IV. OPTICAL AND INFRARED SPECTROSCOPY*

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A. TEMPERATURE DEPENDENCE OF THE FAR INFRARED REFLECTIVITY OF MAGNESIUM STANNIDE

Among the II-IV semiconducting compounds with the antiflourite structure, Magnesium Stannide has the smallest width of the forbidden gap with 0.33-0.36 ev.[1-5] Consequently, at room temperature and above the intrinsic conduction dominates. Measurements of the electrical properties[1-7] cover the range 60°-1000°K. At high temperatures Busch and Winkler[1,2] found a $T^{-2.5}$ law for the mobility for which explanations have been given in terms of optical mode scattering[8,9] and more phonon processes.[10] For the mixed conduction range, however, Lichter[7] reported a $T^{-1.5}$ law in agreement with the theory concerning acoustical mode scattering.[11] Similar results have been obtained for Mg_2Ge and Mg_2Si.[8,9]

With respect to lattice vibrations, Mg_2Sn has for $\vec{g} \approx 0$ an infrared active and a Raman active mode. The frequency of the infrared active mode at room temperature has been determined from the far infrared reflectivity.[12,13]

We have extended the study of the lattice vibrational properties to other temperatures and investigated the electrical properties at infrared frequencies by measuring the reflectivity of Mg_2Sn in the region from 50 cm^{-1}-370 cm^{-1} at various temperatures in the range 100°-600°K. 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 (cf. Fig. IV-1). With increasing temperature the influence of the free carriers becomes more and more important, and above 400°K this is dominant. The reflection spectrum of our samples at room temperature is in good agreement with the data reported previously,[13] except that the subsidiary band in the Reststrahlenband has not been found with our samples.

The reflection spectra were analyzed by means of a classical oscillator fit including Drude terms for electrons, as well as for holes. Details of the dispersion formula and the notation used have been previously published.[14] In this analysis $\epsilon_\infty = 16.4$ was used according to the refractive index of Mg_2Sn in the near infrared,[15] and ϵ_∞ was assumed to be independent of temperature. ϵ_o, ω_o, and γ in the lattice dispersion term were determined from the reflectivity and are shown as a function of temperature in Figs. IV-2 and IV-3. At high temperatures γ is nearly proportional to T^2 which means that predominantly 3-phonon processes via quartic lattice potential terms determine the width

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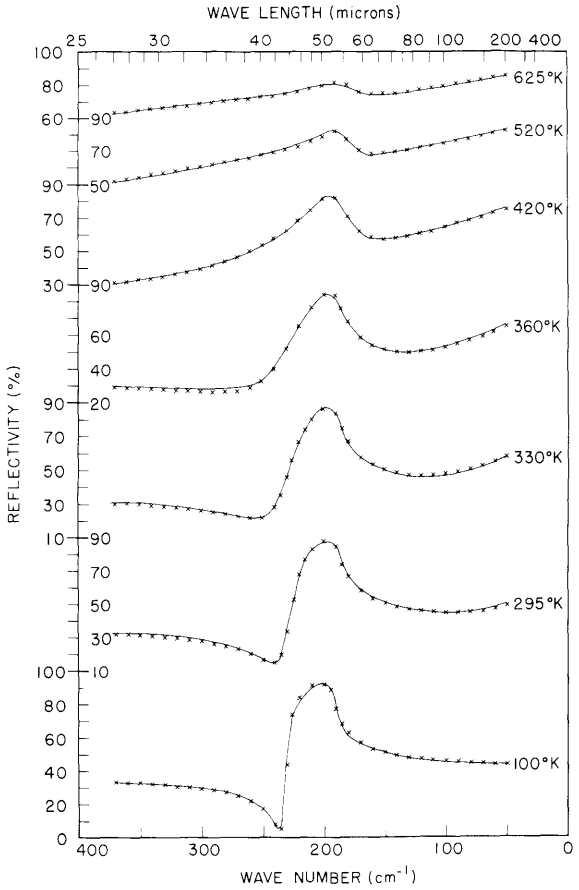

Fig. IV-1.

