$$i(t_{kk}^{-}(\epsilon_k)-t_{kk}^{+}(\epsilon_k))$$
$$+\epsilon\left[\frac{\partial[t_{kk}^{+}(E)+t_{kk}^{-}(E)]}{\partial E}\right]_{E=\epsilon_k}+\sum_{k'}\sigma_{kk'}=0. \quad \text{(C32)}$$

From (134) this may be written

$$2r_k(\epsilon_k)=\sum_{k'}\sigma_{kk'}+s\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{\epsilon=\epsilon_k}. \quad \text{(C33)}$$

If we had started the derivation with the identity

$$1=-\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}R^{-}R^{+}dE, \quad \text{(C34)}$$

then one could easily see that

$$2r_k(\epsilon_k)=\sum_{k'}\sigma_{k'k}+s\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{\epsilon_k} \quad \text{(C35)}$$

replaces (C33). Therefore we have

$$\sum_k\sigma_{kk'}=\sum_k\sigma_{k'k}, \quad \text{(C36)}$$

which becomes for $s\rightarrow 0$

$$\sum_{k'}w_{kk'}=\sum_{k'}w_{k'k}, \quad \text{(C37)}$$

a well-known identity.

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Semiconducting Properties of Mg_2Si Single Crystals*†

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High-purity n-type single crystals of the semiconducting compound Mg_2Si were prepared from melts of stoichiometric proportions of the constituents in graphite crucibles; p-type crystals were obtained when the melt was doped with silver or copper. Carrier concentrations in the saturation region were as low as 8×10^{16} cm^{-3} for n-type and 4×10^{17} cm^{-3} for p-type samples. Electrical resistivity ρ and Hall coefficient R were measured from 77°K to 1000°K. Hall mobility R/ρ showed a temperature dependence in the intrinsic range of approximately $T^{-\frac{3}{2}}$ for all samples. At 300°K, R/ρ was as high as 406 cm^2/volt-sec for n-type and 56 cm^2/volt-sec for p-type material. The ratio of electron mobility to hole mobility was approximately five. The energy gap, determined from the least-square slopes at high temperature of the curves $\log(RT^{\frac{3}{2}})$ *vs* $1/T$, was 0.78 ev. The electron mobility at any temperature in the range 77° to 400°K can be explained quantitatively by a combination of scattering by optical modes and scattering by ionized impurities.

INTRODUCTION

THE compounds Mg_2X, where X is silicon, germanium, or tin, are semiconductors having the antifluorite structure. Single crystals of n-type and p-type Mg_2Sn have been studied by Blunt *et al.*[1] Winkler[2] has investigated polycrystalline Mg_2Sn, Mg_2Ge, and Mg_2Si and Whitsett and Danielson[3] and Nelson[4] have studied single crystals of n-type Mg_2Si. A complete analysis of Hall and resistivity data requires both n-type and p-type material, and measurements on single crystals are more likely to yield carrier mobilities unobscured by the effects of grain boundaries, eutectic inclusions, and dislocations. The present paper reports results of resistivity and Hall effect measurements on high-purity n-type and p-type Mg_2Si single crystals.[5] The following paper[6] reports results for Mg_2Ge.

PREPARATION OF SAMPLES

Sublimed magnesium with a purity of 99.99% or higher, supplied by Dow Chemical Company, and Sylvania transistor-grade silicon were used to prepare Mg_2Si single crystals. Stoichiometric proportions of Mg and Si were melted together in a graphite crucible with a spectrographically-pure graphite liner 6.4 cm long and 1.6 cm in inside diameter. Thermocouples were placed in the crucible wall near the top and bottom

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[1] Blunt, Frederikse, and Hosler, Phys. Rev. **100**, 663 (1955).
[2] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).
[3] C. R. Whitsett and G. C. Danielson, Phys. Rev. **100**, 1261(A) (1955).
[4] J. T. Nelson, Am. J. Phys. **23**, 390(A) (1955).
[5] R. G. Morris, Ph.D. thesis, Iowa State College, 1957 (unpublished). Preliminary results appear in Bull. Am. Phys. Soc. Ser. II, **2**, 120 (1957).
[6] Redin, Morris, and Danielson, Phys. Rev. **109**, 1916 (1957), following paper.

