Hall Effect in Gray Tin Filaments*

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The measurement of the Hall coefficient of gray tin filaments in the temperature range from 70 to 270°K is described. It is found that electron and hole mobilities given by the expressions $\mu_n=3.02\times10^7T^{-1.65}$ cm²/volt sec and $\mu_p=2.18\times10^8T^{-2.0}$ cm²/volt sec combined with an impurity concentration of 2.5×10^{17} cm^{-3} give a good fit to the conductivity and Hall data for pure material in the range extending 110 degrees down from the highest measurement temperature. The intrinsic energy gap at absolute zero is 0.094 ev. If one assumes a temperature dependence of -5×10^{-5} ev/deg, the high-temperature value of the energy gap remains substantially unaltered from that previously reported and the effective masses of charge carriers have the value 0.68 electron masse. Data for the lower temperature range indicate slight degeneracy and impurity scattering of charge carriers. Similar computations and results are discussed for other samples doped with *n*-type impurities. In contradiction to the results for *n*-type samples, *p*-type samples indicate mobility ratios slightly higher than unity. There is no indication, however, of extremely high mobility ratios such as those found in InSb. The field dependence of the Hall coefficient of *p*-type specimens shows a shift of the crossover to higher temperatures with increasing magnetic field, qualitatively in agreement with isotropic theory.

I. INTRODUCTION

STUDIES of the electrical and magnetic properties of gray tin, a group IV semiconductor, have been made by Busch and co-workers[1] using powder samples and by Kendall[2] using pressed-powder rods. Coherent, solid specimens of gray tin were first produced in the form of filaments.[3] More recently, and using different techniques, Becker[4] has produced coherent films of gray tin and studied their properties.

In a previous paper[5] (hereafter referred to as Article I) we have reported measurements of the electrical conductivity and magnetoresistance of filaments. To aid in the interpretation of these data, a method has been devised for measuring the Hall effect in the fine (0.1 mm diameter) wires, and Hall data have been obtained for a number of pure and doped samples of both conductivity types.

II. APPARATUS AND PROCEDURE

The specimen holder for Hall measurements was of special design necessitated by the small lateral dimensions and the brittleness of the gray tin samples. The specimen was supported by the Hall electrodes. These were fine, nonmagnetic spring wires which were parallel to each other, and the specimen was lightly clamped between and perpendicular to them. To provide good electrical contact, the electrodes were wet with a low melting-point solder (1 part indium to four parts gallium) which was liquid at room temperature but solid at the measurement temperatures. Thin-rolled, fine copper wires were used as current leads to prevent excessive stress on the sample due to differential thermal expansion.

Error due to the Ettingshausen effect was eliminated by making measurements with the sample immersed in a liquid bath so that the whole sample was in intimate contact with the liquid and no temperature gradients could build up. The baths used were liquid nitrogen, propane, and butane. To change from liquid nitrogen to liquid propane, gaseous propane was introduced into the nitrogen bath through a glass tube extending below the liquid surface. It was found that under low gas pressure the propane would first freeze, then liquify (mp~83°K) as the nitrogen boiled off with the result that the sample was soon surrounded by liquid propane which warmed up very gradually to its boiling point (~231°K). At this temperature the procedure was repeated with gaseous butane. By using these three baths and by pumping on the liquid nitrogen to reduce the pressure, it was possible to cover the temperature range from 70 to 270°K. To minimize the effect of temperature drift, readings were taken rapidly and in addition a reverse heat leak was used to decrease the rate of temperature rise while readings were being made. The heat leak consisted of a closed glass tube containing liquid nitrogen which was inserted into the bath. At higher temperatures, in the butane bath, where the highest precision was necessary because of the small Hall voltages, the temperature change during an individual measurement was so small as to be undetectable with the thermocouple.