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

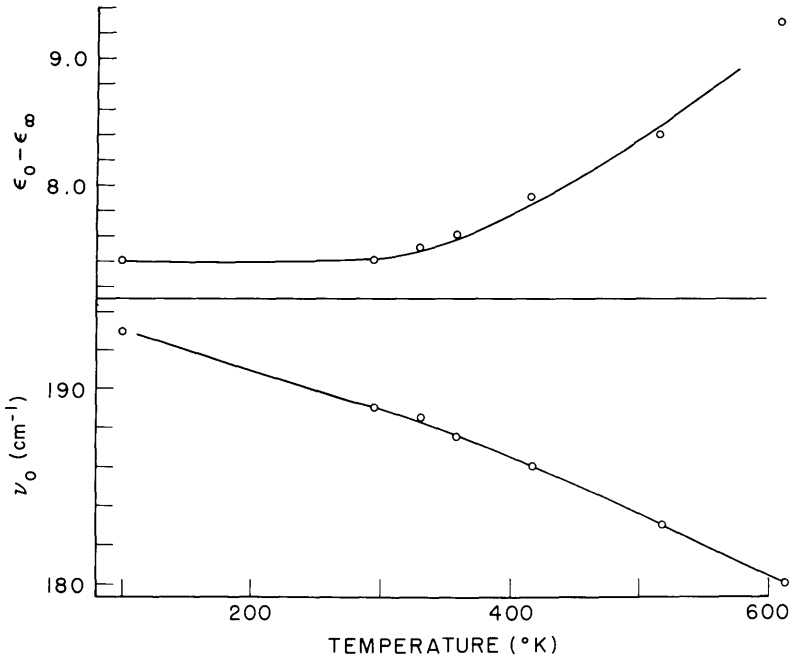

Fig. IV-2. Temperature dependence of the infrared eigenfrequency ω_o and the oscillator strength $(\epsilon_o - \epsilon_\infty)$ of Mg_2Sn.

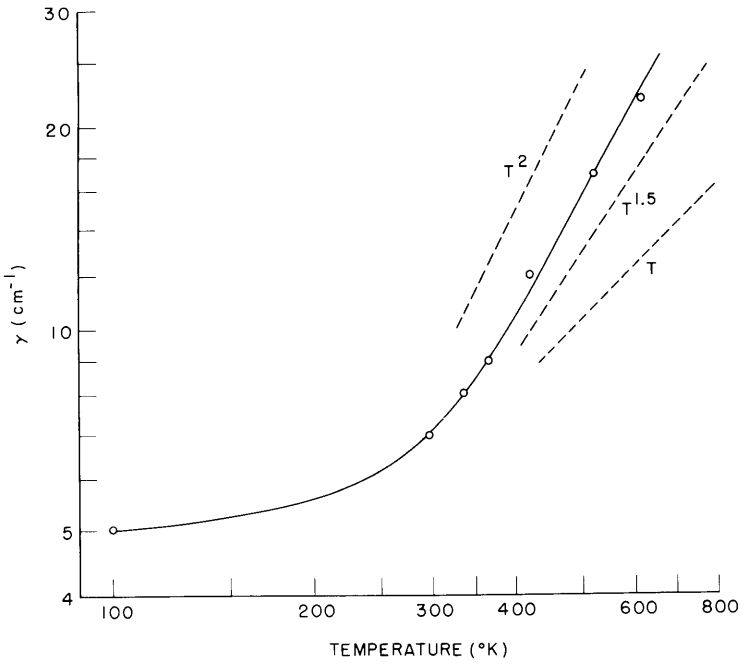

Fig. IV-3. Temperature dependence of the damping constant γ in the lattice dispersion term for Mg_2Sn.

of the fundamental lattice band.[16]

In the free-carrier part of the dispersion formula, too many parameters are involved to determine them all from the reflection spectra. For T = 100°K the free-carrier effects could be neglected completely. At room temperature a reasonable fit was obtained with the values reported from electrical measurements:

A. Intrinsic carrier concentration $N_i = 1.5 \cdot 10^{17}\ cm^{-3}$ [3]

B. Conductivity effective masses of electrons and holes, respectively, $m_e^* = 0.15 m_o$ [3] and $m_h^* = 0.10 m_o$ [3]

C. Mobilities of electrons and holes, respectively, $\mu_e = 370 \frac{cm^2}{V\ sec}$ [3,7] and $\mu_h = 300 \frac{cm^2}{V\ sec}$ [3,7].

