The Hall Effect in Single Crystals of Barium Oxide*

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The Hall effect has been measured as a function of temperature, between 400°K and 800°K, in single crystals of barium oxide using an ac system. Conduction was predominantly N-type. The value of $(\mu_e{}^2-\mu_h{}^2)/(\mu_e+\mu_h)$ was about 3 cm²/volt sec between 600°K and 700°K and varied only slightly with temperature over the entire range studied. μ_e is thought to lie between 3 and 9 cm²/volt sec. There was some evidence that conduction was intrinsic at the higher temperatures in the samples studied.

I. INTRODUCTION

BARIUM oxide has long been a substance of special interest to the physicist.[1] This interest has led to attempts to determine the type of conduction mechanism and the mobility of the current carriers by measuring the Hall effect. Hall effect measurements on powders have been reported.[2] The thermoelectric effect in powder specimens, which gives some of the same information, has also been reported.[3,4]

The present experiment measures the Hall effect in single crystals of barium oxide; it is only by using such specimens that one can be certain he is measuring true bulk properties. The Hall angle and the conductivity have been found as a.function of temperature, the Hall angle being preferred to the Hall constant because of the strong temperature dependence of the latter in semiconductors.

II. DESCRIPTION OF APPARATUS

The ac system used for Hall effect measurements has been described elsewhere.[5] Use of ac minimizes electrolytic effects and transverse voltages caused by thermoelectric effects. Conductivities were measured on an ac bridge at 12 cps, the low frequency permitting measurements to very low conductivities before being limited by the shunt capacitance of the crystal.

The crystal holder, Fig. 1, was machined from solid molybdenum, with MgO insulation to prevent electrical leakage. It was mounted between the poles of a magnet in a flattened portion of a glass, mercury-pump vacuum system, and it could be withdrawn through a lead-gasket seal for insertion of the crystal. Hall data were recorded with a vacuum of about 5×10^{-6} mm of Hg.

All crystals were cleaved to dimensions of about 0.35 in.$\times$0.20 in., and they ranged in thickness from 0.007 in. to 0.050 in. Except for crystal No. 4, they

were mounted on the MgO substrate, about 0.05 in. thick, on which they were grown. Descriptions of the individual crystals are given in Appendix I.

III. CALIBRATION OF SYSTEM AND PRELIMINARY TESTS

The mobility in cm²/volt sec, neglecting the factor $3\pi/8$, is given by the expression

$$\mu=(El/vHdk)\times10^8,$$

where E is the MKS voltage between Hall probes; V, the MKS voltage between the current electrodes; H, the magnetic field strength in oersteds; d, the crystal width; l, the crystal length; and k, a geometry correction factor. This assumes a uniform electric field in the crystal. The experimental determinations of these factors were as follows:

kd/l: d/l was measured with an estimated error of about 1 percent. The geometry correction factor k has been calculated as a function of d/l,[6] and has been experimentally confirmed for tellurium[7] and for germanium.[8] For our d/l of $\frac{1}{2}$, it is 0.93.

H: The magnetic field was calibrated with a ballistic galvanometer and a flip coil, within an accuracy of a few percent.

E/V: The method of calibrating the amplifier was such that the output was given directly in terms of E/V. This calibration was made after every five or six reversals of the magnetic field and included the entire electronic system with the exception of the electrometer stage, which was separately calibrated at less frequent intervals. The maximum estimated error in E/V is 10 percent.

Temperature: The mobility was determined as a function of temperature. Problems of geometry resulted in an oven in which the crystal temperature could not be determined directly in each run but could be found indirectly by applying a correction factor to the oven temperature. The method for determining this correction factor, and also for correcting temperature gradients along the crystal, is described in Appendix II, and the magnitude of the resulting correction to the

[1] See, for example, W. W. Tyler and R. L. Sproull, Phys. Rev. 83, 548 (1951).

[2] D. A. Wright, Nature 164, 714 (1949); and *Semiconductors* (Methuen, London, 1950), p. 71.

[3] J. R. Young (Washington 1951), Phys. Rev. 85, 388 (1952).

[4] K. Noga, J. Phys. Soc. Japan 6, 124 (1951).

[5] E. M. Pell and R. L. Sproull, Rev. Sci. Instr. (to be published).

