INFRARED ABSORPTION IN MAGNESIUM SILICIDE
AND MAGNESIUM GERMANIDE[*]

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ABSTRACT

Infrared absorption spectra of several n-type Mg_2Si and Mg_2Ge
single crystals were obtained in the wavelength regions from 1 micron
to 13 microns and 1 micron to 7 microns, respectively, over the tempera-
ture range from 85°K to 370°K. Free carrier absorption occurred
in Mg_2Si at the longer wavelengths. The absorption edges appeared
to be due to indirect transitions and the shift of the optical energy gap
with temperature is estimated to be -5×10^{-4} ev(K°)$^{-1}$ for Mg_2Si and
-6.5×10^{-4} ev(K°)$^{-1}$ for Mg_2Ge. No values for the gaps were determined
from the present data but they can be seen to be approximately equal to
the gaps determined by electrical measurements. An absorption peak
at 0.40 ev in n-type Mg_2Si was observed and is discussed.

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1. INTRODUCTION

Magnesium silicide and magnesium germanide are semiconducting compounds which crystallize in the antifluorite structure. The temperature dependence of their electrical properties has been studied in some detail by Winkler,[1] Morris, Redin and Danielson,[2,3] and Nelson;[4] but their infrared absorption spectra as functions of temperature have not been available. Nelson[4] obtained an infrared absorption spectrum of an n-type Mg_2Si single crystal at room temperature. The temperature dependence of the optical energy gap was not determined experimentally. On the basis of questionable assumptions, Winkler[1] predicted a temperature coefficient of the energy gap of -6.4×10^{-4} ev per degree K for Mg_2Si and -7.6×10^{-4} ev per degree for Mg_2Ge. The purpose of this research was to study the optical energy gaps in Mg_2Si and Mg_2Ge.

2. EXPERIMENTAL PROCEDURE

The crystals used in this investigation were taken from the same ingots as those used by Morris, Redin and Danielson. The preparation of these crystals is described in their papers.[2,3] For most of the measurements the samples were ground to thin plates, approximately 6 mm, by 6 mm, by 0.3 mm, with silicon carbide paper. Final polishing with a suspension of powdered alumina in distilled water (Mg_2Si) or absolute alcohol (Mg_2Ge) was done on a rotating wheel covered with a short nap cloth.

The optical measurements on these samples were made with a Perkin Elmer Model 13 spectrometer equipped with a KBr or CaF_2

prism, and used in double beam operation in which data proportional to the optical density of the samples were obtained. The samples were mounted in an evacuated metal cryostat provided with NaCl windows. Engelhard CA 9R cement mixed with silver paste held the sample to the temperature bath without cracking due to differential thermal expansion.

Some thinner samples (0.10 to 0.18 mm) were prepared, but these usually broke into very small pieces during polishing. The largest piece of each crystal was mounted in a cryostat built to fit the stage of the microscope attachment of a Perkin Elmer Model 112 spectrometer, used in single-beam operation with a quartz prism. These samples were used to obtain absolute values of the absorption coefficients.

The doping agents and the sample resistivities are given in Table 1. The resistivities were measured by the four probe method described by Valdes.[5] All of the samples were n-type semiconductors.

Table 1. Doping Agents and Resistivities of Samples

| | Sample Number | Doping Agent | | Resistivity ohm cm |
		element	per cent by weight	
Mg_2Si	23B01	silver	0.02	0.18
Mg_2Si	27B01	iron	0.023	0.45
Mg_2Si	28B04	aluminum	0.03	0.16
Mg_2Ge	13B1	none		~1

3. RESULTS

The absorption spectra of two Mg_2Si samples are shown in Figs. 1 and 2. The spectrum of 23B01 was similar to that of 28B04. At high photon energies each spectrum showed an absorption edge caused by electronic transitions across the band gap. At 0.40 ev a broad absorption band, which was observed in the spectra of all three Mg_2Si samples, decreased in height and width with decreasing temperature. It was less prominent in the sample of highest resistivity. At wavelengths beyond 8 microns, the absorption in each sample was proportional to the square of the wavelength, as predicted by the classical Drude theory for free charge carrier absorption.

The Mg_2Ge spectra exhibited an absorption edge at slightly longer wavelengths than the Mg_2Si edge. There was no absorption peak between the edge and 7 microns. Free carrier absorption was not observed for wavelengths shorter than 7 microns.

