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Electrical and Optical Properties of Intermetallic Compounds. IV. Magnesium Stannide*†

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Measurements of electrical and optical properties of this semiconductor have been made over a wide temperature range. Results from conductivity and Hall effect measurements as well as optical absorption data indicate an energy gap of 0.33 ev at $T=0°\text{K}$. Mobility values were found to be $\mu_e=320$ cm^2/volt-sec (for electrons) and $\mu_p=260$ cm^2/volt-sec (for holes) at room temperature. Both parameters are proportional to $T^{-2.2}$. Appreciable photoconductivity is observed at 85°K and at 5°K.

INTRODUCTION

MOTT and Jones[1] point out in their discussion of Brillouin zones in crystals that for several compounds with the fluorite structure "the number of available valency electrons is just equal to the number of states within the zone" and therefore "we are led to expect a small conductivity." They list the following examples: Mg_2Sn, Mg_2Pb, Mg_2Si, Mg_2Ge, Li_2S, Na_2S, Cu_2S, and Be_2C. The experimental work that has been carried out on these compounds is, however, very limited. Two of the magnesium compounds (Mg_2Sn and Mg_2Pb) were investigated in 1948 by Robertson and Uhlig[2] who came to the conclusion that Mg_2Sn is a semiconductor with a forbidden energy gap of 0.26 ev, while Mg_2Pb showed metallic conduction.[3] Recently Busch and Winkler[4] measured the electrical conductivity and Hall coefficient of the compounds Mg_2Si, Mg_2Ge, and Mg_2Sn, and of mixed crystals of the latter two materials.[5] These investigators obtain for Mg_2Sn an energy gap of 0.36 ev at absolute zero. The difference between their result and that of Robertson and Uhlig is due to a different temperature dependence of the mobilities found by Busch and collatorators. The corresponding values of Mg_2Si and Mg_2Ge are listed as 0.77 ev and 0.74 ev, respectively.[4]

This paper deals in detail with the properties of Mg_2Sn.

EXPERIMENTAL PROCEDURES

Magnesium stannide (melting point 780°C[5]) was prepared by melting the two components together under a hydrogen atmosphere. The magnesium metal was obtained from two sources: Dominion Magnesium Limited (purity about 99.7%) and the Dow Chemical Company (purity better than 99.97%). Tin was supplied by the Vulcan Detinning Company (purity 99.997%). Thorough mixing in the molten state is an essential part of the preparation of this compound. The ingots which were pulled from the melt were very hard and brittle and showed a bluish color. These boules contained in most cases large single crystal areas and cleaved very easily along the (111)-plane exhibiting mirror-like surfaces. Contact with water covers the compound immediately with a dark layer quite analogous to the behavior of AlSb.[6]

The purity of the samples prepared in this way is remarkably high in spite of the heavy evaporation of magnesium during preparation. The compound has a tendency to grow crystals of nearly perfect stoichiometry and rejects excess magnesium as well as excess tin. Most crystals showed *n*-type conductivity; *p*-type ingots were obtained by doping with silver (*C*-22) or gold (*C*-23).

Samples for electrical measurements were ground to an approximate size of 1×2×7 mm.

Several attempts to obtain good optical surfaces for transmission measurements by polishing with emery powder or alundum in alcohol were not very successful. The surfaces produced in this way showed large scattering. Excellent results were achieved by cleaving; all optical measurements reported in this paper were made on cleaved samples approximately $\frac{1}{2}$ mm thick.

X-ray analysis confirmed the fluorite structure of the crystals, the lattice constant being 6.7630 A[7] at 26°C.

Detailed descriptions of the equipment used for measuring Hall coefficient and resistivity,[8] optical absorption,[9] and photoconductivity[10] have been presented previously.

RESISTIVITY AND HALL EFFECT

The temperature dependence of the resistivity, ρ, and the Hall coefficient, R, of several *n*- and *p*-type

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† I, II, and III of this series have been published in Phys. Rev. **96**, 571–580 (1954).

[1] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).

[2] W. D. Robertson and H. H. Uhlig, Trans. Am. Inst. Mining Met. Engrs. **180**, 345 (1949).

[3] Their results do not exclude the possibility that Mg_2Pb might be a semiconductor with a very small energy gap.

[4] G. Busch and U. Winkler, Physica **20**, 1067 (1954); Helv. Phys. Acta (to be published).

[5] G. Busch and U. Winkler, Helv. Phys. Acta **26**, 579 (1954).

[6] Blunt, Frederikse, Becker, and Hosler, Phys. Rev. **96**, 578 (1954).

[7] Measurements made by the Microstructure Section of the National Bureau of Standards.

[8] R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).

