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Infrared Absorption in Mg_2Ge*

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Optical-absorption measurements on n- and p-type Mg_2Ge single crystals were made at wavelengths be-between 1.5 and 25 μ at temperatures between 4.2 and 300°K. The absorption edge in p-type crystals arises from allowed indirect transitions. The energy gap is 0.570 eV at 0°K and the phonon involved has an energy of 0.025 eV. At higher temperatures the temperature dependence of the energy gap is -1.8×10^{-4} eV/deg. At longer wavelengths p-type crystals exhibit absorption bands interpreted as being caused by transitions between three valence bands at the center of the Brillouin zone as in germanium. The spin-orbit splitting of these bands is 0.20 eV and the ratio of heavy-hole mass to light-hole mass is 6 ± 1. The n-type samples have an absorption band at 0.58 eV (0°K) of uncertain origin, and $\lambda^{2.5}$ free-carrier absorption, indicating optical-mode scattering.

I. INTRODUCTION

MAGNESIUM germanide is a member of the family of compounds composed of magnesium and elements of column IV A of the periodic table. The compounds are Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb, all of which are semiconductors except Mg_2Pb which exhibits metallic behavior. They are all cubic, crystallizing in the CaF_2 structure. The electrical properties of the magnesium compounds have been the subject of a number of investigations in which determinations of energy gaps and effective masses were made.[1–5]

McWilliams and Lynch[6] and Kahan *et al.*[7] measured the infrared reflectivities of Mg_2Si, Mg_2Ge, and Mg_2Sn and observed reststrahl reflectivity peaks indicating the partially ionic character of the compounds. Koenig *et al.*[8] made infrared-absorption measurements on Mg_2Si and Mg_2Ge. These measurements on the absorption edges could not be fitted to any theoretical model and thus the energy gaps could not be determined, although it appeared that the absorption was due to indirect transitions. Blunt *et al.*[9] and Lawson and coworkers[2] examined the absorption edge in Mg_2Sn. Lipson and Kahan[10] studied the infrared absorption in Mg_2Sn. They concluded that absorption in the edge was due to indirect transitions and determined values of the energy gap as a function of temperature and of the energy of the phonon assisting the indirect transitions.

Relatively little is known about the band structure of the magnesium compounds. Mead[11] made optical-absorption and surface-barrier photoresponse measurements on Mg_2Ge and at 10°K found an indirect transition at 0.57 eV and a direct transition at 1.804 eV. Whitten and Danielson's[12] piezoresistance measurements indicated that the conduction-band minima in Mg_2Si occur along the $\langle 100\rangle$ directions in k space, as is the case for silicon. Umeda[13] reports a $\langle 100\rangle$ conduction-band minimum determined by magnetoresistance measurements on Mg_2Sn. Theoretical investigations of the band structure of the compounds have recently been initiated, with Lee's calculations[14] for Mg_2Si and Mg_2Ge the only results obtained at the time of this writing.

With the quality of crystals currently available, it was felt that considerable information about the band structure of the magnesium compounds could be obtained by a thorough study of the infrared absorption in Mg_2Ge. Preliminary measurements on several of the better Mg_2Si crystals available showed them to be too opaque in the photon energy region below the absorption edge for a fruitful analysis of experimental results.

II. EXPERIMENTAL METHODS

Single crystals of Mg_2Ge were grown by the Bridgman technique. The crystal growth of the magnesium compounds has been described in some detail[5] and will not be discussed here. Thin samples for the optical-transmission measurements were produced by grinding to the desired thickness and then polishing with aluminum oxide abrasive on a wax lap. Measurements were made on the polished surfaces without etching, as a suitable etch for Mg_2Ge was not found.

The optical measurements were made with the samples placed in the monochromatic exit beam of a Perkin-Elmer model 99 single-beam, double-pass mono-

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chromator equipped with a globar source and a thermocouple detector. Prisms of LiF, NaCl, KBr, and CsBr were used in the appropriate spectral regions.

