Energy Gap in β-Ag_2Te†

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(Received 4 October 1965)

The Hall coefficient of a number of samples of β-Ag_2Te has been measured as a function of temperature from 80 to 373°K. The polycrystalline ingots were prepared by direct reaction of the elements either in vacuum or in oxygen gas. Data on seven *p*-type samples prepared from five different ingots have been analyzed in terms of an 0°K energy gap $E_0=(0.064\pm0.009)$ eV including a correction for the effect of degeneracy.

I. INTRODUCTION

THE compound Ag_2Te exists in three polymorphs.[1] The monoclinic β form transforms to the cubic α form at about 140°C; the α form converts to a third phase at a temperature which is between 690 and 800°C. The melting point is approximately 950°C. A hexagonal nonstoichiometric silver-tellurium compound, $Ag_{(2-x)}Te$ ("empressite") has also been reported[2] with $x=0.57$. The monoclinic β form has been reported[3] to be a semiconductor. Values of the energy gap of 0.025 eV[3] and about 0.05 eV[4] at 0°K (using the method of Austin and McClymont[5] to analyze the Hall coefficient data) have been reported. Earlier work by Appel[6] reported a value of the room temperature energy gap of 0.67 eV by analyzing the optical properties of thin films. Böttger and Meister[7] plotted the logarithm of the Hall coefficient versus $(1/T)$ from 110 to 225°K and obtained an activation energy of about 0.032 eV assuming intrinsic conduction. Stating that this value appeared much too small when compared with the value reported by Appel, they reported that an activation energy of about 0.05 eV is obtained if impurity conduction is assumed. No definite conclusion was stated by these workers.

Undoped stoichiometric material has been reported[8] to be *n* type while excess tellurium (less than about 3 atom % excess) produces β-Ag_2Te which is *p* type below about 80°K. Böttger and Meister[7] observed a change of conductivity type from *p* to *n* on heating. The evaporation of tellurium produced tellurium-deficient β-Ag_2Te which was 37.00 weight percent tellurium instead of the stoichiometric composition of 37.16 weight percent. Representative values[3] of the room temperature Hall electron and hole mobilities are 8400 $cm^2\ V^{-1}\ sec^{-1}$ and 1400 $cm^2\ V^{-1}\ sec^{-1}$, respectively. It seemed worthwhile, especially in view of the variation in the reported values of the energy gap, to obtain additional Hall-coefficient data and to analyze it with particular emphasis on the effects of the degeneracy of the semiconductor.

II. EXPERIMENTAL

The polycrystalline ingots of β-Ag_2Te were prepared by reaction of the elements in the liquid state. Stoichiometric quantities of silver (American Smelting and Refining Co. grade A-59, quoted purity 99.999+%) and tellurium (American Smelting and Refining Company grade A-58, quoted purity 99.999+%) were weighed into a clean quartz tube. The tube was then either evacuated to a pressure of about 10^{-5} Torr or was filled with oxygen, generated by the thermal decomposition of $KClO_3$, and sealed off. Two methods of solidification of the liquid were used. The first was the use of a Bridgman-type two-zone furnace in which the liquid mixture of reactants was passed through a freezing plane. The second was a simpler arrangement in which the reactant mixture was allowed to cool slowly after being held at about 1000°C for several hours. In the Bridgman-type preparations, the drive speed was either 0.25 or 0.50 in. per h. After solidification was complete in this method, the ingot was slowly (over about 8–12 h) cooled to room temperature. The oxygen pressures used correspond to about 2×10^{19} molecules present in the ampoule. In all cases, the ampoule was found to be cracked on removing it from the furnace. No evidence of gross oxidation was seen and the cracking of the ampoule probably occurred at the α-β transition temperature of about 140°C. The ingots of β-Ag_2Te used in this work are listed in Table I. Portions of all ingots were analyzed by x-ray diffraction. All were single phase monoclinic β-Ag_2Te except ingot AT-10 which contained about 5 at. % of the hexagonal empressite modification.

The ingots were etched with aqueous HF, followed by a mixture of NH_3 and H_2O_2.[4] Disks of Ag_2Te were then cut from the cylindrical ingot and polished with two grades of alumina to a thickness of about 0.1 cm. These were etched with $H_2O_2+NH_3$ to remove a surface layer and six arm bridge type samples[9] were cut ultrasonically. The configuration is shown in Fig. 1.

