

Thermal Resistance at Indium-Sapphire Boundaries between 1.1 and 2.1°K†

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The thermal resistance at boundaries between indium and single crystal sapphire has been measured with the indium superconducting and normal. The effective temperature at the sapphire side of a boundary was determined from the condition of radiative equilibrium at the surfaces of the crystal. It was found that the thermal conductance of indium-sapphire boundaries can be represented by the sum of a T^2 term and a T^3 term. For two samples, the T^3 terms are, respectively, $0.0295T^3$ and $0.0281T^3 \pm 0.0016T^3$ W/(cm²-deg). These numbers are within the range of possible values expected on the basis of the acoustic mismatch theory of Little. For the two samples the T^2 terms are $0.0059T^2$ and $0.0098T^2 \pm 0.001T^2$ W/(cm²-deg) with the indium superconducting, and are increased by $(1 \pm 0.4) \times 10^{-3}T^2$ when the indium is normal. The values obtained as a matter of course for the thermal conductivity of sapphire are in agreement with the Casimir theory as modified to include the effects of finite crystal length and specular reflection of phonons at the crystal surfaces.

INTRODUCTION

INVESTIGATIONS of the thermal resistance, called the Kapitza resistance, which occurs at a boundary between a solid and liquid helium have been reported by several authors. A brief review of some of these investigations is given elsewhere.¹ A theory by Khalatnikov,² modified by Challis, Dransfeld, and Wilks,³ showed that the Kapitza resistance should arise due to the acoustic mismatch of the solid to the liquid. Calculations by Little⁴ and a suggestion attributed to Bloch⁵ predicted that the conduction electrons of a metal could interact with the phonons of the helium and thus directly contribute to heat transport at a helium-metal boundary. However, none of the reported Kapitza resistance measurements agree with the above theoretical proposals, and it is suspected¹ that other processes contribute to thermal transport at a helium-solid boundary. Furthermore, the work of several authors^{1,3,6,7} demonstrated that the Kapitza resistance of a metal is greatly influenced by surface conditions such as oxidation and work hardening, thus making comparison with any theory difficult.

Little⁸ extended Khalatnikov's theory to the general case of heat transport at a boundary between any two dissimilar, isotropic solids. Little's calculation of the electronic contributions to boundary heat transport could also be generalized to apply to any boundary between a dielectric and a metal, and it would seem

that the proposed mechanism attributed to Bloch could likewise be extended. Thermal resistances have recently been found at boundaries between dissimilar metals.⁹⁻¹¹ However, the electronic thermal transport at such boundaries appears to be different from the above-mentioned mechanisms and thereby these measurements do not serve as a definitive test of the theories of Little.^{4,8} For these reasons it was decided to measure the thermal resistance at a boundary between a metal and a solid dielectric.

EXPERIMENTAL TECHNIQUE

Indium was chosen for the metal because it has a tendency to wet a dielectric surface, and it is superconducting at helium temperatures. The availability and high thermal conductivity of sapphire crystals led to sapphire as the choice of dielectric.

Sample Fabrication

Two samples were made by the following method. Cylindrical sapphire crystals, $1\frac{1}{4}$ in. long by $\frac{1}{4}$ in. diam, were used. These had rough ground sides and polished end faces. Each end face of a crystal was coated with spectroscopically pure indium by an ultrasonic soldering tool in a helium atmosphere. The crystal was then placed in the bottom of a close-fitting Teflon mold. The crystal and mold, with additional pure indium, were baked in a vacuum of 10^{-5} Torr prior to casting the additional indium onto the top precoated end face. The casting was accomplished by repeatedly passing an induction-heated molten zone upward from the top of the sapphire to the free end of the indium. The sample and mold were removed from vacuum and a flat surface was machined on the free end of the indium so as to leave a well-defined area for measurement of its Kapitza

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¹ R. C. Johnson and W. A. Little, *Phys. Rev.* **130**, 596 (1963).

² I. M. Khalatnikov, *Zh. Eksperim. i Teor. Fiz.* **22**, 687 (1952).

³ L. J. Challis, K. Dransfeld, and J. Wilks, *Proc. Roy. Soc. (London)* **A260**, 31 (1961).

⁴ W. A. Little, *Phys. Rev.* **123**, 435 (1961).