The sample was mounted directly on the bottom of the inner chamber of an optical cryostat which contained the coolant at the desired temperature. This was either a dry-ice-acetone mixture (196°K), liquid nitrogen (77°K), or liquid helium (4.2°K). The sample area was surrounded by a small vacuum-tight chamber into which helium exchange gas could be admitted to increase the thermal contact between sample and coolant. Sapphire windows were sealed to this chamber by the method of Roberts.[15] Sample temperatures were measured with an Au 0.07 at.% Fe versus Cu thermocouple calibrated by Finnemore *et al.*,[16] and it was found that with the exchange gas, sample temperatures equal to those of the liquid coolants were achieved even at liquid-helium temperature. The sapphire windows were removed for measurements at longer wavelengths. Without the exchange gas the crystal temperatures were several degrees higher than the refrigerant temperatures.

The sample was mounted with GE 7031 adhesive over one of two identical apertures which were fastened to the cryostat. The cryostat could be moved transverse to the light beam so that either the sample or the blank aperture could be placed in the beam. By this sample-in, sample-out technique, the transmission of the sample was determined. The absorption coefficients were determined from the transmission values from the relation

$$T=(1-R)^2e^{-\alpha d}/(1-R^2e^{-2\alpha d}),$$

where T is the transmission, α the absorption coefficient, d the sample thickness, and R the bulk reflectivity. This expression is derived considering multiple reflections from the sample surfaces but neglecting interference effects. For the sample thicknesses used, the spectral bandwidths were sufficiently large so that no interference effects were actually observed.

The reflectivities of several cleaved and polished surfaces were measured at room temperature in the range of the measured absorption edge and all agreed well with those predicted by the refractive-index measurements of McWilliams and Lynch.[17] These values were used in determining the absorption coefficients at all temperatures.

III. INTRINSIC ABSORPTION EDGE

The absorption spectrum at low absorption levels of an undoped, p-type Mg_2Ge sample with a room-temperature carrier concentration of about 10^{16} cm^{-3} is shown in Fig. 1. The steep increase in absorption at higher photon energies is identified as the intrinsic absorption edge.

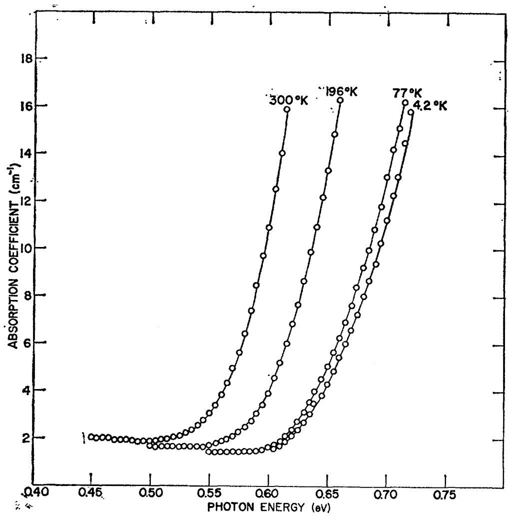

FIG. 1. Absorption edge of p-Mg_2Ge. The sample thickness is 0.232 cm. The room-temperature carrier concentration is about 10^{16}/cm^3.

The experimental data for Mg_2Ge can be interpreted satisfactorily by the theory of allowed indirect electronic transitions across the forbidden energy gap assisted by the absorption and emission of phonons. A least-squares fit to the data of the one-phonon Macfarlane-Roberts expression[18,19] was made. This expression was first used by Macfarlane and Roberts to describe the absorption edges in Si and Ge and later by Braunstein *et al.*[20] for Ge-Si alloys. This expression is

$$\alpha=A\left[\frac{(h\nu-E+K\theta)^2}{\exp(\theta/T)-1}+\frac{(h\nu-E-K\theta)^2}{1-\exp(-\theta/T)}\right],$$

where α is the absorption coefficient, $h\nu$ the photon energy, E the energy gap, $K\theta$ the phonon energy (K being Boltzmann's constant), T the absolute temperature, and A a constant essentially independent of temperature.[21] The first term of the expression is valid for $h\nu\geq E-K\theta$ and corresponds to the absorption of a phonon of energy $K\theta$, while the second term holds for $h\nu\geq E+K\theta$ and corresponds to the emission of a phonon.