No attempt was made to vary the effective masses with temperature, and the room temperature values were used for all temperatures. The mobilities were assumed varying proportional to $T^{-2.5}$ according to the results of Busch and Winkler.[1,2] The mobility ratio used was $\mu_e/\mu_h = 1.23$ independent of temperature.[3,7] The carrier concentration was determined from the reflectivity (cf. Fig. IV-4). For comparison N_i was calculated using the values $m_e^* = 1.20 m_o$ [3] and $m_h^* = 1.30 m_o$ [3] for the density of states effective masses and the value of the band gap energy $E_g = (0.36 - 2.8\ 10^{-4} T)\ ev$ [1-3] (cf. Fig. IV-4).

The agreement of the experimental data with the calculated values is reasonable.

An attempt was also made to fit the reflectivity with mobilities proportional to $T^{-1.5}$ according to the results of Lichter[7] in the mixed conduction range. The calculated

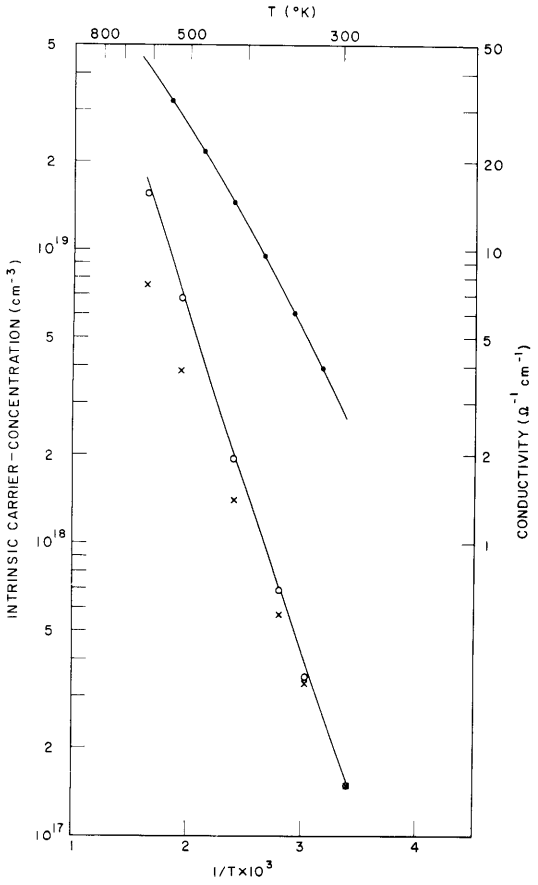

Fig. IV-4.
Intrinsic carrier concentration N_i versus $1/T$ as determined from reflection spectra with $\mu \sim T^{-2.5}$(O) and with $\mu \sim T^{-1.5}$(X), calculated values of N_i (————) and total static conductivity (————·————).

reflectivity is the same as in the former case within 2-3% for all temperatures and consequently, only one calculated value is shown in Fig. IV-1. The carrier concentration deviates systematically from the calculated values, and the ratio of the calculated to the experimental values is proportional to T. The resulting total static conductivity σ_o is the same in both cases and thus the reflectivity is sensitive to the conductivity only. Furthermore, the plot log σ_o versus $1/T$ is not a straight line, which indicates once more a $T^{-2.5}$ law for the mobilities (cf. Fig. IV-4). This means that already in the temperature range covered by our measurements the temperature dependence of the mobility cannot be explained by acoustical mode scattering only,[11] and that optical mode scattering or more phonon processes have to be considered.[8-10]

Because of the relatively low mobility in Mg_2Sn, the free-carrier effects produce no sharp plasma edge in the reflectivity which would have provided additional information.

Such a minimum and a steep vise 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. The corresponding condition is for a lattice dispersion term

$$\frac{(\sqrt{\epsilon_o}-\sqrt{\epsilon_\infty})\omega_o}{\sqrt{\epsilon_\infty}\,\gamma} \gg 1, \tag{1}$$

and for a Drude term

$$\frac{Nm^*\mu^2}{\epsilon_{Lattice}} \gg 1. \tag{2}$$

For Mg_2Sn, condition 1 is fulfilled, but $\frac{Nm^*\mu^2}{\epsilon_{Lattice}} < 1$ for electrons, as well as for holes. Therefore no plasma edge has been found in the spectra.

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