⁵ This is described in Ref. 1.

⁶ L. J. Challis, *Proc. Phys. Soc. (London)* **80**, 759 (1962).

⁷ Kuang Wey-yen, *Zh. Eksperim. i Teor. Fiz.* **42**, 941 (1962)

[English transl.: *Soviet Phys.—JETP* **15**, 635 (1962)].

⁸ W. A. Little, *Can. J. Phys.* **37**, 334 (1959).

⁹ L. J. Barnes and J. R. Dillinger, *Phys. Rev. Letters* **10**, 287 (1963).

¹⁰ V. E. Holt and R. W. Peterson, *Bull. Am. Phys. Soc.* **8**, 474 (1963).

¹¹ L. J. Challis and J. D. N. Cheeke, *Phys. Letters* **5**, 305 (1963).

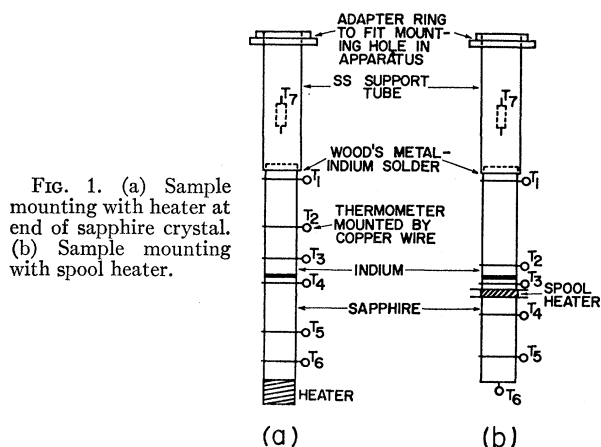


FIG. 1. (a) Sample mounting with heater at end of sapphire crystal. (b) Sample mounting with spool heater.

resistance. The sample, still in the mold, was returned to vacuum and annealed for two hours at 145°C . Finally, the mold was cut away, leaving the sample in the form of a $\frac{1}{4}$ -in.-diam rod with the indium section about $1\frac{1}{2}$ in. long. The grain boundaries indicated that the indium sections of the samples were composed of about ten macroscopic crystals.

Apparatus

The two sample mounting geometries used are shown in Fig. 1. The indium section of each sample was soldered into a 0.010-in. wall stainless-steel support tube with a solder consisting of 25% indium and 75% Wood's metal. Six thermometers, designated as T_1 through T_6 , were attached to the sample. These were nominally $47\ \Omega$, $\frac{1}{10}$ -W Allen-Bradley Ohmite resistors which had been cemented into 0.010-in. wall copper sleeves with G.E. 7031 varnish. Copper wires of 0.010-in. diam had been soldered to the sleeves. These wires were pulled around the circumference of the sample and soldered to the indium or cemented to the sapphire. In various experiments three, four, or five thermometers were used on the sapphire with the remainder on the indium. The support tube was soldered into an apparatus similar to that illustrated elsewhere,⁹ so that liquid helium filled the tube during experimentation. T_7 was a seventh thermometer located within the tube and used for measuring small changes in bath temperature. The seven thermometers were connected in series and carried a current of $0.8\ \mu\text{A}$ dc.

All data were taken with a Leeds and Northrup type K2 potentiometer, although the behavior of any thermometer could be observed with a recording potentiometer. The resistances of the thermometers could be determined to 0.1% at 2°K and to 0.03% at 1.1°K . This contributed an uncertainty of about 1% to the measured boundary resistance at 2°K , and about 0.3% at 1.1°K .

A dummy heater was used in the helium bath so that the sample heater could be switched on and off with no

net change of power expenditure in the bath. Heat fluxes of between 0.6 and $20\ \text{mW}/\text{cm}^2$ were generally used. The heater power could be measured to 0.1%. Obtaining all of the measurements for one value of heater power at one temperature required 15 to 20 min. During this time the bath temperature was held constant to ± 0.15 mdeg by an electronic thermoregulator.

By means of an electromagnet outside the cryostat, up to 8 kOe could be established in the region of the sample in a direction parallel to the plane of the indium-sapphire boundary.