The result of the analysis for Mg_2Ge is shown in Fig. 2, where the square root of the absorption coefficient is plotted versus photon energy after subtraction of a constant background absorption. The absorption curve for each temperature was treated independently without requiring the parameters A and $K\theta$ to be the same at all temperatures. Instead, the values determined for these parameters at different temperatures

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[21] $\alpha h\nu$ is often equated to the quantity on the right in the above equation with theoretical justification. The use of α instead of $\alpha h\nu$ gives essentially the same values of $K\theta$ and E with our data.

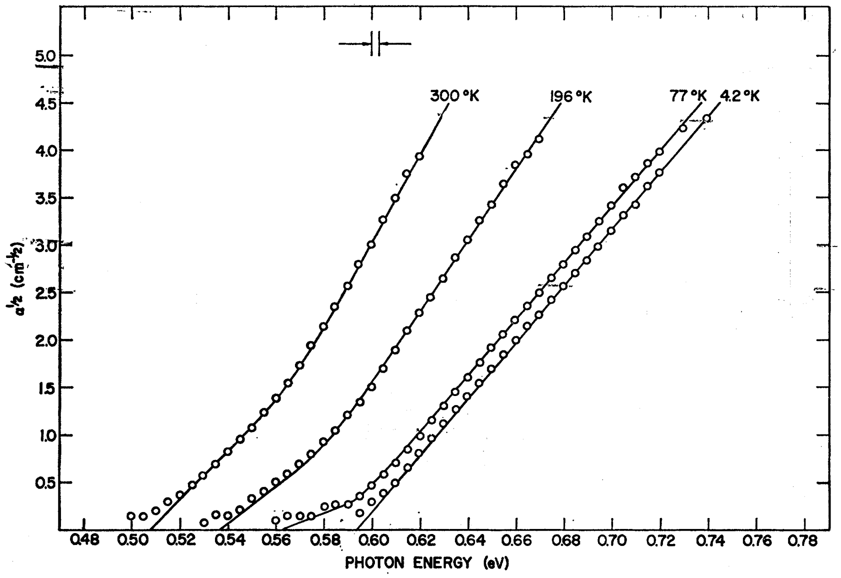

FIG. 2. Comparison of theory (lines) and experimental absorption edge (circles) of Mg_2Ge. The arrows indicate the spectral bandpass.

were compared as a test of how well theory and experiment agree. Over the temperature range from 4.2 to 300°K, the value found for A varied by about 20%. This compares fairly well with the case of Ge where Macfarlane *et al.*[22] found the corresponding quantity to change by about 15% over the same temperature range.

The values found for the phonon energy $K\theta$ at 300 and 196°K differed by about 5% and an average value at these temperatures of 0.025 eV was taken as the energy of the phonon involved in the indirect transitions in Mg_2Ge at all temperatures. This value was used to determine the energy gap at 77 and 4.2°K. This was necessary because at low temperatures, only the quantity $E+K\theta$ can be determined accurately as the magnitude of the phonon absorption term becomes quite small.

Table I shows the value of the phonon energy and energy gaps determined by averaging the results from four crystals. The estimated error in E is about 0.001 eV.

The phonon energy of 0.025 eV was compared with the phonon spectrum of Mg_2Ge calculated by Chung[23] from a point-charge model using elastic constants and optical data, and is representative of his values for phonon energies near the edge of the Brillouin zone. In fact, 0.025 eV agrees within 5% with the energy of the longitudinal acoustic phonon at the edge of the zone in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. Longitudinal optical (LO) modes of large wave vector also appear to have energies near 0.025 eV. The LO modes of small wave vector are believed to interact strongly with the electrons in Mg_2Ge.[4–6]

TABLE I. Energy gap and phonon energy of Mg_2Ge (in eV).