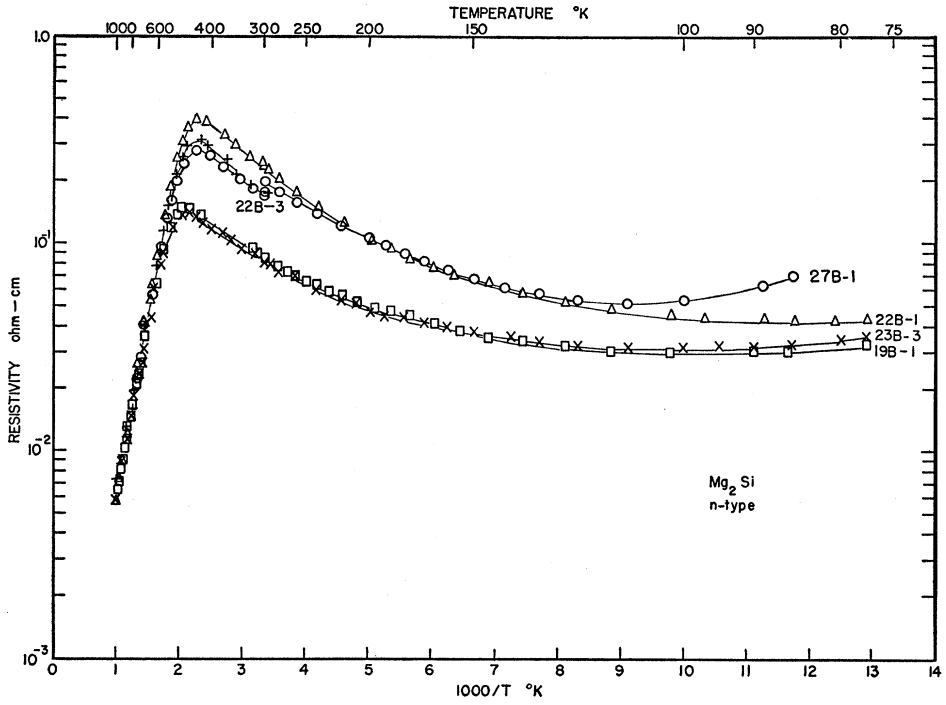

FIG. 1. Resistivity of n-type Mg_2Si.

of the melt. The melting point of Mg_2Si is 1090°C. The melting required about one hour and was carried out under two or three atmospheres of argon in order to reduce the loss of magnesium. A temperature gradient of 25°C/cm was established in the melt with the top at the higher temperature. The melt was then solidified in one more hour and the ingot cooled 50°C/hr to room temperature.

Samples 1 mm by 1 mm by 4 mm to 2 mm by 2 mm by 10 mm were cut from ingots prepared in this way. These samples were always n-type. Samples that were p-type were obtained when the melt was doped with 0.2 to 0.02% by weight of silver or copper. Doping with aluminum or iron did not produce p-type samples. Table I gives, for each of the different samples, the average doping-agent concentration and the impurity concentration obtained from the Hall coefficient in the saturation temperature range (corresponding to complete impurity ionization). Since p-type ingots were generally nonuniform, the average doping-agent concentration did not correspond closely to the impurity concentration in the sample.

TABLE I. Saturation carrier concentrations.

Sample	Doping agent	Average doping-agent concentration in the melt (cm^{-3})	Saturation carrier concentration (cm^{-3})
n-type 19B-1	none		3.5×10^{17}
22B-1	none		8×10^{16}
22B-3	none		10^{17}
23B-3	none		3×10^{17}
27B-1	none		10^{17}
p-type 25B-2	silver	3.7×10^{18}	7×10^{17}
26B-1	copper	7.1×10^{18}	4×10^{17}

Laue back-reflection x-ray photographs were made at three points along a sample and compared. Matching or nearly matching patterns indicated that all the samples were single crystals. X-ray analysis gave a lattice constant of[7] $a=6.35$ A in good agreement with the value 6.338 A obtained by Winkler[2] and by Klemm and Westlinning.[8]

RESISTIVITY AND HALL EFFECT

Electrical resistivity ρ and Hall coefficient R were measured from 77°K to 1000°K by conventional dc methods. A sample holder with phosphor-bronze contact probes was used in the temperature range 77°K to 300°K; for higher temperatures the sample was remounted in a Lavite holder with stainless steel supports and tungsten or molybdenum probes. Measurements at these higher temperatures were carried out with the sample under two or three atmospheres of argon in order to retard evaporation of magnesium.