Procedure

In a given experiment, data were taken at eight or nine different temperatures with the indium superconducting, and then the measurements were duplicated with the indium normal in a 400 Oe field. At each setting of the bath temperature, data were taken for two values of heater power which differed by a factor of 1.5 to 2. For each data point the thermometer current, and the voltages of T_7 , T_1 through T_6 , and again T_7 were measured with the heater off. The heater was switched on and the process repeated. The temperature profile along the sample was thus determined from the rises of the individual thermometers above ambient temperature so that small differences in the absolute calibrations of various thermometers did not affect the data. All data reduction was performed by a digital computer.

At six or seven different temperatures the thermometers were calibrated against the vapor pressure of helium according to the 1958 temperature scale. For each thermometer a least-squares fit of the calibration data to the three-constant formula¹² was calculated for two overlapping ranges of experimental temperatures. The calibration formulas fit the measured calibration temperatures generally within ± 0.5 mdeg. Successive calibration temperatures differed by about 0.15 deg; hence, for the purpose of determining temperature changes of about 0.1 deg, the errors of the calibration formulas were 1% or less. Therefore, one would expect the random scatter of the data to be $\pm \frac{1}{2}\%$ or less below 2°K due mainly to calibration errors. Above 2°K the random scatter could be $\pm 1\%$ due to combined errors of calibration and reduced sensitivity of the thermometers. The actual scatter agreed with this analysis.

Mean-Free-Path Effects

The thermal resistance at a boundary is commonly measured by extrapolating measured thermal gradients to the boundary in question. If this method were used to measure the temperature jump at a boundary between a dielectric crystal and any other substance, spurious results would arise as a consequence of the long mean-free path of the dielectric phonons. The

¹² G. K. White, *Experimental Techniques in Low-Temperature Physics* (Oxford University Press, London, 1961), p. 127.

Casimir theory of thermal conduction¹³ has been modified^{14,15} so as to account for the effects of finite crystal length and specular reflection of phonons at the crystal surfaces. Considering a circularly cylindrical crystal with its axis labeled as the z axis, Berman, Simon, and Ziman¹⁴ showed that one may write for the heat flux which passes through a cross section at $z=0$, and which has been radiated by an elemental ring of surface between z and $z+dz$:

$$dH = QT^4(z) f^2 \sum_{r=0}^{\infty} (1-f)^r E(z/(r+1)) dz, \quad (1)$$

in which $T(z)$ is the temperature of the crystal surface, Q is a constant,¹⁶ $E(z)$ is a geometrical function, and f is the fraction of phonons striking the wall which are absorbed so that $(1-f)$ are specularly reflected.

Consider now the cross section at $z=0$ as the boundary between the dielectric crystal and another substance, and let the crystal be in the region where $z>0$. One can see that the phonon gas impinging on the crystal side of the boundary is not characterized by a single temperature unless the entire surface of the crystal is at one temperature. In particular, if $T(z)$ increases with z , phonons incident upon the boundary at near-normal angles will have originated at higher temperature regions of the crystal surface. The effective temperature on the crystal side of the boundary is not the temperature of the crystal surface extrapolated to the boundary. Furthermore, the thermal gradient along the crystal surface may not be uniform near the ends of the crystal.¹⁴

If one defines a function $G(z)$ such that

$$G(z) = \sum_{r=0}^{\infty} f^2 (1-f)^r E(z/(r+1)), \quad (2)$$

and for the present neglects the nonisotropic distribution of phonon energies, then an average temperature for the phonons incident upon the crystal end located at $z=0$ would be

$$T_{av} = \int T(z)G(z)dz / \int G(z)dz. \quad (3)$$

This end may be regarded as the indium-sapphire boundary, and T_{av} may be regarded as the effective temperature on the sapphire side of the boundary. According to the acoustic mismatch theory,⁸ the boundary heat transport is proportional to $(T_s^4 - T_m^4)$, in which T_s and T_m are the temperatures of the sapphire and metal, respectively. For simplicity of data treat-

ment, T_{av} was computed instead of $\langle T^4 \rangle_{av}$. A rough calculation showed the resulting error to be about 1% and nearly independent of temperature.