$K\theta$	E(4.2°K)	E(77°K)	E(196°K)	E(300°K)
0.025	0.570	0.567	0.550	0.532

Figure 3 shows the values of the energy gap found in the analysis plotted versus temperature. The slope of the straight-line portion of the curve at higher temperatures was calculated to be $\partial E/\partial T = -1.8\times10^{-4}$ eV/°K. This agrees with Mead's[11] value of the slope, but it is lower than the estimate of -6.5×10^{-4} eV/°K given by Koenig *et al.*[8] However, their value was determined by measuring the temperature shift of the point on the absorption edge having a constant absorption coefficient of 100 cm^{-1}. This gives a result higher than the actual shift of the energy gap, as can be seen from the temperature dependence of the Macfarlane-Roberts expression. The straight-line portion of Fig. 3 extrapolates to 0.585 eV at 0°K, and is the value of the gap that electrical measurements should give. Redin[5] found 0.69 eV for this energy, while Winkler[1] obtained 0.74 eV.

High-resolution measurements on the absorption edge of Ge and Si by Macfarlane *et al.* revealed four distinct portions in the curves of $(\alpha)^{1/2}$ versus $h\nu$ instead of just two.[22] [24] These results were interpreted in terms of indirect transitions assisted by the absorption and emission not of one, but of two different types of phonons identified as both the longitudinal and transverse acoustic phonons. No such complex structure is evident in the absorption edge of Mg_2Ge, although the spectral resolution was high enough to see such structure in the absorption edge of a pure Ge crystal at room temperature. It is concluded that if any such fine structure exists in the absorption edge of Mg_2Ge, higher resolution will be needed to see it than is needed for

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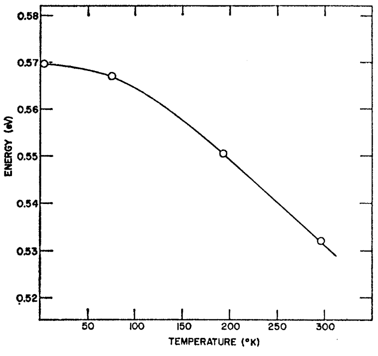

Fig. 3. Energy gap of Mg_2Ge versus absolute temperature.

pure Ge. For these measurements, the slit widths were approximately 0.002 to 0.003 eV compared with 0.001 to 0.0004 eV for the high-resolution work on Si and Ge.

It is felt that this study of the absorption edge establishes reasonably well the fact that Mg_2Ge has an indirect gap and yields useful values for the energy gap as a function of temperature. Although no fine structure due to the absorption and emission of more than one kind of phonon was observed, the phonon energy of 0.025 eV obtained from the one-phonon Macfarlane-Roberts analysis represents an average phonon energy for the indirect interband transitions in Mg_2Ge.

IV. FREE-CARRIER ABSORPTION

1. *p*-Type Mg_2Ge

The absorption spectrum of *p*-type Mg_2Ge at wavelengths longer than that of the absorption edge is dominated by strongly temperature-dependent absorption bands. Figure 4 shows the absorption spectrum of a *p*-type silver-doped Mg_2Ge crystal with a carrier concentration of 9×10^{17} cm^{-3}. There is a strong absorption peak that, as the temperature increases, broadens and shifts from about 0.28 eV at 300°K to 0.22 eV at 10°K. A very weak peak at 0.19 eV is evident at the higher temperatures but disappears entirely at 80 and 10°K. There is a hint of a third absorption band at low photon energies which seems to begin at about 0.10 eV, although it is not completely covered by the energy range measured.

This type of absorption spectrum is similar to those seen in a number of other *p*-type semiconductors, in which the absorption has been interpreted arising from electronic transitions between three germanium-like valence bands.[25–27] Assuming such a valence-band structure for Mg_2Ge, the highest energy peak can be attributed to vertical transitions between the heavy-hole band and the band split off by the spin-orbit interaction, the intermediate energy peak to transitions between the light-hole band and the split-off band, and the low-energy peak to transitions from the heavy-hole to the light-hole band.

The intermediate absorption peak at 0.19 eV, which would correspond to transitions between the light-hole and split-off band, is very weak. In fact, there is some doubt that it exists at all because it occurs in the spectral region in which atmospheric water vapor has a complicated absorption spectrum, making absorption measurements difficult using a single-beam instrument. Interpreting an absorption spectrum as arising from transitions between three germanium-like valence bands even when the intermediate energy peak is absent, is not without precedent. Such is the case for AlSb, where it has been suggested[28] that this missing absorption peak is broadened or obscured by nonvertical transitions between bands due to scattering.