All Hall voltages were measured using a conventional two-probe potentiometric method and a constant sample current of the order of 50 ma. After the sample had been oriented in such a position as to show the greatest Hall voltage, readings were taken with the magnetic field in both the direct and reversed directions and the values averaged to cancel any *IR* mismatch voltage present. Fields used ranged from one to eight kilogauss depending upon the purpose for which the

* This work was supported by the Office of Naval Research.
† Now at Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.
[1] G. Busch and J. Wieland, Helv. Phys. Acta **26**, 697 (1953).
[2] J. T. Kendall, Phil. Mag. **45**, 141 (1954).
[3] A. W. Ewald, Phys. Rev. **91**, 244(A) (1953).
[4] J. H. Becker, Phys. Rev. **98**, 1192(A) (1955).
[5] A. W. Ewald and E. E. Kohnke, Phys. Rev. **97**, 607 (1955).

data were desired. Conductivity values were obtained in the same temperature run with the Hall data. After correction for the appreciable resistance of the fine copper leads extending from the sample to the sample holder, these conductivity values agreed well with those of similar samples previously determined in the work of Article I.

The gray tin filaments were cylindrical in shape and hence the usual expression for the experimentally determined Hall coefficient was modified[6] to

$$R=10^8\pi V_H d/4HI,$$

where R is in cm³/coulomb if V_H is the Hall voltage in volts, d the diameter of the sample in centimeters, H the magnetic field in gauss, and I the sample current in amperes. Sample diameters were determined using a measuring microscope.

III. RESULTS AND DISCUSSION

A. Pure Sample

The analysis of conductivity and Hall data is particularly complex for gray tin because of the overlapping of intrinsic and impurity conduction regions owing to the small forbidden energy gap. In order to quantitatively study the conduction process with the data from only these two types of measurement, certain assumptions were necessary. A particular set of such assumptions, the reasons for making them, and a discussion of the results of computations using them are given in detail for a typical pure gray tin sample prepared from material supplied by Johnson, Matthey, and Company, Ltd. Hall and conductivity values are presented graphically in Fig. 1.

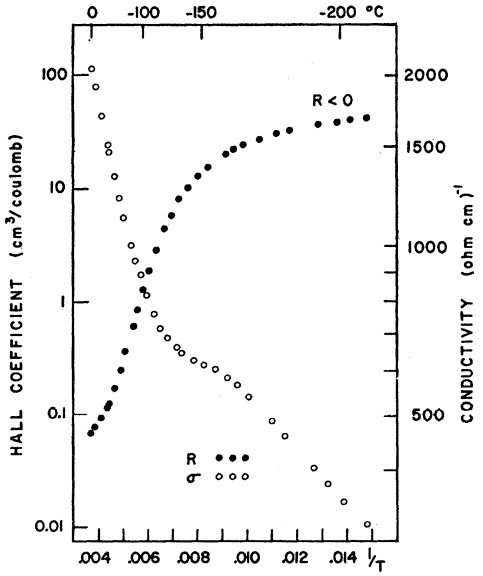

FIG. 1. Hall coefficient and conductivity *vs* reciprocal temperature for pure gray tin.

The common expression for the Hall coefficient

$$R=-\frac{3\pi}{8e}\frac{(n\mu_n^2-p\mu_p^2)}{(n\mu_n+p\mu_p)^2}, \tag{1}$$

in which all symbols have their usual meaning, is based upon the simplifying assumptions of lattice scattering, classical statistics, and low magnetic fields. If N n-type impurities per cc are present and they are all ionized, as seems reasonable for gray tin in the temperature range studied, electrical neutrality requires that

$$n=p+N. \tag{2}$$

The electrical conductivity is expressed as

$$\sigma=e(n\mu_n+p\mu_p). \tag{3}$$

Combination of these three relations with the assumptions that in the high-temperature range

$$\mu_n=AT^{-a} \quad \text{and} \quad \mu_p=BT^{-b},$$

in which A, B, a, and b are constants yields the working equation

$$eNAB=\sigma T^a B-\sigma T^b A-(8/3\pi)R\sigma^2 T^{a+b}. \tag{4}$$

Because the individual terms in this equation are large and the differences small, it was not possible to precisely determine the pair of temperature dependences which gave the best fit to the experimental data. It was found that the value of b must be greater than that of a as is generally true for other semiconductors. Acceptable values of N were restricted to the range determined by the low-temperature Hall coefficient together with the assumption of pure lattice scattering as one extreme and pure impurity scattering as the other. For the sample under consideration, these limits were 1.8×10^{17} and 2.9×10^{17} electrons/cm³, respectively. To carry the analysis further, a was fixed at 1.65 corresponding to recent results for germanium[7] and a value of b was sought such that the data could be fitted for a temperature range extending down approximately 100 degrees from the ice point. A very satisfactory fit to the experimental data of Fig. 1 is given by

