Temperature Dependence of the Far-Infrared Reflectivity of Magnesium Stannide*

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The reflectivity of pure samples of magnesium stannide has been measured in the infrared region from 50 to 370 cm^{-1} at temperatures from 100 to 600°K. The reflection spectra have been analyzed by means of a fit with a classical dispersion formula including Drude terms for the free-carrier effects. At low temperatures the influence of the lattice dispersion on the reflectivity dominates, while at high temperatures the free-carrier effects dominate. The electrical properties of Mg_2Sn in the intrinsic conduction range as determined from the reflectivity are in good agreement with the data obtained by Busch and Winkler from electrical measurements.

INTRODUCTION

AMONG the II–IV semiconducting compounds with the antifluorite structure, Mg_2Sn has the smallest width of the forbidden gap, 0.33–0.36 eV.[1–5] Recent investigations of the electrical properties[6,7] by means of electrical measurements and optical absorption measurements in the near infrared region have shown that below 200°K impurity conduction is important, while at room temperature and above the intrinsic conduction dominates. The electrical measurements cover the temperature range from 60 to 1000°K. At high temperatures in the intrinsic conduction range Busch and Winkler[1,2] found a temperature dependence of the mobility as $T^{-2.5}$, for which explanations have been given in terms of optical-mode scattering[8,9] and multiphonon processes.[10] However, for the mixed conduction range Lichter[7] reported a $T^{-1.5}$ law for the mobility in agreement with the theory about interaction of electrons with long-wavelength acoustical phonons.[11] Similar results have been obtained for Mg_2Ge[8] and Mg_2Si.[9] All previous workers found for Mg_2Sn a temperature-independent ratio of the mobilities of electrons and holes.

With respect to lattice vibrations Mg_2Sn has, for $\mathbf{q}$ near 0, an infrared-active and a Raman-active optical lattice mode. The frequency of the infrared-active mode at room temperature has been determined from the far-infrared reflectivity of Mg_2Sn.[12,13] The purpose of this work was to extend the study of the lattice vibrational properties to other temperatures and to investigate the electrical properties at infrared frequencies by measuring the far-infrared reflectivity of Mg_2Sn.

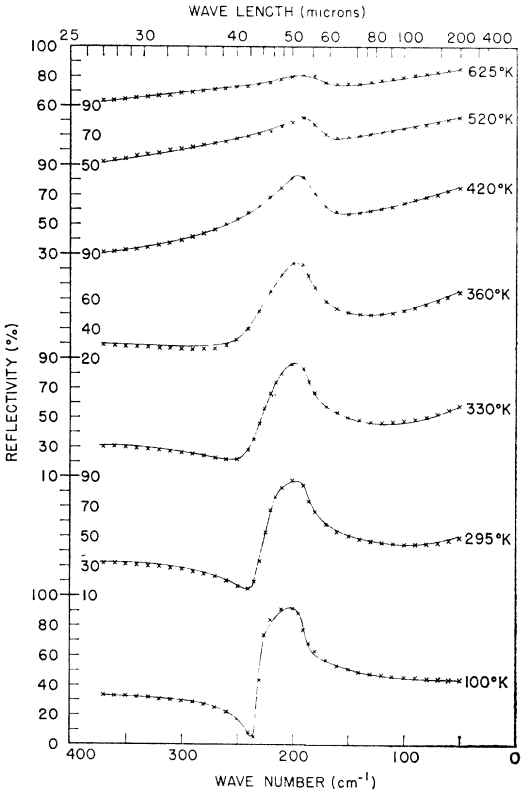

FIG. 1. Reflectivity of Mg_2Sn at various temperatures, experimental data (solid line) and calculated by means of classical dispersion formula (X).