[6] Isenberg, Russell, and Greene, Rev. Sci. Instr. 19, 685 (1948).

[7] W. W. Scanlon, Purdue Signal Corps Report, January, 1948 (unpublished).
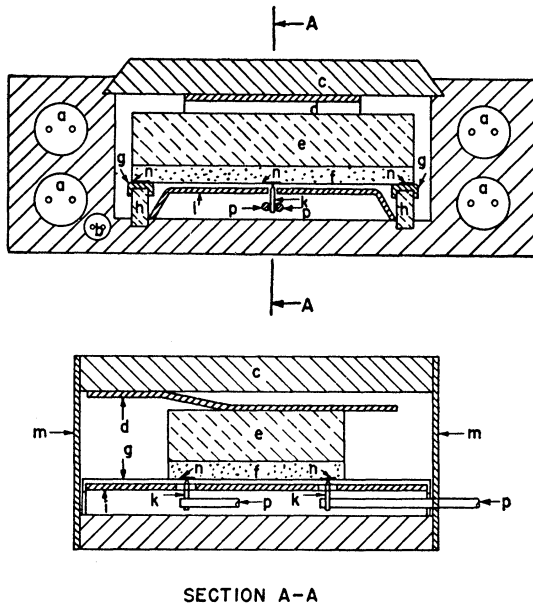
[8] W. C. Dunlap, Phys. Rev. 79, 286 (1950).

SECTION A-A

FIG. 1. Crystal holder. a—tungsten heaters; b—Pt-Pt 10% Rh thermocouple; c—sliding molybdenum cover; d—crystal hold-down spring, molybdenum, spot-welded to c; e—MgO crystal substrate; f—BaO crystal; g—platinum current contacts; h—MgO insulators; i—molybdenum thermionic emission shield; k—platinum hall contact; m—heat shields, with holes for electrical leads; n—platinum contacts sputtered on crystal; p—tungsten springs.

oven temperature data is indicated in Fig. 3. The correction factor is estimated to be accurate to within ±15 percent.

Preliminary Tests: Tests with Aquadag and cesium-antimony films checked the polarity of the Hall apparatus and gave reasonable values of μ.

To minimize thermionic electron currents, Hall data were taken with the crystal biased 45 volts positive with respect to the oven and thermionic emission shield. Probe measurements and considerations of geometry lead to an estimated thermionic current to the probes not exceeding $\frac{1}{2}$ percent of the conduction current, with the crystal at 900°K. By varying the thermionic current with the crystal bias to introduce deliberate and known errors, it was concluded that errors caused by thermionic emission were less than 5 percent at all temperatures.

A dependence of the Hall voltage upon the Hall probe size has been reported.[8] Subsidiary experiments using an electrolytic-tank model of our crystal geometry indicated that such an effect could not be caused by geometrical factors, even with probe diameters as large as one-third of the probe spacing. As a further check, the probe size in the actual experiment was reduced by a factor of two with no change in the measured μ.

To check for thermoelectric effects, the frequency of the current source was varied from 17 to 400 cps, with no change in the measured μ. Calculations indicate that transverse voltages from thermoelectric effects

should not be present at any frequency greater than about 0.01 cps.

A thin, high resistance surface layer under the Hall current contacts would cause an abnormally low Hall voltage since most of the applied voltage would be lost in the IR drop across this barrier. Potentiometric measurements, using a special electrode configuration sputtered on the crystal, indicated that there were no such barriers in crystals No. 1 through No. 4 but that a serious barrier existed in crystal No. 5; visual evidence indicated the presence of a similar barrier in crystal No. 6 and suggested that these barriers were produced by bleaching of the colored crystals proceeding inwards from the surface. Because of these barriers this apparatus was unable to give mobility data for crystals No. 5 and No. 6.

It would also be possible for the crystal to possess a high conductivity surface coating, which would prevent Hall effect measurements by shunting the crystal. Reproducible conductivity data in four runs with the same crystal, and the fact that almost identical conductivities were measured for two crystals of very different thicknesses and surface-to-volume ratios but the same composition, indicate that such coatings were not present.

The measured Hall voltage was directly proportional to the magnetic field, within 3 percent, for fields up to 13,000 gauss, as would be expected from the low μ observed; and it was directly proportional to the applied voltage, within 6 percent, for voltages from 0.25 to 9.6 volts.