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

[10] H. P. R. Frederikse and R. F. Blunt, *Photoconductivity* (John Wiley and Sons, Inc., New York, to be published).

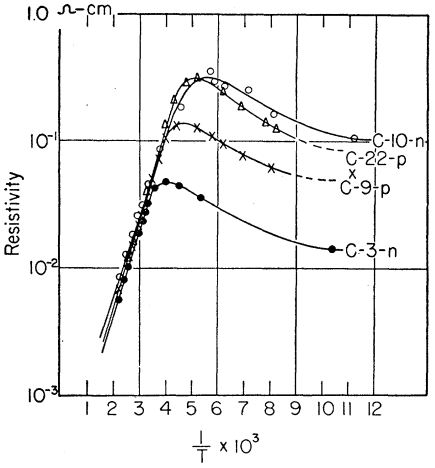

FIG. 1. Resistivity of various Mg_2Sn samples.

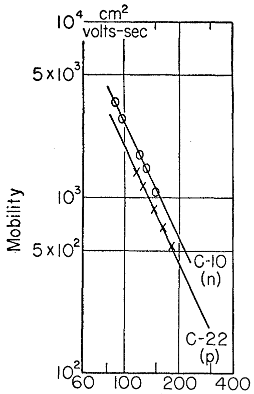

FIG. 3. Charge carrier mobilities of Mg_2Sn.

samples are given in Figs. 1 and 2. These samples contain between 2×10^{16} cm^{-3} and 3.5×10^{17} cm^{-3} impurities as calculated from Hall effect data.

Following the method indicated in reference 9 [Eq. (5)], one finds a ratio of electron to hole mobility of 1.23 (from results on samples *C*-9 and *C*-22). The variations of the mobilities with temperature are plotted in Fig. 3; both mobilities obey a $T^{-2.2}$ law.

In order to determine the value of the energy gap, two different procedures have been followed. For the *p*-type samples, it was possible to calculate the number of electrons (n) and holes (p) at every temperature from the resistivity and Hall coefficient, using the above-quoted value of the mobility ratio and the $T^{-2.2}$ temperature dependence. One can evaluate then the product np which satisfies the following expression[11]:

$$np=4\left(\frac{2\pi m_e kT}{h^2}\right)^3\left(\frac{m_n^* m_p^*}{m_e^2}\right)^{\frac{3}{2}}\cdot e^{-E/kT}, \qquad (1)$$

where m_n^*, m_p^* = effective masses of electrons and holes respectively. Assuming that $E=E_0+\beta T$, it is clear that a plot of $\ln(np/T^3)$ *vs* $1/T$ should yield a straight line with a slope of E_0/k, where E_0 is the energy gap at absolute zero.

This procedure cannot be used for the *n*-type samples. In this case a graph showing $\ln(RT^{\frac{3}{2}})$ *vs* $1/T$ should produce a straight line, the slope being $E_0/2k$.

Plotting the experimental data in the manner indicated, one finds indeed a linear behavior in both cases; resulting values for the energy gap are given in the second column of Table I. Three of the four E_0 values agree fairly well; the average of these three is 0.33 ev.

The above-mentioned plot of $\ln(np/T^3)$ *vs* $1/T$ also enables us to determine the product of the effective masses, $(m_n^* m_p^*)/m_e^2$, from the intercept if the other remaining parameter $\beta(=dE/dT)$ is known. This quantity β may be evaluated from optical absorption

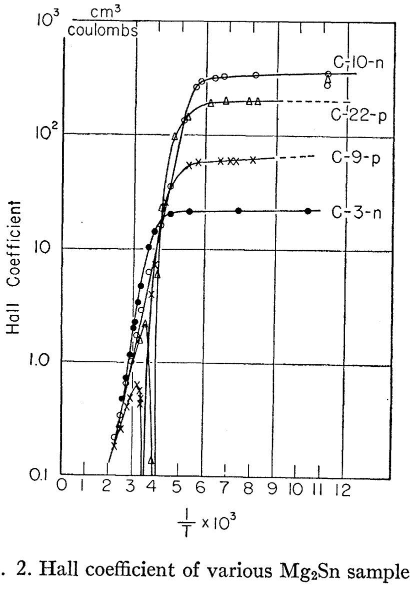

FIG. 2. Hall coefficient of various Mg_2Sn samples.

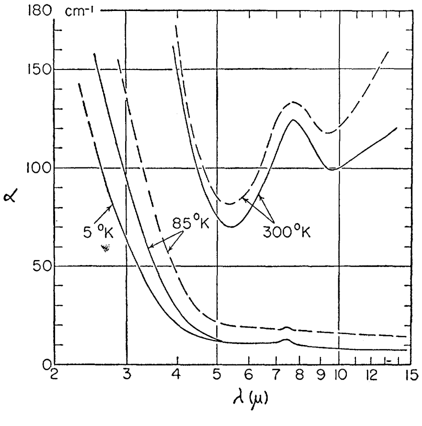

FIG. 4. Absorption spectra of *n*-type Mg_2Sn.
- - - - *C*-10, ——— *C*-20.

