCUSSION/........

(VI) DISCUSSION

(1) INTERPRETATION OF RESULTS

Most of the resistivity vs temperature and resistivity vs time curves are essentially very similar in their general form, differences only being apparent when these are examined in detail; many of the arguments presented here have been derived from these detailed differences. It is difficult to draw definite conclusions from this procedure, for this would require a great deal of speculation on the observed results, and we have attempted to avoid speculation not based on a firm experimental foundation, in so far as it has been possible with the data available.

(2) THE CONDUCTION EQUATION

According to Mathiessen's Rule (Kittel 1967), the resistivity of a conductor may be expressed as the sum of two terms, one of which is temperature dependent, while the other is independent of temperature:-

$$\rho = \rho_0 T + b \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\text{where } \rho_0 = \frac{1}{ne\mu_0} \quad \ldots\ldots\ldots\ldots \quad (2)$$

and ρ_0 = temperature coefficient of resistivity

b = residual/........

b = residual resistivity

n = carrier concentration

μ_0 = temperature coefficient of mobility

e = charge on carriers.

The mobility, $\mu = \mu_0 T$, may be obtained from a plot of ρ vs T if n and e are known, with the relation:-

$$\mu = \frac{1}{ne\rho_0 T}$$

As ρ_0 is proportional to $1/(n\mu)$, the slope of a plot of ρ vs T gives a measure of the product of carrier concentration and mobility at any temperature T. Thus, if μ_0 is known, then n may be determined; alternatively if n is known, then μ_0 (or μ) may be determined.

The constant, b, determines the residual resistivity at T = 0, and appears as a result of lattice defects and interparticle resistances. The potential field in the vicinity of defects in a metal is different from that near the metal atoms; thus defects, acting as scattering centres for electrons, produce deviations from lattice periodicity. Electrons in a metal containing defects are scattered by the defects as well as by the thermal vibrations (phonons) of the atoms (Dekker 1958), and, if the number of defects is unaffected by T, then b will be independent of T.

(3) SUMMARY/........

(3) SUMMARY

Vanadium nitride has been observed to exhibit a roughly linear increase of resistivity with increasing temperature, i.e. metallic behaviour. However, certain deviations from linearity have been observed, and these are assumed to be due to impurities in the VN, or due to temperature effects on the interparticle resistances in the case of low-density samples.

Impurities could affect the bulk conductivity of the VN in three ways:-

(a) If the impurity donates carriers to the conduction band, then the slope of the resistivity vs temperature curve will become less steep or, in extreme cases, the resistivity could actually fall with increasing temperature. A fall in the resistivity vs time curves at constant temperature could thus result if the impurity is slowly absorbed from the ambient atmosphere at the temperature of measurement.

(b) If the impurity withdraws carriers, then the slope of resistivity vs temperature will become steeper, and an increase in resistivity with time at constant temperature may be observed, if there should be slow adsorption of impurity from the ambient atmosphere.

(c) If the incorporation of impurity atoms into the VN structure results in an increase in defect concentration, then the overall resistivity will rise, but the slope of resistivity vs temperature curve will remain constant. An increase in resistivity with time at constant temperature may be observed if absorption from the ambient atmosphere results in an increase in defect concentration.

The above assumes that the conductivity can be strictly divided into a temperature dependent and a temperature independent term and that only one process is operating at one time; however more than one of these effects may operate at the same time, giving rise to apparently contradictory results.

In the present investigation, all three of the types of behaviour described have been observed to some extent, under various conditions, and changes in carrier concentrations required to produce such changes have been examined. Attempts to correlate these effects with oxygen concentrations lead to values for the apparent oxygen content, (assuming that each oxygen atom contributes one or two electrons to the band) which are impossibly high in view of the analytical results for this element. Therefore, concentration is focussed on the possibility of changes in interparticle resistances.

In the case of cold-pressed, low density samples, the interparticle resistances may be very much larger than

the bulk/........

the bulk resistance of the VN, thus changes in the latter may be masked.

The presence of hydrogen in the VN lattice was previously assumed to result in the anomalous resistivity vs temperature behaviour, and in the changes in the resistivity with time of the VN. The presence of hydrogen in the VN was proposed in view of the low analytical results obtained for V, N and O, and of the possibility of its incorporation into the VN during preparation from VCl_3 and its sintering in nitrogen/hydrogen mixtures. However the presence of hydrogen could not account for the anomalous behaviour of the samples, pressed from the VN which had been prepared by the direct nitridation of vanadium, as neither hydrogen or ammonia was involved in preparation or sintering of the material.

(4) GENERAL DISCUSSION OF RESULTS

(a) Hot-Pressed Samples

Hot-pressed samples were pressed from VN which had been prepared by the direct nitridation of vanadium metal. Their stoichiometry, as determined by analysis, was found to be approximately $VN_{0.94}$, and they should not contain impurities other than oxygen due to their

method of/........

method of preparation and pressing. Their density was observed to be close to the X-ray crystal density, thus resistance effects due to interparticle resistances may be expected to be small.

These samples exhibited a very much lower resistivity than the cold-pressed 72-75% dense samples, as expected, and their resistivity vs temperature behaviour may be regarded as the more typical of that of VN itself.

Although their absolute resistivity was lower than that of cold-pressed VN, anomalous resistance/temperature, of types A and B (see later) were still observed in the case of these samples, so that such effects appear to be inherent in the VN itself. These effects could be due to some impurity, such as oxygen, or to deviations from stoichiometry of the VN, but it has not been possible to determine which.

The dense samples have shown no resistance/time effects due to the ambient atmosphere, probably since their high density and non-porosity prevents attack by the ambient atmosphere occuring elsewhere than on the outer surfaces of the samples. This implies too low diffusivity of the reaction products through the VN, which is expected from such a hard and dense material.

(b) Absolute Resistivity/........

(b) Absolute Resistivity

The absolute resistivity of cold-pressed VN at room temperature (about 270 micro-ohm cm) is very much higher than that observed for the hot-pressed material at the same temperature (about 100 micro-ohm cm), probably as a result of large interparticle resistances in the former, and suggests that in the case of cold-pressed samples, the interparticle resistances may be the major component of the overall resistivity.

It appears that very slight differences in nitrogen, or oxygen, content may affect the resistivity to a large extent. Thus the resistivity of $VN_{0.93}$ (85 micro-ohm cm) (Samsonov and Verkhoglyadova 1962) is rather lower than that of the $VN_{0.94}$ (101 micro-ohm cm) observed in the present project; however the oxygen content, about 1%, of the samples used in the present investigation may also have some effect. These large changes of resistivity with relatively small changes in nitrogen, or oxygen, content suggest at first sight that there is a relatively low concentration of carriers in the conduction band, and further suggest that nitrogen and oxygen are electron acceptors if, as appears from thermoelectric power measurements, VN is n-type. However, an increase in nitrogen content could result in an increase in defect concentration and, hence, an increase in resistivity, even if nitrogen (or oxygen) were inert or an electron donor. In order to determine whether nitrogen (or oxygen) is an electron donor or acceptor, it is necessary to examine the changes in the slope of resistivity vs temperature rather than the absolute values of the resistivities.

(c) Temperature Dependent Reversible Behaviour

In the detailed examination of curves of resistivity vs temperature, deviations from linearity have been observed in many cases. Although these deviations, or anomalies, are generally small, they could result from the presence of large concentrations of impurities if it is assumed that VN is a metallic conductor, with a high carrier concentration in the conduction band.

The ambient atmosphere appeared to have little effect on the anomalous behaviour of the VN, but it must be borne in mind that some reaction with the ambient atmosphere occurs in the case of cold-pressed samples, which may cause overall changes in resistivity or in the slopes of resistivity vs temperature curves.

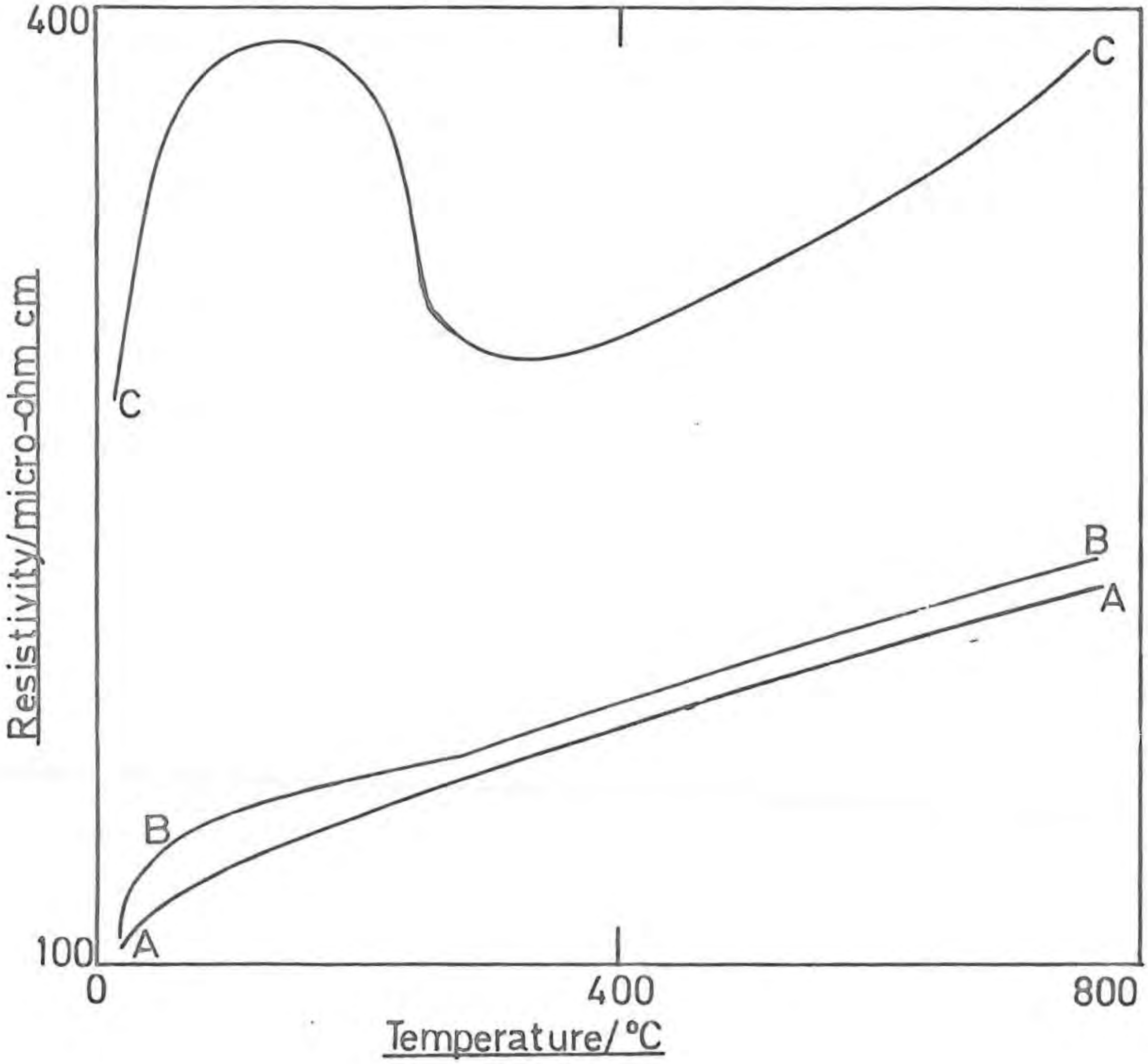
The anomalous behaviour is illustrated in Fig 33, and summarised in Table 2, and was mainly observed between 100 and 250°C.

TABLE 2

SUMMARY OF RESISTANCE VS TEMPERATURE BEHAVIOUR OF VANADIUM NITRIDE

Run No.	Sample No.	Prepared From:-	Pressing Conditions	Type of Anomaly	Temperature at which Anomaly observed /°C	Slope at 100°C		Slope at 500°C	
						$\frac{d\rho}{dT}$ / micro-ohm cm K^{-1} x 10^{-1}	$\frac{1}{\rho}\frac{d\rho}{dT}$ / K^{-1} x 10^{-3}	$\frac{d\rho}{dT}$ / micro-ohm cm K^{-1} x 10^{-1}	$\frac{1}{\rho}\frac{d\rho}{dT}$ / K^{-1} x 10^{-4}
5	VN(XXII)1	NH_4VO_3 & NH_3	Cold	A	100	3.20	1.34	2.40	7.14
19	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.90	0.83	1.30	4.57
20	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.92	0.87	1.30	4.76
21	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	1.87	0.80	1.29	4.52
22	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	A	120	2.00	0.82	1.22	4.15
[illegible]	VNBH1	$^{*}V$ & N_2	Hot	A	100	0.85	0.76	0.72	5.05
33	VNAH1	$^{*}V$ & N_2	Hot	A	100	0.73	0.72	0.66	5.16
[illegible]	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	B	100–350	–	–	1.09	2.62
35	VNBH2	$^{*}V$ & N_2	Hot	B	25–400	–	–	0.60	4.74
36	VNBH3	$^{*}V$ & N_2	Hot	B	25–400	–	–	0.69	4.87
34	VNAC1	$^{*}V$ & N_2	Cold	C	125	10.17	2.99	1.21	3.71
37	VNAC2	$^{*}V$ & N_2	Cold	C	160	3.48	1.12	1.51	4.34
39	VNAC3	$^{*}V$ & N_2	Cold	C	215	4.91	1.58	1.00	2.93
18	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	1.33	5.34
25	VN(XXVI)B1	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	4.00	6.86
27	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	2.13	6.63
28	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	None	–	–	–	1.78	6.08
30	VNBH1	$^{*}V$ & N_2	Hot	None	–	–	–	7.14	5.06
[illegible]	VNBH1	$^{*}V$ & N_2	Hot	None	–	–	–	6.92	5.15

*Supplied to us by Dr. R. Kieffer.



Types Of Anomalous Behaviour In VN

Fig 33

(i) Type A Anomalies

Type A anomalies are characterized by a change in slope in curves of resistivity vs temperature; changes in slope of about 14% in the case of hot-pressed samples and 47% in the case of cold-pressed samples have been observed. If we assume that the carrier mobility is independent of temperature, then the above changes in slope represent changes in carrier concentration of 14 and 47% respectively. If we assume that each VN "formula unit" contributes 2 electrons to the conduction band (Piper 1964), assuming here that donation occurs only above the "knee", then the above changes in carrier concentration represent impurity concentrations of 14 and 47 mole % if each impurity atom also donates 2 electrons to the band. If the impurity is oxygen, then the above impurity levels correspond to about 3.5 and 11.5% by weight respectively. Both the 3.5% by weight of oxygen required in the case of hot-pressed samples, and the 11.5% by weight in the case of cold-pressed samples are excessive in view of the analytical results for this element. In fact, it appears unlikely that any undetected impurities could reach this level and we are led to the conclusion that some other mechanism which may affect the interparticle resistances (small in the case of hot-pressed samples) is involved, or that the changes in slope result from deviations from stoichiometry (i.e. regarding excess V or N as impurity).

(ii) Type B/........

(ii) Type B Anomalies

Type B anomalies, are also reversible anomalies which have been observed in the case of both hot- and cold-pressed samples. In this type of anomaly, the slope of the resistivity vs temperature curve decreases over a range of about 300°, and subsequently rises again, becoming constant. This type of behaviour may be a more pronounced effect than that of type A anomalies, due to the presence of slightly higher impurity levels which donate electrons to the band up to about 350°C, above which temperature the donation ceases, and normal metallic behaviour is observed. Overall changes in slope of about 34% were observed, which would represent an impurity concentration of the same order assuming each impurity atom donates or withdraws two electrons. If the impurity is assumed to be oxygen, then the above concentration corresponds to about 13% by weight, which is excessively high. In the case of hot-pressed samples, the interparticle resistances are fairly low, suggesting that such drastic changes in slope cannot be due to this cause. Another possibility would seem to be semiconducting behaviour of the VN at low temperatures, resulting from deviations from stoichiometry which changes to metallic behaviour at higher temperatures, although why this change should occur is not at all clear.

(iii) Type C/........

(iii) Type C Anomalies

The anomalies of type C are also reversible, and are characterized by a large increase in resistivity followed by a fall, in the temperature range 100 to 200°C, succeeded by, a monotonic, but slightly super-linear, increase of resistivity with temperature. This type of behaviour is similar to the type III behaviour observed by Hoy (1963), but occurs at a much lower temperature. This behaviour was only observed in the case of cold-pressed samples, prepared from VN which was derived from direct nitridation of vanadium metal. The higher oxygen content of these samples (about 3%) than that of the hot-pressed samples from the same source material may have had some effect on their resistivity behaviour. However, even this oxygen content should not result in so profound an effect on the resistivity unless the carrier concentration in the conduction band is low, but as the magnitude of the thermoelectric power of these samples is of the same order as that of the hot-pressed samples, this seems unlikely. Thus we are led to the conclusion that this behaviour is a purely physical effect due to thermal expansion, which affects the interparticle resistances in a reversible way. This assumption is borne out by the fact that Hoy (1963), in a series of measurements on the lattice parameter up to about 500°C, observed no phase change which could lead to this type of behaviour. Also the impurity concentrations required to produce the observed changes in slope (about 400%) would be impossibly high.

The above treatment suggests that, in the case of anomalies of type A, at least, the impurity (probably oxygen) is an electron donor, producing a reduction in the slope of resistivity vs temperature. The effects of impurities on defect concentration, and therefore on the absolute resistivity, has been ignored. If the concentration of impurity in the VN remains constant during measurement, then only the electron donating or withdrawing effects of the impurity on resistivity will be observed and this behaviour should be reversible with respect to temperature. If the impurity concentration changes during the measurements, however, then irreversible changes in the resistance behaviour may be observed.

(d) Irreversible Effects on the Vanadium Nitride Resistance

In determining curves of resistivity vs time on cold-pressed VN samples, a steady increase in resistivity with time was observed in nitrogen, or in

oxygen-doped nitrogen/........