At low temperatures the resistance of the crystal becomes very high and eventually exceeds the reactance of the shunt input capacitance to the electrometer
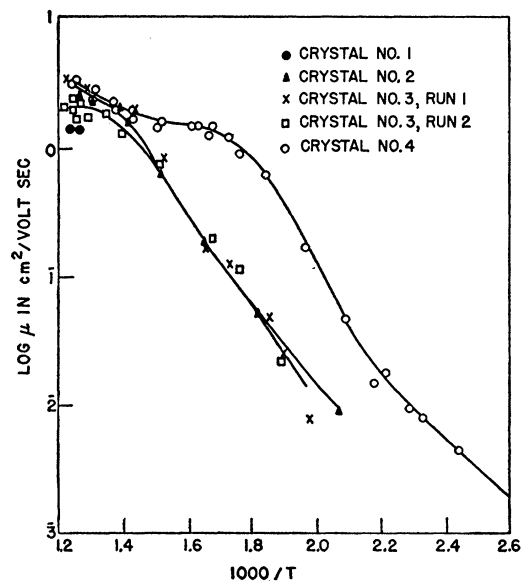

FIG. 2. Mobility data for four single crystals of BaO. The data have not been corrected for shunt capacitance nor for temperature gradients in the crystal.

stage. Below this temperature, the measured Hall voltage should vary inversely with the resistance of the crystal. This was checked experimentally with the electrolytic-tank model, varying the resistance-reactance ratio by changing the frequency. Sufficient confidence in this relation was obtained to justify using it as a means for extending the data in the low temperature region.

Since potentiometric methods were not used, it was necessary to prove that significant rectification did not occur at the current contacts. Direct measurement indicated a rectified signal between the crystal and either probe whose peak value was about 0.2 percent of the peak-to-peak value of the voltage across the crystal. This is negligible in conductivity measurements, and it does not affect the Hall measurements because it is not affected by the magnetic field.

The ac conductivity bridge permitted measuring conductivities as low as 10^{-10} ohm^{-1} cm^{-1}. The range was extended in the case of one crystal by using dc, relying on the overlap of the two sets of data as evidence that polarization effects were not serious.[9]

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. Mobility

The mobility of the current carriers in BaO is the principal result to be obtained from this experiment. Mobility data, uncorrected for shunt capacitance and temperature gradients in the crystal, and neglecting the factor $3\pi/8$ in the formula for Hall angle,[10] are presented for crystals No. 1 through No. 4 in Fig. 2. All data indicated N-type semiconduction throughout the temperature range studied.[11] Fluctuations in the data are larger than the estimated experimental errors and are presumed to be caused by the crystals themselves and the contacts to the crystals.

In Fig. 3, the mobility data for crystal No. 4 has been corrected for shunt capacitance and temperature gradients. The dashed region of the curve is uncertain because of the lack of reliable conductivity data in this region; the available data do, however, indicate the lack of any large sudden changes in mobility in this range.

Because of the above-mentioned possible errors in the conductivity data, the slope of mobility *versus* temperature cannot be found with sufficient accuracy to calculate a value for the characteristic temperature. Such a calculation would assume that the mobility is
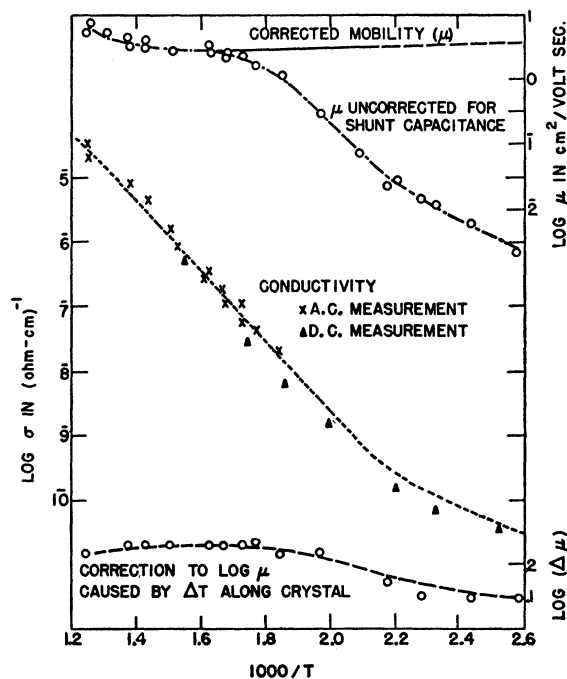

