

that, once E is determined, all the data points taken at each temperature are used in a subsequent reaction rate computation and the analysis can be applied over essentially all of the recovery process.

It should be noted that this analysis applies only in the case in which a single rate process is involved. The

situation becomes more complicated in the case that two or more processes are occurring. At the same time it may be noted that processes more complex than envisioned in Eq. (A1) may be analyzed by the sequential isothermal method providing that the only explicit time dependence is that given in Eq. (A3).

Infrared Reflectivities of Magnesium Silicide, Germanide, and Stannide*

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The room-temperature reflection spectra of Mg_2Si , Mg_2Ge , and Mg_2Sn have been measured at wavelengths between 20 and 50 μ . Reststrahl reflectivity peaks were observed at 36 and 45 μ for Mg_2Si and Mg_2Ge , respectively, and a rising reflectivity in Mg_2Sn is estimated to peak at about 54 μ . The occurrence of peaks indicates that these compounds are partly ionic. The reflection spectra are more like those of the alkali halides than those of the III-V semiconducting compounds. If a simple damped harmonic oscillator is used to describe the reststrahl mode, the three Mg compounds have the same force constant for this mode. Values of dielectric constants and effective charges are estimated for Mg_2Si , and are used to evaluate a previous analysis of electron mobility in this compound. Effects of free carriers on the reflectivity of Mg_2Ge indicate that the effective masses are in rough agreement with the results of transport measurements.

INTRODUCTION

MAGNESIUM silicide, germanide, and stannide are cubic semiconducting compounds with the antiferroite structure. The most recent work on the electrical properties of¹ Mg_2Si and² Mg_2Ge indicates that optical mode scattering is important at room temperature. Morris *et al.* found a reasonable fit of their mobility data with a curve of optical mode-limited mobility versus temperature for longitudinal optical-mode phonons with a characteristic temperature of 400°K. For Mg_2Ge a characteristic temperature of 200°K was assumed. An optical dielectric constant of 19 resulted for Mg_2Si . The mobilities of carriers in Mg_2Sn have not been analyzed in such detail, but this compound is believed to be less ionic than Mg_2Si or Mg_2Ge .³ Reststrahl reflectivity peaks are expected to be observable in crystals in which optical mode scattering is important. The present set of measurements was undertaken to partly characterize the optical mode lattice vibrations in these compounds. By varying the purity of the crystals some information on carrier effective masses might be obtained, but because of the carrier densities obtained and the rather large effective masses ($0.2m_0$ to

$1.3m_0$),^{1,2,4} the effects of the carriers in our samples should not be great in the wavelength region covered.⁵

EXPERIMENTAL DETAILS AND RESULTS

All samples were cleaved faces of single crystals. Polished samples (not etched after polishing) showed a reduced reststrahl peak and were not used. The cleaved faces were not always perfectly plane but consisted of many parallel planes connected by steps. It is estimated that this effect reduced the reflectivity of these samples only a few percent, if at all.

The measurements were made at room temperature at a 12° angle of incidence. Light reflected from the sample or from an aluminum mirror used as a standard passed through a Perkin Elmer 160 fore-prism unit used as a prism monochromator with a thermocouple detector. NaCl, KBr, and CsI prisms were used with appropriate filters. For wavelengths below 30 μ the scattered light was less than 1%. The scattered light rose gradually to about 20% at 47 μ . Corrections based on measurements of scattered light were applied to all data. The corrected reflectivities should be in error by less than 0.05 at 47 μ due to scattered light. Sample-to-sample differences are probably due to differences in surface condition and carrier concentration.