TABLE 4

SUMMARY OF RESISTANCE VS TIME BEHAVIOUR OF VANADIUM NITRIDE

Run No.	Sample No.	Prepared From:-	Pressing Conditions	Temperature of Run /°C	Atmosphere	Increase in Resistivity with Time	
						$d\rho/dt$ micro-ohm cm min^{-1} $x\ 10^{-2}$	$1/\rho\ (d\rho/dt)$ min^{-1} $x\ 10^{-4}$
22.1	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	715	N_2	2.34	0.72
22.2	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	713	N_2/Air	4.53	1.34
22.3	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	715	N_2/Air	9.73	2.69
22.4	VN(XXVI)A1	VCl_3 & (N_2+H_2)	Cold	712	N_2/Air	5.91	1.53
23.1	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	712	N_2	3.58	0.87
23.2	VN(XXVI)A2	VCl_3 & (N_2+H_2)	Cold	712	N_2/Air	15.30	3.56
28.1	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	712	$N_2/8\%H_2$	-0.56	-0.17
28.2	VN(XXVI)B2	VCl_3 & (N_2+H_2)	Cold	713	$N_2/8\%H_2$	0.36	0.11
29.1	VN(XXVI)B3	VCl_3 & (N_2+H_2)	Cold	716	$N_2/8\%H_2$	0.60	0.07
34.1	VNAC1	V & N_2	Cold	700	N_2	1.22	0.40
34.1	VNAC1	V & N_2	Cold	700	N_2/Air	1.75	0.55
34.1	VNAC1	V & N_2	Cold	700	$N_2/30\%H_2$	-0.12	-0.04
32.1	VNBH1	V & N_2	Hot	700	N_2/Air $N_2/30\%H_2$	0	0

oxygen-doped nitrogen atmospheres, see Table 4. This could be due to either an electron-trapping effect of the nitrogen, occurring only at high temperature and not reversible (which would cause changes in the slopes of subsequent resistivity vs temperature curves) or to the incorporation of nitrogen or oxygen atoms as defects in the VN structure (which would not affect the slopes of subsequent resistivity vs temperature curves, but would result in an increase in residual resistivity if it is assumed that the oxygen or nitrogen is electrically neutral). Increases in resistivity of about 3% have been observed during runs in nitrogen or oxygen-doped nitrogen atmospheres, which represents an impurity concentration of about 3 mole %, or about 0.7% by weight of oxygen. However, the slopes of curves of resistivity vs temperature were observed to decrease after heating in a nitrogen or nitrogen-oxygen atmosphere, showing that an increase in carrier concentration had in fact occurred during the heating. Thus the slope in Run 23 was less than that in Run 22, on the same sample which had previously been run in nitrogen and nitrogen-oxygen atmospheres.

While conducting similar measurements in nitrogen/hydrogen atmospheres, however, very much smaller increases or even decreases in resistivity with time were observed. This suggests that the presence of hydrogen in some way inhibits the absorption of nitrogen or oxygen, or even results in its removal from the bulk of the VN, possibly as the result of the formation of ammonia or water from the nitrogen or oxygen contained in the VN. The formation of ammonia should be possible under the prevailing conditions, as VN is a catalyst for its formation (Lotz and Sebba 1957).

Resistance vs time measurements on hot-pressed, dense, VN samples exhibited no effects due to the ambient atmosphere, suggesting that changes in VN due to the effects of the atmosphere are merely surface effects, and can only occur in the case of porous samples in which the gases can reach and react with a larger proportion of the material. This further suggests that all measurements on cold-pressed samples were, in fact, non-equilibrium measurements, which is borne out by the irreversibility of changes observed upon successive heating and cooling cycles on these samples. The dense samples would then be in metastable equilibrium.

(e) A Mechanism for the Effects of Sorbed Gases.

In the case of porous samples, which are affected by the ambient atmosphere, it would appear that both nitrogen and oxygen are electron donors in their effects on VN, but their incorporation into the VN lattice results in an increase in the residual resistivity.

The increase in residual resistivity often masks the effects due to the increase in carrier concentration which, however, is evident from the changes in slope of the resistance/temperature curves, before and after running in nitrogen.

Hydrogen appears to affect the resistivity by inhibiting the absorption of nitrogen or oxygen to some extent, or even resulting in the removal of these elements from the VN, without itself being incorporated into the bulk of the VN.

(f) Thermoelectric Power Measurements

On account of the irreproducibility of the thermoelectric power measurements, little information can be gained from these results other than to suggest that VN appears to be an n-type conductor, which agrees with its behaviour as a metallic conductor. The magnitude of the absolute thermoelectric power, about 3 micro-volts K^{-1}, is also typical of a metallic conductor.

(5) CONCLUSIONS/.......

(5) CONCLUSIONS

In general, VN exhibits metallic behaviour, having a positive temperature coefficient of resistivity, negative charge carriers, and a relatively low thermoelectric power, suggesting a relatively high carrier concentration in the conduction band.

However, the conductivity behaviour of VN is sensitive to impurities, and changes in the slopes of resistivity vs temperature curves corresponding to increases in apparent carrier concentrations of over 50% have been observed in some cases, but in the case of low density samples, these could be due to changes in interparticle resistances rather than changes in the VN itself. In order to observe the latter, it is necessary to examine the effects of impurities on hot-pressed, dense, VN.

The anomalous behaviour (of type A) at 120^{o}C appears to be due to either some impurity which is almost always present in the VN, such as oxygen, or to changes in the interparticle resistances, or a combination of both; probably mainly the former in hot-pressed VN, but which is swamped by the latter in cold-pressed VN. The impurity is thought to be oxygen, as it is very difficult to prepare completely oxygen-free material, and it has been detected by neutron activation analysis in all of the VN samples employed in the present investigation.

It appears that oxygen is an electron donor in its effects on VN, but its presence raises the absolute resistivity due to an increase in defect concentration.

The resistivity increases observed on running samples in nitrogen/oxygen atmospheres may be due to very small increases in nitrogen or oxygen content resulting in large fractional changes in defect concentration and, therefore, of residual resistivity; in many of these cases the residual resistivity is the major component of the resistivity.

(6) COMPARISON OF THE PRESENT INVESTIGATION AND THAT OF HOY

Apart from the work of Hoy (1963) the resistivity of the V—N system does not appear to have been studied with respect to temperature at elevated temperatures.

(a) In both Hoy's and the present investigations, VN has been observed to exhibit more or less metallic

behaviour, i.e./........

behaviour, i.e. increasing resistivity with increasing temperature was observed.

(b) Hoy observed anomalous resistance behaviour at elevated temperatures. This was assumed to be due to impurities in the VN, and oxygen was suggested. Anomalous behaviour has also been observed in the present investigation, but not the anomalies of type I, II and III observed by Hoy. However, the type C behaviour observed in the present investigation resembles the type III behaviour observed by Hoy, except that type C behaviour occurs at a much lower temperature. This difference may reflect the sensitivity of the VN anomalies to the particular preparation and pressing, especially cold-pressing conditions.

(c) Although no resistance variation with time was noted by Hoy, such variation has proved to be significant in the present investigation (in cold-pressed, low density samples) and probably becomes apparent consequent upon the application of the higher temperatures now used, and the present more sensitive technique of conductivity measurement.

(VII) PROPOSAL FOR FUTURE WORK

The sensitivity of VN resistivity to stoichiometry and impurity concentration bears further investigation.

The nitrogen and vanadium analyses performed in the present investigation on samples prepared from VCl_3 leave some doubt as to the stoichiometry of this compound, the atomic ratio V:N being about 1:0.85, which suggests that the temperature of preparation, i.e. 1100°C, may have been too high, (contrary to the results of Epelbaum and Ormont (1947), who predicted the formation of almost stoichiometric $V_{1.0}N_{1.0}$ at this temperature). However, the method of nitrogen analysis, by neutron activation analysis may not be very suitable in the case of this material. Thus an investigation into the relation between stoichiometry and temperature of preparation of this compound employing the modified Dumas technique, in order to determine nitrogen, and neutron activation analysis, to determine oxygen, may prove fruitful.

The effects/........

The effects on the anomalous resistance/ temperature behaviour of dense samples with differing oxygen and nitrogen contents could be investigated. The different oxygen and nitrogen contents would require incorporation during preparation in the case of hot-pressed samples, as "doping" of the ambient atmosphere during measurement appears to have no effect on the resistivity behaviour of these samples.

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APPENDIX/........

APPENDIX

Run 5.

VN(XXII)

Atmosphere: High Purity Nitrogen.

Heating	
Temp. °C	Resistivity micro-ohm cm
21	197.7
64	226.1
102	238.8
165	256.7
211	267.3
253	279.4
300	290.6
352	302.3
403	315.8
451	327.7
500	338.6
555	349.8
601	367.0
650	374.8
700	390.7
752	403.9
801	418.3

Run 16.1./........

Run 16.1.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Current mA	Temp. °C	Resistivity micro-ohm cm
5F	31	307.4
5R	31	312.8
10F	31	308.8
10R	31	312.3
15F	31	314.3
15R	31	312.3
20F	31	310.9
20R	31	312.0
25F	31	310.2
25R	31	315.2

Run 18./........

Run 18.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
803	293.2	172	206.6
803	292.3	172	202.5
733	279.6	247	213.4
733	283.0	247	214.4
663	272.5	311	224.4
663	271.3	311	222.7
593	263.0	456	243.0
593	264.1	456	243.8
521	253.3	524	253.3
521	252.7	524	253.5
447	240.6	601	264.9
447	243.5	601	262.0
375	232.5	670	274.7
375	234.1	670	273.6
283	220.5	755	286.3
283	219.3	755	280.8
212	210.2	363	231.4
212	212.0	363	234.8
148	201.7	21	187.3
148	198.6	21	187.0
118	196.1		
118	197.0		

Run 19./........

Run 19.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
808	308.8	64	217.7
731	300.1	121	228.3
661	289.9	188	240.4
589	282.7	258	249.4
515	273.7	325	259.0
440	264.1	410	271.4
370	265.9	475	280.5
299	257.7	540	289.5
228	247.4	618	299.5
168	238.6	682	309.8
108	230.4	755	321.5
22	210.1		

Run 20./........

Run 20.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp, °C	Resistivity micro-ohm cm
809	310.9	143	227.2
740	305.0	210	236.9
665	296.4	281	245.4
595	286.6	350	254.5
530	278.3	420	263.5
450	267.5	495	272.9
379	258.0	568	282.8
309	249.1	639	291.9
243	241.3	713	304.1
173	232.4	783	312.4
80	216.7	23	204.9

Run 21./........

Run 21.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
811	326.0	143	242.1
735	316.8	207	250.5
671	308.5	280	258.7
600	298.8	351	266.1
525	289.3	427	275.0
456	280.2	505	286.1
382	271.2	576	295.4
310	263.0	640	305.1
237	254.7	715	315.6
172	246.5	787	327.0
87	226.5	23	216.1

Run 22./........

Run 22.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
828	337.9	144	249.0
745	327.0	210	258.9
669	315.9	282	267.4
596	308.3	352	275.4
523	298.4	428	285.2
450	287.4	495	294.7
379	279.4	575	305.3
379	279.2	641	314.0
304	271.1	713	325.0
304	271.1	30	226.0
237	263.2		
237	262.8		
170	254.6		
170	255.4		
83	236.1		

Run 22.1./........

Run 22.1.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Temp. °C	Time min.	Resistivity micro-ohm cm
713	0	325.0
715	30	327.8
715	67	327.3
715	90	328.8
715	120	328.3
715	150	331.0

Run 22.2.

VN(XXVI)A

Atmosphere: Air Doped Nitrogen.

Temp. °C	Time min.	Resistivity micro-ohm cm
713	0	338.2
713	38	340.5
713	60	340.3
713	90	343.9
713	120	344.6
713	150	345.0

Run 22.3/........

Run 22.3

VN(XXVI)A

Atmosphere: Air Doped Nitrogen

Temp. $^\circ$C	Time min.	Resistivity micro-ohm cm
722	0	362.0
715	30	366.0
715	70	372.2
715	90	373.2
715	120	374.7
715	150	376.5

Run 22.4

VN(XXVI)A

Atmosphere: Air Doped Nitrogen.

Temp. $^\circ$C	Time min.	Resistivity micro-ohm cm
718	0	384.1
713	30	387.8
712	60	392.1
712	105	394.3
712	125	395.2
712	150	395.6
713	180	398.1
712	210	398.5
712	270	401.2
713	300	401.0
712	335	404.0

Run 23./........

Run 23.

VN(XXVI)A

Atmosphere: High Purity Nitrogen

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
712	437.0	110	378.2
630	430.1	175	397.8
558	421.3	241	398.7
486	415.4	310	399.9
412	407.0	388	403.2
56	374.8	458	413.3
		527	418.9
		603	427.1
		678	438.5
		23	384.6

Run 23.1.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Temp. °C	Time min.	Resistivity micro-ohm cm
712	0	413.0
712	30	412.5
712	65	418.0
712	135	416.6
712	170	417.8
712	225	418.8
713	310	426.0
713	340	424.0

Run 23.2./........

Run 23.2.

VN(XXVI)A

Atmosphere: High Purity Nitrogen.

Air Injected at 0 min.

Temp. °C	Time min.	Resistivity micro-ohm cm
712	0	429.9
712	5	429.7
712	10	432.4
712	15	437.2
712	20	432.6
712	25	433.4

Run. 25./........

Run 25.

VN(XXVI)B

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
708	636.7	157	480.2
639	618.0	225	504.2
565	594.5	298	530.6
493	570.2	372	556.6
421	548.8	447	581.7
351	525.7	521	603.7
282	505.4	596	630.0
213	483.0	665	651.3
34	433.2	23	444.4
86	454.8		

Run 27./........

Run 27.

VN(XXVI)B

Atmosphere: High Purity Nitrogen Containing 8% Hydrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
711	361.4	118	231.8
640	360.2	184	246.0
568	342.9	250	268.1
496	323.4	328	292.1
424	307.8	398	303.9
353	292.4	471	315.2
282	276.8	542	328.3
215	262.3	620	347.6
54	218.0	689	362.2
		763	371.1
		22	224.9

Run 28./........

Run 28.

VN(XXVI)B

Atmosphere: High Purity Nitrogen
Containing 8% Hydrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
709	329.3	113	218.1
640	317.8	182	232.9
566	304.8	255	247.2
495	292.4	327	261.7
428	278.9	400	274.7
352	265.1	471	288.7
283	252.8	544	300.5
216	239.1	619	312.9
79	209.9	689	325.2
		765	339.1
		22	196.7

Run 28.1./........

Run 28.1.

VN(XXVI)B

Atmosphere: High Purity Nitrogen Containing 8% Hydrogen.

Temp. °C	Time min.	Resistivity micro-ohm cm
712	0	328.9
712	35	329.1
712	60	329.1
713	136	328.5
712	162	327.7
712	196	327.9
712	250	327.4
712	286	327.3
712	330	326.8

Run.28.2./........

Run 28.2.

VN(XXVI)B

Atmosphere: High Purity Nitrogen Containing 8% Hydrogen.

Temp. $^{\circ}C$	Time min.	Resistivity micro-ohm cm
22	---	194.1
713	0	327.2
713	43	327.7
713	68	327.8
713	153	327.7
713	188	328.3
713	213	328.0
713	248	329.2
713	278	328.3
713	313	328.4
713	360	328.4
22	---	194.1

Run 29.1./........

Run 29.1.

VN(XXVI)B

Atmosphere: High Purity Nitrogen Containing 8% Hydrogen.

Temp. °C	Time min.	Resistivity micro-ohm cm
22	---	480.5
713	0	869.0
714	50	868.9
714	75	871.5
716	195	869.9
716	255	871.2
716	335	870.8
716	385	870.6
22	550	497.5

Run 31./........

Run 31.

VN(B)

Atmosphere: High Purity Nitrogen.

Heating		Cooling	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
22	107.2	715	158.4
92	113.4	629	152.0
155	119.5	557	149.8
219	124.7	488	142.5
290	130.3	419	137.0
370	135.9	349	131.8
430	140.6	205	120.5
505	145.8	106	112.9
576	150.7	66	108.4
648	155.2	22	104.9

Run 32./........

Run 32.

VN(3)

Atmosphere: High Purity Nitrogen.

Heating		Cooling	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
22	104.9	656	150.6
117	113.1	584	145.8
181	118.4	515	140.9
252	124.0	448	136.0
318	128.9	381	131.2
406	134.8	309	125.7
466	140.0	225	118.9
531	147.5	159	114.2
608	149.9	51	105.1
681	154.9	25	104.0
752	157.2		

Run 32.1./........

Run 32.1.

VN(B)

Temperature: 700°C.

Atmosphere	Time min.	Resistivity micro-ohm cm	Atmosphere	Time min.	Resistivity micro-ohm cm.
N_2	0	153.5	$N_2/30\%H_2$	1740	147.8
N_2	25	153.0	$N_2/30\%H_2$	1770	148.3
N_2	50	152.8	$N_2/30\%H_2$	1840	147.3
N_2	75	152.6	$N_2/30\%H_2$	2780	148.5
N_2	155	151.9	$N_2/30\%H_2$	2840	148.1
N_2	215	151.4	$N_2/30\%H_2$	3150	148.6
N_2	275	150.8	$N_2/30\%H_2$	3210	148.0
N_2	335	151.0	N_2/Air	4200	148.4
N_2	370	151.3	N_2/Air	4230	148.3
N_2	405	151.0	N_2/Air	4290	148.3
N_2	490	150.5	N_2/Air	4350	148.3
N_2	1290	148.9	N_2/Air	4470	148.3
N_2	1350	148.9	N_2/Air	4530	148.2
N_2	1410	148.7	N_2/Air	4545	148.2
N_2	1470	148.9	N_2/Air	4546	148.1
N_2	1590	148.7	N_2/Air	4595	148.2
$N_2/30\%H_2$	1620	148.3	N_2/Air	4650	148.1
$N_2/30\%H_2$	1650	148.2	N_2/Air	4820	148.1
$N_2/30\%H_2$	1710	148.4	N_2/Air	5625	148.2

Run 33./........

Run 33.

VN(B)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
697	148.0	97	106.9
638	143.8	167	111.4
567	138.7	228	115.8
498	134.2	302	121.1
427	128.4	371	125.8
351	124.6	440	130.7
282	120.0	517	136.0
226	115.4	591	140.7
140	109.9	658	144.9
38	102.6	730	149.7

Run 34./........

Run 34.