FIG. 3. Mobility and conductivity, crystal No. 4. The mobility has been corrected for the shunt capacitance effect and for the temperature gradient in the crystal; the magnitude of the corrections is indicated.

limited by lattice scattering, which seems reasonable because the mobility was substantially the same for all four crystals despite the fact that crystal No. 4 had a larger concentration of the same impurities as the others. Estimates of θ for the longitudinal optical mode based on specific heat data obtained by Anderson[12] indicate that θ probably lies near 700°–800°K for BaO.

The sign of rectification at the current contacts was observed to correspond to that observed for N-type semiconduction in other materials,[13] for crystals Nos. 1, 2, 3, 4, and 6 (no results were obtained for crystal No. 5).

The conductivity may have been intrinsic over the high temperature range (see discussion of conductivity). The data then give $(\mu_e^2-\mu_h^2)/(\mu_e+\mu_h)$[10] instead of μ_e. Over the low temperature range, however, the data probably represent impurity semiconduction.[14] Since there was no jump in the observed μ when impurity conduction began (it is thought that a jump by a factor of three would certainly have been observed), it seems probable from the above expression for observed μ

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[9] The possibility of error in the conductivity data arising from electrical leakage across insulators was checked by substituting an MgO crystal for the BaO. At the highest temperature used, the conductivity measured using the MgO crystal was lower by a factor of 1000 than any conductivity measured on a BaO crystal at the same temperature.

[10] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand and Company, Inc., 1950), p. 278.

[11] Recent experiments by J. R. Young on the thermoelectric effect in powder samples of BaO also gave N-type semiconduction consistently (see reference 3).

[12] C. T. Anderson, J. Am. Chem. Soc. **57**, 429 (1935). See also V. L. Stout, Phys. Rev. **85**, 390 (1952); Stout analyzed luminescence data on BaO to give a $\theta=430°$K.

[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 178.

[14] It may also be ionic conduction. Diffusion data by Redington on quenched crystals made from the same raw material indicate that ionic conductivity was 10^{-7} ohm^{-1} cm^{-1} at 550°K, with a slope of 0.2 to 0.4 ev. This is in the range of our data. The crystals used in the present experiment were annealed, however, and for annealed crystals Redington found no measurable ionic mobility.

for the intrinsic and the impurity regions that $\mu_h \leq 0.6\mu_e$. The fact that the observed μ does not change greatly over a factor of two in T is further evidence for μ_h differing appreciably from μ_e, for since μ_e and μ_h are both temperature dependent—(and probably differently temperature dependent to some extent)—it is unlikely that the difference, $\mu_e^2/(\mu_e+\mu_h)-\mu_h^2/(\mu_e+\mu_h)$, would remain so nearly constant over this T range if it were the difference between two large numbers of nearly equal magnitude. Since μ is proportional to $m^* \exp(-3/2)$ in lattice scattering, the above also implies that $m_h^* \geq 1.3m_e^*$, where m_h^* and m_e^* are the effective masses of holes and electrons, respectively.

The observed rise in μ at high temperatures remains unexplained. The magnitude of the rise is within the sum of the estimated experimental errors, but these errors appear to be incapable of creating a spurious rise in μ. If μ_h is fairly large, even though less than 0.6 μ_e,
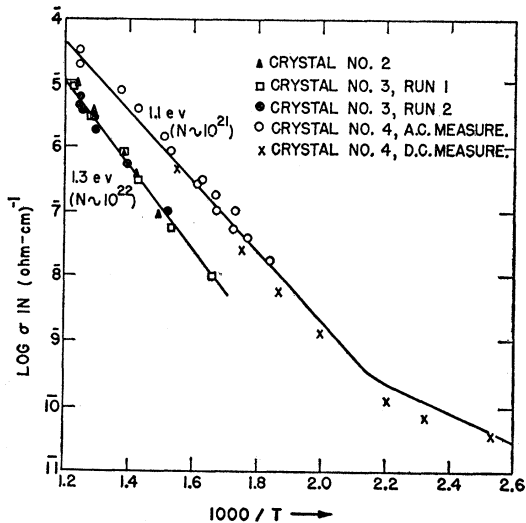

FIG. 4. Conductivity.

a slight increase in μ_e relative to μ_h could account for the rise.