Figure 3 shows the absorption coefficient (α) in the region of the absorption edge for Mg_2Ge 13B1 and Mg_2Si 27B01 at several temperatures. The absorption coefficients were obtained by applying the formula

$$\frac{I}{I_o} = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}$$

to the data taken on the thinnest samples with the microscope attachment, d is the sample thickness. R, the reflection coefficient, was found by applying the above formula to I/I_o far from the absorption
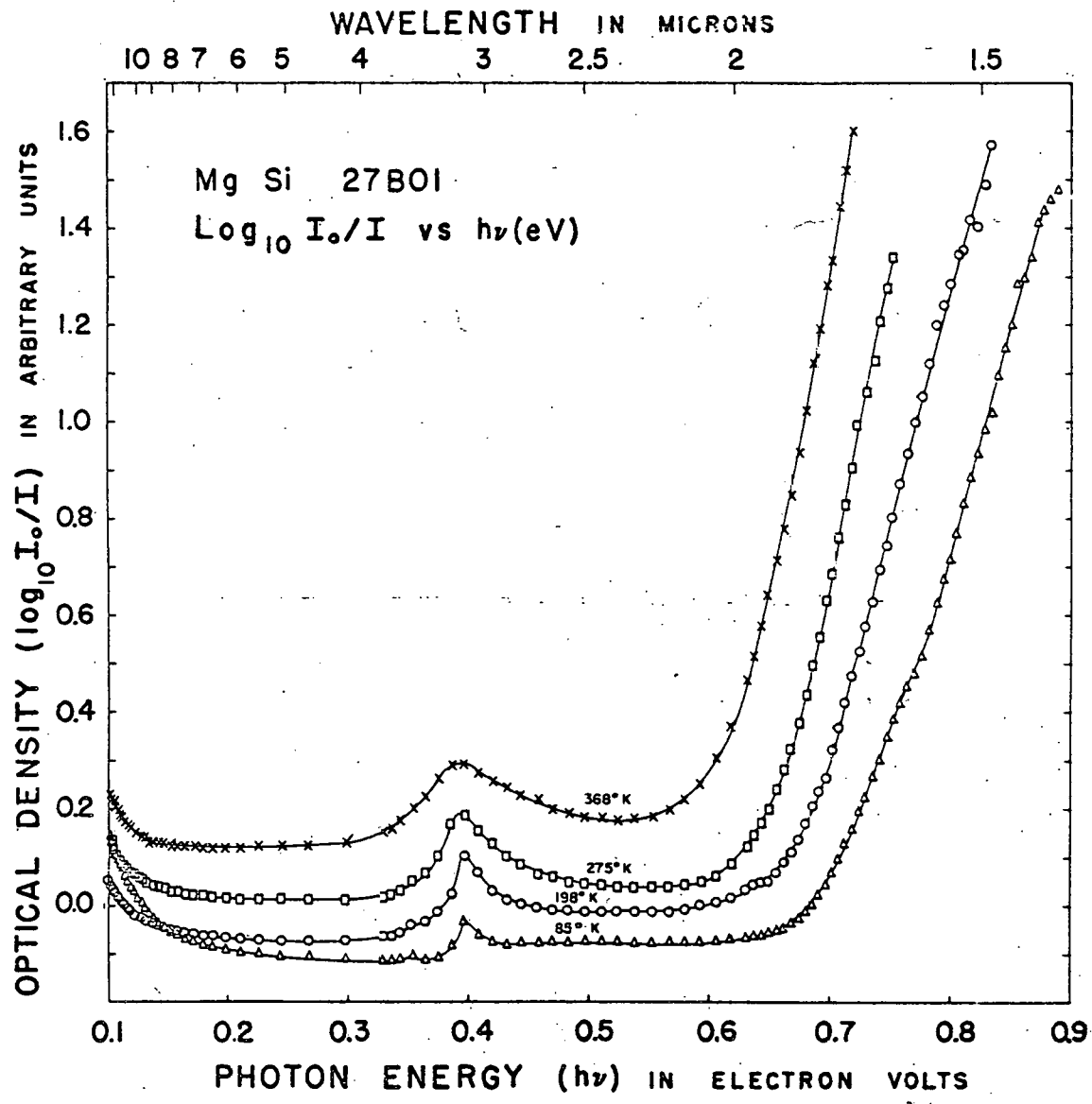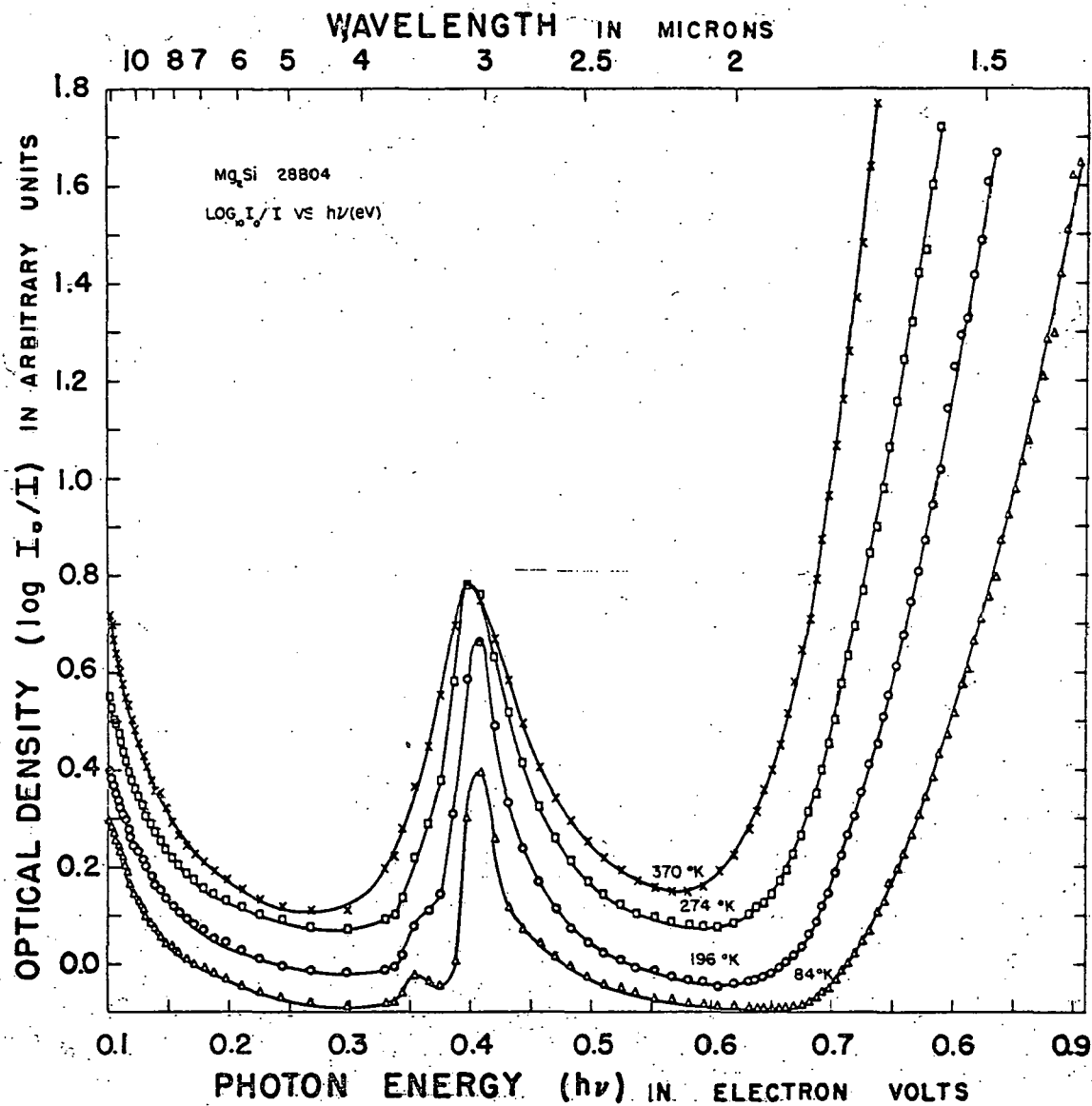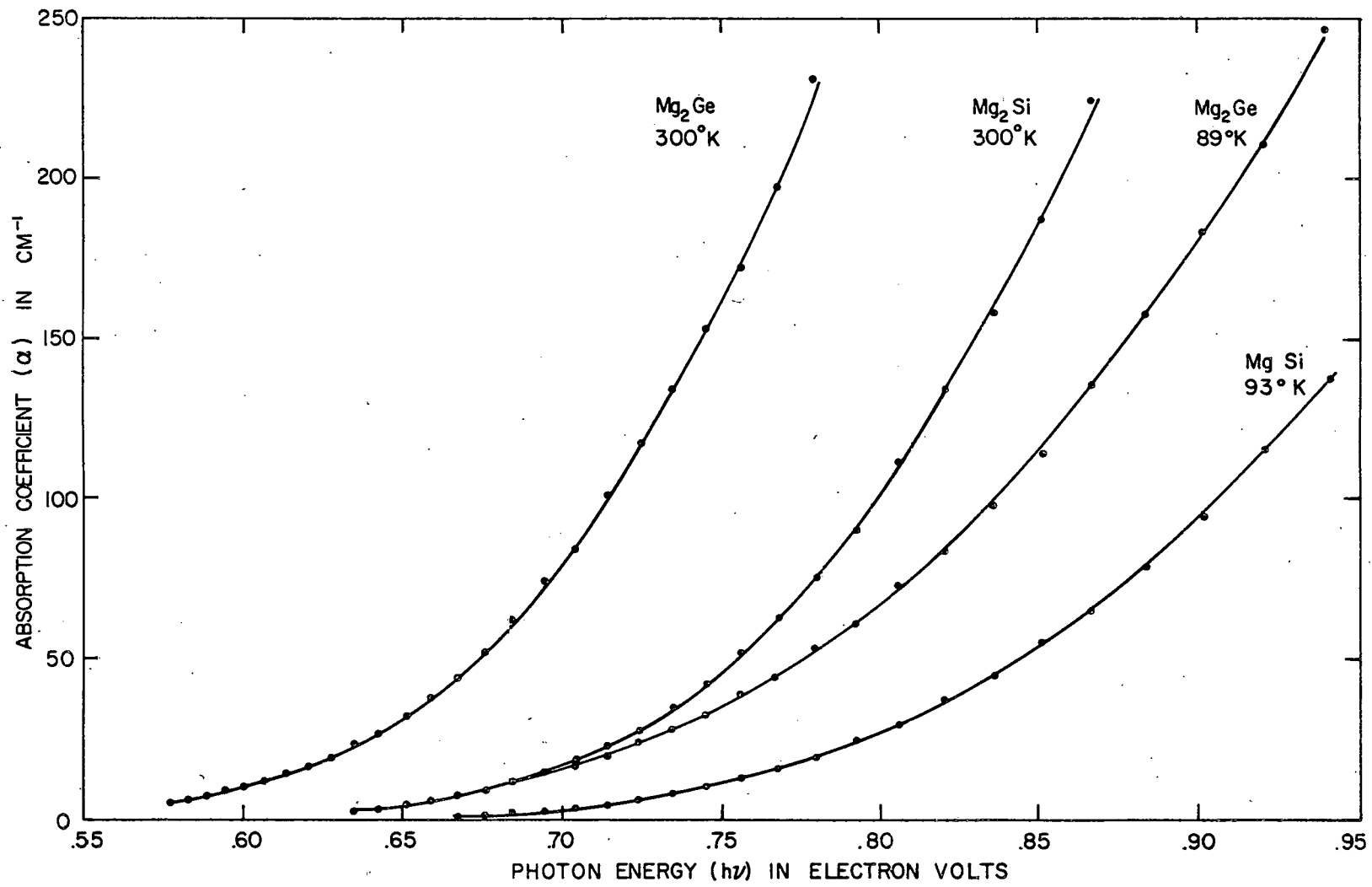
Figure 1