Kahn[29] assumed parabolic bands and derived expressions for the absorption due to transitions between the three valence bands in Ge. These expressions show the temperature and photon-energy dependence of the absorption bands to be dependent on the spin-orbit splitting at the center of the zone and on ratios of pairs of the three hole effective masses. Applying Kahn's expressions to Mg_2Ge, the best fit to the experimental data is found for a spin-orbit splitting of 0.20 eV and a ratio of heavy-hole mass to light-hole mass of 6 ± 1. In making this fit, the position of the trough between the two high-energy peaks and the shift with temperature of the high energy peak were the criteria used. Although such a determination of the effective masses is at best a rough estimate, the observed absorption spectrum in *p*-type Mg_2Ge is, nevertheless, direct evidence of a valence-band structure similar to that of

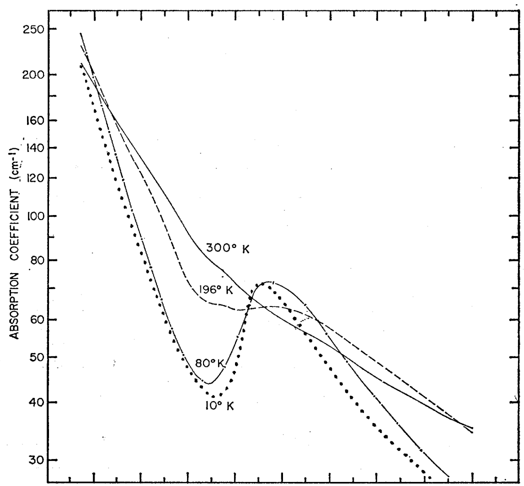

Fig. 4. Free-carrier absorption in *p*-type Mg_2Ge containing $\sim10^{18}$ carriers/cm^3 at room temperature.

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Ge and yields a fairly accurate (10%) value for the spin-orbit splitting at the center of the Brillouin zone.

By a method suggested by Kane,[30] the spin-orbit splitting of a compound can be related to the spin-orbit splittings of the constitutent elements. The spin-orbit splitting of the Γ_{25}' states in the compound is assumed equal to the average of the spin-orbit splittings of the elements weighted by the fraction of time an electron spends on each atom. Applying this to Mg_2Ge, using the spin-orbit splittings of Mg and Ge,[31] respectively, one finds that an electron spends about $\frac{1}{3}$ of the time on an Mg atom and $\frac{2}{3}$ of the time on a Ge atom. Assuming the same sharing time for the other magnesium compounds, one gets spin-orbit splittings of 0.03 eV for Mg_2Si and 0.60 eV for Mg_2Sn. Thus it is unlikely that absorption due to transitions between valence bands can be found in these compounds, because it would be masked by the reststrahl absorption in Mg_2Si and by the absorption edge in Mg_2Sn, in which the energy gap is only about 0.15 eV.

The sharing time of electrons between Mg and Ge should be related in some way to the ionicity of the compound. Naïvely using the $\frac{1}{3}$–$\frac{2}{3}$ sharing time to calculate a static ionic charge, a value of $+0.7e$ for the ionic charge on each Mg ion ($-1.4e$ on each Ge ion) is found, where e is the electronic charge. This ionic charge is important in binding considerations and in some elastic constants.[32,33] It is not equal to the effective charge which includes dynamic polarization effects. McWilliams and Lynch[6] calculated a Mg-ion effective charge of $1.80e$ based on infrared-reflectivity measurements. Chung[23] estimated an effective charge of $0.40e$ for Mg in Mg_2Ge while Whitten[34] found an upper limit of $0.66e$ for Mg_2Si, both values determined by fitting the calculated phonon spectrum to elastic-constant measurements. Because the different effective-charge determinations were made from such widely different considerations, and because effective charge is a vague concept in some of them, it does not seem fruitful to attempt to correlate the different results.