Using data[1] for the photoconductivity in BaO, it is possible to set a lower limit for the product of drift mobility and mean lifetime of a hole-electron pair. By assuming 100 percent quantum efficiency in producing hole-electron pairs a lower limit is obtained for $\mu\tau$ of about 5×10^{-8} cm^2/volt. J. A. Krumhansl reports[15] that a qualitative experiment on bombardment-induced conductivity in BaO gives a value of about 10^{-7} for $\mu\tau$, but with considerable uncertainty.

2. Conductivity

Although experimental conditions were chosen to favor mobility determinations over conductivity, the conductivity data were found to be reproducible, and typical data are presented in Figs. 3 and 4. Data points

were found to be independent of temperature history; if diffusion rates measured by Redington[16] are typical of the diffusion rates of the donors, it is unlikely that donor populations had time to adjust themselves to new equilibria between readings.

The fact that the slopes and magnitudes of conductivity are all about the same at high temperatures for crystals of presumably different impurity content[17] indicates that this may be the region of intrinsic semiconduction. To test this hypothesis further the number of donor centers was calculated[18] on the assumption that conductivity was intrinsic, using μ_{Hall} for μ_{drift} (trapping should be small at these temperatures) and the slope of σ vs log $1/T$ for $E/2kT$ (assumes that E does not vary appreciably with T). The resulting values for N (see Fig. 4) are within the experimental error of the number of barium ions per cc in BaO.

The conductivity slopes observed for crystals No. 5 and No. 6 before prolonged heat treatment, and for crystal No. 4 at low temperatures, are not inconsistent with earlier data obtained by Sproull and Tyler[19] on less pure single crystals.

The activation energy, as defined by b in $\sigma = Ce^{-b/kT}$, is also indicated in Fig. 4. The significance of this value is open to some doubt, for if the activation energy is temperature dependent, the slope of σ will give not E_T but E_0, the value of E obtained by extrapolating the slope of E vs T to $T=0$. Since these measurements were made at high T, E_0 could be quite different from E_T. On the other hand, the preceding paragraph has indicated that the observed slope of σ gives a value for N that is consistent with the other evidence for intrinsic semiconduction; however, this is not strong evidence.

We now consider briefly whether the above thermal activation energies for intrinsic semiconduction would be consistent with the energy-band model for BaO which has been proposed[20] on the basis of previous experiments. This model suggests that the 3.8-volt optical excitation energy[1] corresponds to production of a bound exciton which may produce photoconductivity upon dissociation or by giving its energy to F-center electrons. In the previously mentioned model,[18] the thermal activation energy b in $\sigma = Ce^{-b/kT}$ corresponds to $E/2$, so that our data would give a thermal E of 2.2 to 2.6 ev. If the holes are bound so that the lattice can relax about the bound charge, this thermal E corresponds to a much higher optical E; if the holes are free, the two energies are the same. Since our thermal

[15] Private communication.

[16] R. W. Redington (to be published).

[17] After heat treatment, crystals No. 5 and No. 6 gave conductivity slopes about the same as those in Fig. 4. At the start of the heat treatment, the slope was about half as large.

[18] N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford University Press, London, 1920), p. 157.

[19] R. L. Sproull and W. W. Tyler, Semiconducting Materials, (Butterworths Scientific Publications, London, 1951).

[20] J. A. Krumhansl, Cornell Navy Report No. 3, Cont. N6-ori-91, Task 11, Dec. 1950; E. Steele, Cornell University Thesis (1951).

E would not be much smaller than the optical E, the holes would apparently not be immobile. The slight difference between the two E's would not necessarily be caused by lattice relaxation; the optical transition could be between two states each with wave vector of zero, and these do not lie at the edge of the forbidden band in BaO[20] ($k=0$ would be down about $1\frac{1}{2}$ volts in the filled band on the basis of the above data). It must be emphasized that this experiment cannot be taken as proof that the thermal activation energy for intrinsic semiconduction is 2.2 to 2.6 ev; the above argument merely indicates that such a value would not contradict previous knowledge.