VN(A)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
753	331.8	100	344.5
689	325.0	144	353.8
619	315.6	213	304.3
545	307.2	280	288.8
475	299.2	350	288.9
410	293.0	420	294.4
355	289.1	495	302.1
305	288.1	561	309.5
120	355.5	637	317.9
33	266.9	730	329.1

Run 34.1./........

Run 34.1.

VN(A)

Temperature: 700°C.

Atmosphere	Time min.	Resistivity micro-ohm cm	Atmosphere	Time min.	Resistivity micro-ohm cm.
Ar	0	306.6	N_2	1560	321.4
Ar	60	306.8	N_2/Air	1590	321.2
Ar	150	306.7	N_2/Air	1630	323.6
Ar	195	306.6	N_2/Air	1710	325.9
Ar	270	306.7	N_2/Air	1740	325.5
N_2	330	307.6	N_2/Air	1770	325.6
N_2	390	308.9	N_2/Air	1800	325.6
N_2	450	311.1	N_2/30%H_2	1830	325.3
N_2	540	315.7	N_2/30%H_2	1890	325.6
N_2	600	319.9	N_2/30%H_2	1960	325.7
N_2	720	322.4	N_2/30%H_2	2100	325.2
N_2	1440	321.4	N_2/30%H_2	2840	324.2
N_2	1485	321.1	N_2/30%H_2	2910	324.2
N_2	1520	321.5			

Run 35./........

Run 35.

VN(B)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
747	141.7	101	104.9
680	137.5	165	109.7
611	133.5	227	112.5
542	129.0	299	116.8
475	125.2	370	120.8
403	120.8	441	123.9
332	118.8	555	130.2
236	112.7	585	131.6
181	110.5	655	135.5
109	105.8	748	140.9
23	96.6		

Run 36./........

Run 36.

VN(B)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
705	156.6	120	117.1
638	150.0	195	122.9
213	122.9	259	126.9
32	110.1	350	132.4
		420	136.8
		492	140.6
		565	144.8
		685	154.6
		779	160.7

Run 37./........

Run 37.

VN(A)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
707	380.1	35	279.0
633	368.3	94	309.8
569	357.7	143	321.6
494	346.3	205	316.8
429	336.8	305	321.0
340	324.3	422	336.0
259	317.6	527	352.4
146	322.7	665	372.9

Run. 38./........

Run 38.

VN(A)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
697	140.0	35	95.4
630	135.6	117	102.3
565	131.8	288	113.2
499	127.1	490	126.5
429	122.6	727	142.0
361	117.9		
304	114.2		
213	108.1		
101	101.4		

Run 39./........

Run 39.

VN(A)

Atmosphere: High Purity Nitrogen.

Cooling		Heating	
Temp. °C	Resistivity micro-ohm cm	Temp. °C	Resistivity micro-ohm cm
701	361.8	97	309.9
572	349.2	35	278.9
494	341.5	90	308.8
440	336.3	360	328.3
405	332.8	480	340.1
288	329.0	660	357.7
193	354.0		

Run T/P 1./........

Run T/P 1.

VN(XXVII)A

Atmosphere: Argon.

Thermoelectric Power of VN(XXVII)A vs. Cu.

Mean Sample Temp. °C	Thermoelectric Power micro-volts/°C
25	1.10
32	1.06
51	1.25
71	1.40
95	1.58
130	1.54
156	1.82
169	1.70
194	2.04
224	2.07
204	2.21
191	2.13
180	2.13
165	1.98
148	1.95
133	1.84
114	1.85
102	1.65
71	3.21

Run T/P 2./........

Run T/P 2.

VN(A)

Atmosphere: Argon.

Thermoelectric Power of Cold-Pressed VN(A) vs. Cu.

Mean Sample Temp. °C	Thermoelectric Power micro-volts K^{-1}
33	2.67
39	2.84
45	2.76
50	2.72
61	2.52
76	2.29
82	2.16
87	2.07
92	2.05
97	1.97
101	1.90
95	0.76
102	1.62
110	1.87
128	1.50
147	1.16
170	0.81
193	0.85
215	0.77
205	1.17
183	1.12
161	1.27
139	1.42
118	1.49
97	1.69
77	1.50
53	1.52

Run T/P 3./........

Run T/P 3.

VN(A)

Atmosphere: Argon.

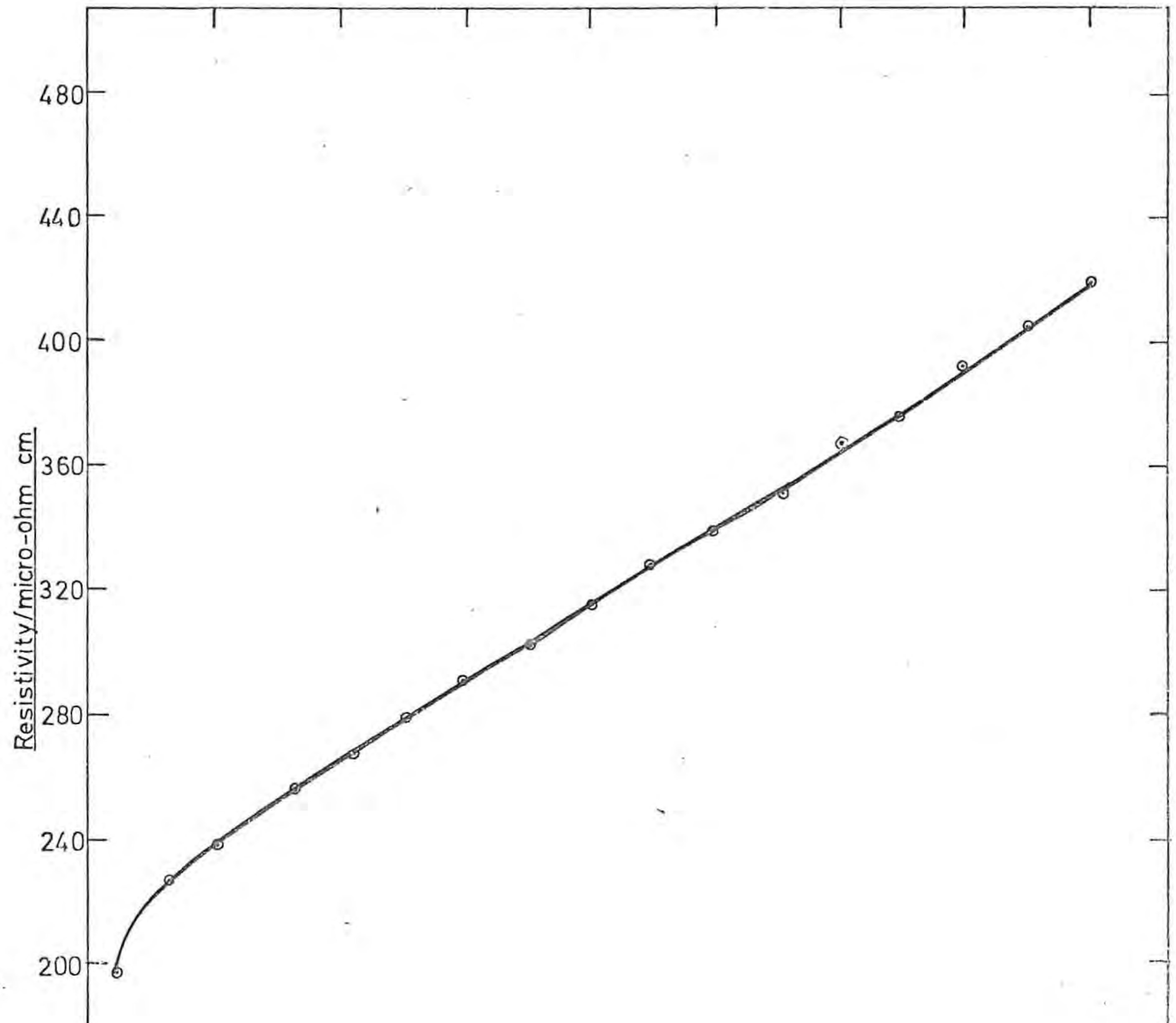
Thermoelectric Power of Hot-Pressed VN(A) vs. Cu.

Mean Sample Temp. °C	Thermoelectric Power micro-volts K^{-1}
45	3.00
67	3.28
85	2.62
104	2.64
124	2.56
145	2.40
166	2.33
186	2.40
207	3.00
198	4.00
178	4.69
158	4.44
137	4.39
117	4.36
96	4.31
75	4.18
53	4.67

RUN 5

VN(XXII)