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[11] See reference 9 [Eq. (9a)].

data (see below); calculation then yields a value of 1.5 for the product $(m_n^* m_p^*)/m_e^2$. Combining this result with the relation[9]

$$\mu_n/\mu_p = (m_p^*/m_n^*)^{5/2} \qquad (2)$$

leads to the following values of the effective masses: $m_n^* = 1.17 m_e$ and $m_p^* = 1.28 m_e$.

OPTICAL ABSORPTION

Infrared absorption spectra of four Mg_2Sn samples have been measured at three different temperatures. The results are given in Figs. 4 and 5.[12] Several features are immediately apparent. The absorption at 300°K is much larger than at low temperatures. This is due to the high number of intrinsic carriers (about 4×10^{17} cm^{-3} electrons and holes). Both n- and p-type samples show at room temperature a relatively strong absorption band with a maximum at about 7.5μ. No indication of this band was found in any of the spectral curves of the p-type samples at lower temperatures; a faint band is still observable in the spectra of the n-type samples at 85°K and at 5°K. The origin of this band (imperfections or lattice vibrations) is still an open question and can only be solved by means of additional experiments.

TABLE I. Values of the energy gap (ev) calculated from electrical and optical data.

	From electr. meas.	From optical absorption measurements			From photoconductivity measurements	
	$T=0°K$	$T=300$	$T=85°K$	$T=5°K$	$T=85°K$	$T=5°K$
C-3(n)	0.33^5					
C-9(p)	0.28^5					
C-10(n)	0.32^5	0.23	0.29		0.28	0.30
C-20(n)		0.22	0.31	0.33	0.29	0.30
C-22(p)	0.34	0.21	0.30	(0.30)		0.30
C-23(p)		0.21	0.30	0.33		

A point of major interest is the value of the intrinsic energy gap as derived from transmission measurements. In the absence of any well-founded criterion, we have determined our values of the energy gap by extrapolating the absorption edge to α (absorption coefficient) $=0$. The extrapolation consists of extending the linear part of the absorption edge towards the axis of abscissas; in this process considerable weight has been given to points with high α. Values for the energy gap obtained in this way are tabulated in Table I.[13] (Results on sample C-10 have to be regarded with much reservation due to the nonuniform thickness of the specimen.)

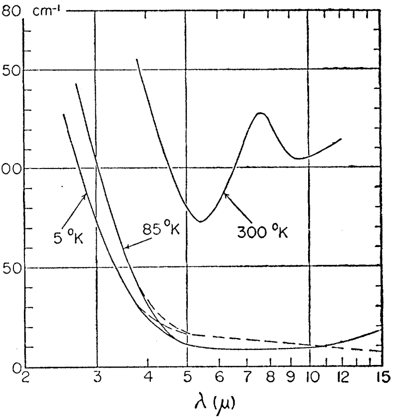

FIG. 5. Absorption spectra of p-type Mg_2Sn. ——— C-22, - - - - C-23.

The shift of the absorption edge is -3.5×10^{-4} ev/deg between 85°K and 300°K.

PHOTOCONDUCTIVITY

The photoconductive response of two Mg_2Sn samples is shown in Fig. 6. The ordinate, $\delta R/U$, represents the relative change of resistance ($\Delta r/r$) per incident photon (total flux or total number of photons $=U$). These measurements were made with a 0.5-mm slit opening of the monochromator at a modulation frequency of 510 cps. The signal at low temperature is several orders of magnitude above the noise; no photoconductivity could be detected at room temperature.

The photoresponse at 85°K is independent of the chopping frequency up to 510 cps, indicating a time constant smaller than 1 millisecond. The lifetime τ

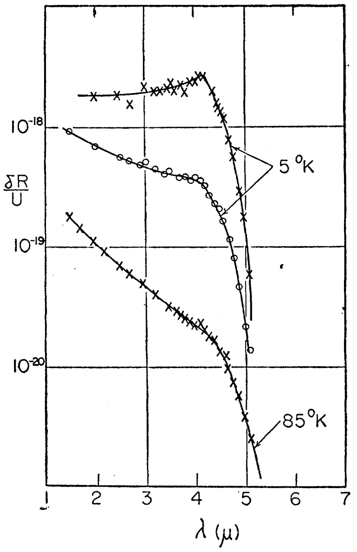

FIG. 6. Spectral response of two Mg_2Sn samples. × $C-10$, o $C-22$.