$$\mu_n=3.02\times10^7 T^{-1.65} \text{ cm}^2/\text{volt sec},$$
$$\mu_p=2.18\times10^8 T^{-2.0} \text{ cm}^2/\text{volt sec},$$
$$N=2.5\times10^{17} \text{ cm}^{-3}.$$

It may be noted that, in contrast to most other semiconductors, the electron mobility is less than the hole mobility, the ratio becoming unity (by extrapolation) just slightly above the transition temperature. Also, mobility values calculated from the above expressions are generally greater (by factors as large as 3 in one

[6] R. Landauer and J. Swanson, Phys. Rev. **91**, 555 (1953).

[7] F. J. Morin, Phys. Rev. **93**, 62 (1954).

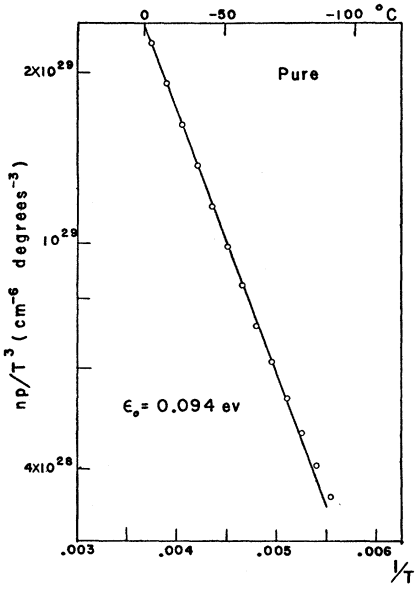

FIG. 2. Product of carrier densities divided by cube of temperature plotted against reciprocal temperature for pure material. The slope shows the energy gap at absolute zero to be 0.094 ev.

case) than those found by other investigators[1,2] using powder or compressed powder samples of gray tin.

Once μ_n and μ_p were determined, it was possible to evaluate n and p in the high-temperature range by substitution into Eqs. (2) and (3). According to theory[8] based on classical statistics,

$$np/T^3=2.33\times10^{31}(m_nm_p/m^2)\exp(-\epsilon_i/kT), \quad (5)$$

and the slope of the np/T^3 *vs* $1/T$ curve on a semilogarithmic plot will give the value of ϵ_0, the intrinsic energy gap at absolute zero, if ϵ_i is assumed to have the linear temperature dependence

$$\epsilon_i=\epsilon_0-\beta T.$$

The plot of Eq. (5) in Fig. 2 shows ϵ_0 to be 0.094 ev. The value of β is lumped together with the values of the effective masses of the charge carriers in the expression for the intercept of this curve. Since no independently determined values of these quantities yet exist for gray tin, assumptions were made based on the following considerations. Lark-Horovitz[9] has tabulated values of β determined by various methods for other semiconductors showing that it is of the order of 10^{-4} ev/deg for silicon and germanium, apparently smaller for germanium with its smaller forbidden gap. Furthermore, as the mobility ratio is about unity for gray tin, one would expect an effective mass ratio near unity. In consideration of the extremely small forbidden energy gap of gray tin, β was set equal to 5×10^{-5} ev/deg, yielding values of the effective masses: $m_n=m_p$ $0.68m$. The latter value is quite insensitive to the value of β, varying only from $0.56m$ to $0.80m$ as β goes from 10^{-4} to 10^{-5} ev/deg. Experimental verification of the assumed temperature coefficient of change of energy gap awaits optical transmission measurements. Using $\beta=5\times10^{-5}$ ev/deg, the energy gap at 250°K has the same value as that previously determined (Article I) from the slope of the conductivity curve, namely 0.082 ev.

