Semiconducting Properties of Mg_2Ge Single Crystals*

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Single crystals of Mg_2Ge have been obtained from melts of the constituents, and Hall effect and electrical resistivity measurements have been made from 77°K to 1000°K. Undoped crystals were n-type and had saturated impurity carrier concentration as low as 3×10^{15} cm^{-3}; silver-doped crystals were p-type and had saturated impurity carrier concentrations roughly proportional to the amount of added silver. The room-temperature Hall mobilities were observed to be 280 cm^2/volt-sec for electrons and 110 cm^2/volt-sec for holes. The hole mobility observed in the extrinsic region (120°K to 350°K) of the highest purity p-type sample and the mobility difference observed in the intrinsic region (350°K to 700°K) of the n-type samples varied with temperature as $T^{-2.0}$. The mobility difference was found to decrease faster than $T^{2.0}$ above 700°K. The width of the energy gap at absolute zero, as determined from the temperature dependence of both the resistivity and the Hall effect in the intrinsic region, was 0.69 ± 0.01 ev.

INTRODUCTION

THIS paper reports the results of a study[1] of the Hall effect and electrical resistivity of n-type single crystals of Mg_2Ge. Magnesium germanide is a member of the series Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb. These compounds have the antifluorite structure and all except Mg_2Pb are semiconductors. The results of measurements on Mg_2Si are given in the preceding paper. Polycrystalline samples of all the members of this series were studied by Busch and Winkler[2] and Winkler.[3] For Mg_2Ge Busch and Winkler obtained an energy gap of 0.74 ev. The mobility obtained from the ratio of the Hall coefficient to the electrical resistivity was found to vary as $T^{-2.5}$ between 700°K and 900°K. Whitsett and Danielson[4] made Hall effect and electrical resistivity measurements on a single crystal of Mg_2Ge. It had an impurity electron density of 3×10^{17} cm^{-3}. They concluded that at high temperatures the Hall mobility varied as $T^{-\frac{3}{2}}$ and on this basis found an energy gap of 0.63 ev.

The single crystals of Mg_2Ge were prepared in the same way as were the Mg_2Si crystals described in the preceding paper.[5] Sublimed magnesium with a stated purity of 99.99% was obtained from the Dow Chemical Company. Germanium of the same purity was obtained from the Eagle Picher Company. The melt was doped with silver to obtain p-type samples.

ELECTRICAL MEASUREMENTS

Hall effect and electrical resistivity measurements were made by standard dc methods from 77°K to 1000°K. The results are given in Figs. 1 and 2. All samples had a negative Hall coefficient in the intrinsic region. The silver-doped samples had a positive Hall coefficient at low temperatures. A magnetic field of 10 kilogauss was used. No field dependence of the Hall coefficient was observed up to 16 kilogauss. The impurity concentrations in the samples as determined from the Hall coefficient in the saturation region are listed in Table I. N_D is the donor concentration and N_A is the acceptor concentration. The amount of silver added is also given. It appears that nearly all of the silver that was added to the melt was effective in producing acceptor levels. Since it was not known how well the silver was distributed through the melt, this is only an order of magnitude estimate. The source of the donor levels is not known. The measurements do not extend to temperatures low enough to determine accurately the impurity levels. The slow rise of the Hall coefficient below room temperature suggests the presence of at least two impurity levels in both the p-type and n-type samples.

MOBILITY

The ratio of the Hall coefficient R to the resistivity ρ is given in Fig. 3. This ratio may be called the Hall mobility. In the extrinsic region, $|R|/\rho=G\mu$, where μ is the conductivity mobility of the impurity carriers and G is a factor depending on the scattering mechanism and the applicable statistics. The value $3\pi/8$ was used

TABLE I. Impurity concentrations.