V. CONCLUSIONS

1. In the BaO single crystals studied, conduction is predominantly N-type. This is true in the high temperature region of steep conductivity slope and also in the low temperature region between 400°K and 450°K, where the slope of log σ vs $1/T$ is small because of either impurity or ionic conduction.

2. The value of $(\mu_e{}^2-\mu_h{}^2)/(\mu_e+\mu_h)$ is about 3 cm^2/volt sec between 600°K and 700°K.

3. At lower temperatures, down to 400°K, the data do not contradict a model of mobility limited by lattice scattering by the longitudinal polarization modes. Evidence indicates it is not caused by impurity scattering. At higher temperatures there is an observed rise in the mobility to about five at 800°K. This has not been explained.

4. There is some evidence, not conclusive, that the crystals were intrinsic semiconductors in the high temperature region. The conductivity slopes correspond to a thermal activation energy (b in $\sigma=Ce^{-b/kT}$) of 1.1 to 1.3 ev. If intrinsic, this corresponds to an energy gap for thermal transitions of about 2.5 volts. At lower temperatures, slopes corresponding to activation energies of roughly 0.5 ± 0.2 ev were measured.

5. If the slope corresponding to 0.5 ev is caused by impurity semiconduction, and the higher slope of about 1.2 ev is caused by intrinsic semiconduction, then $m_h{}^*\geq1.3m_e{}^*$, and μ_e lies between 3 and 9 cm^2/volt sec. If the low slope is caused by ionic conduction, this conclusion is invalid. If the steep slope is caused by impurity semiconduction, then μ_e is about 3 cm^2/volt sec.

6. Analysis of available data on photoconductivity in BaO, combined with an extrapolated value for the mobility of about 4 at 100°C, indicates that the mean lifetime of an electron in the conduction band is $\geq10^{-8}$ second.

ACKNOWLEDGMENTS

APPENDIX I. DESCRIPTION OF CRYSTALS

Crystals Nos. 1, 2, and 3: These were high purity crystals grown by W. C. Dash[21] from BaO containing a few hundredths percent of calcium and strontium and less than 0.01 percent of all other metallic impurities. The crystallization process resulted in some further purification. Crystals No. 1 and No. 2 were single crystals free from visible flaws; crystal No. 3 contained visible flaws. Similar samples have given x-ray diffraction pictures typical of single crystals. All three crystals cleaved along orthogonal planes.

Crystal No. 4: This was a clear crystal made from less pure BaO containing tenths of a percent of silicon, iron, and alkaline earth impurities. This crystal contained many visible flaws.

Crystal No. 5: This was a red crystal grown in molten barium by G. Libowitz, using a method suggested by the work of Schriel.[22] Spectrographic analysis of a sample crystal gives 1–5 percent strontium, of the order of 0.1 percent calcium, and less than 0.01 percent of any other metal. There is some evidence that the red color may be caused by F centers or interstitial atoms produced by excess barium.[23] If so, optical absorption measurements indicate a 0.02 percent barium excess; chemical analysis by G. Libowitz indicates <0.1 percent barium excess. This crystal was very brittle and fractured at irregular angles, indicating very imperfect crystal structure.

Crystal No. 6: This was a blue crystal produced by heating crystal No. 3 for 15 hours at about 1000°C in an atmosphere of barium inside a cylinder of compressed BaO. The cause of the blue color is not known, but it is felt that it arises because of the presence of the excess barium.

All crystals were polished with emery in a dry-box using BaO for a desiccant. Platinum contacts were sputtered on in an atmosphere of dry hydrogen. Mounting of the crystals in the oven was done in the dry-box. Although the total exposure of the crystal to room atmosphere during these transfers was less than a minute, a small amount of barium hydroxide inevitably formed on the surface. This was reduced to the oxide by heat treatment previous to taking Hall data. Examination of the crystal surface after a data run indicated little deterioration. Hall and conductivity data were found to be closely repeatable when using the same crystal in separate runs.