Voltages were measured in a sequence suggested by Lindberg[9] in order to eliminate all spurious emf's other than that due to the Ettingshausen effect. An estimate of the error in the Hall coefficient resulting from the Ettingshausen effect, according to the method of Johnson and Shipley,[10] indicated an error less than

[7] P. Farrell (private communication).
[8] W. Klemm and H. Westlinning, Z. anorg. Chem. **245**, 365 (1941).
[9] Olof Lindberg, Proc. Inst. Radio Engrs. **40**, 1414 (1952).
[10] V. A. Johnson and F. M. Shipley, Phys. Rev. **90**, 523 (1953).

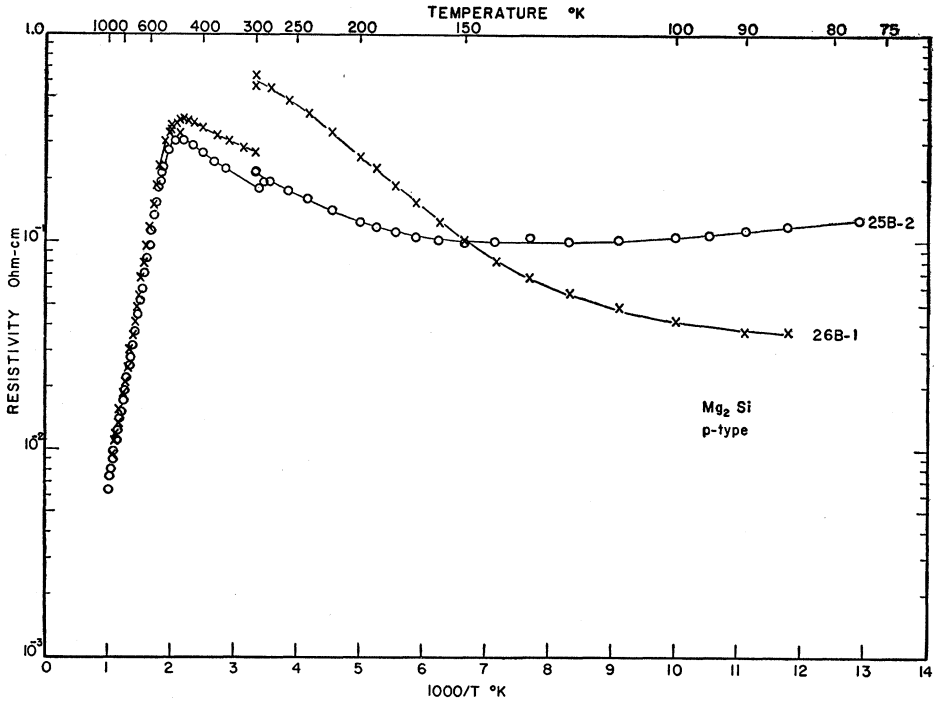

FIG. 2. Resistivity of p-type Mg_2Si. Different sample holders were used above and below 300°K. The change in probe locations and slight nonuniformity in impurity distribution caused the small breaks at 300°K in the curves for sample 25B-2. Sample 26B-1 was heated to 1000°K between measurements taken below and above 300°K, and this heat treatment caused the large breaks at 300°K in the curves for this sample.

4% below 800°K and less than 10% from 800°K to 1000°K.

Results for the resistivity are given in Figs. 1 and 2; the Hall coefficients are shown in Figs. 3 and 4; Figs. 5 and 6 show the quotient R/ρ. The curves $\log(R/\rho)$ *vs* $\log T$, where T is the absolute temperature, exhibit slopes at temperatures above 500°K between -1.9 and -2.9, depending on the sample.

The ratio of the electron mobility to the hole mobility $b=\mu_n/\mu_p$ was obtained from the graphs of the Hall coefficient *vs* $1/T$ for p-type samples according to a method given by Breckenridge *et al.*[11] From the equation