The near normal reflectivities of Mg_2Si , Mg_2Ge , and

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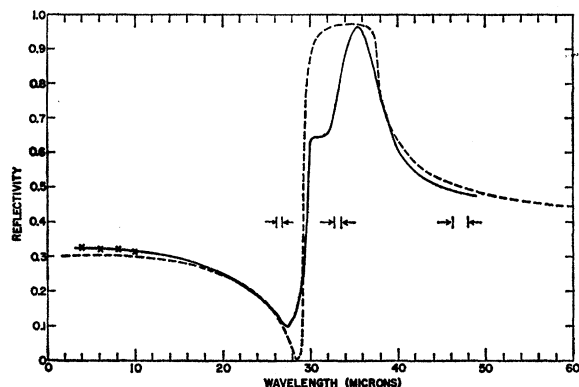


FIG. 1. Reflectivity of Mg_2Si II, n type, carrier concentration believed to be less than $10^{17}/cm^3$ (solid line) and reflectivity of a damped harmonic oscillator with $\nu_0=8.0 \times 10^{12} \text{ sec}^{-1}$, $\rho=0.63$, $\gamma=0.01$, $\epsilon_\infty=13$ (dashed line). The parameters are defined in the Appendix. The crosses are reflectivities calculated from the index of refraction determined by the method of minimum deviation in reference 6. The arrows indicate the spectral band pass of the monochromator.

Mg_2Sn are shown as solid curves in Figs. 1–4. The crosses represent reflectivities calculated from the index of refraction measured by a prism method.⁶ The carrier concentrations were determined from the room temperature Hall coefficients using $N=(R_{He})^{-1}$.

DISCUSSION

A. Lattice Vibrations

Strong reststrahl reflectivity is observed in all three compounds. The shape of the reflectivity curves is quite unlike that of the III-V compounds⁷ whose room-temperature reflection spectra can be approximated by that of a single damped harmonic oscillator. (At lower temperatures the III-V compounds' reflection spectra exhibit more structure.⁸) As is evident in Figs. 1–4, there occurs a subsidiary bump on the high-energy side of the maximum reflectivity, like the subsidiary peak in the reflection spectrum of an alkali halide⁹ or an alkaline earth fluoride.¹⁰ Lax and Burstein¹¹ have ascribed this subsidiary peak to two-phonon effects and for KBr the phonon spectrum obtained by Woods *et al.*¹² from inelastic neutron scattering can be used to find several modes of equal wave vector whose energies add up to the photon energy of this subsidiary maximum. In the III-V compounds the multiple-phonon processes do not give rise to a subsidiary reflectivity peak at room tem-

perature, but to a series of absorption peaks.^{13–15} Some preliminary transmission measurements on Mg_2Si and Mg_2Ge between 1.5 and 20μ revealed no peaks ascribable to lattice vibrations. (A previously unobserved peak near 3μ occurred in all Al-doped Mg_2Ge , but it cannot be attributed to lattice vibrations because it was not observed in p -type samples.)

A simple harmonic oscillator (see Appendix) was fitted to the reflectivity peaks of the magnesium compounds. In choosing a best fit the suggestions of Spitzer, Kleinman, and Walsh¹⁶ were followed and the subsidiary peaks were ignored. The harmonic oscillator reflectivities are shown dashed in Figs. 1 and 2. The purpose of the fitting was to decide on a characteristic frequency for the reflectivity maximum of each crystal. These frequencies, shown in Table I, represent the frequency of the optically active transverse optical mode of lattice vibration with $\lambda \rightarrow \infty$. The reduced mass for this mode,

$$\mu = \frac{Mm}{2M+m}, \quad (1)$$

where M is the mass of Mg and m the mass of the other element, is also listed in Table I. The simplest model of the reststrahl vibration would have a frequency

$$\nu_{TO} = \frac{1}{2\pi} \left(\frac{K}{\mu} \right)^{1/2}, \quad (2)$$

where K is a force constant. As can be seen in Table I the quantity $\mu\nu_{TO}^2$ is approximately constant for all