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[1] G. Busch and U. Winkler, Physica **20**, 1067 (1954).
[2] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).
[3] H. G. Lipson and A. Kahan, Phys. Rev. **133**, A800 (1964).
[4] R. F. Blunt, H. P. R. Frederikse, and W. R. Hosler, Phys. Rev. **100**, 663 (1955).
[5] W. D. Lawson, S. Neilson, E. H. Putley, and V. Roberts, J. Electron. **1**, 203 (1955).
[6] H. P. R. Frederikse, W. R. Hosler, and D. E. Roberts, Phys. Rev. **103**, 67 (1955).
[7] B. D. Lichter, J. Electrochem. Soc. **109**, 819 (1962).
[8] R. D. Redin, R. G. Morris, and G. C. Danielson, Phys. Rev. **109**, 1916 (1958).
[9] R. G. Morris, R. D. Redin, and G. C. Danielson, Phys. Rev. **109**, 1909 (1958).
[10] Ch. Entz, Physica **20**, 983 (1954); Helv. Phys. Acta **27**, 199 (1954).
[11] F. Seitz, Phys. Rev. **73**, 549 (1948).
[12] D. McWilliams and D. W. Lynch, Phys. Rev. **130**, 2248 (1963).
[13] A. Kahan, H. G. Lipson, and E. V. Loewenstein, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964*, edited by M. Hulin (Academic Press Inc., New York, 1965), Vol. I, p. 1067.

EXPERIMENTAL

The reflectivity of Mg_2Sn has been studied in the infrared region from 50 to 370 cm^{-1} at various temperatures in the range from 100 to 600°K. The instrument used was a Michelson-type Fourier-spectrophotometer with a reflection attachment having an angle of incidence of about 15°. For the measurements above room temperature the sample holder was mounted to a heater for which the power was regulated by a temperature-control unit. Two samples of different origin yielded the same reflectivity within experimental error. Both were pure material, and their reflectivities at 100°K exhibited no indication of free-carrier effects. The mobility and some other properties of one of the samples were known from previous electrical measurements.[14] The results of the reflection measurements are given in Fig. 1. With increasing temperature the influence of the free carriers becomes more and more important, and above 400°K this is dominant. Because of the relatively low mobility in Mg_2Sn, the free-carrier effects produce no sharp plasma edge in the reflectivity which will be discussed in more detail later. The reflection spectrum of our samples at room temperature is in good agreement with the data reported by Kahan, Lipson, and Loewenstein,[13] except that the subsidiary band in the reststrahlen band has not been found with our samples.

ANALYSIS OF THE EXPERIMENTAL DATA

The reflection spectra were analyzed by means of an optimum fit with a classical dispersion formula for the reststrahlen band and with Drude terms for the free carriers. For a semiconductor in which both electrons and holes contribute to the conductivity, the complex dielectric constant in the infrared spectral region may

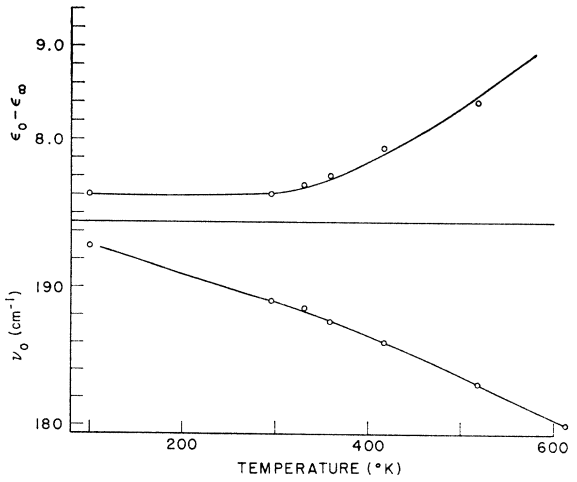

FIG. 2. Temperature dependence of the infrared eigenfrequency ν_0 and the oscillator strength $(\epsilon_0-\epsilon_\infty)$ of Mg_2Sn.

[14] J. T. Nelson, Ph.D. thesis, Oregon, 1955 (unpublished).

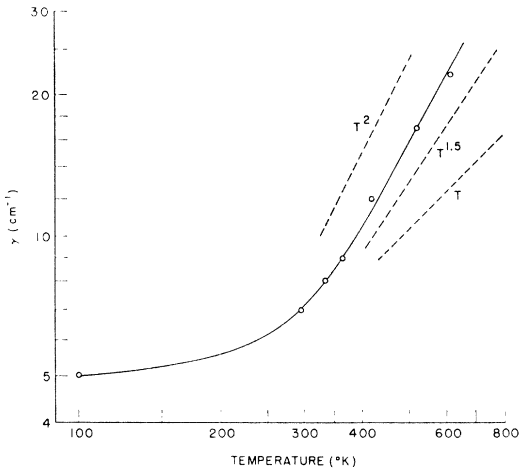

FIG. 3. Temperature dependence of the damping constant γ in the lattice dispersion term for Mg_2Sn.