Figure 2

Figure 3

edge so that $\alpha \sim 0$. This method could be used only on the purer samples which had less free-carrier absorption; and in the case of Mg_2Si, only when the peak around 0.40 ev was small. In these samples there was a wavelength region throughout which I/I_o was constant. This region of maximum transmission was used to obtain R, which varied from 0.45 to 0.75. A series of spectra on different samples at room temperature gave nearly identical α vs ν curves even though R varied from sample to sample. It should be noted that the approximate expression, $I/I_o = (1-R)^2 \exp(-\alpha d)$, is not always valid in the present work because of the large reflection coefficients. Thus the ordinates in Figs. 1 and 2 are not directly proportional to α for the smaller values of I_o/I.

4. DISCUSSION

The transitions in the edge appear to be indirect transitions involving the creation or destruction of a phonon in the absorption process. Indirect transitions are inferred from plots of log α vs log $(h\nu-h\nu_t)$ where $h\nu_t$ is taken to be the photon energy at which the curve of I/I_o vs $h\nu$ begins to depart from a straight line, i.e. the low energy limit of edge transitions detectable in our samples. These plots were linear with slopes, n, in the range 2.5 to 3.5 for both compounds at all temperatures. The values of n obtained are sensitive to the choice of $h\nu_t$ but remain within the above limits for all reasonable values of $h\nu_t$. For direct transitions one expects n to be 1/2 or 1/3 while an n of 2 or 3 is expected for indirect transitions.[6]