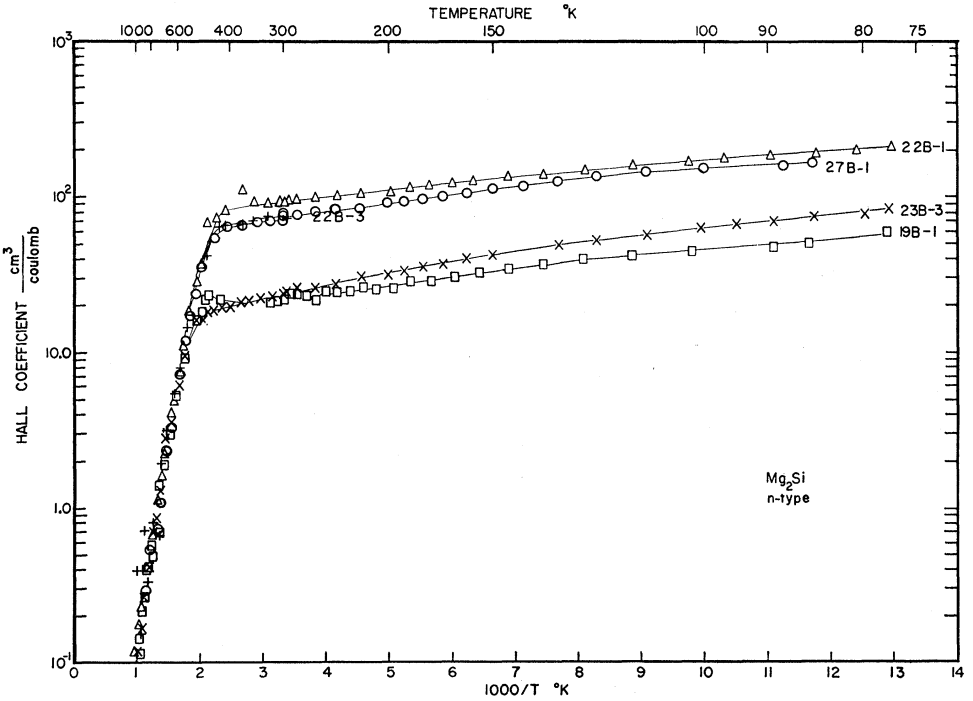

FIG. 3. Hall coefficient n-type Mg_2Si.

[11] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. **96**, 571 (1954).

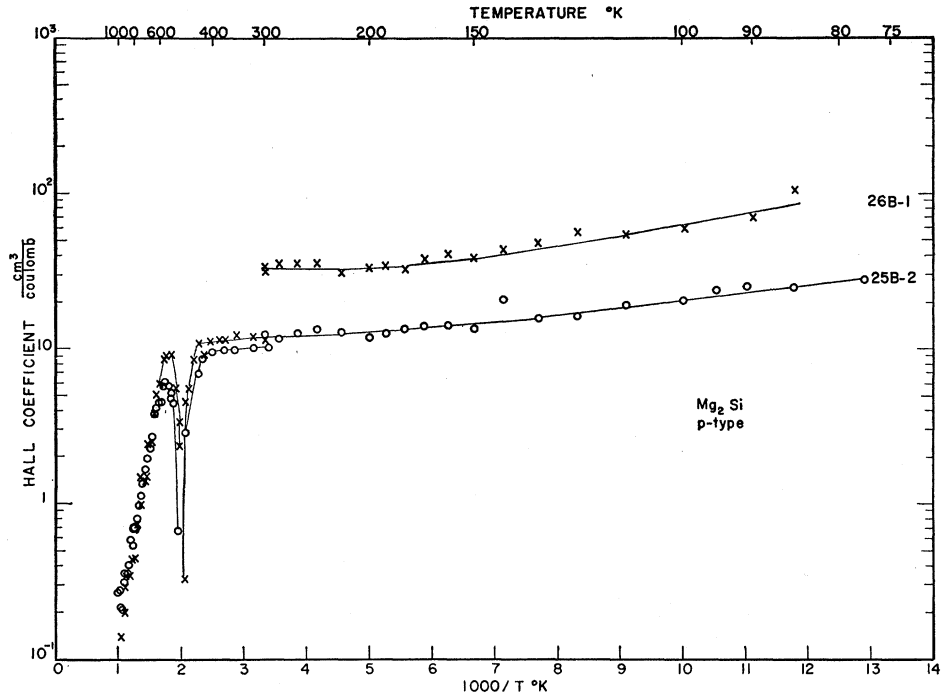

FIG. 4. Hall coefficient of p-type Mg_2Si.

$R_{max}/R_{sat}=-(b-1)^2/4b$, where R_{max} is the peak absolute value of R after the sign change and R_{sat} is the value of R from the flat saturation region of the curve, the mobility ratio b equals 4.2 and 5.0. An alternative method similar to one outlined by Shockley[12] gives the equation $(b-1)^2/b=-R_i/R_{sat}$, where R_i is obtained from the extrapolation of $RT^{\frac{3}{2}}$ in the intrinsic region to the temperature where the Hall coefficient changes sign. This equation gives $b=5.0$ and 5.2. An average of the four values gives $b=4.8$.