Sample No.	N_D-N_A (cm^{-3})	Silver added (atoms/cm^3)
7B-1	3.2×10^{15}	none
7B-3	2.5×10^{15}	none
11B-1	3.1×10^{16}	none
9B-1	-2.4×10^{17}	7.4×10^{17}
8B-1	-2.5×10^{18}	3.5×10^{18}

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[1] R. D. Redin, Ph.D. thesis, Iowa State College, 1957 (unpublished). Preliminary results appear in Bull. Am. Phys. Soc. Ser. II, **2**, 120 (1957).
[2] G. Busch and U. Winkler, Physica **20**, 1067 (1954).
[3] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).
[4] C. R. Whitsett and G. C. Danielson, Phys. Rev. **100**, 1261(A) (1955).
[5] Morris, Redin, and Danielson, Phys. Rev. **109**, 1909 (1958), preceding paper.

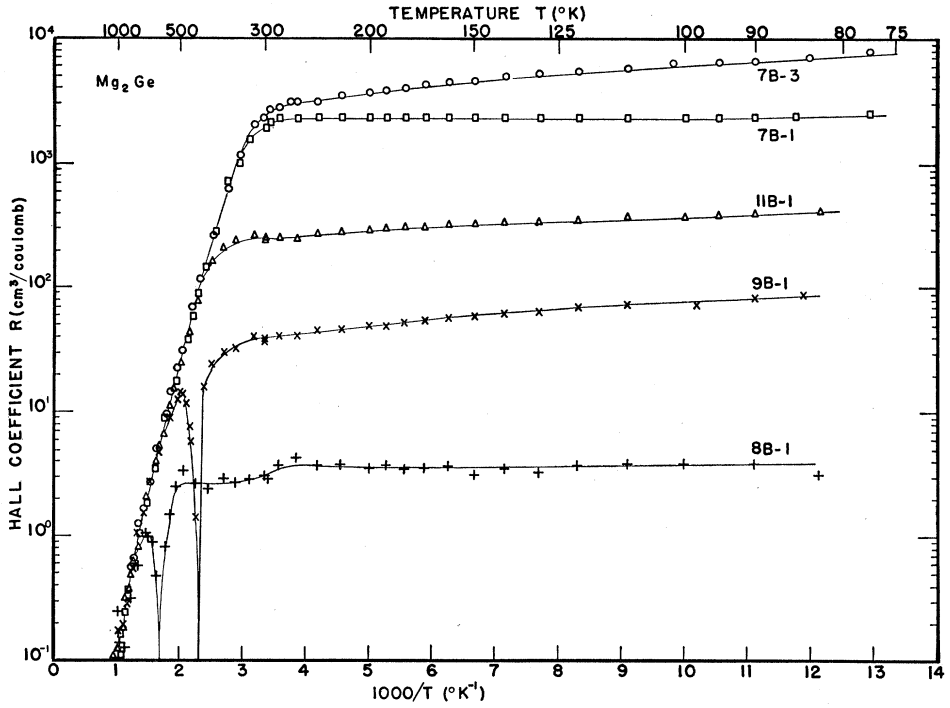

FIG. 1. Temperature dependence of the Hall coefficient in Mg_2Ge.

for G throughout. The low-temperature behavior of the electron Hall mobility in samples 7B-1, 7B-3, and 11B-1 (see Table I and Fig. 3) was unusual in that the mobility did not increase with increasing purity as determined from the Hall effect. It is possible that samples 7B-1 and 7B-3 had more neutral impurities such as dislocations or had many compensated donors and acceptors. These types of impurities would reduce the mobility without decreasing the Hall coefficient.

The data for sample 9B-1 in the temperature range 120°K to 350°K could be represented by

$$\mu_p = 0.848 \times 10^7 T^{-2.0}. \quad (1)$$

In the intrinsic region $n \cong p$ and $R/\rho = -G(\mu_n - \mu_p)$.