† The research reported in this paper was sponsored by the Advanced Research Projects Agency through the U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

[1] A. J. Frueh, Jr., Z. Krist. **112**, 44 (1959).
[2] G. Donnay *et al.*, Am. Mineralogist **41**, 722 (1956).
[3] G. E. Gottlieb, *et al.*, J. Phys. Chem. Solids **15**, 183 (1960).
[4] C. Wood, *et al.*, Phys. Rev. **121**, 978 (1961).
[5] I. G. Austin and D. R. McClymont, Physica **20**, 1077 (1954).
[6] J. Appel, Z. Naturforsch. **10a**, 530 (1955).
[7] O. Böttger and W. Meister, Ann. Physik **9**, 367 (1962).
[8] P. F. Taylor and C. Wood, J. Appl. Phys. **32**, 1 (1961).
[9] See, for example, W. C. Dunlap, Jr., *An Introduction to Semiconductors* (New York, John Wiley & Sons, Inc., 1957), pp. 185–187.

TABLE I. β-Silver telluride preparation.

Ingot	Reaction ambient	Solidification method	Temperatures employed	X-ray diffraction analysis
AT-1	Vacuum	Bridgman	1000°/900°C	β-Ag_2Te
AT-4	O_2, $p=185$ Torr	Bridgman	1000°/900°C	β-Ag_2Te
AT-9	Vacuum	Simple freezing	1000°C	β-Ag_2Te
AT-10	O_2, $p=155$ Torr	Bridgman	1000°/900°C	β-Ag_2Te+5 at. % "empressite"
AT-11	O_2, $p=170$ Torr	Simple freezing	1000°C	β-Ag_2Te

The length-to-width ratio is 5.2; this figure satisfies the criterion given by Dunlap[9] in which the length-to-width ratio of the sample must be greater than about 3 in order that a spuriously low value of the Hall coefficient not be obtained. The sample thicknesses were about 0.1 cm. All dimensions were measured with a calibrated microscope. Three types of soldered contacts to the Ag_2Te samples were used. All were metallic materials which melted well below the α-β transition temperature of Ag_2Te. The first was the intermetallic compound InBi, which has metallic properties[10] and melts at about 110°C. The second was an alloy of 40 weight % Bi, 40 weight % Pb, and 20 weight % Sn which melted at about 100°C. The third was a binary alloy of 22 at. % bismuth with indium. This alloy melted at 73°C. All types of contact were found to be ohmic up to current densities of about 20 A cm^{-2}. The contacts were made using the ultrasonic soldering technique.

Measurement of the Hall coefficient and resistivity were made using standard dc methods. A block diagram of the apparatus is shown in Fig. 1. A constant current supply provided the sample current. The current density in the sample was about 6 A cm^{-2}. The very high input resistance (100 000Ω minimum) of the Keithley dc microvoltmeters used insured that very low currents were drawn during the measurements of Hall voltages. The output of the microvoltmeter was displayed on a 10-in. recorder to obtain greater accuracy.

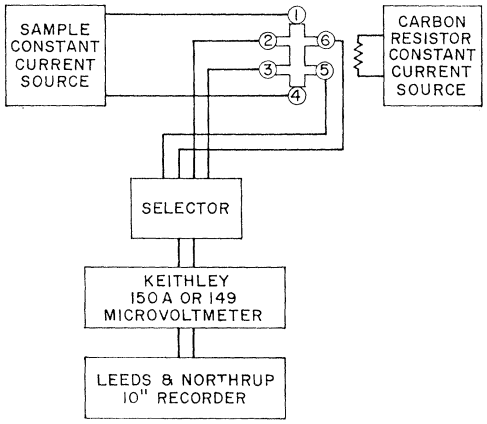

FIG. 1. Hall sample configuration and measurement apparatus.

[10] G. S. Cooper, *et al.*, J. Phys. Chem. Solids **25**, 1277 (1964).