Mean-free-path effects of a different sort can arise in the metal. Little⁸ has pointed out that the finite phonon-electron relaxation time could cause an additional thermal resistance which is experimentally indistinguishable from the true boundary resistance. Although this proposed additional resistance would be small, it would be different for the superconducting and normal states of indium and it might thereby lead to a misinterpretation of the data if it were in fact included in the measurements. However, the quantity one wishes to measure is the temperature of the phonons incident upon the boundary from within the metal. These have been scattered within the metal and should be characterized by the temperature of the electrons near the boundary. Since, as shown by the present experiments, heat is transported across the boundary mainly by phonons, the thermal gradient of the electron gas increases rapidly with increasing distance from the boundary as the thermal current is transferred to the electrons. In the present experiments the thermal gradients in the indium were very small; hence the temperature of the phonons incident upon the metal side of the boundary could be estimated reliably. This would not have been true for an impure metal specimen which had both a macroscopic mean-free path for phonon collisions with electrons and a large thermal resistivity.

EXPERIMENTAL RESULTS

Thermal Conductivity and Kapitza Resistance of In

The small temperature drops along the indium section of either sample suggested that the thermal conductivity was under all circumstances greater than 20 W/cm-deg. In one experiment where larger heat fluxes were used the normal state conductivity (uncorrected for the 400-Oe transverse field) was found to be about 70 W/cm-deg. One can therefore assume that for either sample the purity of the indium was comparable to that of the spectroscopically pure specimens used by Jones and Toxen¹⁷ or Guenault.¹⁸

Although a previous report¹⁹ mentions no difficulty with reproducibility, it was observed that the Kapitza resistance of indium was quite irreproducible. It increased by as much as 20% as a sample remained undisturbed in the cryostat for a few weeks. For one sample it was near $6T^{-3}$ (deg-cm²)/W, while that of the other sample was near $20T^{-2.7}$ (deg-cm²)/W for either the superconducting or normal state.

¹³ H. B. G. Casimir, *Physica* **5**, 495 (1938).

¹⁴ R. Berman, F. E. Simon, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A220**, 171 (1953).

¹⁵ R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A231**, 130 (1955).

¹⁶ It appears that the factor Q was accidentally omitted from the corresponding expression in Ref. 14.

¹⁷ R. E. Jones and A. M. Toxen, *Phys. Rev.* **120**, 1167 (1960).

¹⁸ A. M. Guenault, *Proc. Roy. Soc. (London)* **A262**, 420 (1961).

¹⁹ J. I. Gittleman and S. Bozowski, *Phys. Rev.* **128**, 646 (1963).

Thermal Conductivity of Sapphire

The measurements of the thermal conductivity of sapphire, which resulted as a matter of course during the experiments, represent quantitative support for the theory.¹⁴ From published data,²⁰ one may represent the specific heat of sapphire below 25°K by $3.66 \times 10^{-5} T^3$ J/(cm³-deg). Using this value, and the theoretical curves presented in Ref. 15, one can predict that the thermal conductivity of a sapphire crystal with perfectly rough surfaces, a $\frac{1}{4}$ -in. diam, and a radius to length ratio of 0.1 should be $4.4 \times 10^{-2} T^3$ W/(cm-deg). The measured conductivity of the crystal in sample 1 was $4.81 \times 10^{-2} T^{2.89}$, and that of the crystal in sample 2 was $4.78 \times 10^{-2} T^{2.84}$ W/(cm-deg). These values represent the averages of the thermal conductivities of the sections of crystal between successive thermometers. For different sections of the same crystal, the coefficients of T differed from these values by as much as 6%, due in part to the uncertainties of thermometer positions. However, for a given sample, the powers of T always agreed within 1%. The fact that the magnitudes of the conductivities are greater than the theoretical value, while the exponents of T are less than 3, indicates that some specular reflection of phonons took place at the crystal surfaces. An expression for f of Eq. (1) can be determined from a graph in Ref. 15. When the ratio of crystal radius to length is 0.1, f is given by

$$f = 1.87 - 1.28(K/K_c) - 0.279(K/K_c)^2, \quad (4)$$

in which K is the measured thermal conductivity and K_c is the conductivity predicted by the Casimir theory. Due to the uncertainty in determining Eq. (4) from the curves, the uncertainty in the specific-heat data, and the experimental errors in K , the error in the values of f may be as large as 15%. However, since f is approximately linear with K/K_c in the narrow region of interest, the temperature dependence of f could be determined to sufficient accuracy for purposes of making small corrections to the boundary-resistance data. Since the values of f were all in the range $0.9 \leq f \leq 1$, the present measurements of the thermal conductivity of sapphire are considered to be in quantitative agreement with the theory.