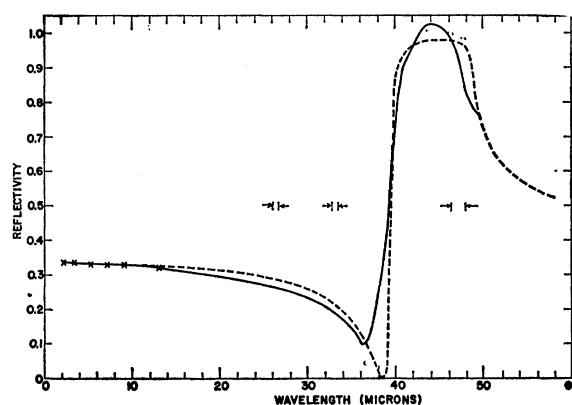


FIG. 2. Reflectivity of Mg_2Ge (0.1 Al), $2.75 \times 10^{16} \text{ electrons}/cm^3$ (solid line), and reflectivity of a damped harmonic oscillator with $\nu_0=6.2 \times 10^{12} \text{ sec}^{-1}$, $\rho=0.5$, $\gamma=0.007$, $\epsilon_\infty=14$ (dashed line). The parameters are defined in the Appendix. The crosses are reflectivities calculated from the index of refraction determined by the method of minimum deviation in reference 6.

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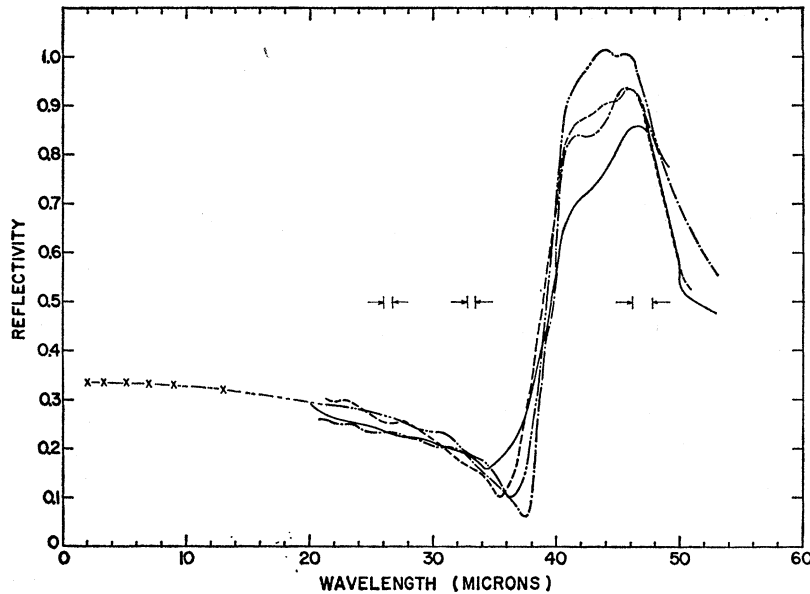


FIG. 3. Reflectivity of Mg_2Ge . n type: 2.75×10^{16} carriers/cm³ (dash-double dot) and 9.2×10^{17} carriers/cm³ (dash). p type: 2.8×10^{17} carriers/cm³ (dash-dot) and 2.75×10^{18} carriers/cm³ (solid).

three compounds investigated. The interatomic forces for long-wavelength transverse optical modes are thus about the same for all three compounds.

One can estimate the static dielectric constant, ϵ_0 , of Mg_2Si in several ways. If the imaginary part of the index of refraction, k , vanishes then the long-wavelength reflectivity becomes

$$R = \left(\frac{\epsilon_0^{1/2} - 1}{\epsilon_0^{1/2} + 1} \right)^2. \quad (3)$$

At $\lambda = 46 \mu$, k for the classical oscillator shown dashed in Fig. 1 is negligible and the free carriers do not cause an appreciable value of k if they can be treated classically.⁵ Using R between 0.42 and 0.45 yields ϵ_0 between 22 and 26, with the lower value being preferred since uncompensated scattered light tends to raise R , and furthermore the reflectivity probably decreases slightly at

wavelengths longer than 46μ . The carriers, if treated classically,⁵ contribute a term to ϵ_0 of about -1 . This method then gives $\epsilon_0 \approx 20$ or 22 without free-carrier effects. (The harmonic oscillator used in Fig. 1 gives $\epsilon_0 = 20.9$.) A second estimate can be made from a Kramers-Kronig analysis¹⁷⁻¹⁹ of the reflectivity data, giving both n and k from R when R is known over a sufficiently large frequency range. The result of such an analysis is $k = 1.14$, $n = 4.61$, $\epsilon_0 = 20$ at $\lambda = 46 \mu$. This ϵ_0 should also be reduced by subtracting the free-carrier contribution from it. The Kramers-Kronig analysis gives no more accuracy for ϵ_0 than the previous method, since it depends on the accuracy of R near 46μ , but it does indicate that $k^2 \ll n^2$, as assumed earlier. A few details of this analysis are discussed in the Appendix. The best estimate of the static dielectric constant of Mg_2Si is $\epsilon_0 = 20$.