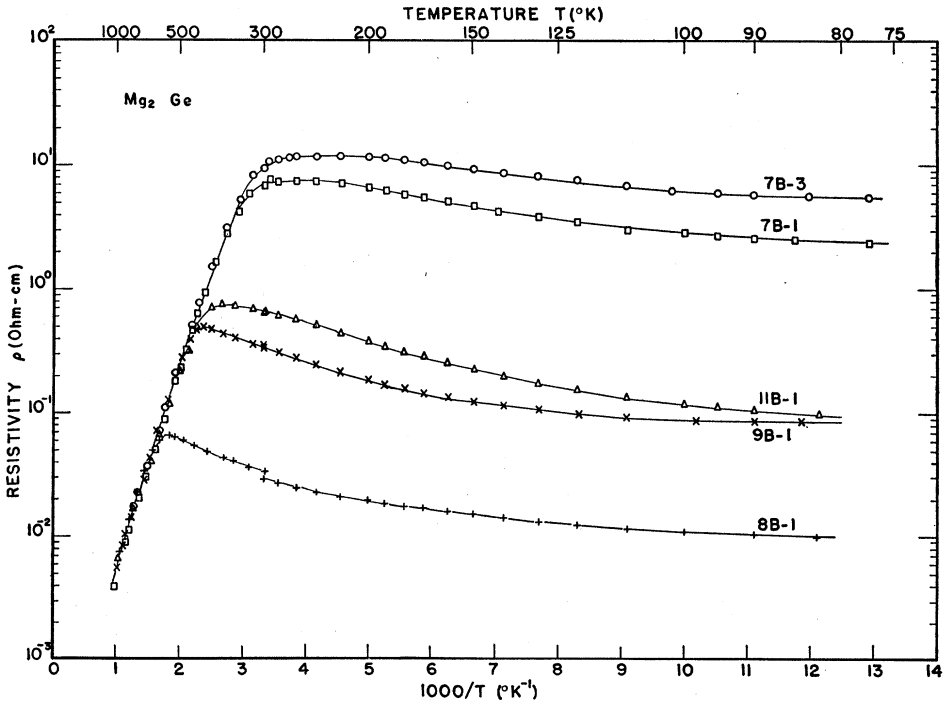

FIG. 2. Temperature dependence of the resistivity in Mg_2Ge.

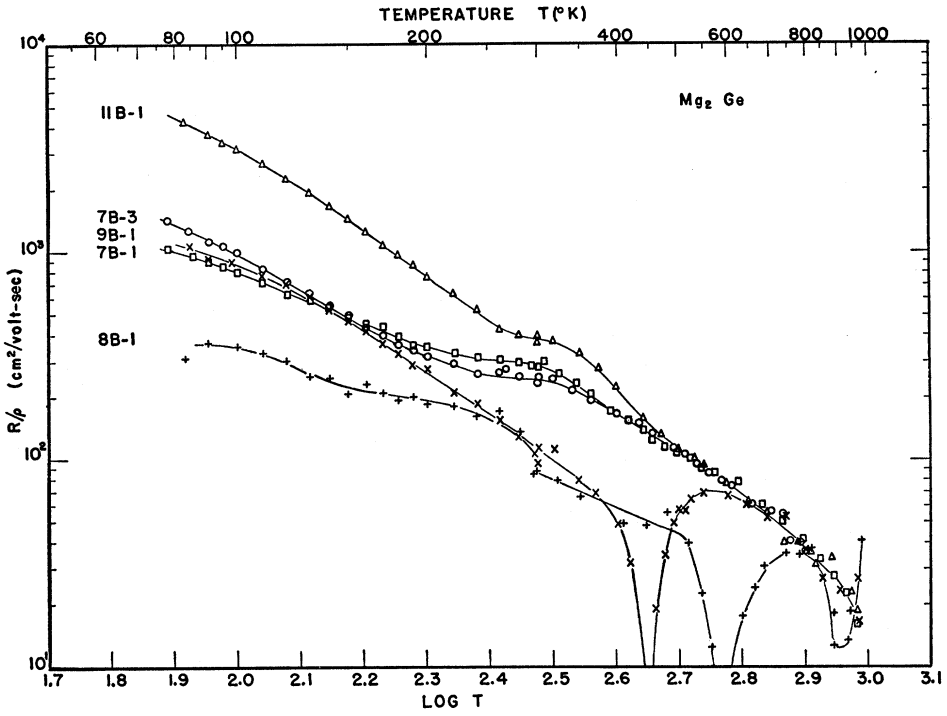

FIG. 3. Temperature dependence of Hall mobility R/ρ in Mg_2Ge.