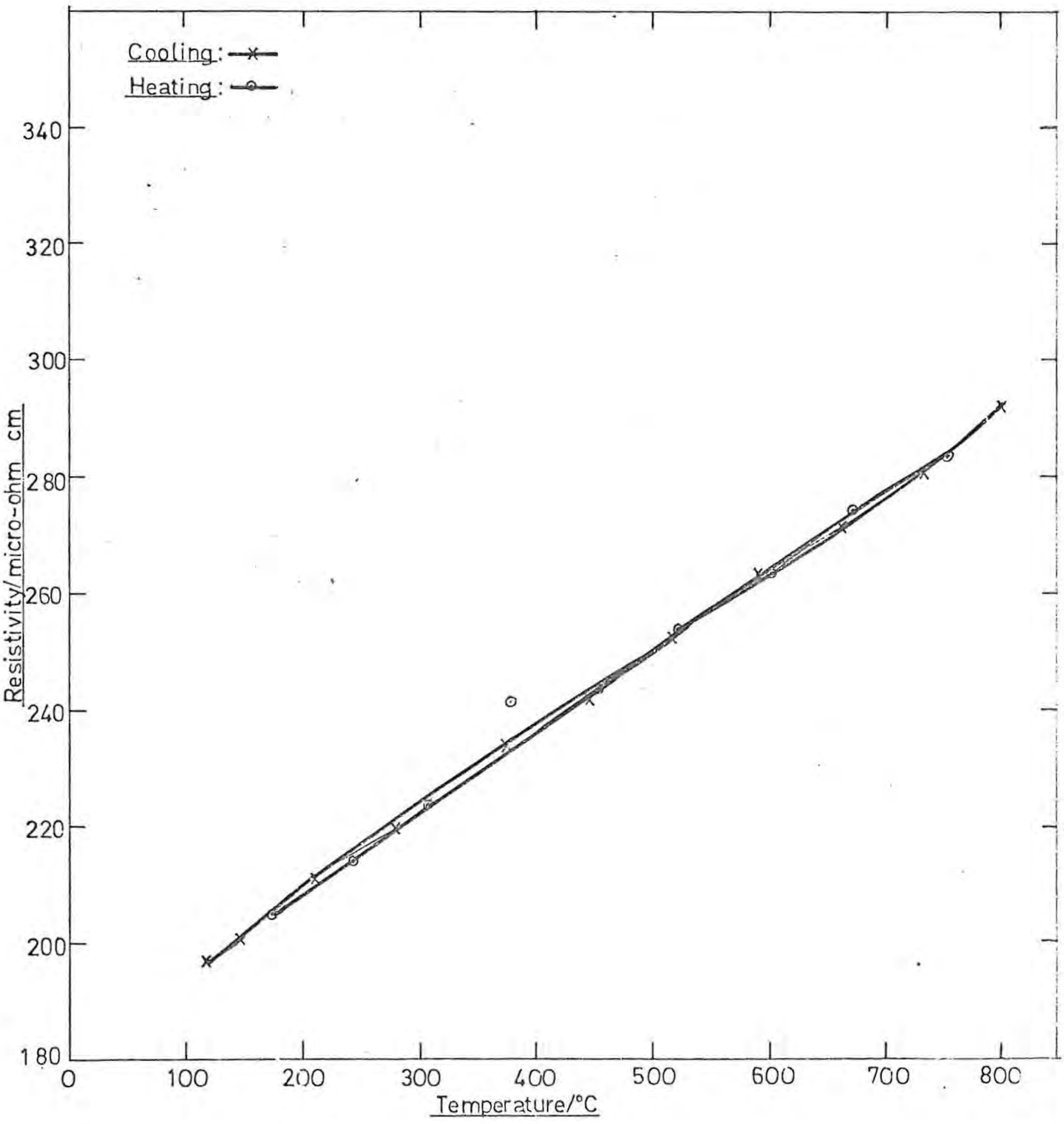
Atmosphere: High purity nitrogen



RUN 18

VN(XXVI)A

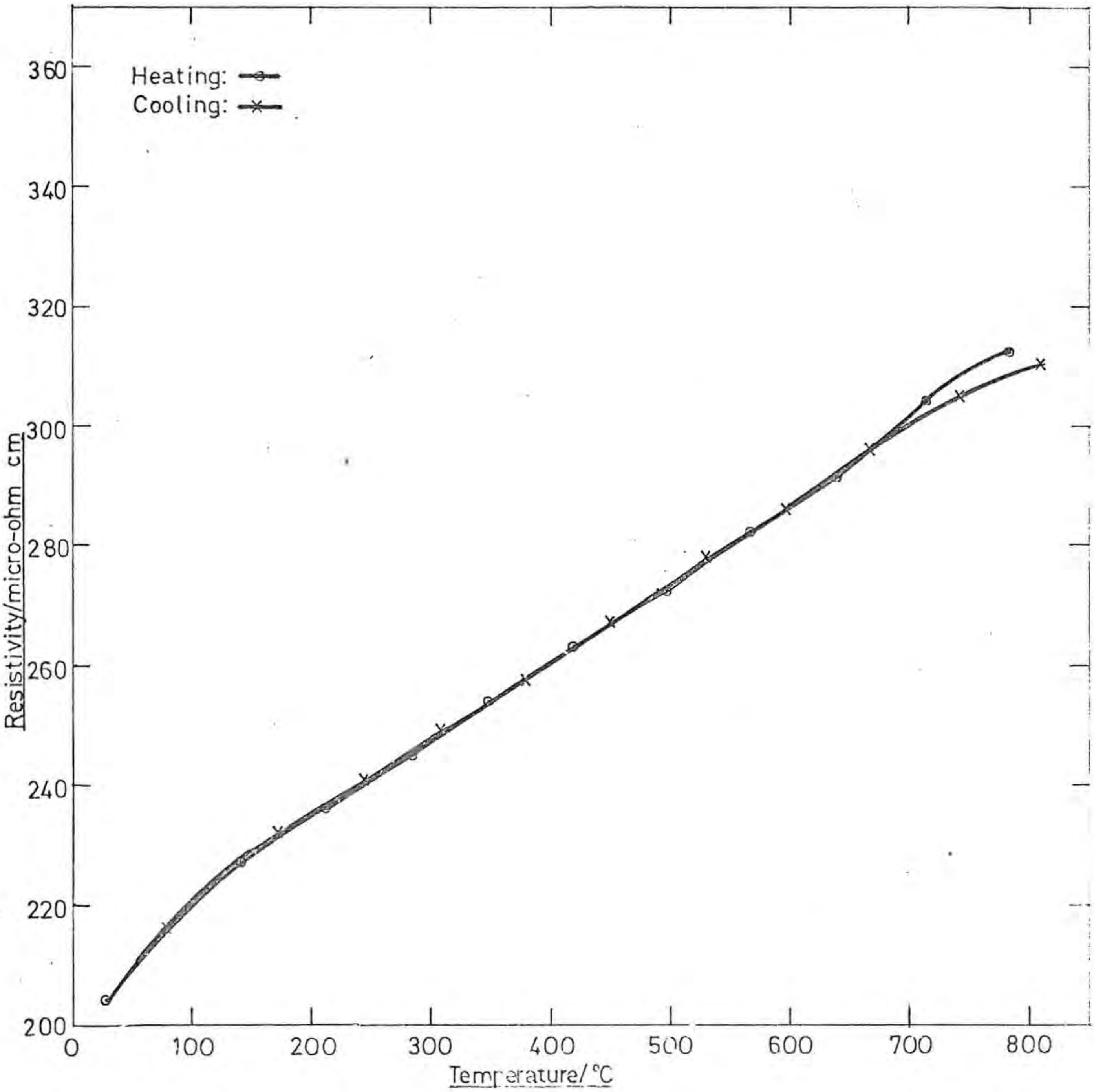
Atmosphere : High purity nitrogen



RUN 20

VN(XXVI)A

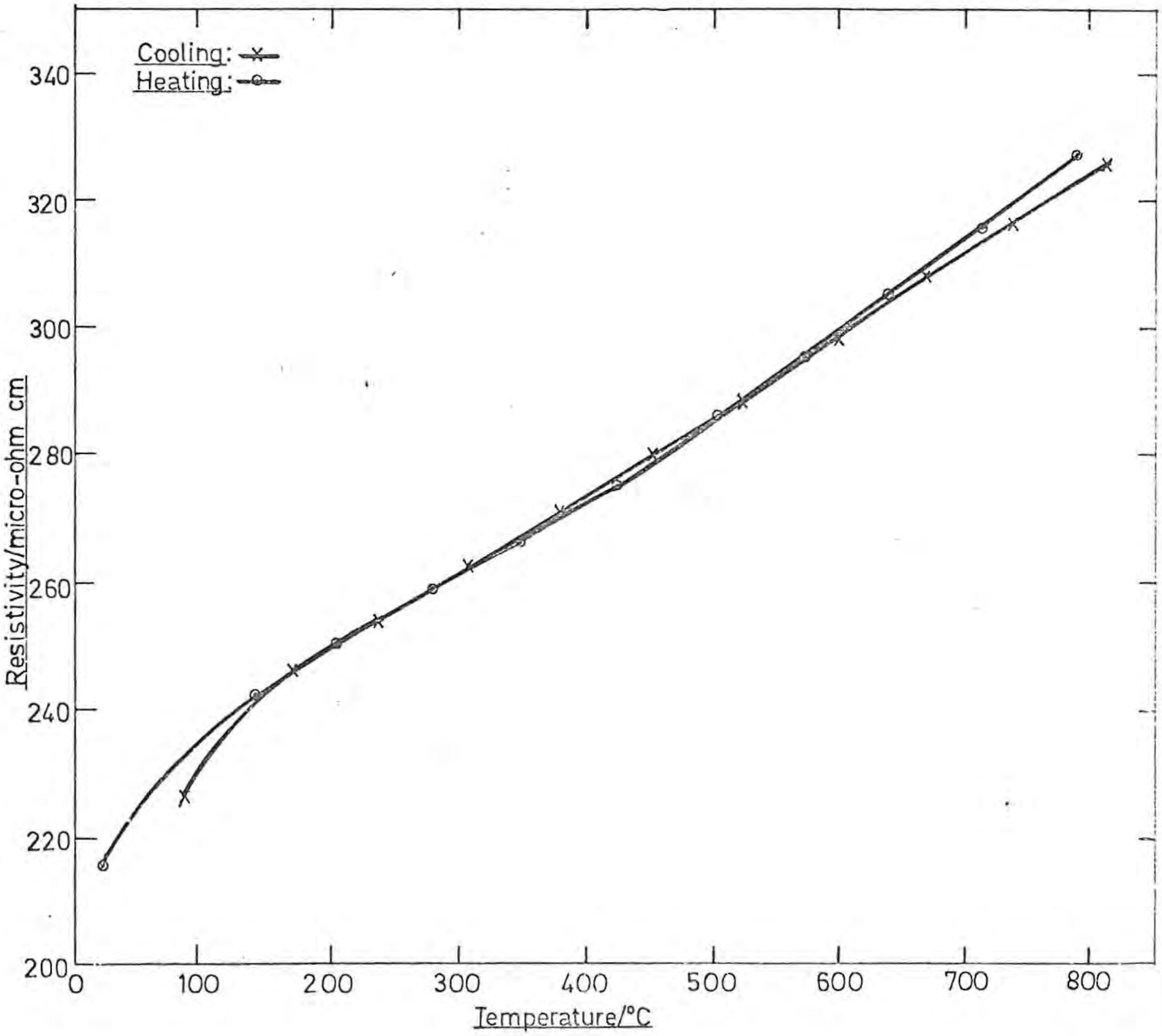
Atmosphere: High purity nitrogen



RUN 21

VN(XXVI) A

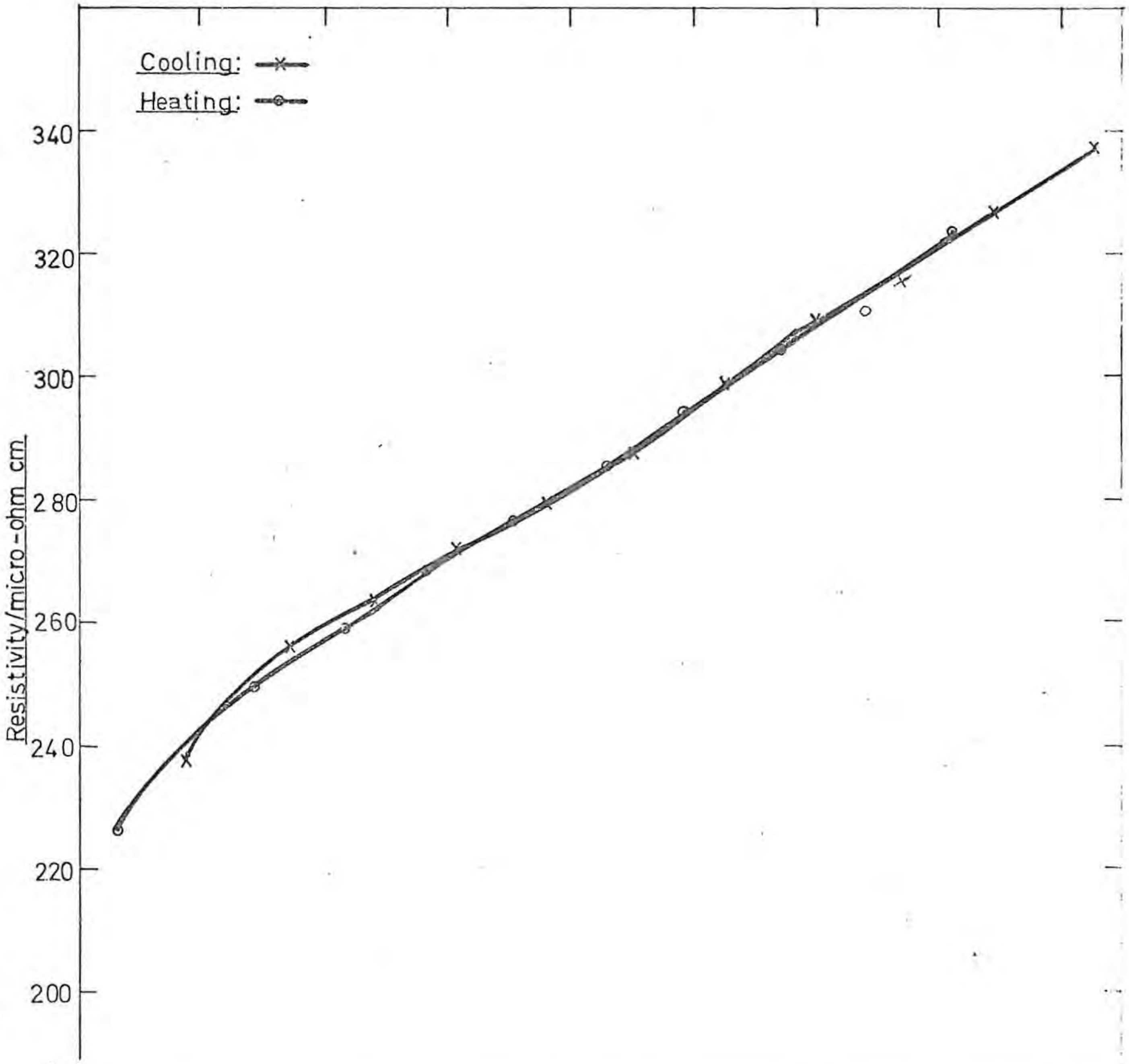
Atmosphere: High purity nitrogen



RUN 22

VN(XXVI)A

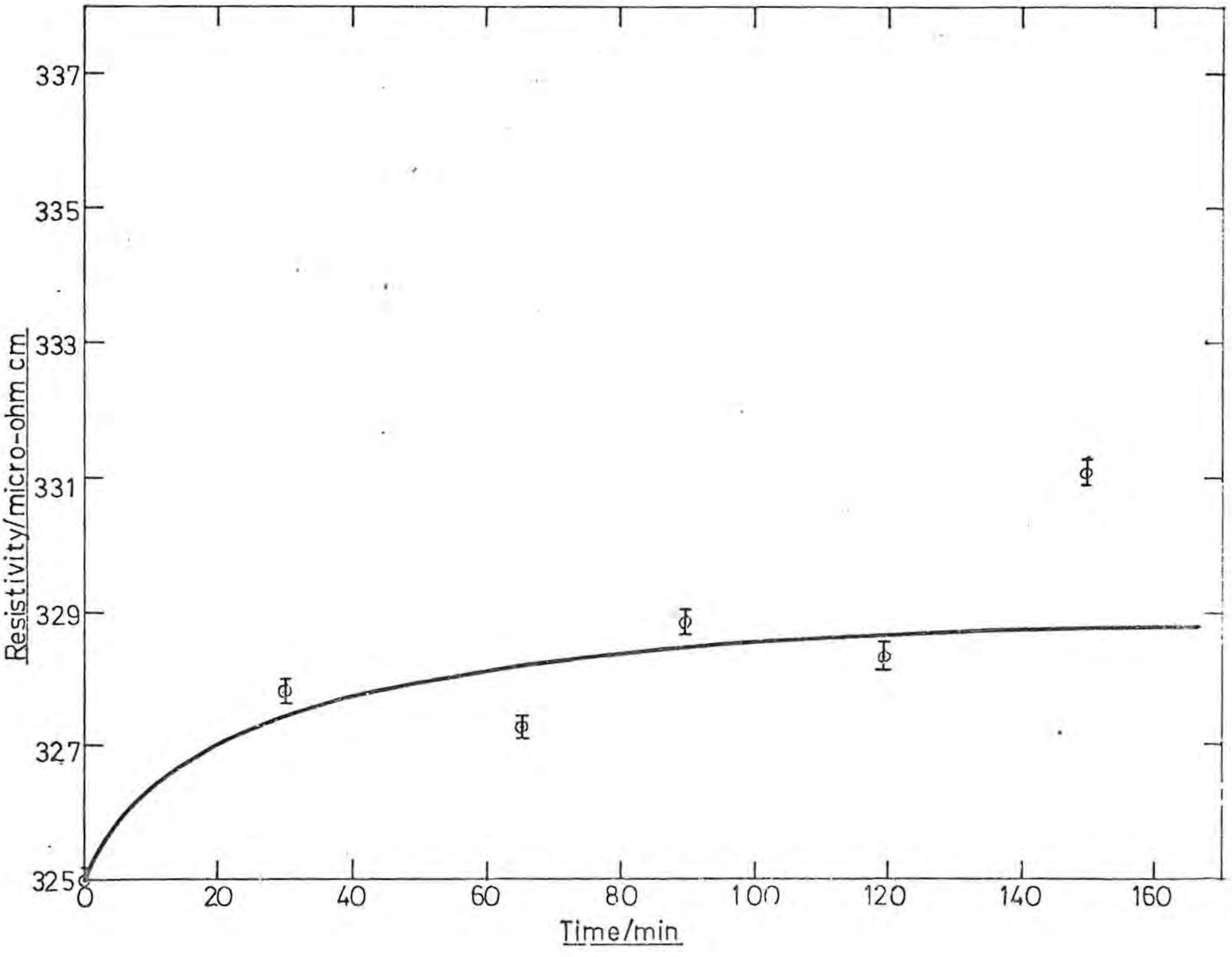
Atmosphere: High purity nitrogen



RUN 22.1

VN(XXVI)A

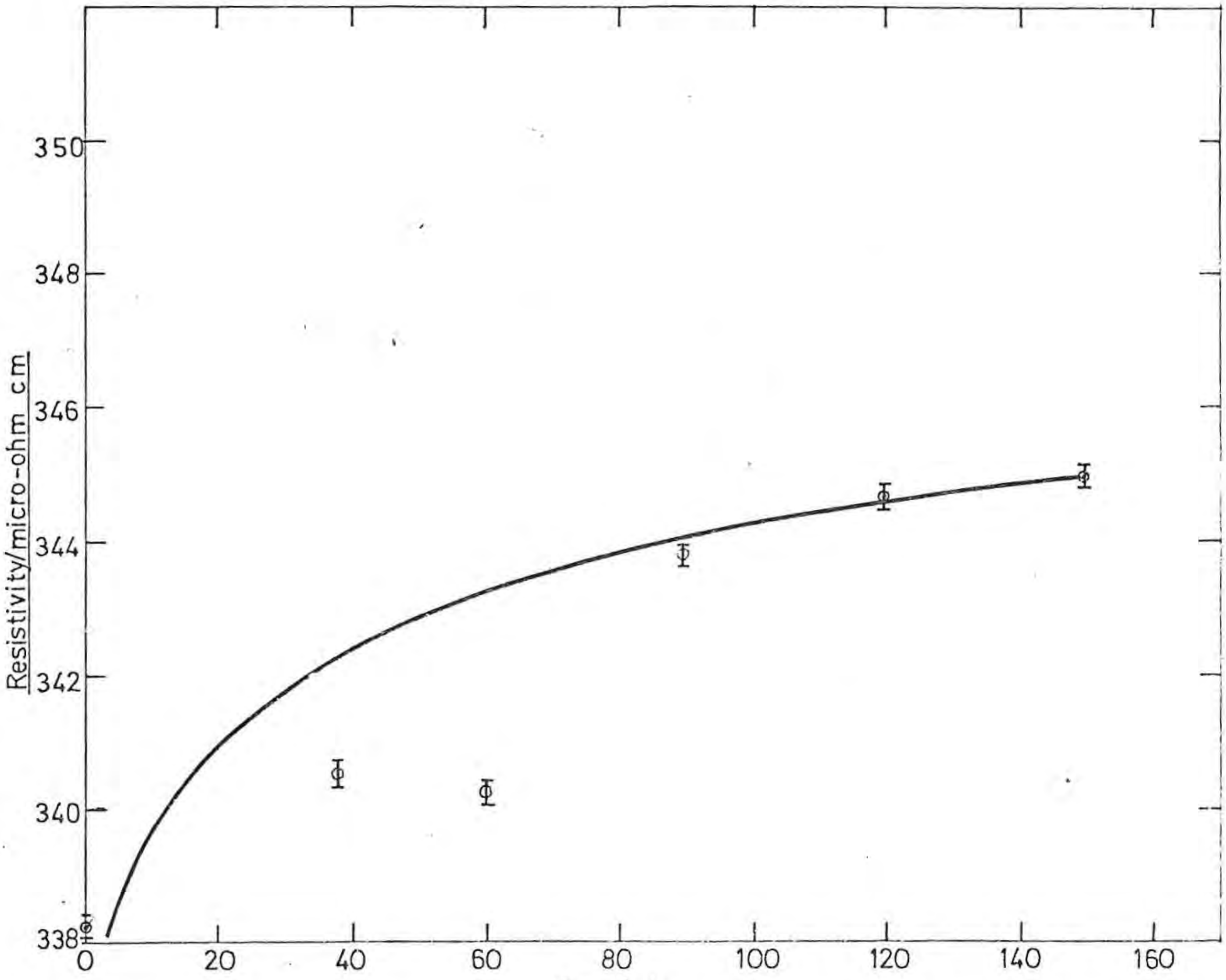
Atmosphere: High purity nitrogen