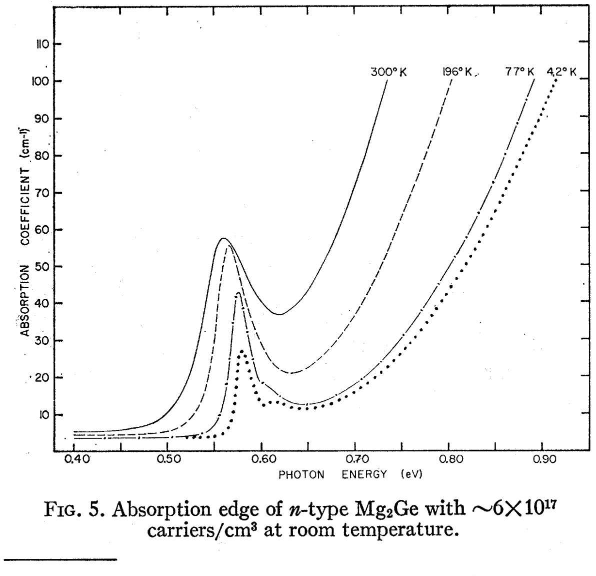

FIG. 5. Absorption edge of n-type Mg_2Ge with $\sim 6\times10^{17}$ carriers/cm^3 at room temperature.

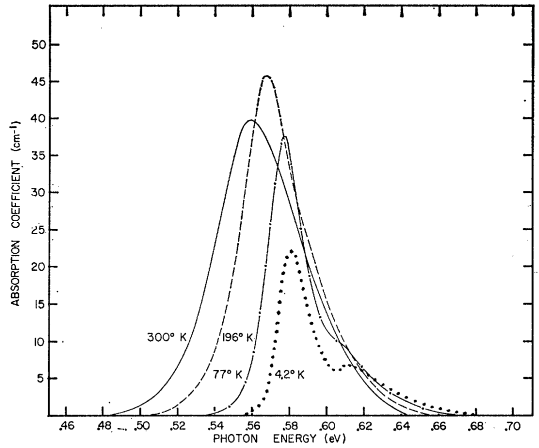

FIG. 6. Absorption band of Fig. 5 after subtraction of edge absorption.

2. n-Type Mg_2Ge

In n-type material, the absorption edge of Mg_2Ge is masked by an absorption band at about 0.57 eV. Figure 5 shows the absorption spectrum of an aluminum-doped crystal with a room-temperature carrier concentration of 6×10^{17} cm^{-3}. Figure 6 shows the absorption band after subtraction of the intrinsic edge absorption. This absorption was not seen in any p-type material with hole concentrations ranging from 10^{16} to 10^{19} cm^{-3} at temperatures from 4.2 to 400°K. The absorption appeared to be roughly proportional to the electron concentration and was independent of the doping material, being seen in crystals doped with Al, Ga, In, As, and Sc.

The absorption band is similar to those seen in the other magnesium compounds. Bands were seen at 0.40 eV in n-type[8] Mg_2Si and at 0.16 eV in[10] Mg_2Sn. In these cases it was suggested that the bands arose from electronic transitions within the conduction band, although the transitions were not positively identified.

It is difficult to attempt an explanation of the absorption band in Mg_2Ge without a more detailed knowledge of the band structure. However, the explanation Paul proposed[35] for an absorption band in several n-type III–V compounds and n-Si may be extended to Mg_2Ge if Lees' band structure[14] is correct. If the conduc-