be written as a function of frequency ν (in cm^{-1}) in the following form:

$$\epsilon(\nu)=\epsilon_L(\nu)+\sigma_e(\nu)/i\nu+\sigma_h(\nu)/i\nu, \qquad (1)$$

where $\epsilon_L(\nu)$ is the complex dielectric constant due to lattice vibrations, $\sigma_e(\nu)$ and $\sigma_h(\nu)$ are the complex conductivities due to electrons and holes respectively. Equation (1) is based on the assumption that the lattice vibrational part and the free-carrier parts can be superimposed linearly and that there are no interaction terms.

Quantum-mechanical treatment[15] of the lattice dispersion and absorption leads to a frequency-dependent damping function, apart from frequency-dependent terms in the oscillator strength and normalization terms in the fundamental lattice frequency. Finer details in the absorption spectrum are caused by the damping function, and generally these are not observed in the reflectivity curve. The measured reflectivity of Mg_2Sn shows a typical reststrahlen band only, and therefore, $\epsilon_L(\nu)$ was approximated by a classical dispersion formula with a constant damping term

$$\epsilon_L(\nu)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)\nu_0^2/(\nu_0^2-\nu^2+i\gamma\nu), \qquad (2)$$

where ϵ_∞ and ϵ_0 are the optical and static dielectric constants, respectively. ν_0 is the frequency (in cm^{-1}) of the infrared-active transverse optical mode and γ is the damping constant.

The free-carrier terms in Eq. (1) were approximated by Drude terms with constant relaxation time τ although a more rigorous treatment would also lead to a more complicated dispersion formula with frequency-dependent τ. However, since no essential deviations were found between the frequency dependence of the reflectivity computed by means of the Drude terms and the frequency dependence of the

[15] R. A. Cowley, Adv. An. Phys. 12, 421 (1963); Phil. Mag. 11, 673 (1965).

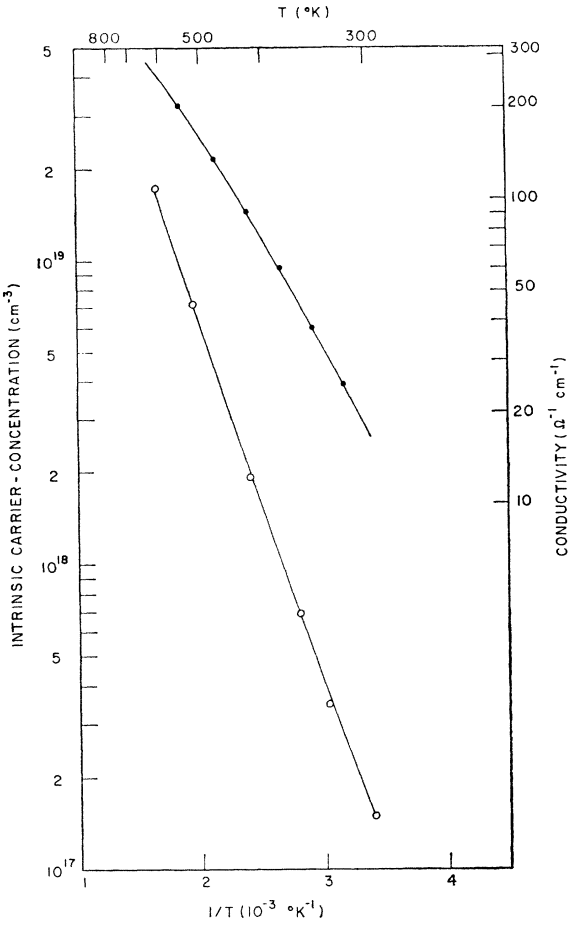

FIG. 4. Intrinsic carrier concentration N_i versus $1/T$ as determined from reflection spectra (0), calculated values of N_i (solid line with circles) and total static conductivity σ_0 (solid line with dots).

experimental data, this approximation seems justified. In detail the Drude terms are

$$\frac{\sigma_e(\nu)}{i\nu}=-\frac{N_i e^2/4\pi^2c^2m_e^*}{\nu^2-i\nu e/2\pi c m_e^*\mu_e},$$

and (3)

$$\frac{\sigma_h(\nu)}{i\nu}=-\frac{N_i e^2/4\pi^2c^2m_h^*}{\nu^2-i\nu e/2\pi c m_h^*\mu_h},$$

where N_i is the intrinsic carrier concentration and μ_e μ_h, m_e^*, and m_h^* are the mobilities and conductivity effective masses of electrons and holes, respectively, c is the velocity of light, and e the electronic charge.