RUN 22·2

VN(XXVI)A

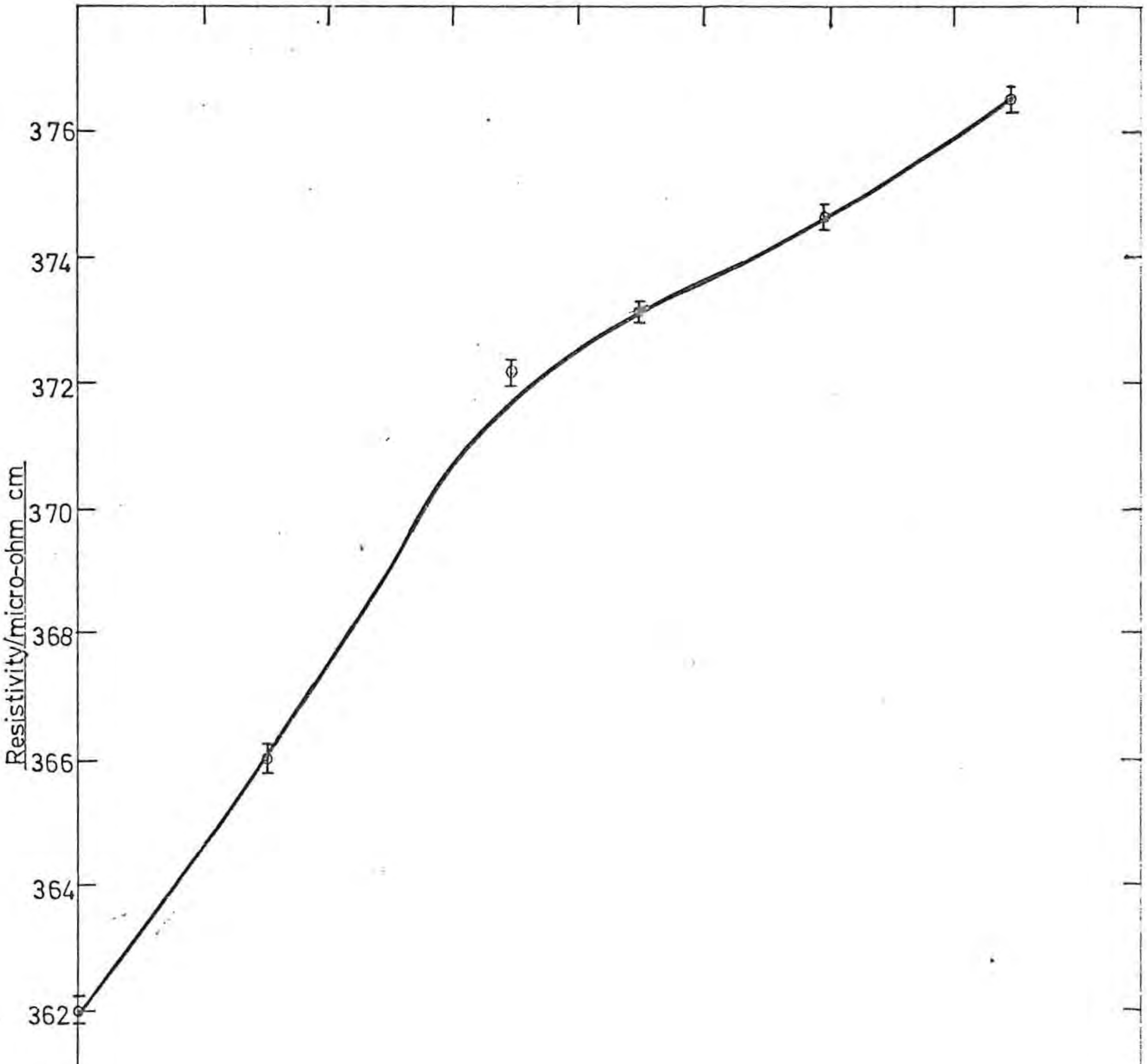
Atmosphere: Air doped nitrogen



RUN 22·3

VN(XXVI)A

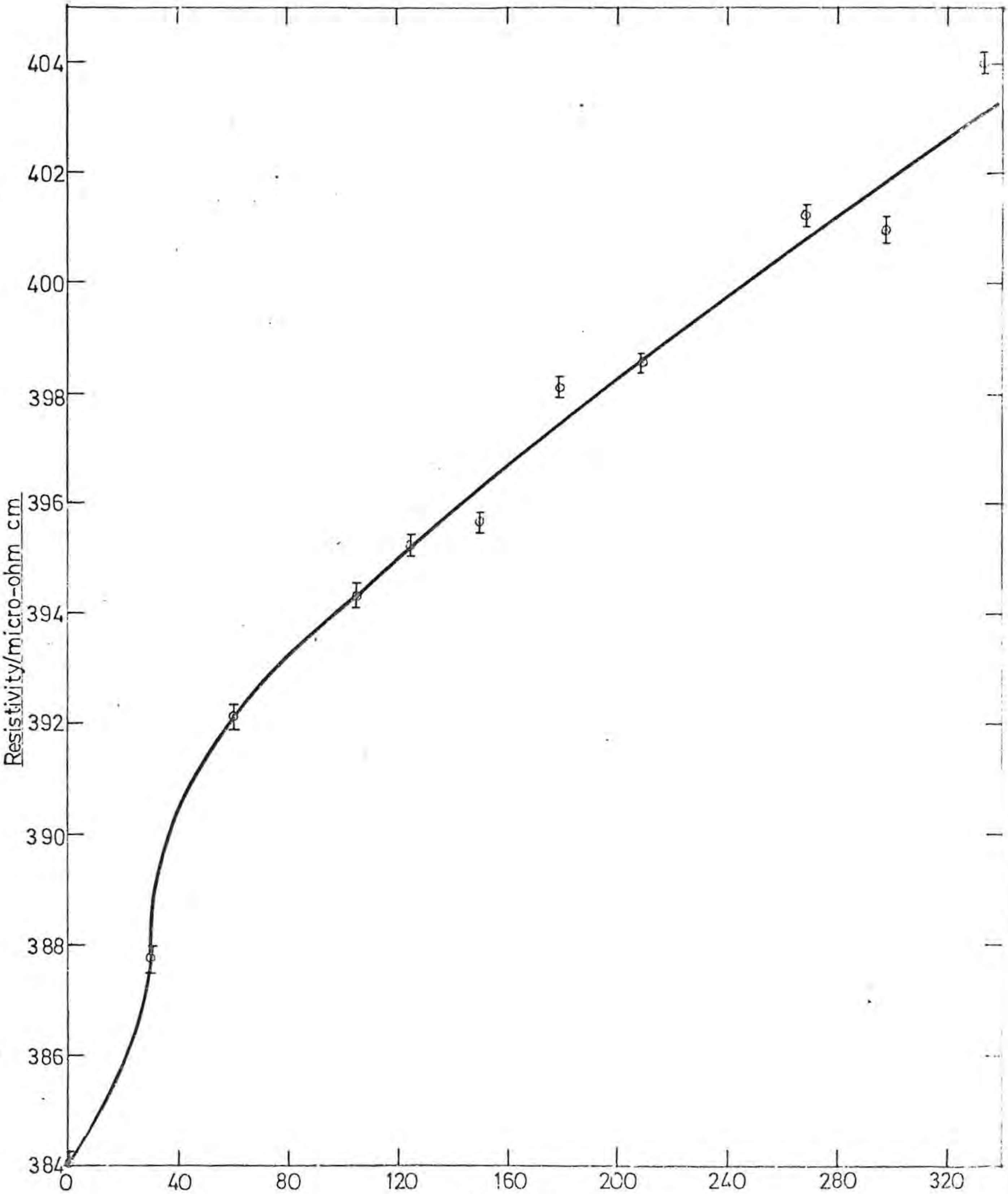
Atmosphere: Air doped nitrogen



RUN 22.4

VN(XXVI)A

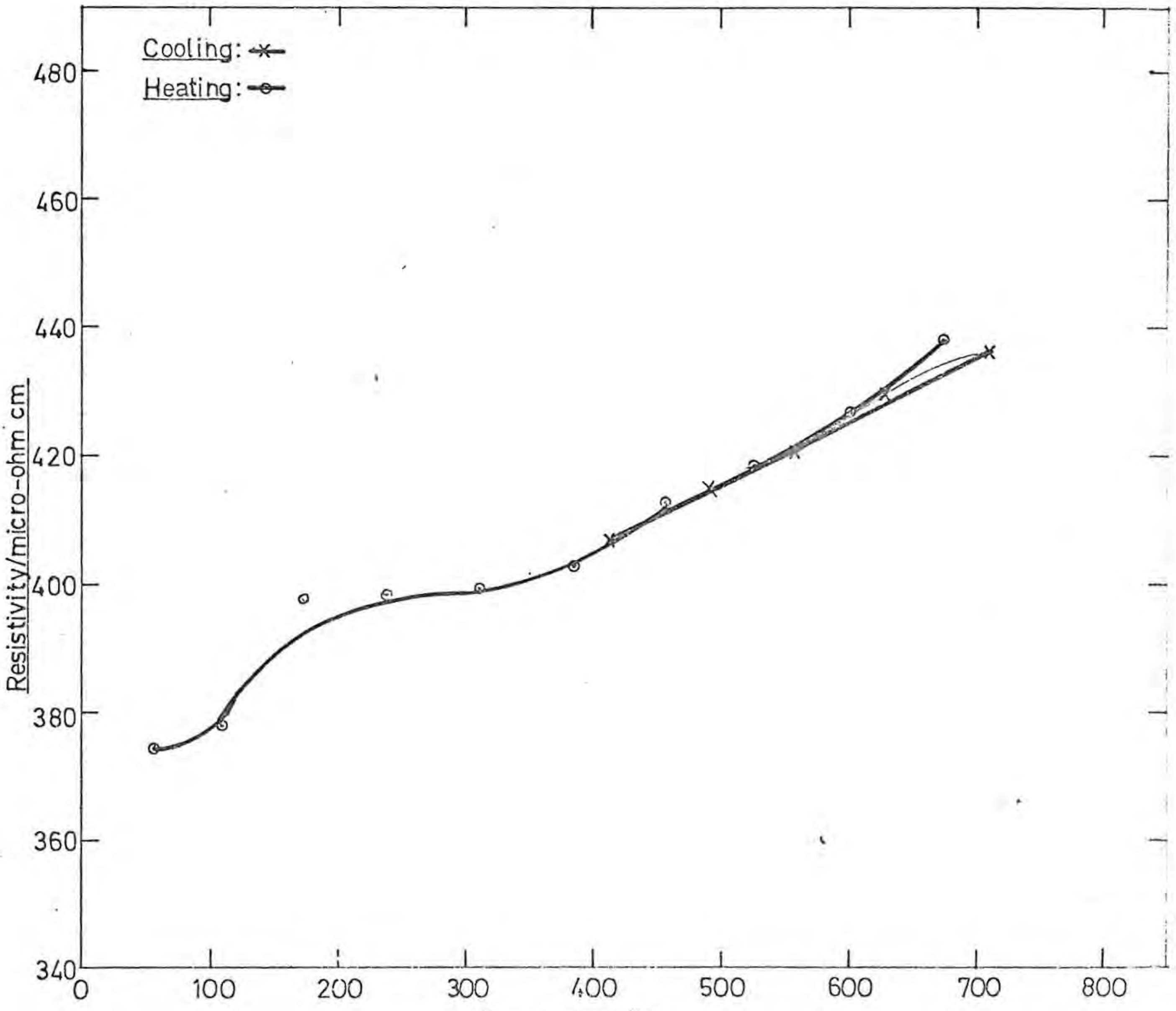
Atmosphere: Air doped nitrogen



RUN 23

VN(XXVI)A

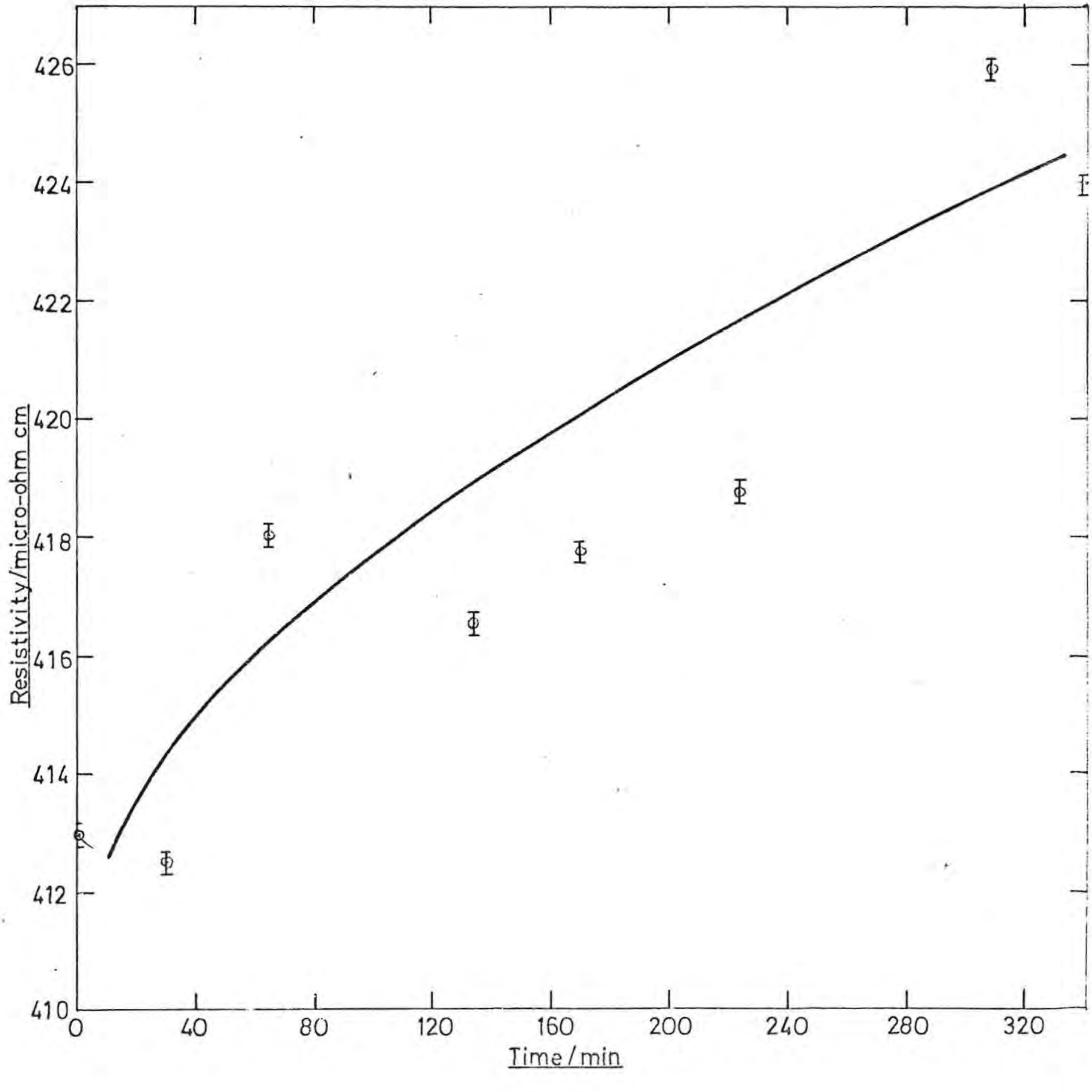
Atmosphere:High purity nitrogen



RUN 23·1

VN(XXVI) A

Atmosphere: High purity nitrogen

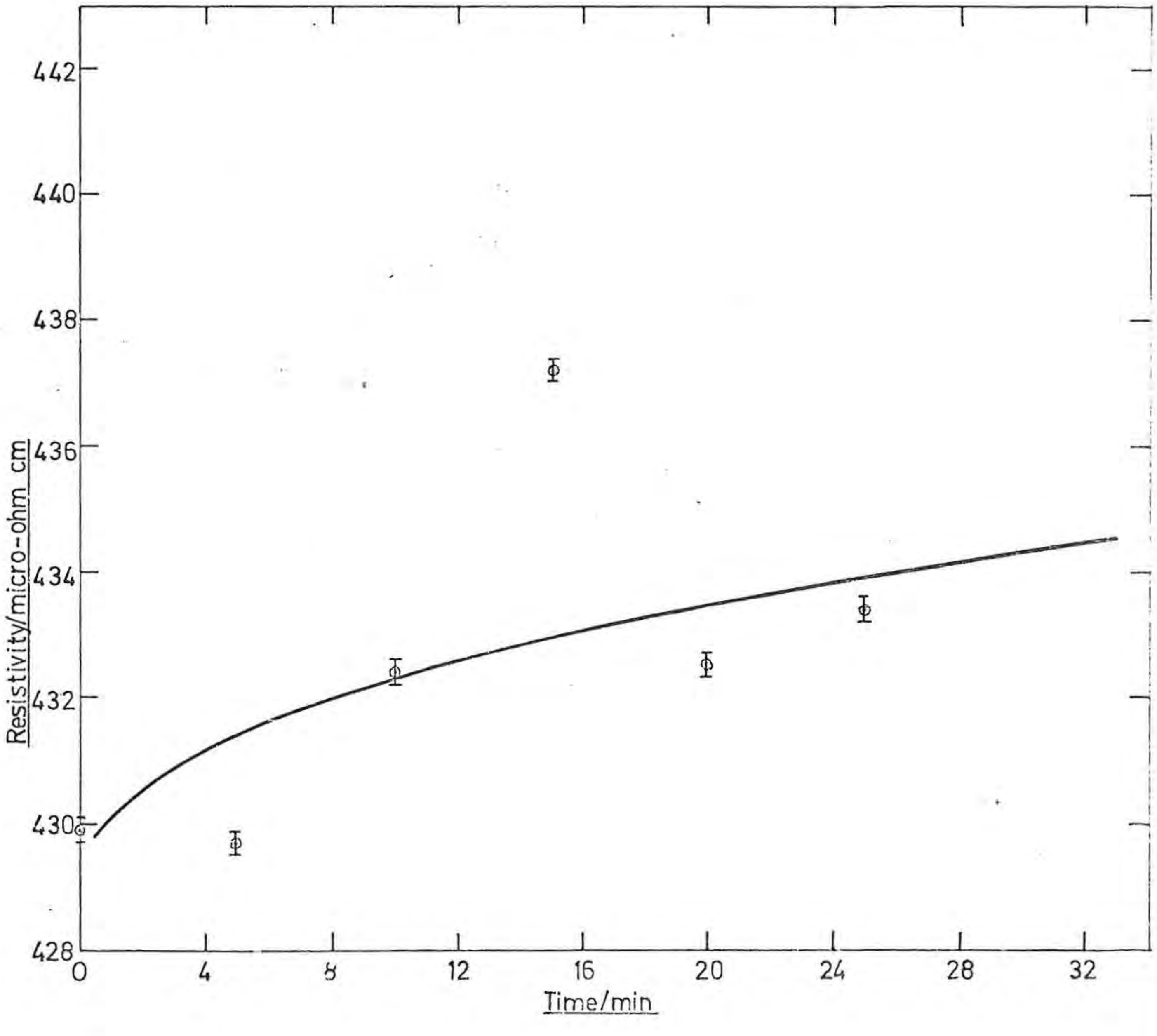


RUN 23.2

VN(XXVI)A

Atmosphere: High purity nitrogen