As can be seen from Fig. 3, all of the samples approached the same curve at high temperatures. The data of samples 7B-1 and 7B-3 in the temperature range 350°K to 700°K could be represented by the expression

$$\mu_n-\mu_p=2.28\times10^7T^{-2.0}. \quad (2)$$

All of the samples showed a more rapid decrease than $T^{-2.0}$ above 800°K. This rapid decrease was caused by a decrease in the Hall coefficient and not by an increase in the resistivity. In this temperature region the resistivity was proportional to $(\mu_n+\mu_p)$ and the Hall coefficient was proportional to $(\mu_n-\mu_p)/(\mu_n+\mu_p)$. These facts suggest that the rapid decrease was due to μ_n approaching μ_p rather than to μ_n and μ_p both decreasing rapidly. To obtain the electron mobility the expression for the hole mobility found for sample 9B-1 was assumed to hold above 350°K, and Eqs. (1) and (2) were added to give

$$\mu_n=3.13\times10^7T^{-2.0}. \quad (3)$$

The electron mobility over the entire temperature range is plotted in Fig. 4. The dashed lines represent the experimental results as obtained from the data for sample 7B-1 below 300°K, and from Eq. (3) above 300°K. The $T^{-2.0}$ dependence above 300°K does not agree with the ordinary formula for acoustic-mode scattering. The bend in the electron mobility curve between 200°K and 300°K was suggestive of the behavior one would expect for strong optical-mode scattering and this possibility was considered. An expression for the mobility when the scattering is by the optical modes of the lattice vibrations based on the theory of Howarth and Sondheimer is given in the preceding paper. The constant coefficient and the Debye temperature θ were used as parameters to fit this expression to the experimental mobility. The best fit

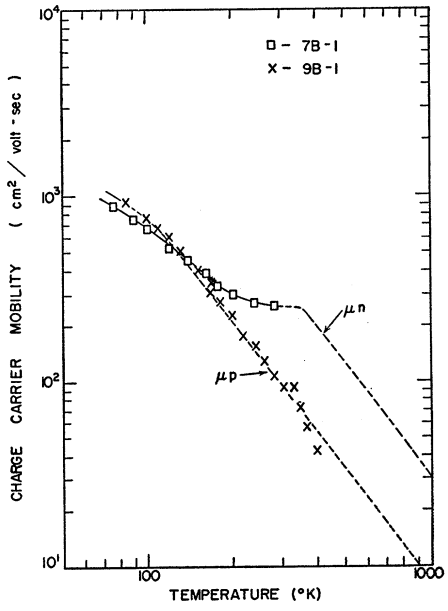

FIG. 4. Electron mobility, μ_n, and hole mobility, μ_p in Mg_2Ge. $\mu_p=0.848\times10^7T^{-2}$ in the range 120° to 350°K and is assumed to hold for higher temperatures. The dashed portion of the μ_n curve is obtained by addition of μ_p to $\mu_n-\mu_p=2.28\times10^7T^{-2}$ as obtained in the range 350° to 700°K from Fig. 3.