Based on these assumptions a calculated reflectivity curve was obtained from the dielectric-constant data which had in turn been computed by inserting values for the various constants in Eq. (1) together with Eqs. (2) and (3). On a trial and error approach a best fit to the experimental data was obtained and the results are shown in Fig. 1. The most reliable values from the results of previous measurements[1–3,7,14] were used for the free-carrier terms. For the lattice-vibrational part, $\epsilon_\infty=16.4$ (assumed to be temperature-independent) was used according to the refractive-index measurements of Mg_2Sn in the near infrared.[16] ϵ_0, ν_0, and γ were determined from the reflectivity and are shown as a function of temperature in Figs. 2 and 3. ν_0 decreases with temperature while ϵ_0 and γ increase. At high temperatures γ is nearly proportional to T^2. This indicates that predominantly three-phonon processes via quartic lattice potential terms determine the width of the fundamental lattice band.[17] The accuracy of these values decreases with increasing temperature as the reflectivity becomes more and more insensitive to the lattice-vibrational properties.

At 100°K the free-carrier part of Eq. (1) was neglected completely. For room temperature and above the temperature-independent ratio of the mobilities $\mu_e/\mu_h=1.24$ was used,[3,7,14] according to the electrical data of one of our own samples and of many samples of different origin. The values of the conductivity effective masses $m_e^*=0.15m_0$ and $m_h^*=0.10m_0$ were taken as the most reliable values from the results of electrical and optical measurements in the infrared by Lipson and Kahan.[3] The effective masses were assumed to be temperature-independent. The intrinsic carrier concentration N_i and one of the mobilities (μ_h) were determined from the reflectivity. The results are shown as a function of temperature in Figs. 4 and 5. For comparison, the carrier concentration was calculated using the value $E_p=(0.36-2.8.10^{-4}T)$ eV[1–3] for the band-gap energy and $m_e^*=1.20m_0$[3,14] and $m_h^*=1.30m_0$[3,14] for the density-of-states effective masses (of Fig. 4). In Fig. 5 the hole mobility deduced from electrical measurements on one of our samples[14] is also shown and here the agreement between these values and those obtained from the reflectivity is reasonable in the overlapping temperature range. In the mixed conduction range (200–300°K) μ_h is nearly proportional to $T^{-1.5}$ in accordance with the results of Lichter.[7] However from 300 to 600°K in the intrinsic range, μ_h follows almost a $T^{-2.5}$ law in agreement with the results of Busch and Winkler.[1,2]

The reflectivity above 400°K proved to be rather insensitive to variations of N_i and μ_h as long as the product $N_i\mu_h$ was kept constant. The total static conducitivity $\sigma_0=N_ie(\mu_h+\mu_e)$ is also shown in Fig. 4 and this is the most reliable quantity determined from the reflectivity as it is independent of the accuracy of the values for N_i and μ_h. In Fig. 4 the plot $\log\sigma_0$ versus $1/T$ also indicates a $T^{-2.5}$ law for the mobility as $\log(T\sigma_0)$ versus $1/T$ approaches a straight line and the same result was found by Busch and Winkler[1,2] from conductivity measurements in the same temperature region. Furthermore, if μ_h is taken to be very different

[16] D. McWilliams and D. W. Lynch, J. Opt. Soc. Am. **53**, 298 (1963).

[17] D. W. Jepsen and R. F. Wallis, Phys. Rev. **125**, 1496 (1962).

TABLE I. Roots of the equation $\epsilon=0$.