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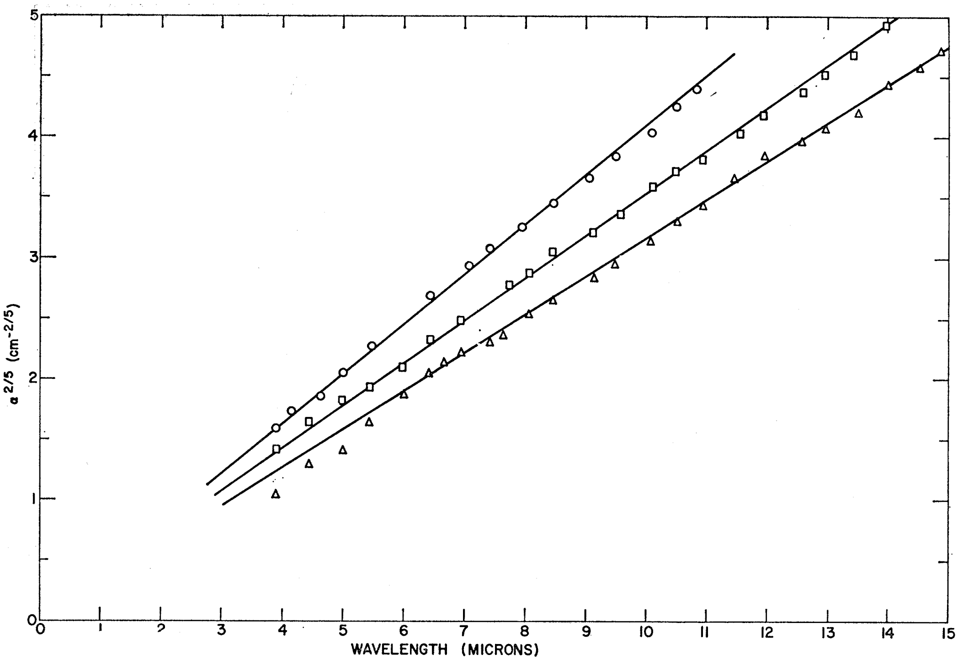

FIG. 7. Free-carrier absorption in n-type Mg_2Ge, ~6×10^{17} carriers/cm^3 at room temperature. ○, 300°K; □, 196°K; △, 80°K.

tion-band minimum is actually located in the ⟨100⟩ direction at the point X, as his calculations indicate, then there is the possibility of vertical transitions from this minimum (X_1) to the higher X_3 band, although Lee places no confidence in the position of the X_3 level. However, the absorption band is photoconductive, as shown by Stella and Lynch,[36] which would indicate that the absorption results in new charge carriers in the conduction band. Such a strong photoconductivity signal would not likely be produced by a change in mobility, as electrons are excited to a different conduction band.

Transitions from deep-lying impurity levels to the conduction-band minimum do not seem likely as there is no evidence of such levels in Mg_2Ge from electrical measurements. Transitions from the valence band to empty donor levels also seem unlikely, since at 4.2°K most of the donor levels would be full, when actually the absorption peak is still strong.

Structure appears in the absorption at 77 and 4.2°K in the form of a secondary peak about 0.03 eV higher than the main peak. This suggests the possibility that the secondary peak is due to a transition from an impurity level 0.03 eV below the conduction-band minimum to a higher conduction band, while the main peak is due to transitions from the conduction-band minimum. This is in agreement with the results of Redin,[37] who made estimates of from 0.03 to 0.077 eV for donor ionization energies. If this were the case, one would expect the primary peak to be smaller at 4.2°K when few electrons from the relatively deep level of 0.03 eV would be thermally excited to the conduction band. Such a trend is evident in Fig. 6, but it could also arise from other factors, such as diminishing phonon population or smaller spread in electron wave vectors at low temperatures.

In short, there is no preponderance of evidence supporting any one mechanism as giving rise to the absorption band in n-type Mg_2Ge. However, the most likely possibilities remain transitions in which the final state is a higher conduction band.

The absorption coefficient of n-type Mg_2Ge at wavelengths longer than that of the absorption edge increases monotonically with increasing wavelength. This can be described by a λ^p wavelength dependence, where the power p varies from 2.35 at 300°K to 2.50 at 80°K. This is best fit by the theory of optical-mode scattering of Visvanathan,[38] who found for scattering by longitudinal optical modes a free-carrier absorption of $\lambda^{2.5}$ for $h\nu \gg kT$. The $\lambda^{2.5}$ behavior of the free-electron absorption in Mg_2Ge is shown in Fig. 7, where $\alpha^{2/5}$ is plotted versus wavelength for an n-type aluminum-doped crystal with an electron concentration of 6×10^{17} cm^{-3}.

This interpretation of optical-mode scattering is consistent with the partially polar character of Mg_2Ge and with electrical measurements in which it was suggested that optical-mode scattering is important at low temperatures.[5] However, the possibility of a combination of other scattering mechanisms giving rise to the $\lambda^{2.5}$ free-electron absorption cannot be discounted.

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