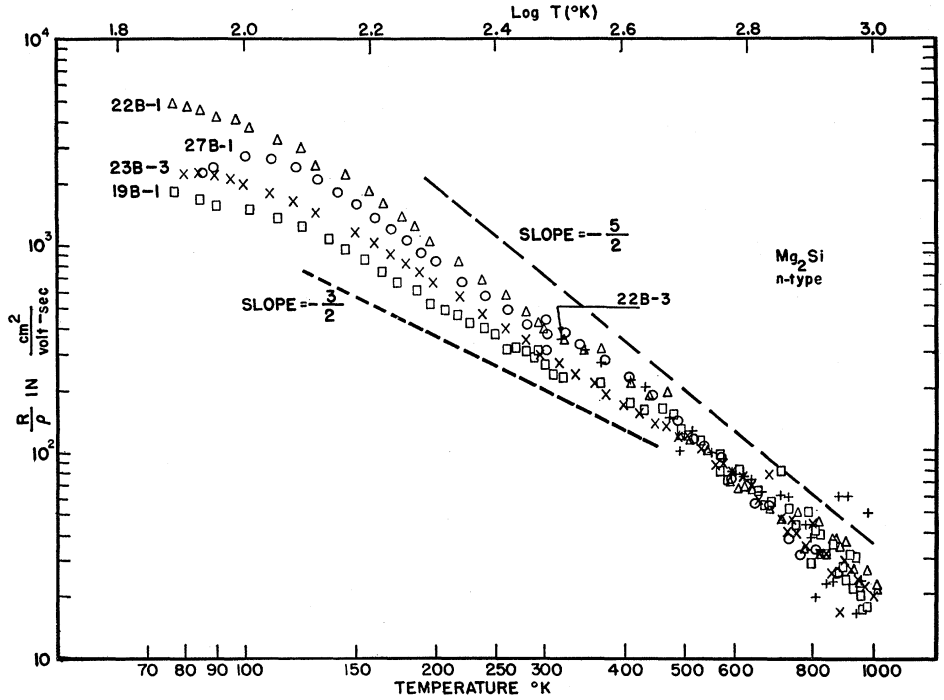

FIG. 5. Hall mobility R/ρ for n-type Mg_2Si.

[12] W. Shockley, in *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, 1950), p. 218.

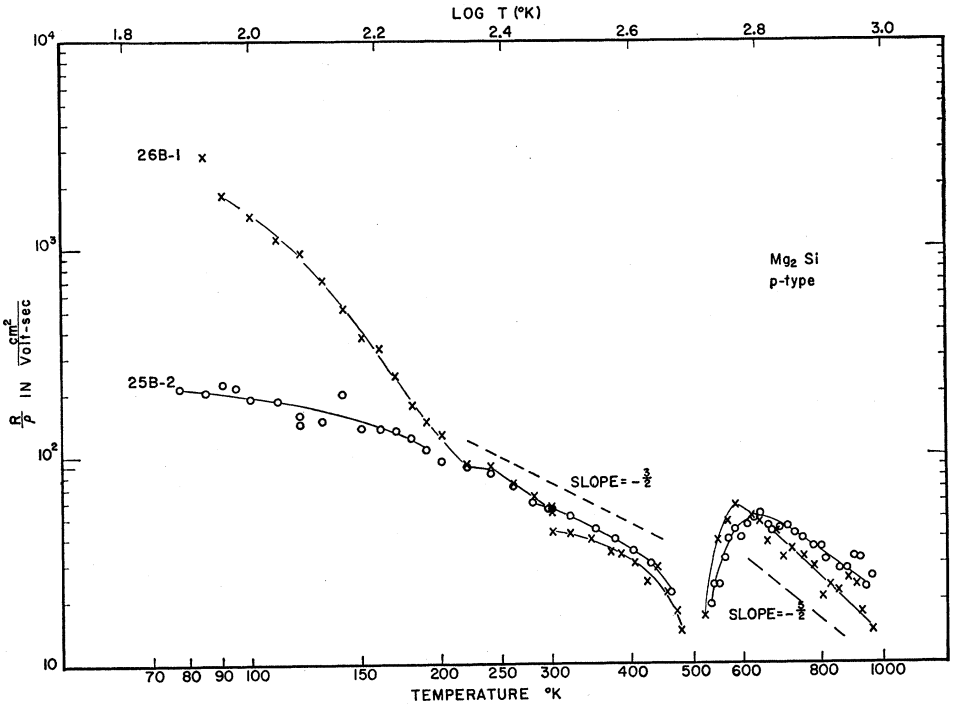

FIG. 6. Hall mobility R/ρ for p-type Mg_2Si.