The above analysis is based entirely on the temperature range from 0° to −110°C within which the data could be fitted by the mobility expressions. At lower temperatures one would expect departures from this simple mobility behavior due to impurity scattering and also that the assumption of classical statistics might no longer be valid. To extend the analysis to this temperature range, the temperature variation of the Fermi level was first determined by substituting the values of ϵ_0, β, N, and the effective mass ratios as determined above into the following expressions[8] together with Eq. (2), and eliminating n and p.

$$n=5.54\times10^{15}T^{\frac{3}{2}}(m_n/m)^{\frac{3}{2}}F_{\frac{1}{2}}(\eta^*), \quad (6)$$

$$p=5.54\times10^{15}T^{\frac{3}{2}}(m_p/m)^{\frac{3}{2}}F_{\frac{1}{2}}(-\eta^*-\eta_i). \quad (7)$$

In these, $\eta_i=\epsilon_i/kT$ and similarly η^* is the reduced Fermi level. $F_{\frac{1}{2}}(\eta^*)$ and $F_{\frac{1}{2}}(-\eta^*-\eta_i)$ are Fermi-Dirac functions, values of which have been tabulated by McDougall and Stoner.[10] Results of this calculation shown in Fig. 3 indicate that only slight degeneracy occurs and only at the lowest and highest temperatures, where the Fermi level comes within $2kT$ of the conduction band. Knowing the Fermi level at each tempera-

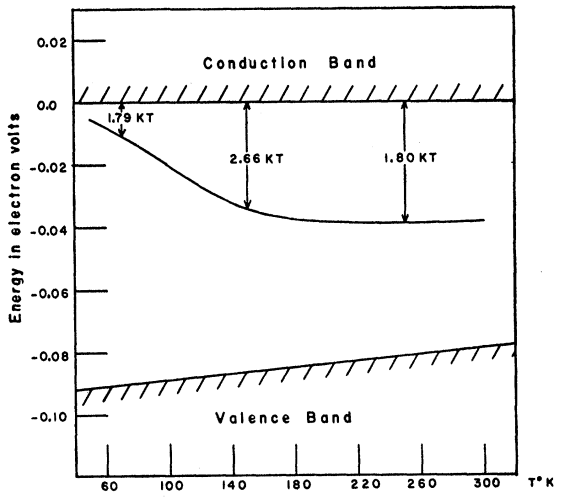

FIG. 3. Temperature dependence of the Fermi level in pure gray tin. Slight degeneracy occurs at the lowest and highest temperatures where the Fermi level comes within $2kT$ of the conduction band.

[8] See, for example, J. S. Blakemore, Elec. Commun. **29**, 131 (1952).

[9] *The Present State of Physics* (Am. Acad. Arts Sci. Publication, Washington, D. C., 1954), p. 93.

[10] J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) **A237**, 67 (1938).

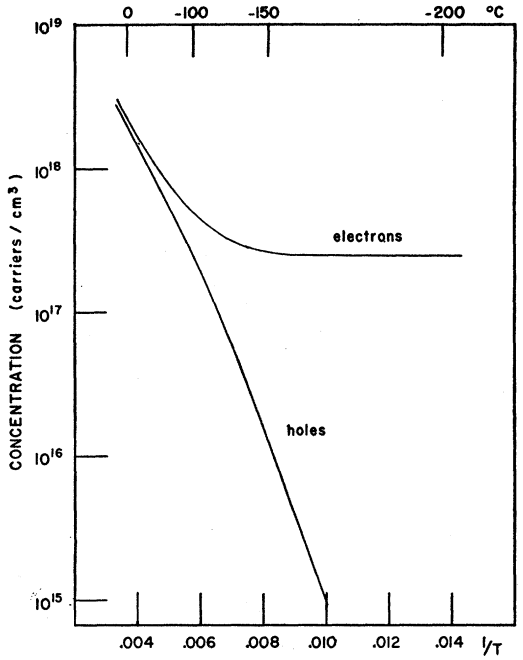

FIG. 4. Electron and hole concentrations in pure material, plotted against reciprocal temperature.