It is difficult to associate a part of the absorption edge with the band gap. Plots of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ vs $h\nu$ yielded two straight line segments which made a fit of the data to the formula of Macfarlane and Roberts,[7]

$$\alpha h\nu = A \left[\frac{(h\nu - E_G + k\theta)^n}{\exp(\theta/T) - 1} + \frac{(h\nu - E_G - k\theta)^n}{1 - \exp(-\theta/T)} \right] , \quad n = 2 \text{ or } 3,$$

seem likely. The fit with least scatter was obtained with the Mg_2Si data using $n = 2$. This fit gave a gap energy, E_G, which extrapolated to 0.71 ev at $0°K$, a phonon energy of about 0.053 ev, corresponding to $\theta = 600°K$, but values of A which varied widely with temperature. Better data for small absorption coefficients are needed before a reliable fit to the above formula can be made. Our absorption coefficients in the beginning of the edge could be in error due to the imprecise knowledge of R and its unjustified extrapolation to shorter wavelengths. It is clear from Fig. 3 that the absorption edge at $90°K$ begins near the photon energies corresponding to the gaps at $0°K$ determined from electrical measurements by Morris, Redin, and Danielson, [2, 3] 0.69 ev and 0.78 ev for Mg_2Ge and Mg_2Si, respectively.

The shift of the energy gap with temperature, $\left(\frac{\partial E_G}{\partial T} \right)_p$, is of interest in connection with the transport properties. One way to determine this shift is to use the displacement with temperature of of a point on the edge having constant absorption coefficient. [8] This method is more reliable if the shift is the same for all values of α or

if the absorption coefficient curves for various temperatures can be made to coincide by horizontal and vertical translations. The Mg_2Ge and Mg_2Si edges cannot be made to coincide by any shift or even by a rotation and translation. If a value of $\alpha = 100 \text{ cm}^{-1}$ is chosen the resultant temperature shift of the corresponding point on the edge of each compound is linear between 90° and 370°K. The shifts are -5×10^{-4} ev/K° and -6.5×10^{-4} ev/K° for Mg_2Si and Mg_2Ge respectively. See Fig. 4. If the intercepts with the $h\nu$ axis of the plots of $(\alpha h\nu)^{1/2}$ or $(\alpha h\nu)^{1/3}$ va $h\nu$ are used as a measure of the gap the resultant temperature shifts are about half the above values. The fit to the formula of Macfarlane and Roberts yields temperature shifts also about half the above values, but the latter methods of describing the gap rely on small values of α which are not reliable in the present work. It should be noted that the analysis of Fan usually gives larger values of $(\frac{\partial E_G}{\partial T})_p$ than does the analysis of Macfarlane and Roberts. (Compare $(\frac{\partial E_G}{\partial T})_p$ of Ref. 8 with those of Ref. 7 and 9.)