It has been suggested^{1,2} that long-wavelength longitudinal optical modes limit the mobility of carriers in Mg_2Si and Mg_2Ge for temperatures above room temperature. The frequency of these modes is given by

$$\nu_{LO} = \nu_{TO} (\epsilon_0 / \epsilon_\infty)^{1/2}, \quad (4)$$

where ν_{TO} is the frequency of long-wavelength transverse optical modes, determined in the present work. ϵ_∞ is the optical dielectric constant and is equal to the square of the index of refraction. Using 20 for the static dielectric constant of Mg_2Si and 13.3 for its optical dielectric constant⁶ one obtains the value of ν_{LO} shown in Table I. For Mg_2Ge and Mg_2Sn ϵ_0 cannot be estimated reliably so all that is known is that $\nu_{LO} \geq \nu_{TO}$. Characteristic LO phonon temperatures are also listed.

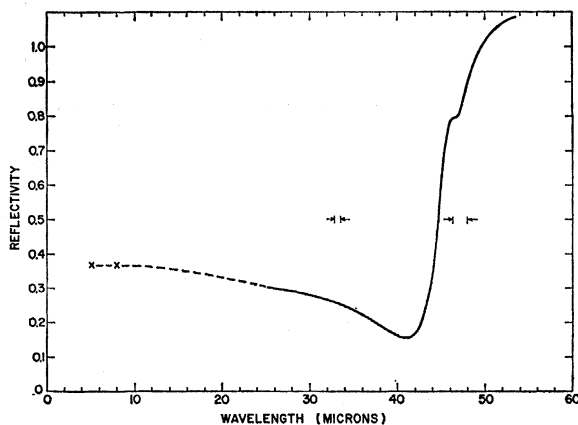


FIG. 4. Reflectivity of Mg_2Sn , 3×10^{18} electrons/cm³.

¹⁷ T. S. Robinson, Proc. Phys. Soc. (London) **B65**, 910 (1952).

¹⁸ T. S. Robinson, Proc. Phys. Soc. (London) **B66**, 962 (1952).

¹⁹ F. C. Jahoda, Phys. Rev. **107**, 1261 (1957).

TABLE I. Lattice vibration parameters in the Mg_2X compounds.

Compound	ν_{TO} (10^{12} sec $^{-1}$)	μ (10^{-26} kg)	$\mu\nu_{TO}^2$ (kg sec $^{-2}$)	ϵ_∞^a	ϵ_0	ν_{LO} (10^{12} sec $^{-1}$)	θ_{LO} ($^\circ K$)
Mg_2Si	8.0	1.47	0.94	13.3	20	9.8 ^b	470 ^b
Mg_2Ge	6.2	2.42	0.93	13.9	...	≥ 6.2	≥ 300
Mg_2Sn	5.6	2.86	0.90	17.0	...	≥ 5.6	≥ 270

^a Reference 6.
^b Using $\epsilon_0 = 20$.

The characteristic temperatures assumed in references 1 and 2 are thus seen to be too low, and the importance of optical-mode scattering compared to ionized impurity scattering in Mg_2Si and Mg_2Ge is less than indicated in those papers unless the effective ionic charge is increased from the values they find.

By use of the expression

$$\rho = \frac{\epsilon_0 - \epsilon_\infty}{4\pi} = \frac{2Ne_B^{*2}}{4\pi^2\mu\nu_{TO}}, \quad (5)$$