ture, carrier concentrations could be calculated from Eqs. (6) and (7) and are shown in Fig. 4. Finally, the mobilities plotted in Fig. 5 were determined by using the carrier concentrations in Eqs. (1), (2), and (3). The decrease of electron mobility below -170°C is probably due to the increased scattering of charge carriers by ionized impurities. Such an increase in impurity scattering would also explain the rising Hall coefficient in the low-temperature range where the number of carriers is constant. Between -110°C and -135°C the electron mobility rises more rapidly than $T^{-1.65}$. This may indicate optical mode scattering,[11] but verification of this is made difficult by the uncertainty in the Debye θ for gray tin.[12]

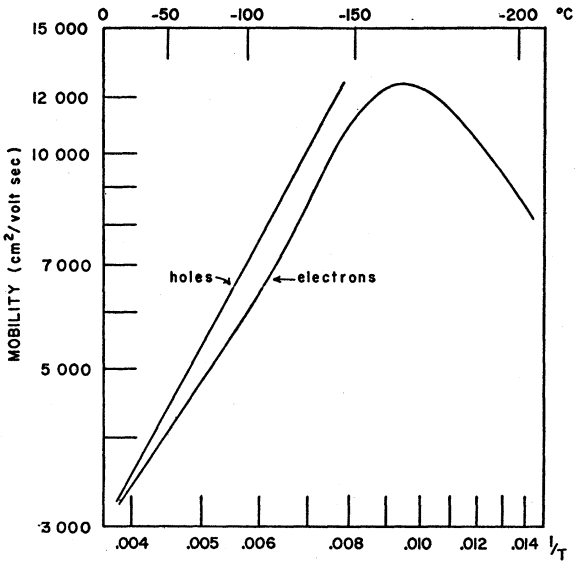

FIG. 5. Electron and hole mobilities *vs* reciprocal temperature.

B. Samples Containing Added *n*-Type Impurities

The sample As[11] (Fig. 6) contained 1.2×10^{18} added arsenic atoms per cubic centimeter. It was found that the high temperature Hall and conductivity data could be fitted by using

$$\mu_n = 2.48\times10^{7}T^{-1.65}\ \text{cm}^2/\text{volt sec},$$
$$\mu_p = 1.81\times10^{8}T^{-2.0}\ \text{cm}^2/\text{volt sec},$$
$$N = 3.5\times10^{17}\ \text{cm}^{-3}.$$

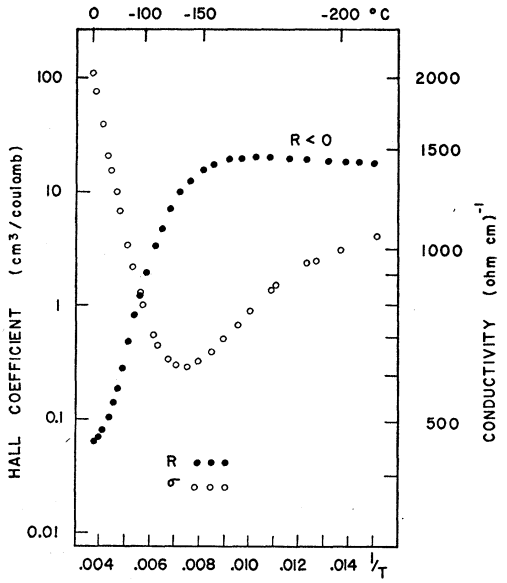

FIG. 6. Hall coefficient and conductivity *vs* reciprocal temperature for an *n*-type sample containing 1.2×10^{18} arsenic atoms per cc.

Thus the mobility temperature dependences are the same as those for the pure sample but there is a discrepancy in the coefficients. This can probably be attributed in large part to errors in measurement of sample dimensions which could not easily be further reduced because of the small size. Despite the differences in absolute values, the temperature at which the mobility ratio becomes unity is the same as for pure material. When the value of N for pure material is subtracted from the above value and the difference compared with the number of added arsenic atoms per cc, one finds that only one arsenic atom in twelve is effective as a donor. This low effectiveness of arsenic as a source of substitutional impurity atoms could be

[11] F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954).
[12] F. Lange, Z. physik Chem. **110**, 343 (1924).

inferred from the conductivity curves of Article I. The indicated energy gap at absolute zero is 0.104 ev. Assuming again a value for β of 5×10^{-5} ev/deg, the energy gap at 250°K is 0.092 ev, the same as previously reported on the basis of conductivity measurements alone.