The absorption band at 0.40 ev in Mg_2Si appears to be due to transitions from a conduction band minimum to a higher conduction band. Such transitions are believed to occur in n-type Si,[10] n-type GaAs,[11] and n-type AlSb.[12] For each Mg_2Si sample the temperature dependence of the peak height of the 0.40 ev band was roughly correlated with the temperature dependence of the concentration of conduction electrons as determined from Hall coefficient measurements on samples cut from adjacent parts of
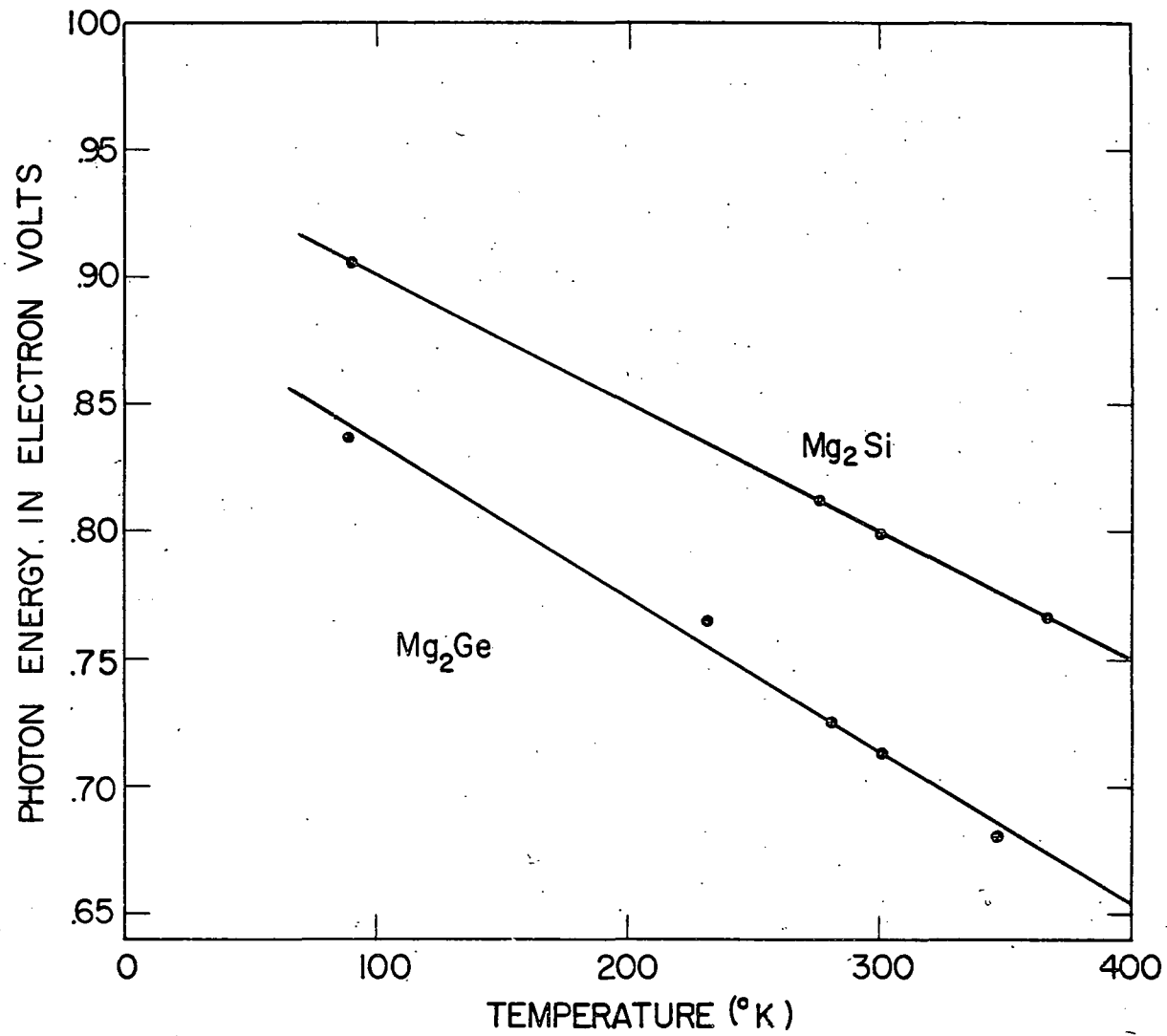
Figure 4

the same ingots. [2]   This band appeared in all n-type samples regardless of doping agent but not in a p-type sample doped with Cu.   The band shifts to higher energy as the sample is cooled, but the shifts vary from 0.012 ev (28B01) to 0.06 ev (23B01) for the interval from 370° to 84°K.   Low temperature Hall coefficients are not amenable to analysis for activation energies and do not seem to have the same general characteristics in the three samples. [2, 13]   Thus the shift of the 0.40 ev band upon cooling cannot be correlated yet with the capture of conduction electrons by donors.

The very small absorption maximum near 0.35 ev has not been positively identified.   It may be caused by a trapping level whose absorption is masked at high temperatures by the increased width of the 0.40 ev absorption band.

Further work is being undertaken to obtain more reliable values of the absorption coefficient in the low energy part of the edge.   Purer crystals are now available*. and it is hoped that reflection coefficients can be measured.   Photoconductivity measurements are also being undertaken to obtain information on the gap energy and the nature of the 0.40 ev peak in Mg_2Si.

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* Room temperature resistivities of ~ 1 ohm-cm for Mg_2Si and ~ 10 ohm-cm for Mg_2Ge. [14]

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FIGURE CAPTIONS

Fig. 1. Optical density vs photon energy of Mg_2Si sample 27B01.
The ordinates shown are for a temperature of 368°K; the
other curves are displaced downward for clarity.

Fig. 2. Optical density vs photon energy of Mg_2Si sample
28B04. The ordinates shown are for a temperature of
370°K; the other curves are shifted downward for clarity.

Fig. 3. Absorption edge of Mg_2Si and Mg_2Ge at 300° and 90°K.

Fig. 4. Shift with temperature of the point on the absorption edge
for which $a = 100$ cm^{-1}.