where the terms are defined in the Appendix, one estimates $e_B^* = 1.80e$, where e is the charge on an electron. $\rho = 0.63$ was used, corresponding to the harmonic oscillator of Fig. 1. If ϵ_0 is less than 20.9, the following effective charges will all be reduced. Equation (5) does not use the Lorentz-Lorenz correction for the internal field and hence does not give the usual Szigeti effective charge^{20,21} which in this case is $e_S^* = 0.34e$. The above effective charge, e_B^* , first discussed by Born,²² would be $2e$ if the crystal were purely ionic and the ions did not deform during lattice vibrations. Brodsky and Burstein²³ indicate that e_B^* is more appropriate for semiconducting compounds although it is e_S^* that usually is tabulated.⁸ The effective charge for optical-mode scattering is discussed by Callen^{24,25} and it is $e_C^* = e_B^*/\epsilon_\infty$, which is $0.13e$ for Mg_2Si . Reference 1 gives²⁶ $e^* = 1.60e$ which should correspond to e_B^* since the ϵ_∞ factor was explicitly used in the expression for the mobility. However, this number should be revised upward to produce a better fit with experiment when the higher phonon temperature is used. This revision further improves agreement with the value of e_B^* determined optically, and tends to restore the mobility due to optical-mode scattering to the importance given it in reference 1. A good fit to the experimental mobility for n - Mg_2Si (Fig. 7 in reference 1), can be made between 90 and 400 $^\circ K$ by using $\epsilon_0 = 20$, $\epsilon_\infty = 13.3$ and $e_B^* = 1.8e$ in the expressions¹ for mobilities limited by ionized impurity and optical mode scattering.

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²¹ B. Szigeti, Proc. Roy. Soc. (London) **A204**, 52 (1950).

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²⁴ H. B. Callen, Phys. Rev. **76**, 1394 (1949). See also reference 25.

²⁵ H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1957).

²⁶ The effective charge on a Mg ion, e_B^* , is given as $2Fe$ in reference 1.

Whitten and Danielson²⁷ discuss further the effective charges in Mg_2Si in relation to the elastic constants and binding energy.

B. Carrier Effects

To estimate m^* of the carriers in Mg_2Ge , a damped harmonic oscillator reflectivity curve was fitted to the reflectivity curve of the purest sample (Fig. 2). To the susceptibility and conductivity of this oscillator were added terms due to the free carriers, treated classically:

$$\chi = \frac{Ne^2}{m^*} \tau^2 (1 + \omega^2 \tau^2)^{-1}, \quad (6)$$

$$\sigma = \frac{Ne^2}{m^*} \tau (1 + \omega^2 \tau^2)^{-1}. \quad (7)$$

N was taken to be the carrier concentration determined from Hall coefficient measurements. τ , a relaxation

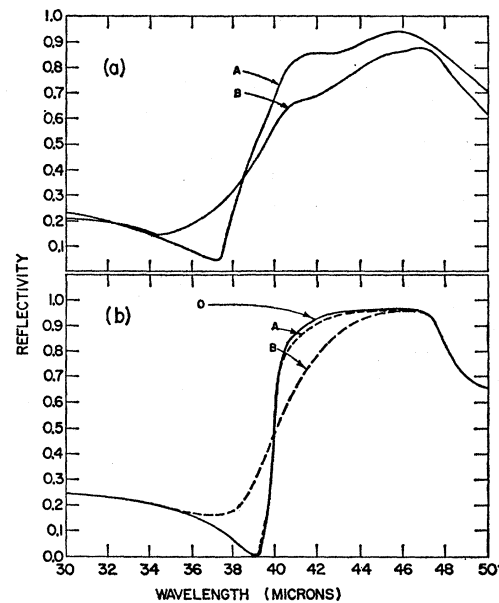


Fig. 5(a). Reflectivity of two p -type Mg_2Ge crystals with carrier concentrations of (A) 2.4×10^{17} cm $^{-3}$ and (B) 2.75×10^{18} cm $^{-3}$. (b) Reflectivity of a damped harmonic oscillator (same parameters as in Fig. 2) and classical free carriers with $m^* = 0.5m_0$, $\tau = 10^{-14}$ sec and concentrations equal to zero (curve 0) and those in the samples of Fig. 4(a).