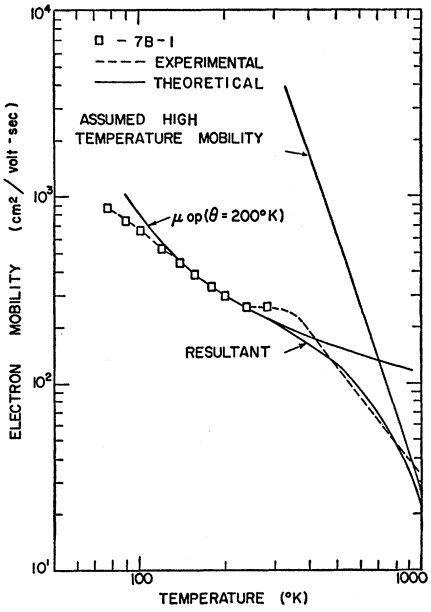

FIG. 5. Approximation to the experimental electron mobility (dashed curve) by a combination of scattering by optical modes (μ_{op}) and an arbitrary high-temperature scattering mechanism ($\mu \sim T^{-4.2}$).

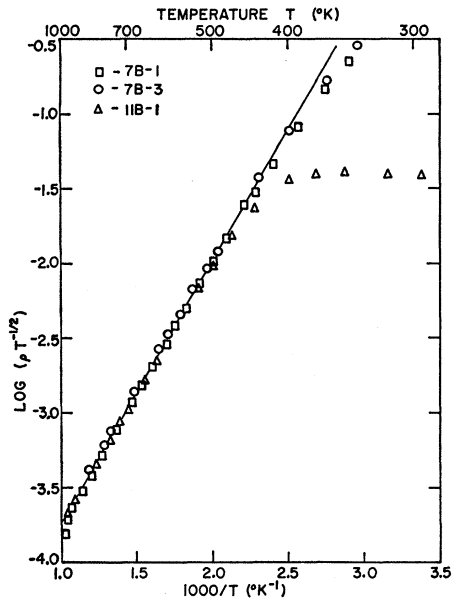

FIG. 6. Temperature dependence of $\log(\rho T^{-\frac{1}{2}})$. Energy gaps obtained from the slopes are listed in Table II.

was obtained for $\theta = 200°K$ and this fit is shown in Fig. 5. The Debye temperature for Mg_2Ge is not known.

In order to make the theoretical mobility approach a T^{-2} dependence at high temperatures, it was necessary to assume that a second scattering mechanism was producing a mobility with a $T^{-4.2}$ temperature dependence. One scattering mechanism which would give this high-temperature dependence is electron-hole scattering. This type of scattering was considered for the case of germanium by Morin and Maita.[6] They found that it had only a small influence on the observed mobility at high temperatures. The magnitude of electron-hole scattering depends essentially on the dielectric constant and the intrinsic concentration of electrons and holes. The dielectric constant of Mg_2Ge was not known, but it would not be expected to differ too much from that of germanium. The intrinsic concentration of electrons and holes was very nearly the same for Mg_2Ge and germanium. Therefore, electron-hole scattering would not be expected to be important in Mg_2Ge. Therefore, although optical-mode scattering could possibly explain the low-temperature data, it does not seem possible to explain the high-temperature data by existing theories.

ENERGY GAP

In the intrinsic region ($n=p$), the energy gap at absolute zero, ΔE_0, may be determined from the slope of a plot of $\log(RT^{\frac{3}{2}})$ *vs* $1/T$ or from the slope of a plot of $\log(\rho T^{\alpha+\frac{3}{2}})$ *vs* $1/T$ (see preceding paper). The assumption has been made that both the electron mobility and the hole mobility vary as T^{α}. For Mg_2Ge this appears to be true between 350°K and 700°K where $\alpha = -2$. Such plots are shown in Figs. 6 and 7. The energy gap, as obtained by least-squares fits to the data in the linear region, is given in Table II.