The numbering system used for the contacts to the sample is also shown. Thus R_{26} is a value of the Hall coefficient calculated from voltages measured between contacts 2 and 6 on the sample. Heating of the sample for the experiments above room temperature was done using a high intensity lamp. The sample was enclosed in a brass can and was in a helium atmosphere during all measurements. The temperatures reported, measured with a calibrated copper-constantan thermocouple, are estimated to be accurate to about ±1°K. In the conventional[11] manner, the directions of both the magnetic field and the sample current were reversed to cancel various errors due to thermoelectric effects, probe misalignment, etc. Two runs over the temperature range being covered were necessary to obtain data for both magnetic field directions. Each Hall voltage used is the arithmetic mean of the appropriate four values of the measured voltage. A field of 5000 G was used. An estimate was made of the magnitude of the Ettingshausen effect, in which a longitudinal electric current produces a transverse temperature gradient which, in turn, can produce a spurious thermoelectric component

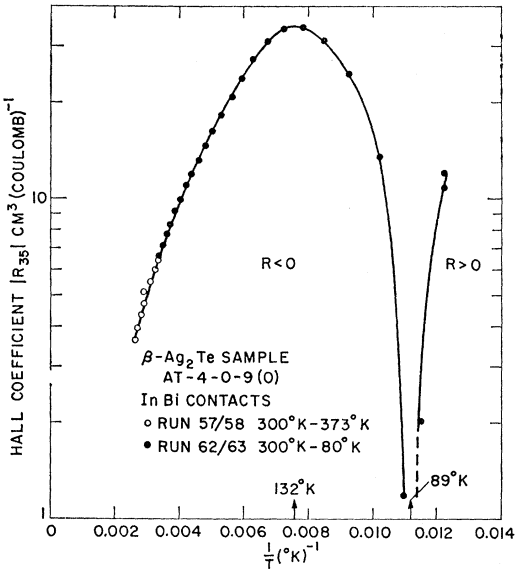

FIG. 2. Hall coefficient $|R_{35}|$ versus $(1/T)$ for β-Ag_2Te sample AT-4-0-9(0)

[11] E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths Scientific Publications Ltd., London, 1960), pp. 42–43.

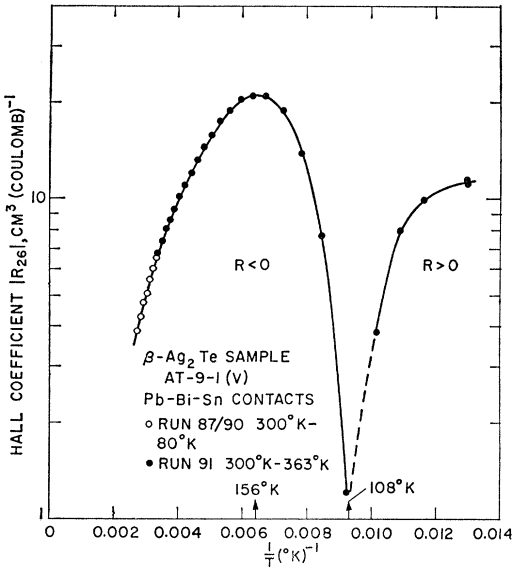

FIG. 3. Hall coefficient $|R_{26}|$ versus $(1/T)$ for β-Ag_2Te sample AT-9-1(V).

V_0 in the Hall voltage. V_0 was found to be of the order of 10^{-7} V, which is much less than the measured Hall voltages.

III. RESULTS

From the five ingots listed in Table I, seven samples for measurement of the Hall coefficient R were prepared. The Hall coefficient of each sample was measured, at two points on the sample (R_{26} and R_{35}), from 80 to 300°K and from 300 to about 370°K. All the samples were found to be n type between 370°K and the neighborhood of the 100°K, below which temperature they were p type. We estimate the uncertainty in our measured values of R to be about $\pm 10\%$. The Hall coefficient was measured as a function of magnetic field from 1000 to 5000 G for samples AT-4-0-5 (77°K) and AT-9-1 (300 and 77°K). The maximum variation

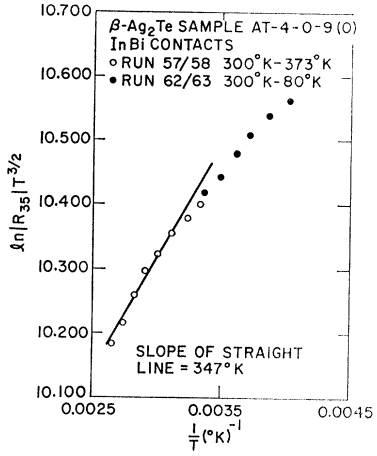

FIG. 4. $\ln|R_{35}|T^{3/2}$ versus $(1/T)$ for β-Ag_2Te sample AT-4-0-9(0).