Hall measurements on samples doped with antimony gave results which were similar in nature but showed antimony to be much more effective as a source of substitutional impurity atoms, again in agreement with previous conductivity results.

C. *p*-Type Samples

As yet, *p*-type samples have not yielded to a similar type of analysis. Figure 7 shows the results for a sample containing 1.2×10^{18} added indium atoms per cubic centimeter. The fact that the Hall coefficient changes sign from plus to minus with rising temperature is an indication that the electron mobility is greater than the hole mobility in contradiction to the results of *n*-type sample analysis. Results obtained on other specimens doped with zinc showed the same general pattern, and the relative magnitudes of the negative and positive maxima of the Hall curves were such that any computation of the mobility ratio using the analysis developed by Breckenridge *et al.*[13] for *p*-type InSb yielded results more nearly in line with those found for Ge than for InSb.

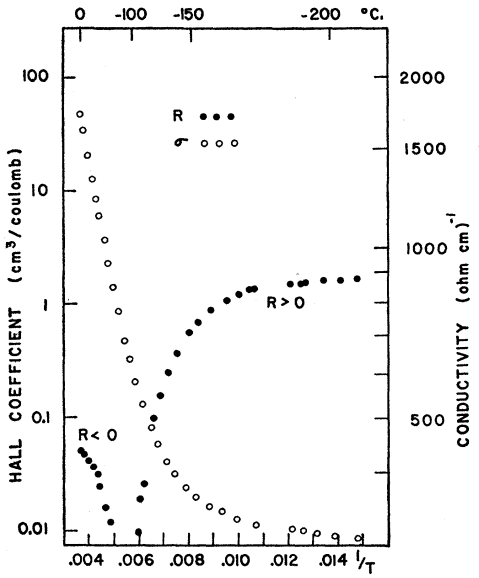

FIG. 7. Hall coefficient and conductivity *vs* reciprocal temperature for a *p*-type sample containing 1.2×10^{18} indium atoms per cc.

[13] Breckenridge, Blunt, Hosler, Frederickse, Becker, and Oshinsky, Phys. Rev. 96, 571 (1954).

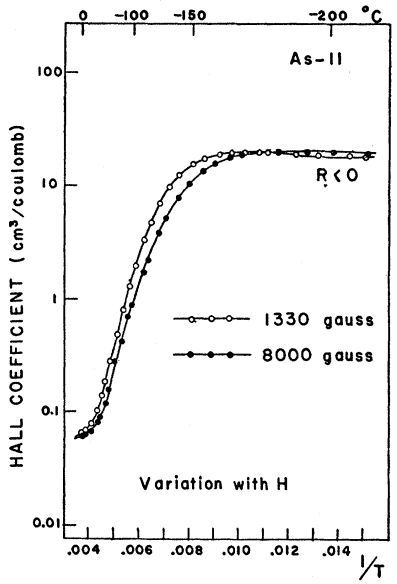

FIG. 8. Field dependence of the Hall coefficient for the *n*-type sample containing 1.2×10^{18} arsenic atoms per cc.

D. Field Dependence of the Hall Coefficient

Hall data used for computations on *n*-type samples were taken at a magnetic field of 1330 gauss, approximately the lowest field it was possible to use with the experimental setup to attain reproducible results. The trend of R with increasing field was such as to indicate that this field strength was low enough so that no appreciable improvement could be realized by extrapolating values to zero field. At much higher fields the

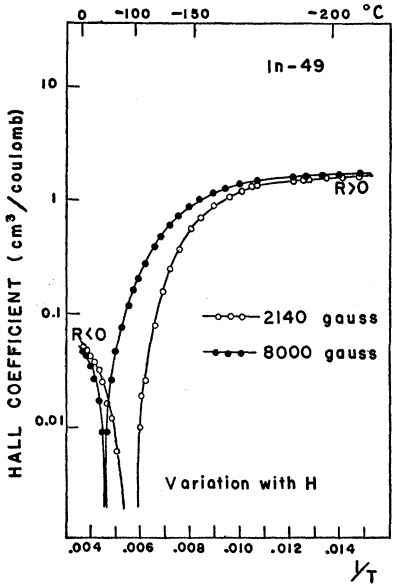

FIG. 9. Field dependence of the Hall coefficient for the *p*-type sample containing 1.2×10^{18} indium atoms per cc.

field dependence became significant especially in the intermediate temperature range as is shown for sample As[11] in Fig. 8.