In the case of sample 9B-1, the intrinsic region was too short to apply the above analysis. Therefore, a different procedure was followed. It was assumed that

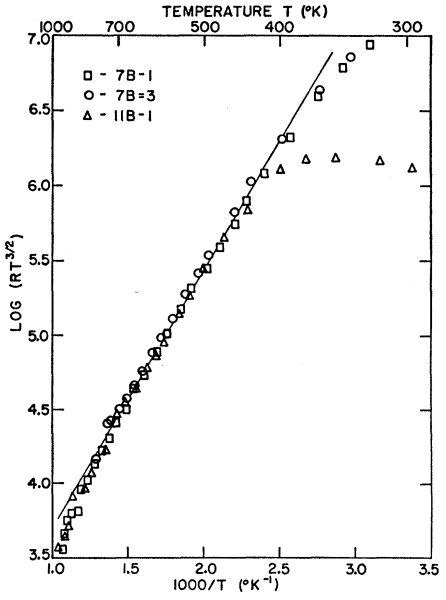

FIG. 7. Temperature dependence of $\log(RT^{\frac{3}{2}})$. Energy gaps obtained from the slopes are listed in Table II.

[6] F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954).

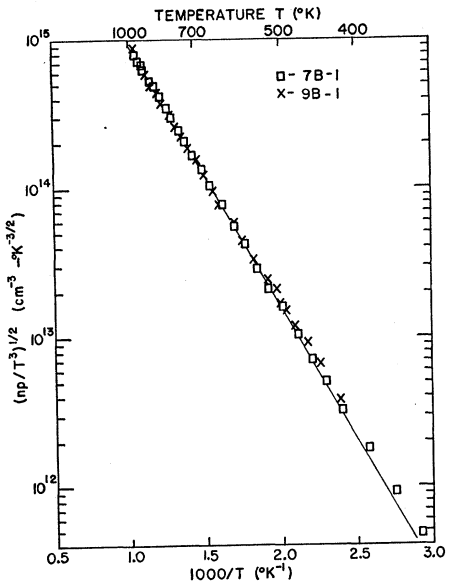

FIG. 8. Temperature dependence of $(np/T^3)^{\frac{1}{2}}$. The energy gap obtained from the slope is listed in Table II.

all the acceptors were ionized, so that

$$n=p-N_A. \tag{4}$$

The hole density is then given by

$$p=[1/e\rho(\mu_n+\mu_p)]+N_A\mu_n/(\mu_n+\mu_p). \tag{5}$$

The experimental resistivity values for sample 9B-1 were used to evaluate p. The value of N_A was obtained from Table I with the assumption that N_A was much greater than N_D. The mobilities μ_n and μ_p were obtained from Eqs. (2) and (3). The electron concentration was then obtained from Eq. (4) and a plot of $\log(np/T^3)^{\frac{1}{2}}$ *vs* $1/T$ was made. This plot is shown in Fig. 8. The energy gap obtained from a least-squares fit to these data is given in Table II. A similar plot for sample 7B-1 is given in Fig. 8. Sample 8B-1 was not analyzed because of its low purity. These methods of obtaining the energy gap are not entirely independent since the temperature dependence of the mobility which was used in analyzing the resistivity data was obtained from the ratio of the Hall coefficient to the resistivity. A simple average of the seven values of the energy gap was made and the standard deviation was computed. This gave $\Delta E_0=0.69\pm0.01$ ev.

TABLE II. Energy gap ΔE_0 (ev).

Sample No.	From plot of $\log(\rho T^{-\frac{3}{2}})$ *vs* $1/T$	From plot of $\log(RT^{\frac{3}{2}})$ *vs* $1/T$
9B-1	0.69	...
11B-1	0.70	0.67
7B-1	0.70	0.68
7B-3	0.69	0.69

The effective masses can be estimated from the values of $\log(RT^{\frac{3}{2}})$ and $\log(\rho T^{\alpha+\frac{3}{2}})$ at $1/T=0$, the temperature dependence of the energy gap, and the relation $\mu_n/\mu_p=(m_n/m_p)^{-\frac{5}{2}}$. Winkler[2] gives for the temperature dependence of the energy gap: 7.6×10^{-4} ev/°K. From these expressions the effective masses were found to be: $m_n=0.18m$, $m_p=0.31m$, where m is the free-electron mass.