Thermal Resistance at the Boundaries

The results of four final experiments will be discussed. Experiments with sample 1 will be designated as 1A and 1B; experiments with sample 2 will be designated as 2A and 2B.

The effective temperature at the sapphire side of the boundary was determined according to Eq. (3) with the limits of the integrals at zero and infinity. The small contribution from the end face opposite the boundary was considered to be the same as that from an infinite

extension of crystal at constant temperature. If one writes the following for P , the boundary power transport per unit area:

$$P = R_0^{-1}(T_{av}^4 - T_m^4), \quad (5)$$

and computes R_0 to second order in $(T_{av} - T_m)$; then R , the boundary resistance in the limit of infinitesimal P , will be given by:

$$R = \frac{1}{4} R_0 T_m^{-3}. \quad (6)$$

In experiments 1A and 2A, which were conducted with the arrangement shown in Fig. 1(a), the thermal gradients were linearly interpolated and extrapolated between and beyond thermometers, and R_0 was determined for each data point. Since there was a possibility that the thermal gradient in the sapphire was non-uniform near the crystal ends, experiment 1B was conducted in similar fashion, but with five thermometers on the sapphire. Three thermometers were located within the first mean-free path of the boundary, and no unusual thermal gradient was detected. The results of experiments 1A and 1B agree within experimental error. The fact that f was less than unity added at most 2.5% to R_0 . This is less than the uncertainty in the measured magnitude of R_0 ; however, the temperature dependence of the contributions of the specularly reflected phonons was significant.

The fact that the phonons incident upon the boundary had a nonisotropic distribution of energies has been thus far neglected. Any effects caused by this could have been investigated by reversing the heat current or changing the form of the thermal gradient. For reasons of experimental convenience the latter course was chosen. For experiment 2B a heater in the form of a narrow copper spool was soldered around the circumference of the sapphire near the boundary, as shown in Fig. 1(b). About half of the phonons incident upon the sapphire side of the boundary originated between the boundary and the lower edge of the spool heater. Due to the conditions of radiative equilibrium, the temperature in the region below the heater gradually decreased with increasing distance from the boundary when the heater was on. The temperature of the portion of crystal surface to which the heater was soldered was estimated from the condition of radiative equilibrium with no heat flow in the region between the heater and the free end of the crystal. The temperature profile along the sapphire was approximated by several constant temperature sections. The boundary resistance as determined in experiment 2B was a constant 10% larger than the result of experiment 2A, but had almost exactly the same temperature dependence. The factor of 10% was considered within the uncertainty of the approximate data treatment.

A plot of R_0 versus T more clearly illustrates the deviation of the boundary resistance from perfect T^{-3} behavior than a plot of R versus T . The results of

²⁰ D. C. Ginnings and G. T. Furukawa, J. Am. Chem. Soc. **75**, 522 (1953).

TABLE I. Experimental values of the boundary resistance (units of R are deg-cm²/W).

Experiment	Superconducting	RMS	Normal	RMS
1A	$R=27.9T^{-2.88}$ $1/R=0.0299T^3+0.00602T^2$	0.8% 0.7%	$R=27.2T^{-2.84}$ $1/R=0.0294T^3+0.00727T^2$	1.1% 1.1%
1B	$R=28.5T^{-2.88}$ $1/R=0.0294T^3+0.00585T^2$	0.5% 0.4%	$R=28.0T^{-2.86}$ $1/R=0.0292T^3+0.00666T^2$	0.6% 0.5%
2A	$R=26.6T^{-2.81}$ $1/R=0.0282T^3+0.00982T^2$	0.5% 0.5%	$R=26.1T^{-2.80}$ $1/R=0.0280T^3+0.0108T^2$	0.5% 0.4%
2B	$R=29.3T^{-2.81}$ $1/R=0.0252T^3+0.00943T^2$	1.2% 1.2%	$R=28.7T^{-2.78}$ $1/R=0.0252T^3+0.00997T^2$	0.8% 0.7%

experiment 1B are shown in Fig. 2. The data of the other experiments presented similar appearances.