ENERGY GAP

The expressions for the Hall coefficient and the resistivity are given by[13]

$$R=-G(n\mu_n^2-p\mu_p^2)/e(n\mu_n+p\mu_p)^2, \quad (1)$$

$$\rho=1/(ne\mu_n+pe\mu_p), \quad (2)$$

where G is a factor depending on the scattering mechanism and the applicable statistics, e is the absolute value of the electronic charge, and n and p are the electron and hole concentrations. In the intrinsic range n and p are approximately equal and each is proportional to $T^{\frac{3}{2}}\exp(-\Delta E_0/2kT)$. The quantity ΔE_0 is the energy gap at $T=0°K$; the energy gap at any temperature is assumed to be linear in the temperature: $\Delta E=\Delta E_0+\text{const}T$. If μ_n and μ_p vary with the temperature in the same manner, say as T^α, plots of both $\ln(RT^{\frac{3}{2}})$ and $\ln(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$ will have as their slopes $\Delta E_0/2k$. ΔE_0 from the slopes of least-square straight-line fits to the curves $\log(RT^{\frac{3}{2}})$ *vs* $1/T$ are given in Table II along with ΔE_0 from the graphical slopes of the curves $\log(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$ for three assumed values of α.

The experimental value of α was between -1.9 and -2.9 from the (R/ρ) curves. Table II indicates that ΔE_0 obtained from the slopes of $\log(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$ for α between -2.0 and -2.5 would indeed be consistent with those obtained from the slopes of $\log(RT^{\frac{3}{2}})$ *vs* $1/T$. The values of ΔE_0 obtained from the Hall data are considered more reliable since they do not depend on α, but only on the assumption that $(\mu_n-\mu_p)/(\mu_n+\mu_p)$ is temperature independent.

Winkler[2] obtained 0.77 ev for ΔE_0 in polycrystalline Mg_2Si by using the same analysis. Whitsett and Danielson[3] took $\alpha=-1.5$ and found $\Delta E_0=0.48$ ev from the slope of $\log\rho$ *vs* $1/T$. The consistency of the present values of ΔE_0 obtained from Hall data and from $\log(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$, where α is near the observed value of temperature dependence for (R/ρ) and for μ_n, points to the validity of $\Delta E_0=0.78$ ev.

MOBILITY

Simultaneous solution of Eqs. (1) and (2), the charge conservation expression $n=p+N$, the equation $R_{\text{sat}}=-G/eN$, and the definition $b=\mu_n/\mu_p$ yields expressions for n, p, μ_p and μ_n. The equation for μ_n is

$$\mu_n=\left\{\frac{R_{\text{sat}}(b-1)}{2G\rho}\right\}\left\{1-\left[\frac{4Rb}{R_{\text{sat}}(b-1)^2}\right]^{\frac{1}{2}}\right\}. \quad (3)$$

TABLE II. Energy gap obtained from Hall and resistivity data.

Sample	ΔE_0 (ev) from slope $\log(RT^{\frac{3}{2}})$ *vs* $1/T$	ΔE_0 (ev) from slope $\log(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$ $\alpha=-1.5$	-2.0	-2.5
n-type 19B-1	0.81	0.70	0.75	0.85
22B-1	0.79	0.69	0.75	0.89
22B-3	0.74	0.70	0.76	0.82
23B-3	0.86	0.68	0.77	0.84
27B-1	0.79	0.69	0.77	0.83
p-type 25B-2	0.70	0.71	0.78	0.84
26B-1	0.80	0.72	0.77	0.82
Average	0.78			

[13] See, for example, W. Shockley, in *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), Chap. 8.

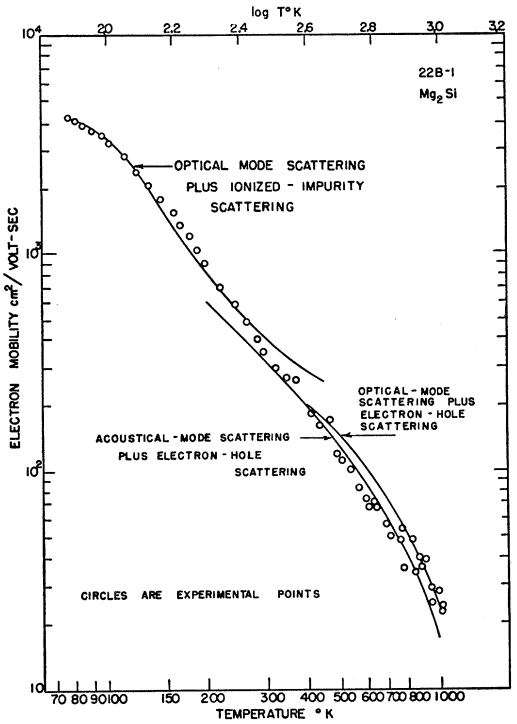

FIG. 7. Approximations to the experimental electron mobility. The fit in the range 77° to 400°K requires a dielectric constant of 20; the fit in the range 400° to 1000°K requires a dielectric constant 3.