²⁷ W. B. Whitten and G. C. Danielson (to be published).

time, and m^* were varied. The experimentally observed shift in the wavelength of the reflectivity minimum and the decrease of the peak reflectivity as N increases [Fig. 5(a)] could be reproduced [Fig. 5(b)] for holes in Mg_2Ge only for values of τ in the range $5-10 \times 10^{-15}$ sec and m^* in the range $0.2-0.3m_0$. The data of reference 2 give $m^*=0.31m_0$ and $\tau=2 \times 10^{-14}$, but the relaxation time at the surface could be shorter than in the volume. The effects of adding electrons were not reproduced by any combination of τ between 10^{-16} and 5×10^{-14} sec and m^*/m_0 between 0.1 and 0.5. These combinations shifted and raised the reflectivity minimum too much compared to the experimental curves (not shown). Attempts to use a larger N in Eq. (7) than in Eq. (6) did not help much. (This is equivalent to using $\sigma_0 > \sigma_{dc}$ in the expression $\sigma = \sigma_0(1 + \omega^2\tau^2)^{-1}$ [Eq. (7)]. Visvanathan²⁸ showed that this can be valid for III-V compounds.) No attempt was made to let τ vary with ω .²⁹ One can only conclude that the observed changes in reflectivity with carrier concentration are consistent with a classical description of the carriers using the known properties of holes in $p\text{-Mg}_2\text{Ge}$, and that in $n\text{-Mg}_2\text{Ge}$ the changes probably are due to the free electrons but not in the expected manner. The reflectivity of Mg_2Si may also contain some effects of the free carriers but only at the longer wavelengths, since $m^*=0.46$ for electrons in this compound.¹

APPENDIX

Classical dispersion theory³⁰ gives, for a system of N charged, damped harmonic oscillators per unit volume, a dielectric constant

$$\epsilon = \epsilon_\infty + 4\pi\chi = \epsilon_\infty + \frac{4\pi\rho(1-\nu^2)}{(1-\nu^2)^2 + \gamma^2\nu^2}, \quad (\text{A1})$$

and conductivity

$$\sigma = \frac{2\pi\rho\gamma\nu^2}{(1-\nu^2)^2 + \gamma^2\nu^2}, \quad (\text{A2})$$

where ν is the frequency divided by ν_0 , the resonance

frequency, and

$$\rho = \frac{2Nq^2}{4\pi^2\mu\nu_0^2}, \quad (\text{A3})$$

where μ is the reduced mass of the oscillator and q its charge. [The 2 in Eq. (A3) results from the fact that there are two dipoles per molecule in the CaF_2 lattice.] γ is related to the damping constant of the oscillator, ϵ_∞ is the high-frequency dielectric constant. From these one gets the real and imaginary parts of the complex index of refraction, $N = n + ik$:

$$n^2 = \frac{1}{2} \{ [\epsilon^2 + 4\sigma^2/\nu^2]^{1/2} + \epsilon \}, \quad (\text{A4})$$

$$k^2 = \frac{1}{2} \{ [\epsilon^2 + 4\sigma^2/\nu^2]^{1/2} - \epsilon \}. \quad (\text{A5})$$

Finally the normal reflectivity is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (\text{A6})$$

When free carriers are also to be considered, their σ and χ are to be added to the above values and new n , k , and R calculated.

The Kramers-Kronig analysis was undertaken primarily to see whether free-carrier absorption was affecting the value of ϵ_0 . A computer program,³¹ kindly supplied by Professor J. J. Hopfield, was used to yield n and k vs λ for the entire range of reflectivity measurements. For $\infty > \lambda > 50 \mu$, R was assumed to increase from 0.42 to 0.45. Slight variations of these values altered n but not k . No changes in n and k for $\lambda > 2 \mu$ were caused by the neglect of the absorption edge. This was tested by assuming R rose to 0.6 at $\lambda = 1 \mu$ and remained constant to $\lambda = 0.3 \mu$, and comparing the result to that obtained by letting $R = 0.336$ between 0.3 and 2μ . A correction term³¹ to compensate for the finite wavelength range of the data was applied to make $k = 0$ at $\lambda = 1.6 \mu$, 8μ , and 14.5μ where the crystal is known to be transparent.³² The result of the analysis is that k is constant, ~ 1.1 , for $\lambda > 40 \mu$, and n decreases as λ increased until $\lambda > 50 \mu$. Experimental errors leading to an altered shape of R vs λ for $\lambda > 40 \mu$ can be responsible for k being as large as it is.

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