T (°K)	Longitudinal lattice frequency (cm^{-1})	Plasma frequency (cm^{-1})
100	$232\pm 2.5i$	0
295	$232\pm 8.7i$	$\simeq 0$
331	$234\pm 17.5i$	$49.8\pm 118i$
359	$232\pm 34.5i$	$121\pm 136i$
417	$190\pm 37.3i$	$299\pm 221i$
518	$183\pm 22.3i$	$589\pm 436i$
613	$179\pm 20.8i$	$872\pm 676i$

from the values in Fig. 5, the fit to the experimental data for high temperatures leads to a temperature dependence of N_i such that the band gap energy E_g deduced from N_i disagrees appreciably with the value found for all samples by previous workers.

DISCUSSION

Apart from the temperature dependence of the fundamental lattice vibration, the analysis of the reflection spectra of Mg_2Sn with respect to free carriers is in reasonable agreement with the data of Busch and Winkler[1,2] obtained from electrical measurements. For reasons of the low mobility, we were unable to deduce more information from the reflectivity which would have been contained in a sharp plasma edge. Such a minimum and a steep rise of the reflectivity always occur when the real part of the dielectric constant changes from positive to negative values with increasing wavelength and the imaginary part is sufficiently small. For a lattice dispersion term the corresponding condition is

$$[(\epsilon_0)^{1/2}-(\epsilon_\infty)^{1/2}]\nu_0/(\epsilon_\infty)^{1/2}\gamma\gg 1, \quad (4)$$

and for a Drude term

$$N m^*\mu^2/\epsilon_{\text{lattice}}\gg 1. \quad (5)$$

In the case of Mg_2Sn, Eq. (4) is valid but $Nm^*\mu^2/\epsilon_{\text{lattice}}<1$ for electrons as well as for holes and consequently no plasma edge was observed in the reflection spectra.

In order to get some insight into the longitudinal frequencies (longitudinal lattice mode and plasma frequency) of this highly damped system, the complex ν roots of the equation $\epsilon=0$ [cf. Eq. (1)] were evaluated using the set of data with $\mu\sim T^{-2.5}$. $\epsilon=0$ is the condition for a longitudinal mode in the limits of the phenomenological treatment of infrared absorption and dispersion.[18] Apart from two roots with zero real part which are omitted here, there are two pairs of conjugate complex roots, one of which is the plasma frequency with large imaginary part and the other the longitudinal lattice frequency with small imaginary part(cf. Table I). Here the imaginary part is a measure of the reciprocal of the lifetime of the vibration and consequently the longitudinal lattice frequency is of more interest in this discussion. In the range 100 to 360°K the calculated value of this frequency corresponds closely to the high-frequency edge of the reststrahlen band. At temperatures above 500°K it corresponds to the reflectivity minimum at frequencies somewhat lower than the eigenfrequency and so the high conductivity of the material at these temperatures seems to cause a longitudinal lattice frequency lower than the transverse lattice frequency.

[18] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Oxford University Press, London, 1962).

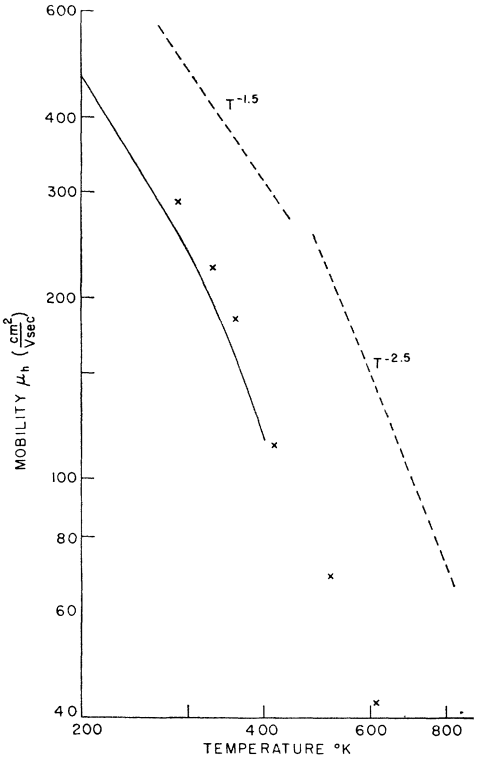

FIG. 5. Hole mobility μ_h as determined from the reflectivity (X) and from electrical measurements on one of our samples Ref. (14) (solid line).

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