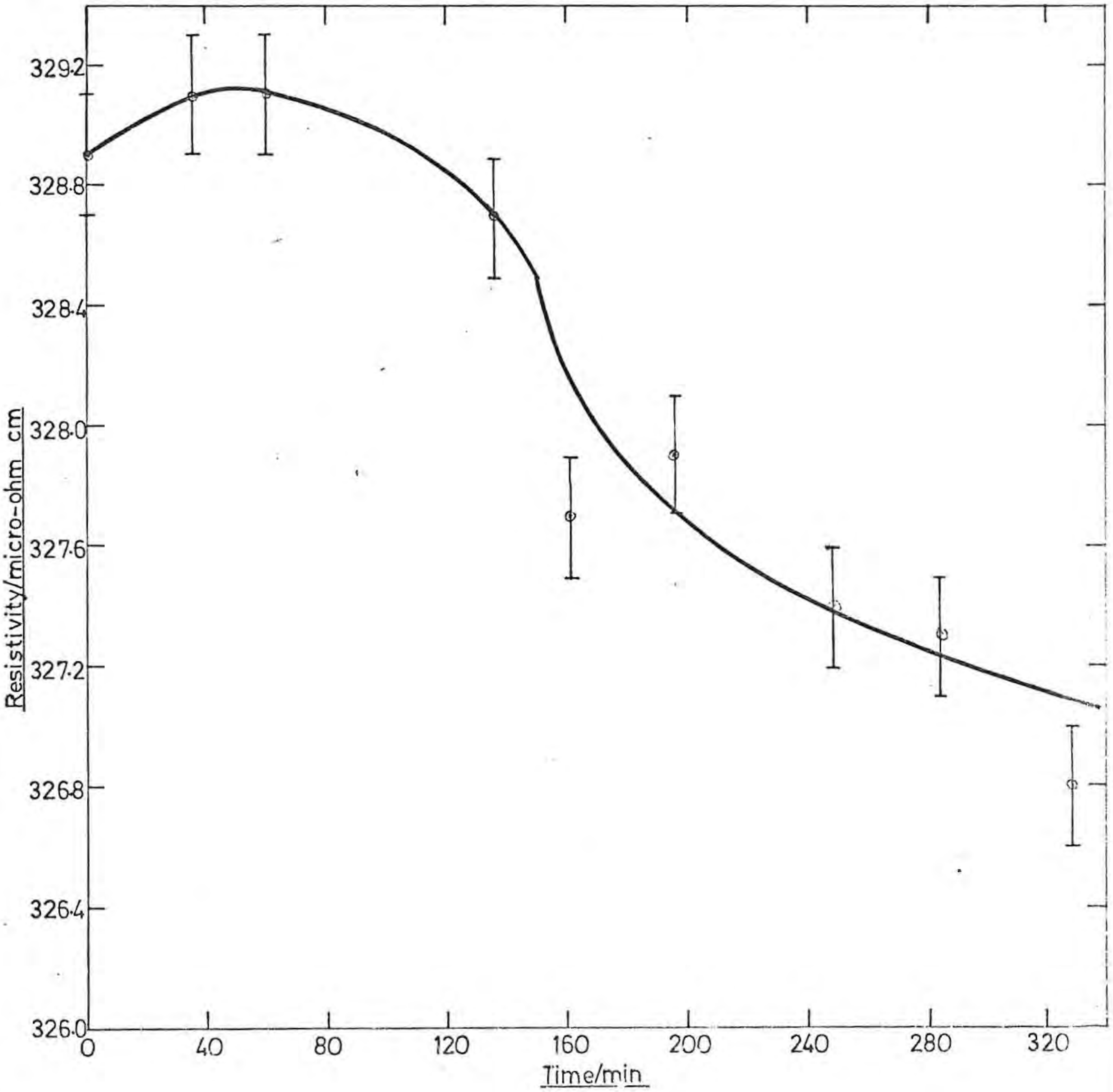
Air injected at 0 min



RUN 28·1

VN(XXVI)B

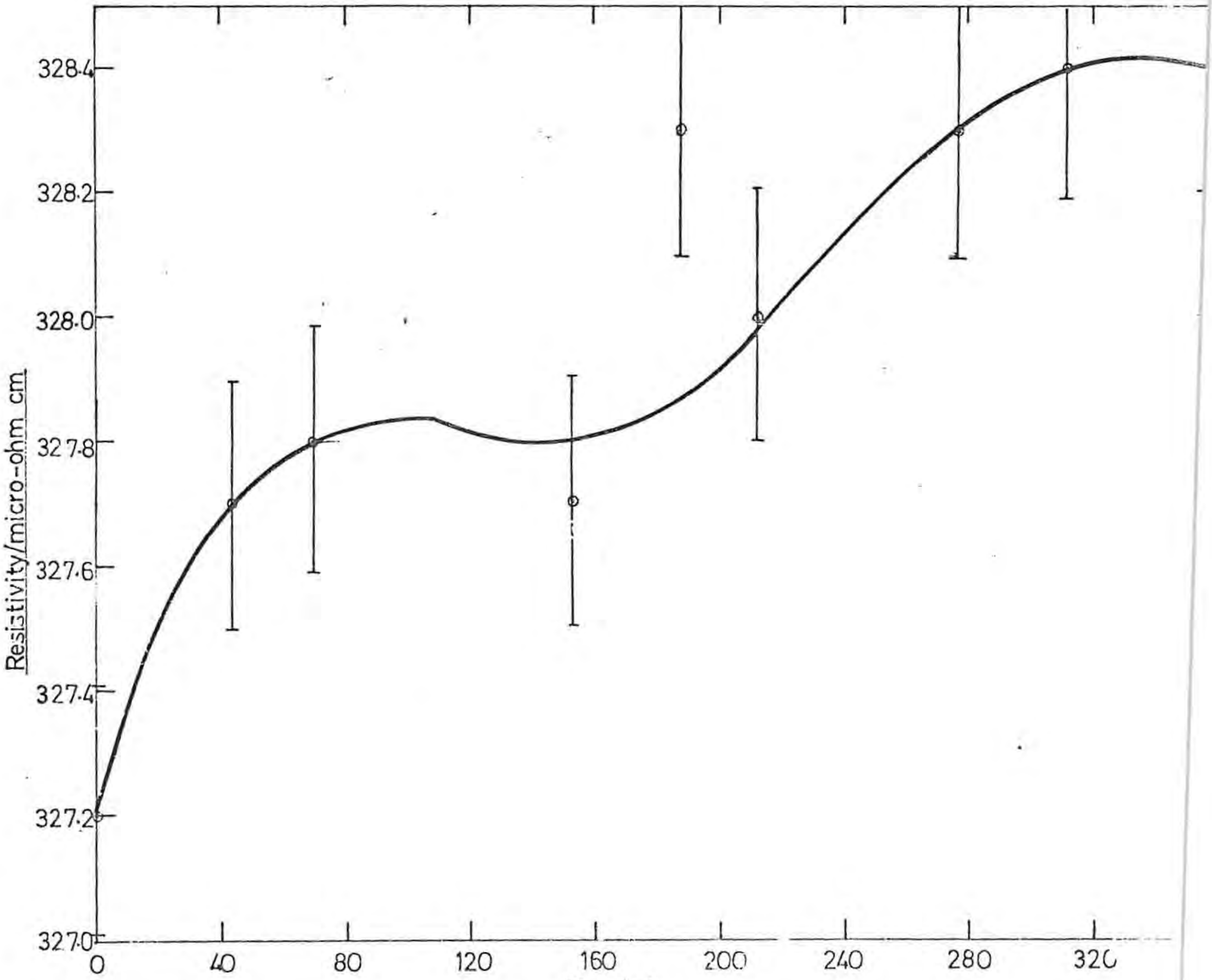
Atmosphere: Nitrogen/8% Hydrogen



RUN 28·2

VN(XXVI)B

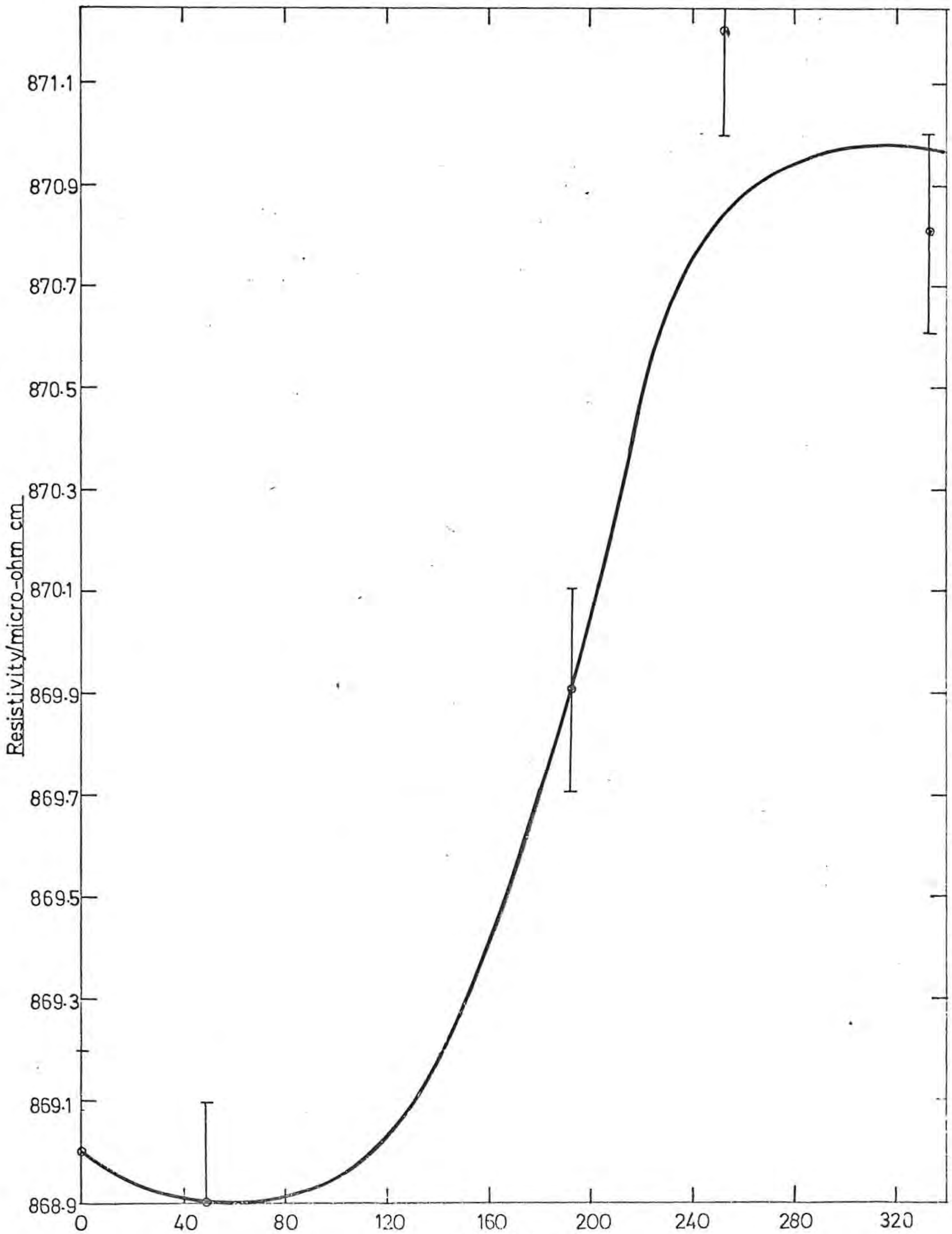
Atmosphere: Nitrogen/8%Hydrogen



RUN 29.1

VN(XXVI) B

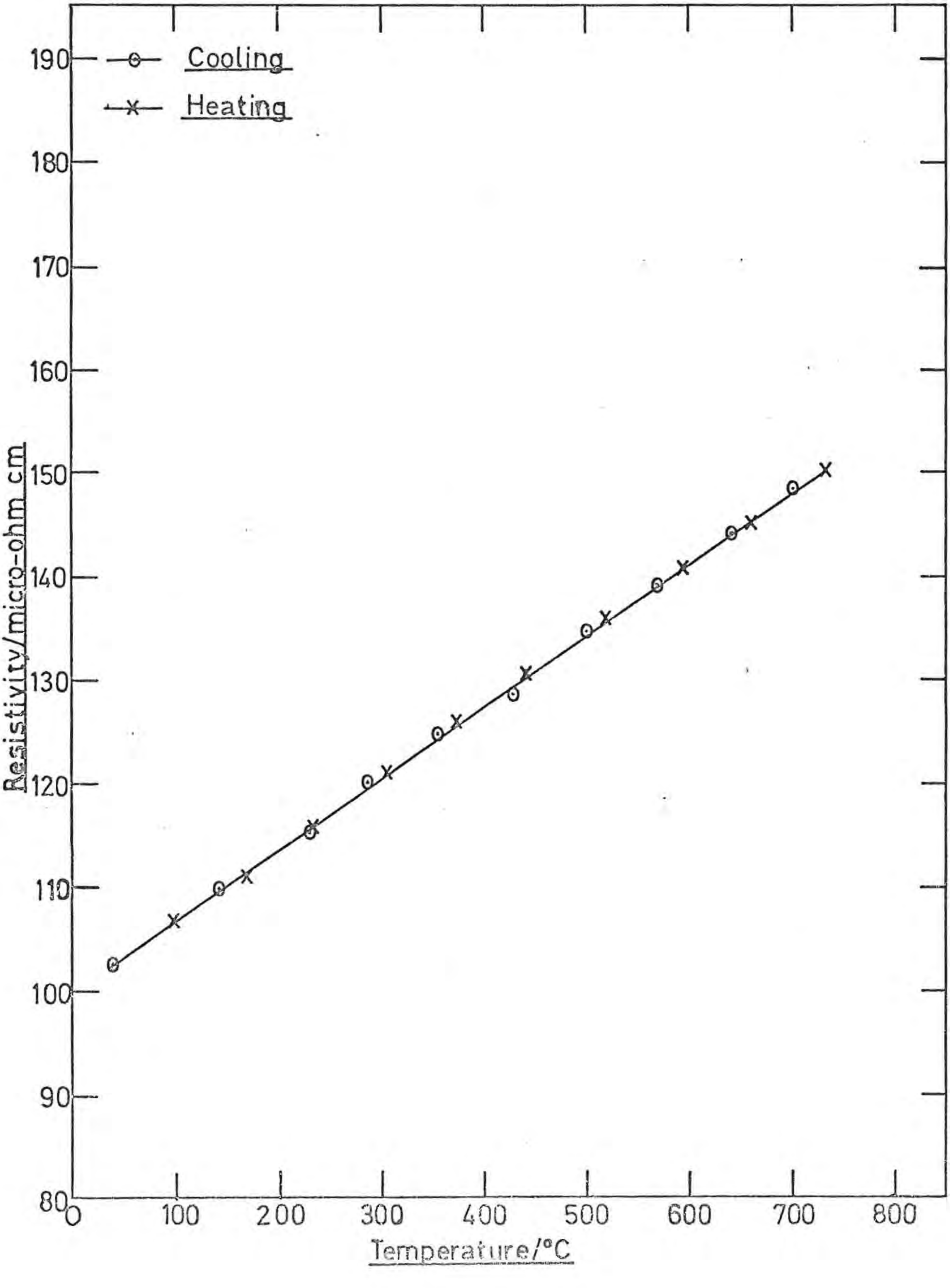
Atmosphere: Nitrogen/8% Hydrogen



RUN 33

Hot pressed VN(B)

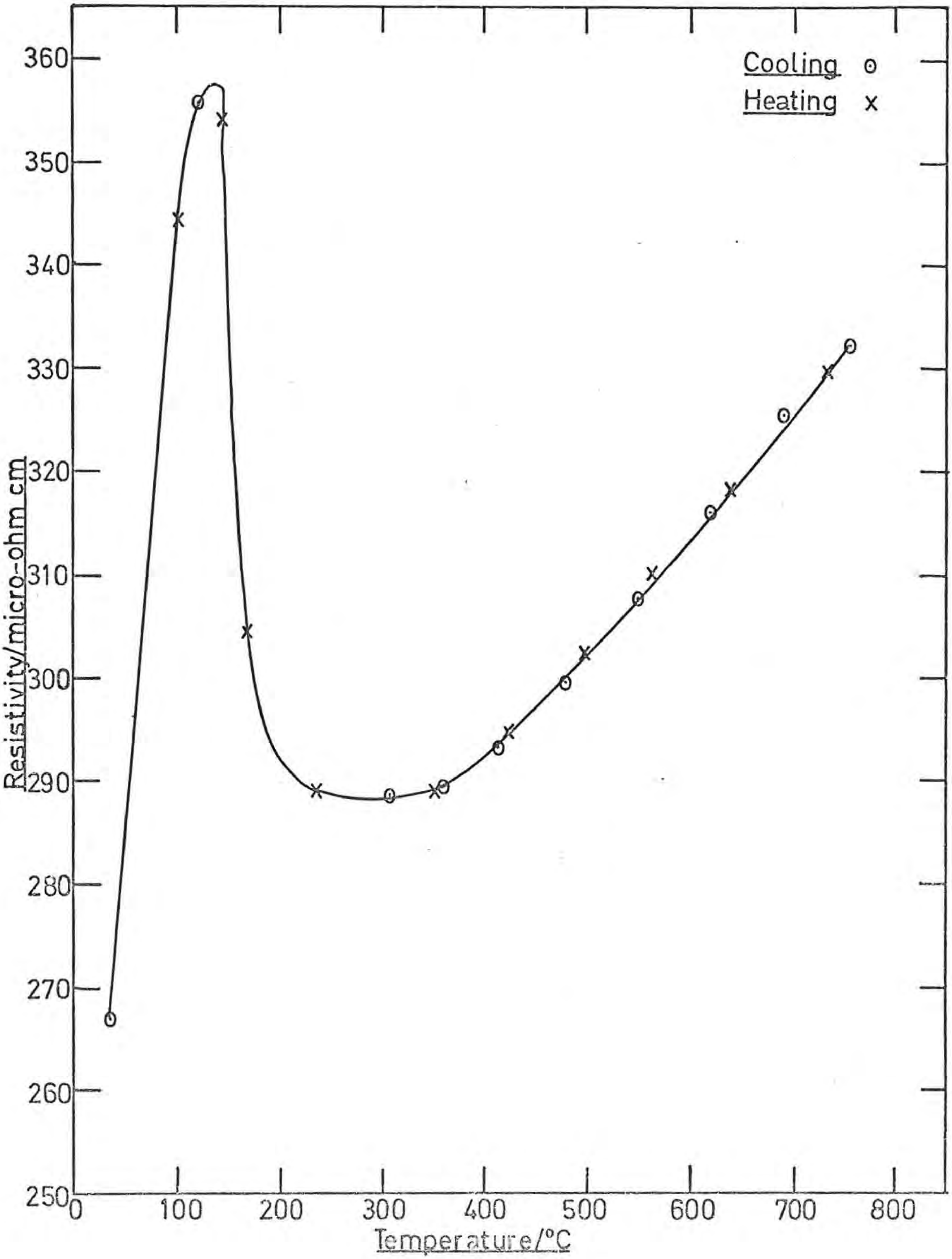
Atmosphere:High purity nitrogen



RUN 34

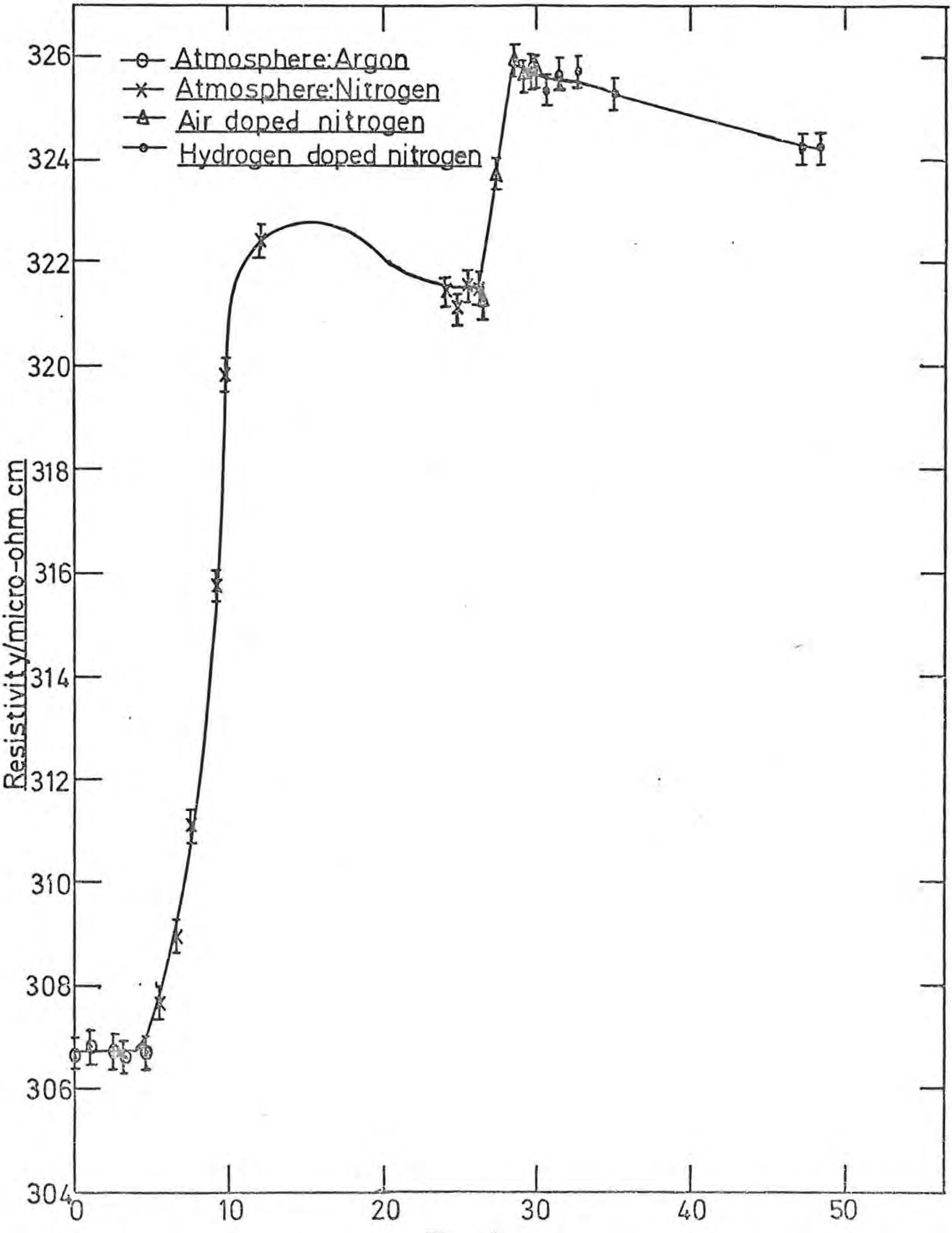
Cold pressed VN(A)