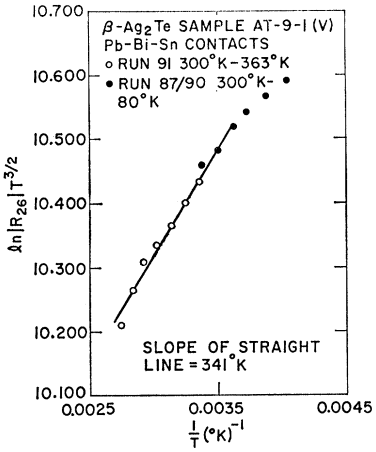

FIG. 5. $\ln|R_{26}|T^{3/2}$ versus $(1/T)$ for β-Ag_2Te sample AT-9-1(V).

in the Hall coefficient R was $\pm 5\%$, justifying the statement that R is independent of the magnetic field within the precision of our measurements. Since thermal expansion data for β-Ag_2Te are not available, no corrections for the change in sample dimensions with temperature were made. Typical Hall-coefficient data are shown in Figs. 2 and 3. These illustate the magnitude of the data, the temperatures of the maximum in the magnitude of the negative Hall coefficient, the inversion temperature, etc. We have calculated $\ln|R|T^{3/2}$ for each of our measurements of R: a total of 16 measurements on seven p-type samples from five ingots. Figures 4 and 5 show representative plots of $\ln|R|T^{3/2}$ versus $(1/T)$; in each case, a straight line was fitted through the data. The slope in degrees Kelvin of this straight line, whose interpretation is discussed below, was calculated. The results are summarized in Table II. In each case, data from 250 to about 370°K were plotted; the high temperature points were weighted more than those below room temperature because the sample is more likely to be intrinsic at high temperature than at low. We note in Figs. 4 and 5 that the

TABLE II. Measured values of the slope S of plots of $\ln|R|T^{3/2}$ versus $(1/T)$. The mean value of $S = (335 \pm 48)$ °K.

Number	Sample	Measurement	Temperature range (°K)	Contacts	S (°K)
1	AT-4-0-5	R_{35}	250–373	InBi	329
2	AT-4-0-5	R_{35}	250–373	InBi	225
3	AT-4-0-5	R_{26}	250–373	InBi	220
4	AT-4-0-9	R_{35}	250–373	InBi	347
5	AT-4-0-9	R_{35}	250–373	InBi	295
6	AT-4-0-9	R_{26}	250–373	InBi	329
7	AT-4-0-9	R_{26}	250–373	InBi	272
8	AT-4-0-10	R_{26}	250–373	InBi	410
9	AT-10-1	R_{35}	250–363	Pb-Bi-Sn	312
10	AT-10-1	R_{26}	250–363	Pb-Bi-Sn	312
11	AT-1-1	R_{35}	250–363	Pb-Bi-Sn	347
12	AT-1-1	R_{26}	250–363	Pb-Bi-Sn	347
13	AT-9-1	R_{26}	250–363	Pb-Bi-Sn	341
14	AT-9-1	R_{35}	250–363	Pb-Bi-Sn	399
15	AT-11-4	R_{26}	250–363	Pb-Bi-Sn	422
16	AT-11-4	R_{35}	250–363	Pb-Bi-Sn	445

points are beginning to deviate from our assumed intrinsic line as the importance of extrinsic carriers becomes more pronounced when the temperature is lowered. The mean value of the measured slopes S was (335±48)°K based on 16 measurements.

IV. DISCUSSION

The data consist of plots of $\ln|R|T^{3/2}$ versus $(1/T)$ from 250 to about 370°K. The consensus of the previous work[3,4,6,7] is that β-Ag_2Te is a semiconductor with an energy gap of less than 0.1 eV at 0°K. Assuming that the width of the energy gap ΔE decreases with increasing temperature, ΔE will be less than about $4kT$ at 250°K and will be less than about $3kT$ at 370°K. Classical statistics are a poor approximation to Fermi statistics if the Fermi level is about $2kT$ or less from the band edge and thus will probably fail in both the valence and conduction bands of β-Ag_2Te above 250°K. If, because of the value of the ratio of the carrier effective masses, the Fermi level is close to, say, the conduction band, it may be far enough from the valence band so that classical statistics might apply in the latter band. This is less likely at 370 than at 250°K because of the smaller ratio $(\Delta E/kT)$ at 370°K. Hence, it is possible that classical statistics might hold in one band but not in the other at the lower end of the temperature range we are considering. However, the more general case is that this semiconductor is very probably degenerate (i.e., classical statistics do not hold) in both the conduction and valence bands in this temperature range. We conclude also that our samples are intrinsic above about 250°K. Evidence for this statement is in the representative data in Figs. 2 and 3, in which the variation of the Hall coefficient with reciprocal temperature is consistent with this view. These curves are indicative of a p-type semiconductor, extrinsic at low temperatures, becoming intrinsic and n type at higher temperatures.