Expressions of the form $R=R_1T^n$ and $1/R=aT^3+bT^2$ were fit by least squares to the data with R_1 , n , a , and b as adjustable parameters. These expressions are presented in Table I, together with the rms percent deviations of the data from the expressions.

The first mechanism proposed by Little⁴ for boundary thermal transport due to electrons would not be operative at an indium-sapphire boundary as the totally reflected phonons are within the indium. Nevertheless, the effect of the magnetic field on the electronic processes which were operative was investigated. Any change in the boundary resistance due to an 8 kOe transverse field was less than 0.8%.

DISCUSSION

Changes in the boundary resistance could be measured to better than 1%. For separate experiments the uncertainties in the thermometer locations could cause an uncertainty in the measured boundary resistance of $\pm 2\%$. The calculated value of the absolute contribution to T_{av} made by phonons reflected at the crystal surfaces could be too small by 1% of T_{av} , and the contribution made by phonons radiated from the end face of the crystal opposite the boundary could be in

error by $\pm 1\%$ of T_{av} . Finally, the actual area of each boundary could be 3% less than the area inferred from the diameter of the crystal. From these considerations, with the exception of experiment 2B, the values of R_1 given in Table I are considered accurate to $\pm 5\%$, but the values of n are accurate to $\pm 1\%$.

In order to evaluate the acoustic mismatch theory⁸ for an indium-sapphire boundary, it is necessary to know the velocities of sound in each medium. The velocities of sound in sapphire, doped with 0.08% Cr₂O₃, at 3 kMc/sec along the C axis have been supplied by Dransfeld and Ciccarello.²¹ They are $c_l=11.6\times 10^5$ cm/sec and $c_t=6.1\times 10^5$ cm/sec, in which c_l and c_t are the velocities of longitudinal and transverse waves, respectively. The velocities of sound in indium are reported elsewhere.²² Since in indium $1.7\leq c_l/c_t\leq 4.4$, one must consider the transmission coefficients given in Ref. 8 with either 0.33 or 0.44 as Poisson's ratio for indium. From these transmission coefficients, one would expect the boundary conductance to be in the range $2.2\times 10^{-2}T^3$ to $3.6\times 10^{-2}T^3$ W/(cm²-deg).²³

The T^3 terms presented in Table I for experiments 1A, 1B, and 2A agree within the experimental error, and fall within the above range of theoretical values. The T^2 terms indicate that another mechanism for boundary heat transport operates in parallel with the direct transmission of phonons. The T^2 terms are unquestionably different for the two samples, and may be due to static defects near the boundaries.²⁴

If one assumes that the electronic contribution to the boundary conductance is proportional to the number of excited quasiparticles, then at all experimental temperatures this contribution would have been reduced by more than 99% in the superconducting state. Within the accuracy of the data, the super-

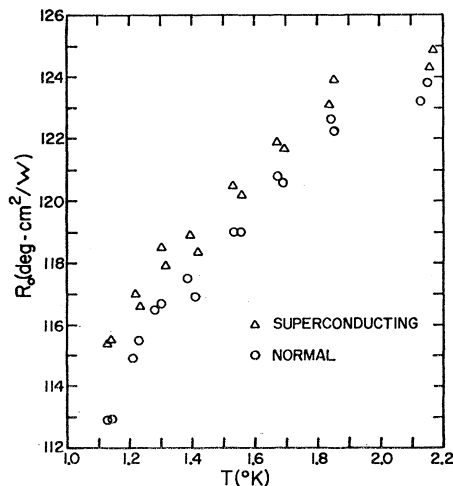


FIG. 2. R_0 versus temperature, experiment 1B.

²¹ K. Dransfeld and I. Ciccarello (private communication).

²² B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. **124**, 1011 (1961).

²³ The transmission coefficients are given in Ref. 8 only for $c_2/c_1 > 0.5$. Little (private communication) has pointed out that in some regions of the graphs the coefficients change only slightly if one varies ρ_1 , ρ_2 , c_1 , and c_2 in such a way that $\rho_1 c_1 / \rho_2 c_2$ is constant, in which ρ_1 and ρ_2 are the densities of sapphire and indium, respectively. This approximation may not be entirely valid in the region of present interest.