Atmosphere:High purity nitrogen



RUN 34.1

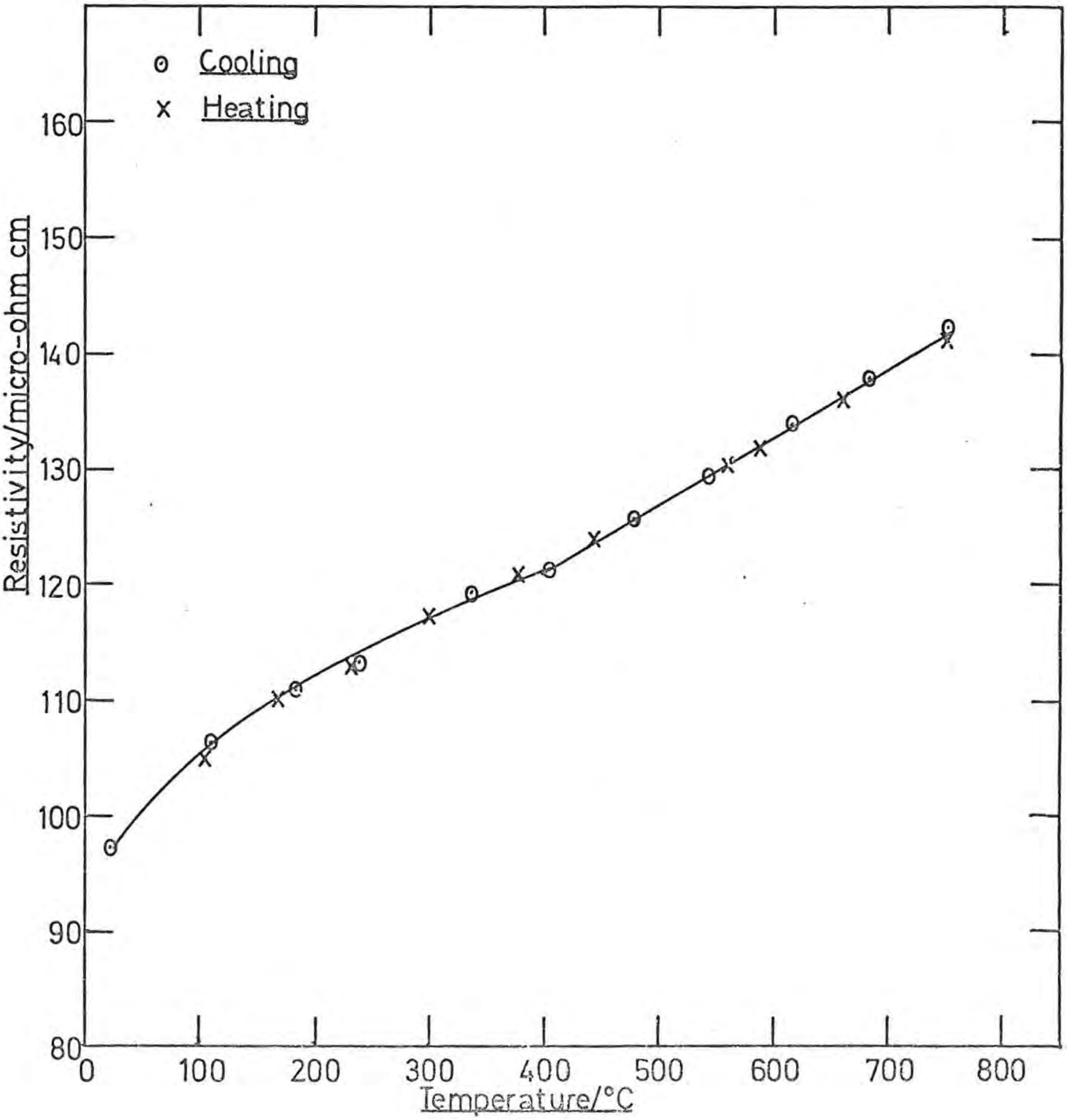
Cold pressed VN(A)



RUN 35

Hot pressed VN(B)

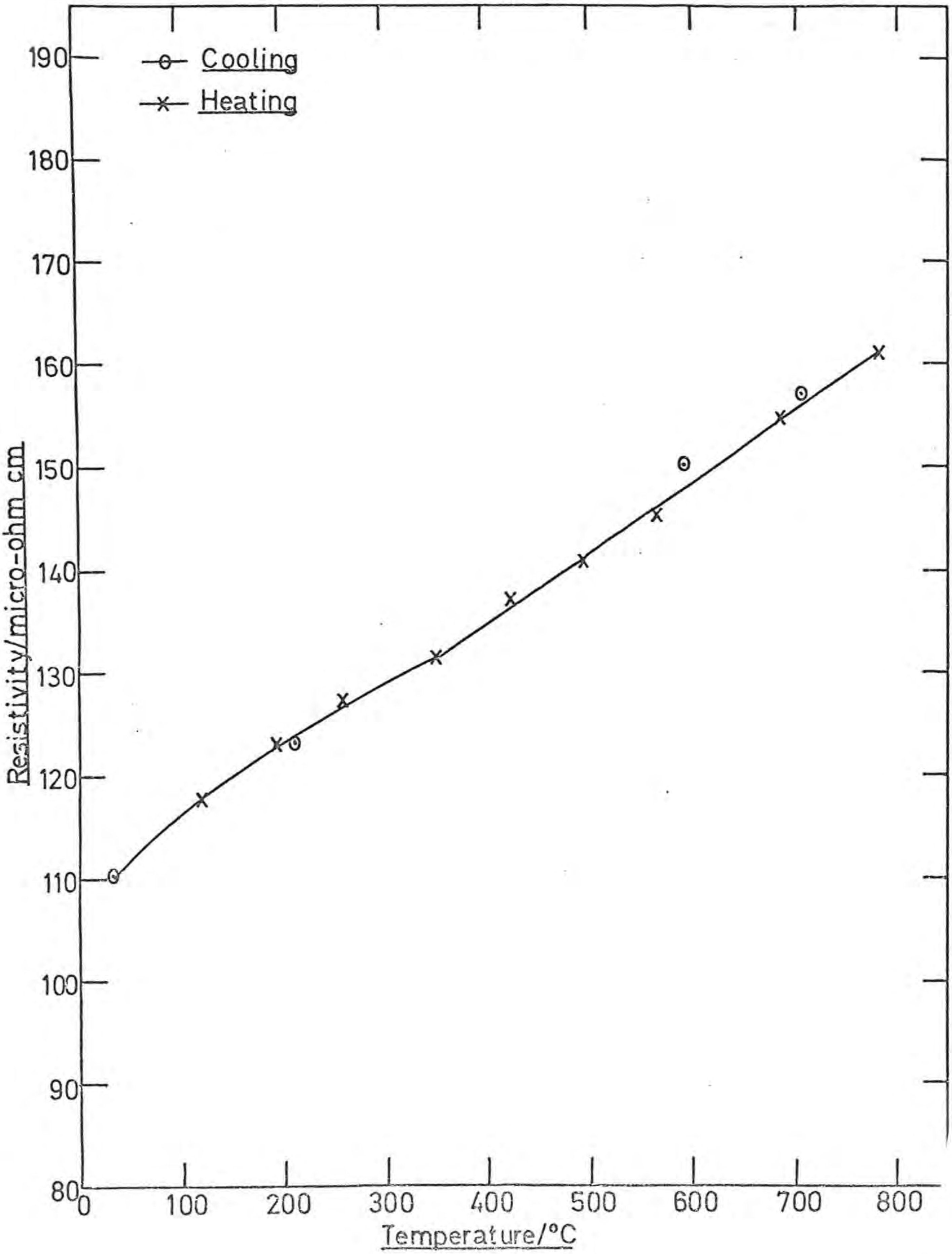
Atmosphere:High purity nitrogen



RUN 36

Hot pressed VN(B)

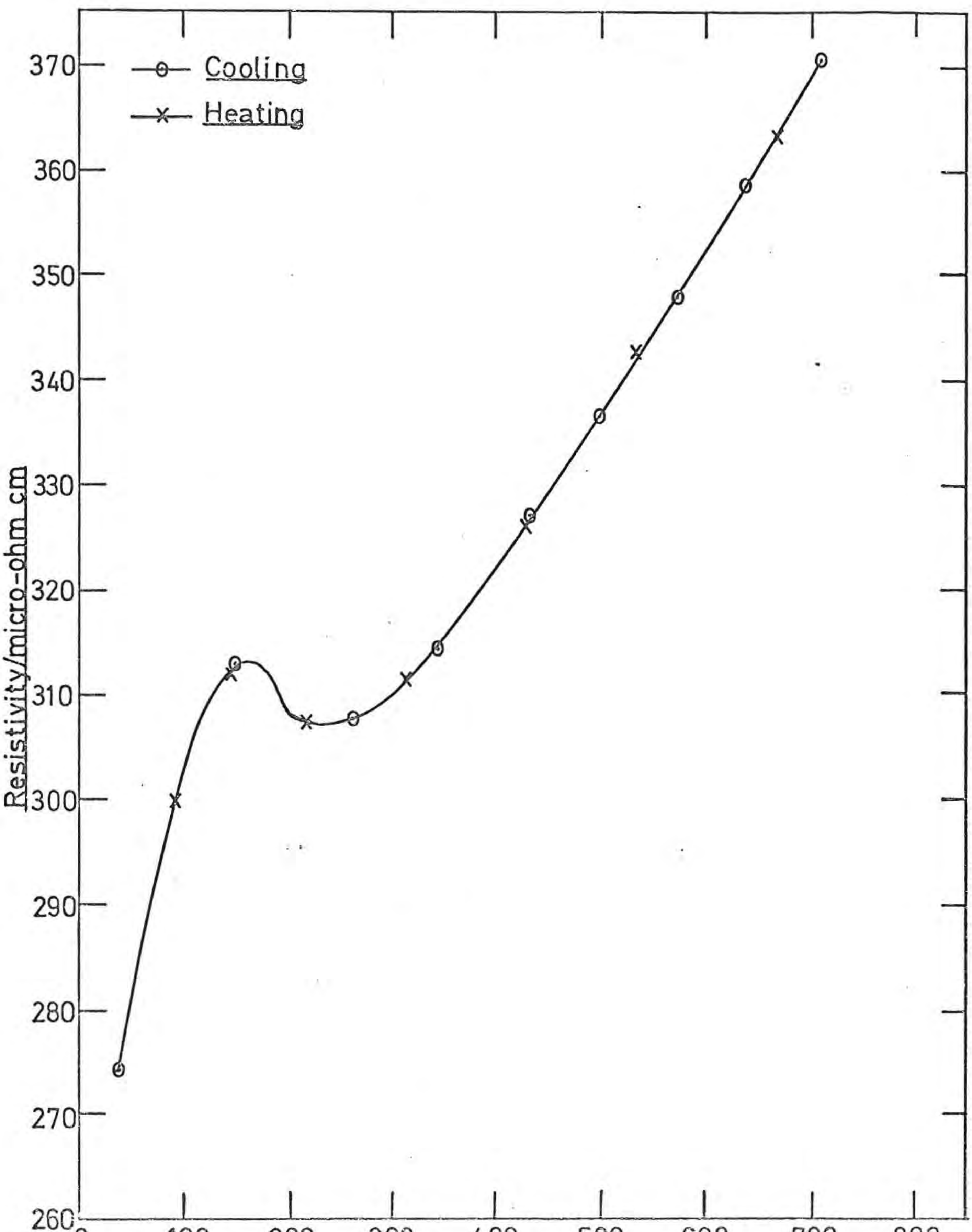
Atmosphere:High purity nitrogen



RUN 37

Cold pressed VN(A)

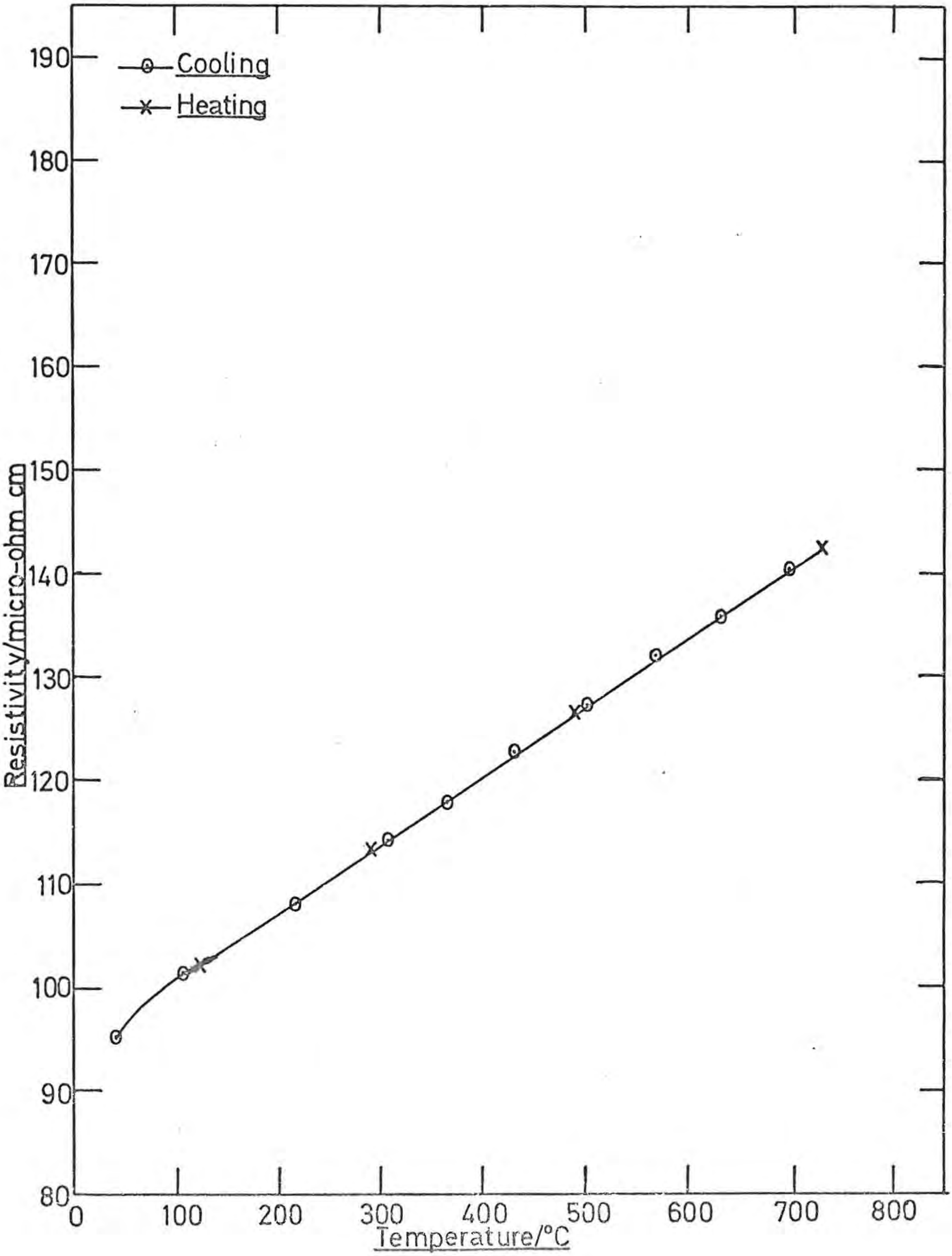
Atmosphere: High purity nitrogen



RUN 38

Hot pressed VN(B)

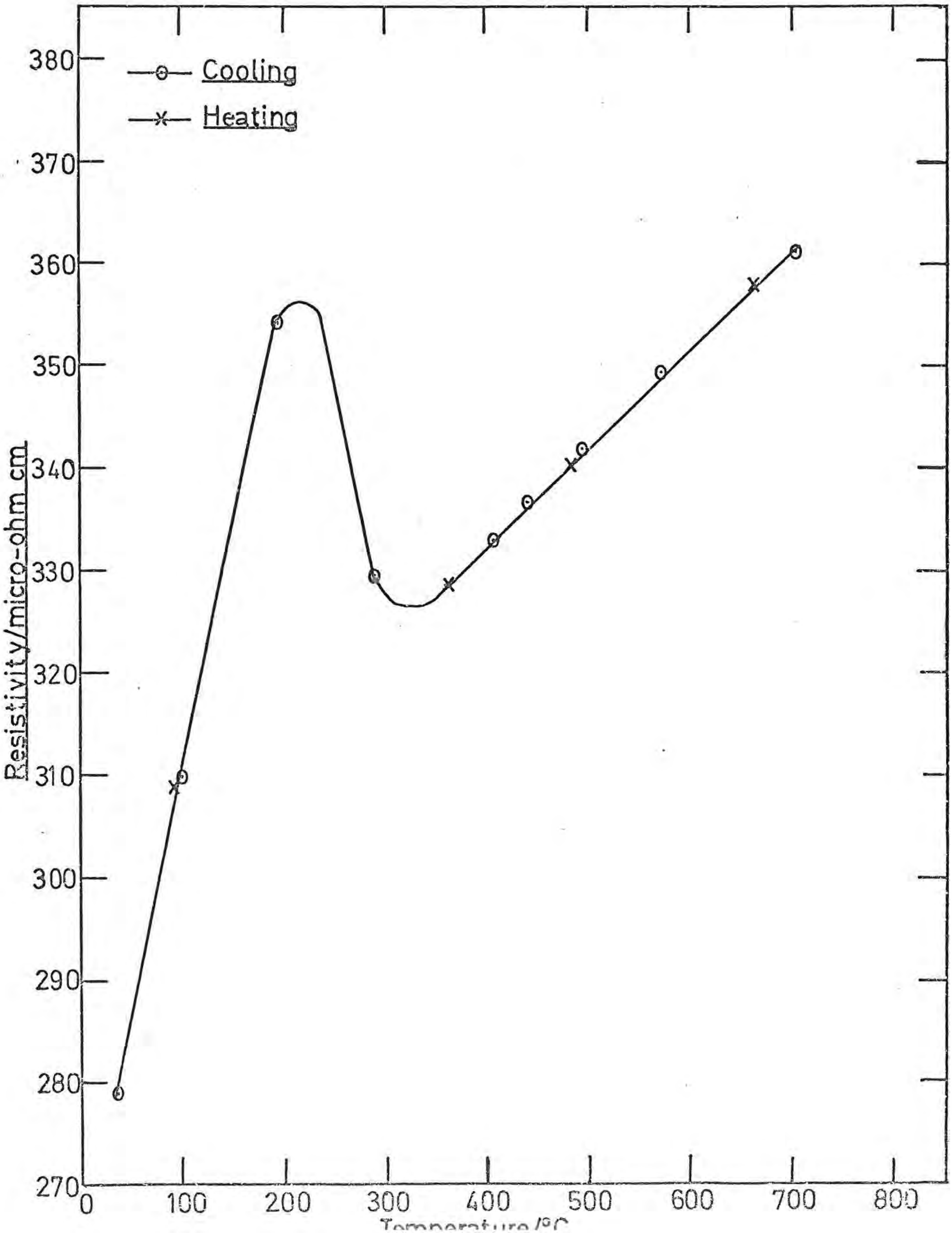
Atmosphere: High purity nitrogen



RUN 39

Cold pressed VN(A)

Atmosphere:High purity nitrogen



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R 334

Philips Res. Repts 13, 1-9, 1958

A METHOD OF MEASURING SPECIFIC RESISTIVITY AND HALL EFFECT OF DISCS OF ARBITRARY SHAPE

by L. J. van der PAUW

537.723.1:53.081.7+538.632:083.9

Summary

A method of measuring specific resistivity and Hall effect of flat samples of arbitrary shape is presented. The method is based upon a theorem which holds for a flat sample of arbitrary shape if the contacts are sufficiently small and located at the circumference of the sample. Furthermore, the sample must be singly connected, i.e.. it should not have isolated holes.