N is the compensated impurity concentration; G was taken as $3\pi/8$. μ_n is shown as a function of the temperature in Fig. 7 for one sample. At 300°K, μ_n was 350 cm²/volt-sec. The temperature dependence of μ_n for $T>160$°K was $T^{-2.3}$. Similar departure from the $T^{-\frac{3}{2}}$-dependence predicted by acoustical-mode lattice scattering theory[14] has been observed by Blunt *et al.*[1] for Mg_2Sn and by Winkler[2] for Mg_2Sn, Mg_2Ge, and Mg_2Si.

An attempt to explain the temperature dependence of the mobility has been made. The mobility ratio b and the scattering factor G were taken as constant with temperature. Since the antifluorite structure has more than one atom per unit primitive cell (*viz.*, three), one might expect scattering of charge carriers by optical-mode lattice vibrations. The scattering theory applicable to crystals with parabolic energy surfaces and two atoms per unit cell has been developed by Howarth and Sondheimer.[15] The mobility μ_0 may be obtained from their Eq. (43) for the conductivity. For the case where Maxwell-Boltzmann statistics apply, μ_0 can be expressed by the equation

$$\mu_0=4\Omega M\epsilon_0^2k\theta(kT)^{\frac{1}{2}}(e^{\theta/T}-1)\chi(\theta/T)/3Q^2e(2\pi m_n)^{\frac{3}{2}}, \quad (4)$$

where Ω is the primitive unit cell volume, M is the reduced mass of the atoms in the unit cell, ϵ_0 is the high-frequency dielectric constant, k is Boltzmann's constant, θ is the Debye temperature for the material, Q is the effective ionic charge, m_n is the electron mass, and $\chi(\theta/T)$ is a slowly varying function given by Howarth and Sondheimer. The inclusion of ϵ_0 in Eq. (4) is a correction due to Callen.[16]

Equation (4) represents the mobility due to scattering of electrons by polarization waves in the case of two atoms per unit cell. In the fluorite structure two of the three atoms per unit cell are identical, have half the charge of the third and are symmetrically placed with respect to it. By using the method of Frölich[17] one may then write the polarization per unit cell in the same form as for two atoms per unit cell except that it is a factor of two greater. For Mg_2Si, $2Q$ must be used instead of Q since Mg is divalent. $Q=Fe$ where F is an ionicity parameter: $0\leq F\leq 1$. The scattering matrix element for Mg_2Si is thus increased by a factor of $2\times2=4$; and the scattering probability is increased and thus the mobility [Eq. (4)] is decreased by a factor of $(2\times2)^2=16$. The reduced mass for the mode having an electric moment is $1/M=1/2m_1+1/m_2$, where m_1 and m_2 are the atomic masses of magnesium and silicon, respectively.

A plot of $T^{\frac{1}{2}}(e^{\theta/T}-1)\chi(\theta/T)$ *vs* $1/T$ is given in Fig. 8 for four values of θ. The experimental mobility curve is also given, drawn to the same scale. It is seen that

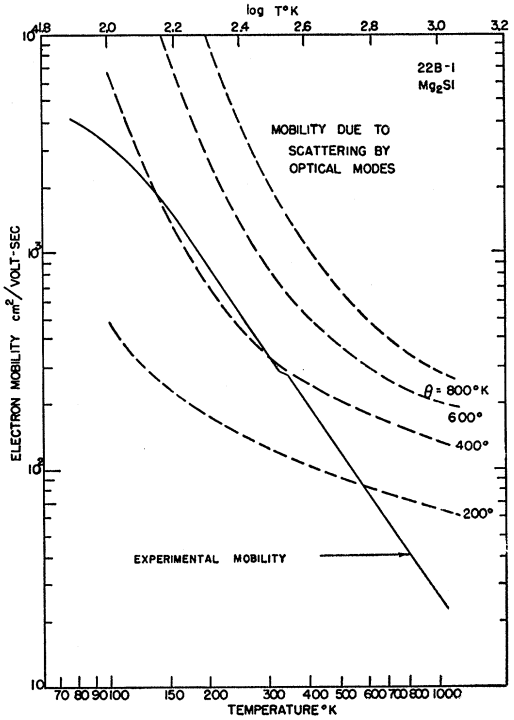

FIG. 8. Temperature dependence of electron mobility caused by scattering by optical modes.