²⁴ W. A. Little, *Seventh International Conference on Low Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 482.

conducting transition affects only the T^2 term. Very roughly, the electronic contribution may be represented by $1 \times 10^{-3} T^2$ W/(cm²-deg).

CONCLUSIONS

Between 1.1 and 2.1°K, the thermal conductance of indium-sapphire boundaries can be represented by the sum of a T^2 term and a T^3 term. For two samples the T^3 terms are, respectively, $(0.0295 \pm 0.0016) T^3$ and $(0.0281 \pm 0.0016) T^3$ W/(cm²-deg). These numbers are within the range of possible values expected on the basis of the theory of Little. For one sample the T^2

term is $0.0059 T^2$ or $0.0069 T^2$ W/(cm²-deg) for the indium superconducting or normal, respectively. For the second sample this term is $0.0098 T^2$ or $0.0108 T^2$, respectively. These values are uncertain by $\pm 1 \times 10^{-3} T^2$, but the change caused by the superconducting transition is believed accurate to $\pm 4 \times 10^{-4} T^2$.

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Magnetic Properties of a Single Crystal of Manganese Phosphide

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Magnetic measurements were made on a spherical single crystal of high-purity stoichiometric MnP with a vibrating-sample magnetometer which was modified to allow precise temperature control and temperature cycling from 4 to 500°K. Anisotropy, saturation magnetization, and susceptibility data were obtained over this temperature range. The ferromagnetic Curie temperature was found to be 291.5 ± 0.2 °K. Evidence is presented which shows that MnP is neither ferrimagnetic nor antiferromagnetic, as has been previously supposed. Strong ferromagnetic coupling between spins may be assumed from the fact that the $1/\chi$ versus T curve has strong concave-up curvature above the Curie point. A magnetic transformation, not previously reported, was observed at 50°K which may be interpreted in terms of temperature-dependent, competing antiferromagnetic-ferromagnetic interactions. Below 50°K, MnP is metamagnetic, i.e., it exhibits an antiferromagnetic-ferromagnetic transition which is a function of applied field and temperature.

I. INTRODUCTION

THE principal results of magnetic measurements on a single crystal of MnP have been reported in abbreviated form elsewhere.¹ In that report a preliminary suggestion was made that the magnetic properties of MnP could be explained on the basis of temperature-dependent, competing antiferromagnetic-ferromagnetic interactions. The experimental results led to this hypothesis on comparison of the magnetic data with the theoretical predictions made by Enz,² Yoshimori,³ and others for competing-interaction models. The purpose of this paper is to present some of the magnetic data in more detail and to develop more completely an explanation in terms of temperature-dependent competing interactions.

Structural considerations, coupled with inconsistencies in the previous magnetic data, have led certain investigators to attempt to explain the magnetization of MnP on the basis of either ferrimagnetism or antiferromagnetism with weak, superimposed ferromagnetism (canted spins). MnP has an orthorhombic, slightly distorted NiAs structure,^{4,5} and there is some indirect evidence to indicate that it is an intermetallic compound with a narrow range of composition.⁶ The structure is shown in Fig. 1 where the displacements of the ions from their positions in an ideal NiAs structure are indicated.

Definition of the orthorhombic axes is ambiguous in the literature. The axis convention $a > b > c$ is used in this investigation. In MnP the Mn atoms form zigzag chains along the a and b axes, which allows the Mn sublattice to be separated into two sublattices. If the Mn atoms of each sublattice are similar, antiferromagnetism is possible and canting would give rise to a superimposed ferromagnetism. If the Mn atoms

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¹ E. E. Huber, Jr., and D. H. Ridgley, *J. Appl. Phys.* **34**, 1099 (1963).

² U. Enz, *J. Appl. Phys.* **32**, 22S (1961).

³ A. Yoshimori, *J. Phys. Soc. Japan* **14**, 807 (1959).

⁴ H. Nowotny, *Z. Elektrochem.* **49**, 254 (1943).

⁵ H. Nowotny, *Z. Physik, Chem. ABT B38*, 356 (1937).

⁶ K. H. Sweeny and A. B. Scott, *J. Chem. Phys.* **22**, 917 (1954).