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[12] The absorption coefficients are calculated on the basis of n (index of refraction) $=4.4$; this value was obtained from preliminary reflectivity measurements.

[13] The very gradual change of slope of the absorption edge for low α makes an exact determination of the energy gap of Mg_2Sn very difficult. It has been suggested [G. G. Macfarlane (private communication)] that the rather long tail of the edge is due to indirect transitions between the valence and the conduction band [Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954)]. On the basis of this suggestion the energy gap would be considerably smaller. A critical evaluation of our electrical and optical data does not support such a small value of the energy gap.

may be estimated from the magnitude of the photoconductive signal on the basis of unity quantum efficiency.[14] The result of such a calculation applied to the largest response observed at 85°K (sample C-20) yields a value for τ of 250 μsec (for 4 μ radiation). As yet no theoretical expression for the photoconductive threshold has been derived; the situation here is as unsatisfactory as for the absorption edge. It has been customary in recent years to use a criterion formulated by Moss[15] for the correlation of the energy gap with the cutoff of the photoresponse. According to this rule the energy gap is determined by that wavelength for which the response has fallen to one-half of its maximum value. Indeed, this rule has been applied with reasonable success to several elements and compounds. Loferski,[16] however, has shown that this criterion leads to significant disagreement in the case of tellurium; extrapolating to absolute zero, one finds the photoconductive threshold of tellurium at 0.30 ev, while electrical measurements indicate a value for E_0 of 0.34 ev. According to Loferski the energy gap is more closely connected with the maximum of the spectral distribution.

Identifying the width of the energy gap with either the maximum or the "break" of the photoconductive response, we find values of E as indicated in the last two columns of Table I. These figures are somewhat lower than the results from electrical and transmission data.

CONCLUSIONS

The compound Mg_2Sn appears to be a semiconductor, which obeys the "simple" theory rather well. Hall effect and conductivity data, as well as optical absorption data, indicate an energy gap of about 0.33 ev at absolute zero. The value deduced from the photoconductive threshold (4.2 μ) is, however, about 0.03 ev lower. An explanation of this discrepancy will probably have to await a better understanding of the correlation between optical transitions and band structure. The magnitude of the photoresponse is quite sizable at low temperatures.

The authors are greatly indebted to Mr. D. E. Roberts for preparing most of the crystals used.

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[14] A. Rose, *Photoconductivity* (John Wiley and Sons, Inc., New York, to be published).

[15] T. S. Moss, *Photoconductivity in the Elements* (Butterworth Scientific Publications, London, 1952).

[16] J. J. Loferski, Phys. Rev. **93**, 707 (1954).

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Effect of Point Imperfections on the Electrical Properties of Copper. II. Thermoelectric Power*

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The changes in the thermoelectric power of copper due to the presence of interstitials and vacancies have been calculated in the free electron approximation. It is found that the changes for concentrations of defects encountered in experiments on radiation damage due to massive charged particles are, at liquid nitrogen temperature, of the same magnitude as the absolute thermoelectric power of pure copper. Both interstitials and vacancies tend to reduce the absolute thermoelectric power of copper, and this effect should be readily observable in a suitably designed experiment. It is suggested that the effect may also be used to throw additional light on the processes which occur in the annealing of an irradiated sample.

The calculated changes in the thermoelectric property of copper due to Frenkel defects are also of such magnitude as to make adequate precautionary measures necessary whenever the thermocouple, which is used to measure the temperature of the specimen, is also in the beam of the massive charged particles. Unless the thermocouple is suitably screened from the beam, unreliable temperature measurement is likely to result. Curves showing the predicted temperature and concentration dependence of the thermoelectric power change due to Frenkel defects are presented.

The effect of small concentrations of arsenic in solid solution in copper on the thermoelectric power of copper has also been calculated by the same procedure. The calculated results are in satisfactory agreement with experiment, indicating that the results for interstitials and vacancies are probably of the correct magnitude.

I. INTRODUCTION

IT has been known for many years that impurities exert a considerable influence on the thermoelectric properties of metals. For example, Norbury[1] found that almost all dilute binary alloys of the noble metals are thermoelectrically negative compared to the pure metal. There have been attempts to formulate empirical rules relating the thermoelectric power of a dilute alloy to that of the pure metal; but these, apart from their failure to be satisfying from a fundamental point of view, are not universally applicable. For example, Kohler[2] is able to account for most of Norbury's results, but copper-manganese alloys form a notable exception to his additivity rules.

In the case of copper, at any rate, the change of

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* Supported by the Office of Naval Research.

[1] A. L. Norbury, Phil. Mag. **2**, 1188 (1926).

[2] M. Kohler, Z. Physik **126**, 481 (1949).