APPENDIX II. TEMPERATURE CALIBRATION

In the temperature range used, the crystal temperature was determined chiefly by the difference between conduction heating through the oven structure and conduction losses through the electrical leads. Since it

[21] Sproull, Dash, Tyler, and Moore, Rev. Sci. Instr. **22**, 410 (1951).
[22] M. Schriel, Z. anorg. u. allgem. Chem. **231**, 313 (1937).
[23] E. O. Kane, J. Appl. Phys. **22**, 1214 (1951).

was impractical to imbed thermocouples in the crystals for each run, the oven temperature was monitored, and later a calibration curve of crystal temperature *versus* oven temperature was obtained. Although this produces some uncertainty, the reproducibility of the data indicates that changes in thermal contacts were small and had little effect upon the data.

The thermocouple imbedded in the oven, which was of Pt *vs* Pt 10 percent Rh, was checked against a Leeds and Northrup optical pyrometer at 960°C. Using an emissivity of 0.37 for molybdenum and an estimated glass transmission factor of 90 percent, the two readings differed by only 4°C.

In the calibration experiments, the crystal temperature was found both by imbedding 4-mil thermocouples in holes in the crystal and also by using small platinum plates, in thermal contact with the crystal, to transfer heat to the thermocouples; the two methods gave similar results. The temperature gradient along the crystal was measured by two thermocouples, one at the end and one in the middle of the crystal. This gradient will produce an exponential conductivity gradient along the crystal, and the electric field in the crystal will hence be non-uniform, thus affecting the Hall voltage. An appropriate correction factor has been calculated and is plotted in Fig. 3.

The Coherent Neutron Scattering Cross Sections of Nitrogen and Vanadium*

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Neutron diffraction measurements on vanadium nitride, vanadium carbide, and potassium azide show the coherent neutron scattering cross section of nitrogen to be 11.1± 0.3 barns, positive phase and that of vanadium to be 0.029±0.01 barn, negative phase.

THE coherent neutron scattering cross sections of nitrogen and vanadium have been evaluated from neutron diffraction patterns of vanadium nitride VN and confirmed by similar data from potassium azide KN_3 and vanadium carbide VC. Vanadium nitride was prepared by the reaction of pure V_2O_5 with NH_3 gas at 1100°C for 6 to 8 hours. Neutron diffraction patterns with neutron wavelength 1.16A were obtained from samples sealed in aluminum cells shortly after preparation. The technique for making neutron diffraction measurements will be described elsewhere.

VN crystallizes with the rocksalt structure, for which structure factors are of two types, corresponding to even-index and odd-index reflections. Integrated reflections of three odd-index and four even-index reflections were measured and converted to absolute structure-factor values by comparison with the (111) reflection from nickel powder, for which the coherent cross section was taken as 13.4 barns.[1] The (311) reflection was corrected for contamination by (222) by computing the intensity of the latter from its interpolated structure factor. The resulting values of $F^2/16$ are plotted in Fig. 1 against $\sin^2\theta$. Extrapolation of each family to zero angle yields values proportional to the squares of the structure factors corrected for the effect of temperature and zero-point motion in the crystal and equal, respectively, to the sum (even reflections) and difference (odd reflections) of the scattering amplitudes of V and N. It is immediately apparent that the amplitude of vanadium is of negative sign, opposite to that of nitrogen which is known to be positive.[1] Values of the coherent amplitudes f and cross sections σ yielded by the data are the following:
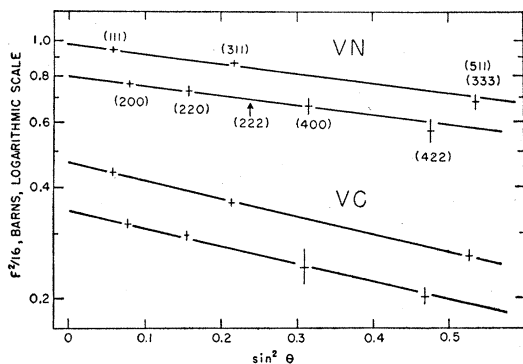

FIG. 1. A plot of observed neutron diffraction values of $F^2/16$ against $\sin^2\theta$ for vanadium nitride and vanadium carbide. The vertical lines indicate the estimated precision of the individual values.

For nitrogen:

$$f_N = 0.940 \pm 0.015, \qquad \sigma_N = 11.1 \pm 0.3 \text{ barns.}$$

For vanadium:

$$f_V = -0.048 \pm 0.010, \qquad \sigma_V = 0.029 \pm 0.01 \text{ barn.}$$

[1] C. G. Shull and E. O. Wollan, Phys. Rev. 81, 527 (1951).