Given the assumption that the semiconductor is intrinsic and nondegenerate, one generally assumes spherical energy surfaces, dominance of lattice scattering, temperature-independent electron and hole effective masses, and a linear variation of the energy gap with temperature. With these assumptions, a plot of $\ln|R|T^{3/2}$ versus $(1/T)$ should be a straight line whose slope is $(E_0/2k)$, where E_0 is the value of the energy gap at 0°K and k is Boltzman's constant. This interpretive scheme for Hall coefficient data has been applied to, among other substances, β-Ag_2Se.[12] This interpretation of the data, applied to our average linear slope of (335±48)°K, gives $E_0=(0.058\pm0.008)$ eV. As discussed above, we believe our samples to be intrinsic but also believe them to be degenerate simultaneously in both the conduction and valence bands. Hence, we do not believe that the approach used by Austin and McClymont[5] in discussing InSb, which assumes degeneracy only in the conduction band, is appropriate for β-Ag_2Te.

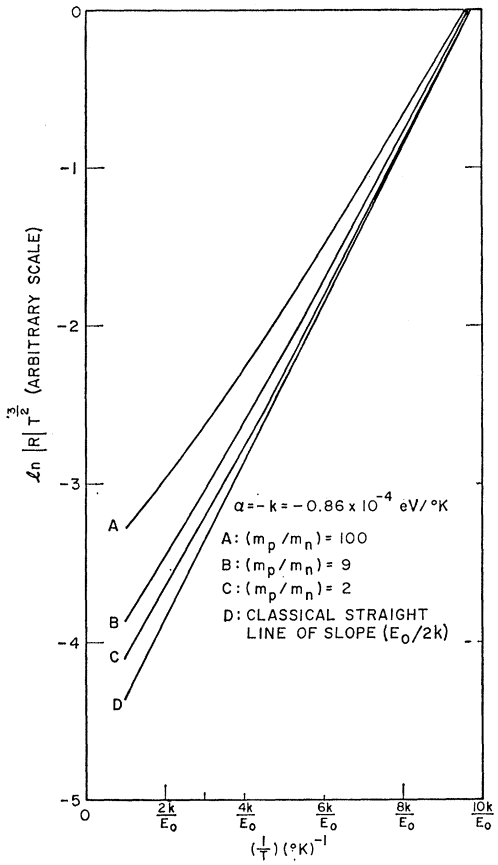

FIG. 6. Calculated values of $\ln|R|T^{3/2}$ versus $(1/T)$ for a degenerate intrinsic semiconductor with $\alpha=-0.86\times10^{-4}$ eV/°K for several values of (m_p/m_n).

No calculation of the Hall coefficient of an intrinsic semiconductor, degenerate in both bands, is known to us. Hence, we have calculated,[13] in the weak-field approximation, the Hall coefficient of a degenerate intrinsic semiconductor, assuming in this model (a) two bands and mixed conduction; (b) spherical energy surfaces, (c) dominance of acoustic lattice scttering; (d) linear variation of the energy gap with temperature. A part of our results is shown in Fig. 6, where we present plots of $\ln|R|T^{3/2}$ versus $(1/T)$. We express $\ln|R|T^{3/2}$ as a function of the parameters (m_p/m_n) and α, where m_p and m_n are the hole and electron effective masses and $\alpha=(\partial\Delta E/\partial T)$ is the constant temperature shift of the energy gap ΔE. The temperature is expressed in units of (E_0/k) and the $\ln|R|T^{3/2}$ scale is given in "arbitrary units" since different shifts of this scale for different values of (m_p/m_n) were necessary to give the three cases a common fictitious nondegenerate limit at low temperatures. The limiting values are really

[12] P. Junod, Helv. Phys. Acta 32, 567 (1959).