For the p-type sample discussed in the preceding section, Fig. 9 gives the results of similar measurements. Particularly noteworthy is the shift of the Hall crossover (sign change) to higher temperatures with increasing field strengths. The direction of this shift is that qualitatively predicted by a strong-field, isotropic theory treatment such as given by Madelung.[14] Willardson, Harmon, and Beer[15] point out that though InSb has a similar shift, the shift observed in germanium is in the opposite direction. To explain this fact they introduce the concept of "fast holes," showing that the results can be explained by assuming a mixture of ordinary and high mobility holes taking part in the conduction process. At present, such a model seems unnecessary for gray tin.

[14] O. Madelung, Z. Naturforsh. **8a**, 791 (1953).
[15] Willardson, Harmon, and Beer, Phys. Rev. **96**, 1512 (1954).

ACKNOWLEDGMENTS

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Magnetic Susceptibility of Copper Metal at Low Temperatures

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The total magnetic susceptibility of high-purity copper has been measured between 300°K and 1.45°K using the Gouy method. It is found that the mass susceptibility can be represented by $\chi=(-0.083+0.023/T)\times10^{-6}$ cgs unit. This temperature dependence is much smaller than that found by previous workers, whose data extends only down to 14°K. An anomaly in the susceptibility at low temperatures, previously reported, was not found. The nuclear susceptibility of copper is responsible for about one-fifth of the temperature dependence found in the present work; the remainder can be explained by a paramagnetic impurity content which is plausible for the particular copper used. It is concluded that the susceptibility of pure copper is substantially independent of temperature in the measured range.

I. INTRODUCTION

THERE have been reported in the literature two measurements of the temperature dependence of the magnetic susceptibility of copper between room temperature and 14°K.[1,2] No measurements at lower temperatures have been published.[3] The two measurements down to 14°K are in substantial disagreement with each other. According to de Haas and van Alphen,[1] the magnitude of the susceptibility of copper increases monotonically with decreasing temperature, the value at 14°K being 12% higher than at room temperature. On the other hand, Bitter *et al.*[2] found that the susceptibility first increases about 3% as the temperature is reduced from 300°K to 63°K, but subsequently gets rapidly smaller, decreasing by 35% between 63°K and 14°K.

Either of these results, if correct, would be difficult to understand because one would expect the magnetic susceptibility to be substantially independent of temperature. Using a free-electron picture, the only temperature dependence expected would be due to the effect of changes in bulk density on the Fermi level and the total effect of this would be less than 2%. Most of this change would be concentrated at the higher temperatures. Even a theory which takes into account the energy band structure of copper does not suggest a temperature-dependent susceptibility. A more refined model of a metal can, however, lead to a temperature-dependent susceptibility at very low temperatures, if the density of states is affected by a temperature-dependent electron-phonon interaction.[4] Anomalies in the magnetic susceptibility of copper would be of particular interest inasmuch as the noble metals are considered to have a relatively simple electronic structure.[5]

In the experiments to be described in this paper, the magnetic susceptibility of very pure copper has been

[1] W. J. de Haas and P. M. van Alphen, Leiden Comm. 225b (1933).
[2] Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).
[3] Some indication of the behavior of the susceptibility in the liquid helium range can be obtained from experiments by L. Mackinnon [Ph.D. thesis, Cambridge University, 1949 (unpublished)]. His results suggest that the susceptibility decreases by about 5% between 4.2°K and 1.4°K. Because of experimental difficulties, this result is not well established.
[4] M. J. Buckingham, Nature, **168**, 281 (1951); M. J. Buckingham and M. R. Shafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954).
[5] H. M. Krutter, Phys. Rev. **48**, 664 (1935); D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).