Résumé

On présente une méthode pour mesurer la résistance spécifique et l'effet Hall d'un échantillon plat de forme quelconque. La méthode est fondée sur un théorème qui est appliquable si l'échantillon est plan-parallèle, si les contacts sont suffisamment petits et se trouvent à la périphérie de l'échantillon. Enfin l'échantillon doit être simplement connexe, c-à-d. sans trous isolés.

Zusammenfassung

Es wird eine Methode zur Messung des spezifischen Widerstandes und des Halleffektes einer planparallelen Probe willkürlicher Form angegeben. Die Methode gründet sich auf eine These, die anwendbar ist wenn die Kontakte genügend klein sind und sich am Rande der Probe befinden. Schließlich soll die Probe einfach zusammenhängend sein, d.h. sie darf keine Löcher haben.

1. Introduction

In many cases the specific resistivity and the Hall effect of a conducting material are measured by cutting a sample in the form of a bar. Current contacts A and B and voltage contacts C, D, E and F are attached to the bar as shown in fig. 1. The specific resistivity is then derived from the

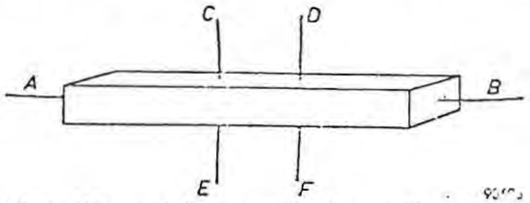

Fig. 1. The classical shape of a sample for measuring the specific resistivity and the Hall effect.

potential drop between the points C and D or E and F and from the dimensions of the sample. On the other hand, the Hall voltage can be measured between the points C and E or D and F. The current contacts must be far away from the points C, D, E and F in order to ensure that the lines of flow are sufficiently parallel and are not changed on application of a magnetic field.

For the measurement of the specific resistivity and Hall effect of semiconductors a more complicated shape of the sample has often to be used. A well-known example is the bridge-shaped sample shown in fig. 2. The large areas at the ends have the task to provide low-ohmic contacts. Furthermore, when making these contacts a heat treatment is often necessary which in this case can be done without heating that part of the sample which is under measurement.

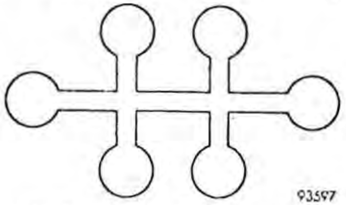

Fig. 2. The bridge-shaped sample, furnished with large areas for making low-ohmic contacts.

It will be shown that the specific resistivity and the Hall effect of a flat sample of arbitrary shape can be measured without knowing the current pattern if the following conditions are fulfilled:

(a) The contacts are at the circumference of the sample.
(b) The contacts are sufficiently small.
(c) The sample is homogeneous in thickness.
(d) The surface of the sample is singly connected, i.e., the sample does not have isolated holes.

2. A theorem which holds for a flat sample of arbitrary shape

We consider a flat sample of a conducting material of arbitrary shape with successive contacts A, B, C and D fixed on arbitrary places along the circumference such that the above-mentioned conditions (a) to (d) are fulfilled (see fig. 3). We define the resistance $R_{AB,CD}$ as the potential difference

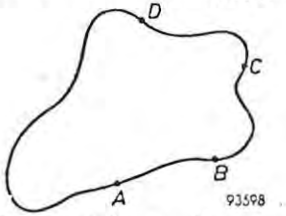

Fig. 3. A sample of arbitrary shape with four small contacts at arbitrary places along the circumference which, according to this paper, can be used to measure the specific resistivity and the Hall effect.

$V_D - V_C$ between the contacts D and C per unit current through the contacts A and B. The current enters the sample through the contact A and leaves it through the contact B. Similarly we define the resistance $R_{BC,DA}$. It will be shown that the following relation holds:

$$\exp(-\pi R_{AB,CD}\, d/\varrho) + \exp(-\pi R_{BC,DA}\, d/\varrho) = 1, \tag{1}$$

where ϱ is the specific resistance of the material and d is the thickness of the sample.

To prove eq. (1) we shall first show that it holds for a particular shape of the sample. The second step is to prove that if it holds for a particular shape it will hold for any shape. For our particular shape we choose a semi-infinite plane with contacts P, Q, R and S along its boundary, spaced at distances a, b and c respectively (see fig. 4). A current j enters the sample at the contact P and leaves it at the contact Q. From elementary theory it follows that

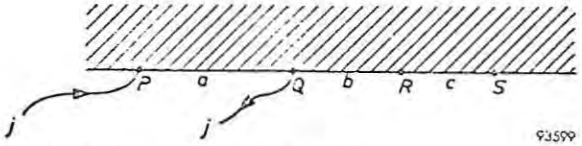

Fig. 4. A sample in the form of a semi-infinite plane with four contacts along its boundary for which eq. (1) is proved first.

$$V_S - V_R = \frac{j\varrho}{\pi d} \ln \frac{(a+b)(b+c)}{b(a+b+c)}.$$

Hence

$$R_{PQ,RS} = \frac{\varrho}{\pi d} \ln \frac{(a+b)(b+c)}{b(a+b+c)}. \tag{2}$$

In the same way, we have

$$R_{QR,SP} = \frac{\varrho}{\pi d} \ln \frac{(a+b)(b+c)}{ca}. \tag{3}$$

Moreover,

$$b(a+b+c) + ca = (a+b)(b+c). \tag{4}$$

From the eqs (2), (3) and (4) eq. (1) follows immediately.

Using the same arguments it can also be shown that

$$R_{PQ,RS} = R_{RS,PQ}, \tag{5}$$

$$R_{QR,SP} = R_{SP,QR}, \tag{6}$$

$$R_{PR,QS} = R_{QS,PR}, \tag{7}$$

$$R_{PQ,SR} + R_{QR,SP} + R_{PR,QS} = 0. \tag{8}$$

The last four relations, however, are of a much more general nature than (1) and follow also from the reciprocity theorem of passive multipoles.

We shall now proceed with the second step and show that eq. (1) holds quite generally. To that end we make use of the well-known technique of conformal mapping of two-dimensional fields *). We assume that the semi-infinite sample considered above coincides with the upper part of the complex z-plane, where $z = x + iy$.

We introduce a function $w = f(z) = u(x,y) + iv(x,y)$, where u and v are both real functions of x and y. The function $f(z)$ is chosen in such a way that u represents the potential field in the sample. The functions u and v satisfy the Cauchy-Riemann relations:

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y}, \tag{9}$$

$$\frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x}. \tag{10}$$

If we now travel from an arbitrary point T_1 in the upper half-plane to another point T_2 in the upper half-plane (see fig. 5), the net current which traverses our path from right to left is given by

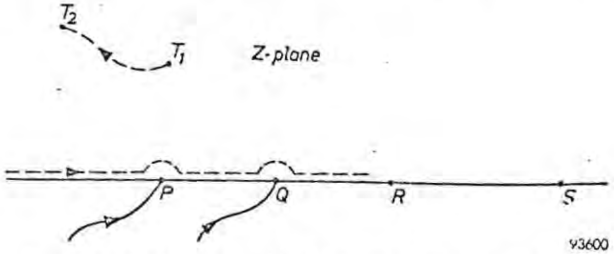

Fig. 5. The same sample as in fig. 4, coinciding with the upper part of the complex z-plane.

$$j_{T_2,T_1} = \frac{d}{\varrho} \int_{T_1}^{T_2} E_n \, ds,$$

where E_n is the normal component of the field strength. This expression is readily verified to be equal to

$$j_{T_2,T_1} = \frac{d}{\varrho} \int_{T_1}^{T_2} \left(-\frac{\partial u}{\partial y}\,dx + \frac{\partial u}{\partial x}\,dy\right) = \frac{d}{\varrho} \int_{T_1}^{T_2} \left(\frac{\partial v}{\partial x}\,dx + \frac{\partial v}{\partial y}\,dy\right) = \frac{d}{\varrho}\left(v_{T_2} - v_{T_1}\right).$$

Hence if we travel along the real axis from $-\infty$ to $+\infty$ the value of v remains constant until we pass the point P. When passing the point P along a small half-circle in the upper half-plane the value of v will increase by $\varrho j/d$. Similarly when passing the point Q the value of v will decrease by $\varrho j/d$. We consider now a sample of arbitrary shape, lying in a different complex plane which we shall call the t-plane (see fig. 6), where $t = r + is$.

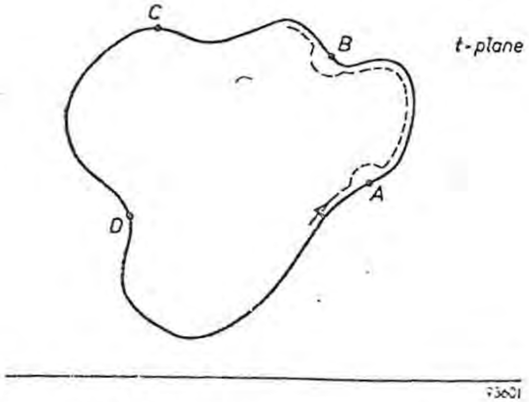

Fig. 6. A sample of arbitrary shape, lying in the complex t-plane.

By a well-known theorem, it is always possible to find an analytic function $t(z)$ such that the upper half-plane in the z-plane is mapped onto the sample in the t-plane. There are some restrictions as to the shape of the sample in the t-plane which are, however, not of physical interest. In particular, let A, B, C and D in the t-plane be the images of the points P, Q, R and S respectively in the z-plane. Furthermore, let $k(t) = l + im$ be identical with $f(z) = f(z(t)) = k(t)$. Hence by definition m remains constant when travelling in counter-clockwise direction along the boundary of the sample in the t-plane; it only increases by $\varrho j/d$ when passing the point A and it decreases by the same amount when passing the point B.

From the theory of conformal mapping it follows that if m in the t-plane is interpreted in the same way as v in the z-plane, then l will represent the potential field in the t-plane. Consequently if a current j' enters the sample at the contact A and leaves it at the contact B and if we choose $j'\varrho'/d' = j\varrho/d$, where ϱ and d' are the specific resistivity and the thickness of the sample in the t-plane, then the voltage difference $V_D - V_C$ will be equal to the voltage difference $V_S - V_R$. Hence $(d/\varrho)\ R_{AB,CD}$ is invariant under conformal transformation. The same is true for $(d/\varrho)\ R_{BC,DA}$. From this it follows that eq. (1) is of general validity.

3. Practical applications

From the above section it follows that for measuring the specific resistivity of a flat sample it suffices to make four small contacts along its circum-

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*) L. V. Bewley, Two-dimensional fields in electrical engineering, The MacMillan Company, New York, 1948.

ference and to measure the two resistances $R_{AB,CD}$ and $R_{BC,DA}$ (see fig. 3) and the thickness of the sample. Equation (1) determines uniquely the value of ϱ as a function of $R_{AB,CD}$, $R_{BC,DA}$ and d. In order to facilitate the solution of ϱ from eq. (1) we write it in the form

$$\varrho = \frac{\pi d}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} f\left(\frac{R_{AB,CD}}{R_{BC,DA}}\right), \tag{11}$$

where f is a function of the ratio $R_{AB,CD}/R_{BC,DA}$ only and satisfies the relation

$$\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = \frac{f}{\ln 2} \operatorname{arccosh} \left\{\frac{\exp(\ln 2/f)}{2}\right\}. \tag{12}$$

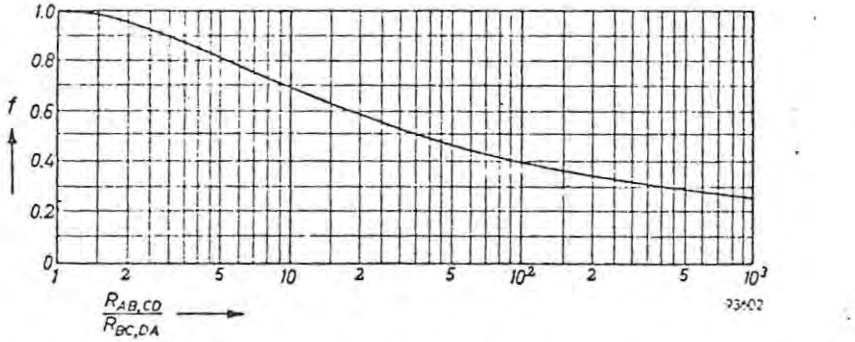

Fig. 7. The function f used for determining the specific resistivity of the sample, plotted as a function of $R_{AB,CD}/R_{BC,DA}$.

In fig. 7 a plot is given of f as a function of $R_{AB,CD}/R_{BC,DA}$. If $R_{AB,CD}$ and $R_{BC,DA}$ are almost equal, f can be approximated by the formula

$$f \approx 1 - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}}\right)^2 \frac{\ln 2}{2} - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}}\right)^4 \left\{\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right\}.$$

The Hall mobility can be determined by measuring the change of the resistance $R_{BD,AC}$ when a magnetic field is applied perpendicular to the sample. The Hall mobility is then given by

$$\mu_H = \frac{d}{B} \frac{\Delta R_{BD,AC}}{\varrho}, \tag{13}$$

where B is the magnetic induction and $\Delta R_{BD,AC}$ the change of the resistance $R_{BD,AC}$ due to the magnetic field.

Equation (13) is based upon the following argument: If we apply a field perpendicular to the sample the equations

$$\operatorname{div} \mathbf{j} = 0, \tag{14}$$

$$\operatorname{curl} \mathbf{j} = 0, \tag{15}$$

where $\mathbf{j}$ represents the current density, remain valid. Furthermore if the contacts are sufficiently small and at the circumference of the sample the outer lines of flow, which must follow the circumference of the sample, fully determine our boundary conditions. Hence the lines of flow do not change when a magnetic field is applied. However, the effect of the magnetic field on the electric potential is such that between two arbitrary points an additional potential difference ΔV is built up which is equal to

$$\Delta V = \frac{\mu_H B j \varrho}{d}, \tag{16}$$

where j is the current which passes between the two points. Equation (13) follows immediately from (16).

In order to estimate the order of magnitude of the error introduced if the contacts are of finite size and not at the circumference of the sample we derived an approximation formula for a few special cases. In all cases we assumed that the sample had the form of a circular disc with contacts spaced at angles of 90°. Furthermore we assumed that the area over which the contact is made is an equipotential area. We shall denote by $\Delta\varrho/\varrho$ and $\Delta\mu_H/\mu_H$ the relative errors introduced in the measurement of the specific resistivity and the Hall mobility, respectively.

In fig. 8a is presented the case in which one of the contacts is of finite length d; it is assumed to lie along the circumference of the sample. The other contacts are infinitely small and located at the circumference. The diameter of the sample will be denoted by D. In this case for a small value of d/D and of μB the following relations may be shown to hold:

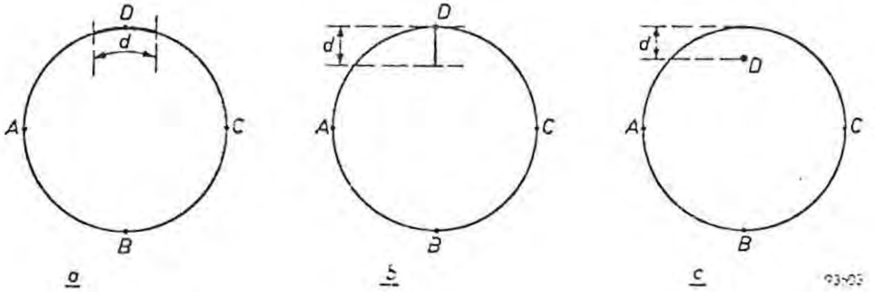

Fig. 8. Some special cases for which the error in the measurement of ϱ and μ_H due to the finite length or the finite distance to the circumference of one contact has been calculated.