[13] R. Dalven, Bull. Am. Phys. Soc. 11, 33 (1966).

different because of the different values of (m_p/m_n). This figure is designed to show how $\ln|R|T^{3/2}$ deviates from the nondegenerate value for given values of (m_p/m_n) and α at constant temperature. Several conclusions may be noted. First, the deviations from classical (slope $S=E_0/2k$) behavior increase as the temperature is increased and the material becomes more degenerate as $(\Delta E/kT)$ decreases. The same effect occurs as the ratio of m_p to m_n increases at constant temperature and the Fermi level moves toward the conduction band, which is the band of lighter carrier carrier mass in this model. Second, the deviations are positive; $\ln|R|T^{3/2}$ is larger than predicted by the nondegenerate equation. Third, the slope of the plot of $\ln|R|T^{3/2}$ versus $(1/T)$ is always less than or equal to $(E_0/2k)$. If the sample is intrinsically degenerate, setting the slope equal to $(E_0/2k)$ gives too small a value of E_0. Hence we see that the value of E_0 obtained from the classical analysis is a lower limit to the 0°K band gap.

We now apply these conclusions to the analysis of our data for β-Ag_2Te. Our measured slope $S=(335\pm48)$°K and we note that a value of $(m_p/m_n)=2$ has been reported[3] for β-Ag_2Te. We must now specify the second parameter α, whose value has not been measured. To estimate α, we note that, since β-Ag_2Te shows semiconductor behavior at 375°K, $\Delta E>0$ at 375°K. Since ΔE is approximately 0.06 eV at 0°K, $|\alpha|<1.5\times10^{-4}$ eV/°K, assuming $\alpha<0$. We have used a value of $\alpha=-k$ eV $(°K)^{-1}=-0.86\times10^{-4}$ eV $(°K)^{-1}$ and have calculated the slope S of the plot of $\ln|R|T^{3/2}$ versus $(1/T)$ for $(m_p/m_n)=2$ and $\alpha=-k$ eV $(°K)^{-1}$ at $(1/T)=(5k/2E_0)$. This value of $(1/T)=0.0036$ when $E_0\cong0.06$ eV and is about the center of the reciprocal temperature range covered. The slope of the plot of $\ln|R|T^{3/2}$ versus $(1/T)$, at $(1/T)=0.0036$, for $(m_p/m_n)=2$ and $\alpha=-k$ eV $(°K)^{-1}$, is 0.90 $(E_0/2k)$. We propose that the relation between our observed linear slope S and E_0 is $S=0.90$ $(E_0/2k)$ and not the classical result $S=(E_0/2k)$. The data appear linear because of experimental scatter and the relatively small $(1/T)$ interval available before extrinsic carriers become important. Using $S=(335\pm48)$°K, this approach yields a value of $E_0=(0.064\pm0.009)$ eV, corrected for intrinsic degeneracy, which we propose for the energy gap of β-Ag_2Te at 0°K.

The treatment above explicitly assumes that β-Ag_2Te is a conventional semiconductor with a positive energy gap. Recently, Groves and Paul[14] proposed a new type of band structure for grey tin which had previously been thought to be a semiconductor with an energy gap of about 0.08 eV at 0°K. The new band structure has an energy gap fixed at the value zero at the zone center: the highest valence band overlaps or is tangent to the conduction band. At the zone edge in the (111) direction there is a conduction band minimum less than about 0.09 eV above the highest valence band. We cannot determine from our data the possible applicability of the Groves-Paul band structure to β-Ag_2Te. We conclude that our measured thermal activation energy corresponds to thermal excitation of carriers across an energy gap. However, at this time, the band structure of β-Ag_2Te is not known and the place of this 0.064-eV energy gap in the band structure cannot be ascertained.

ACKNOWLEDGMENTS

The authors would like to thank R. J. Paff for the x-ray analyses and J. O. Schroeder and R. Wasserman for assistance with the instrumentation.

[14] S. Groves and W. Paul, Phys. Rev. Letters **11**, 194 (1963).

Errata

Piezoresistance in *p*-Type ZnTe, A. SAGAR AND W. LEHMANN [Phys. Rev. **140**, A923 (1965)]. At the top of columns 5, 6, and 7 in Table II, (10^{+12} cm²/dyn) should read (10^{-12} cm²/dyn).