[14] F. Seitz, Phys. Rev. **73**, 549 (1948).
[15] D. Howarth and E. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).
[16] Herbert B. Callen, Phys. Rev. **76**, 1394 (1949).
[17] H. Fröhlich, Proc. Roy. Soc. (London) **A160**, 230 (1937).

for $\theta=400°K$ the optical-mode curve approximates the shape of the experimental curve between 125°K and 300°K. No reasonable value of θ, however, leads to an optical-mode curve which will have a slope comparable to the experimentally observed slope for higher temperatures.

For $\theta=400°K$, consistent with an estimate of 430°K from the melting point of Mg_2Si,[18] Eq. (4) becomes

$$\mu_0=0.0226A_1T^{\frac{1}{2}}(e^{\theta/T}-1)\chi(\theta/T), \tag{5}$$

where $A_1=\epsilon_0^2/F^2$. The parameter m_n was determined from the general expression for $\log(RT^{\frac{3}{2}})$ for $1/T=0$, in combination with the relation $b=(m_p/m_n)^{\frac{3}{2}}$. Winkler's[2] value of the temperature dependence of $\Delta E(-6.4(10)^{-4}$ ev/deg K) was used to obtain $m_n=0.46\,m$, where m is the electron rest mass.

Acoustical-mode scattering or a combination of acoustical-mode and ionized-impurity scattering cannot at all explain a temperature dependence steeper than $T^{-\frac{3}{2}}$ since they vary only as $T^{-\frac{3}{2}}$ and $T^{+\frac{3}{2}}$, respectively. Combinations of optical-mode and acoustical-mode scattering gave only poor mobility fits to the experimental curve. A combination of optical-mode and ionized-impurity scattering was more successful. The Conwell-Weisskopf[19] expression for the mobility due to scattering by ionized impurities is in the present case given by

$$\mu_I=0.0610A_2T^{\frac{3}{2}}/\ln(1+3.52\times10^{-3}T^2), \tag{6}$$

where $A_2=\epsilon^2$; ϵ is the static dielectric constant. The quantity ϵ was taken as 14 in the denominator of Eq. (6), where the logarithm is relatively insensitive to ϵ. The value of A_2 which provided a good fit to the experimental curve justified this choice.

The resultant mobility was approximated by

$$1/\mu=1/\mu_0+1/\mu_I, \tag{7}$$

and solved for A_1 and A_2 when two experimental values of μ and T were substituted. A reasonable fit to the experimental curve, when $A_1=550$ and $A_2=355$, gave $\epsilon=18.8$. For $\epsilon\cong\epsilon_0$ (as in the case for valence crystals), $F=0.8$; the fit is shown in Fig. 7. The fit offers a quantitative explanation of the experimental electron mobility from 77°K to 400°K especially since a value of dielectric constant near 20 agrees with ϵ values for other semiconductors, tabulated by Winkler.[2]

At higher temperatures, electron-hole scattering may become important. A combination of electron-hole scattering with acoustical-mode or with optical-mode scattering gave the fits also shown in Fig. 7. The Conwell-Weisskopf formula [Eq. (6)] was adapted for electron-hole scattering when the impurity concentration was replaced by $(np)^{\frac{1}{2}}$ and the electron effective mass replaced by $m_nm_p/(m_n+m_p)$, where $m_p=0.87m$ is the effective hole mass. The formula $\mu_a=A_jT^{-\frac{3}{2}}$ was used for the mobility due to acoustical scattering.

Electron-hole scattering produces a steep mobility curve, but for $400°K<T<1000°K$ fits to the experimental data requires $\epsilon\cong3$ for either electron-hole plus optical-mode or electron-hole plus acoustical-mode scattering. A value of nearly three for the dielectric constant seems to be unreasonably low in light of the knowledge of other semiconductors. It appears that an explanation of the temperature dependence of the mobility, especially at high temperatures, must await a determination of the true shape of the energy surfaces.

[18] N. F. Mott and H. Jones, in *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), pp. 12–15.

[19] E. M. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).