This disseration has been 63-1588 microfilmed exactly as received

McWILLIAMS, Donald Arthur, 1929– INFRARED INDICES OF REFRACTION AND REFLECTIVITIES OF Mg<sub>2</sub>Si, Mg<sub>2</sub>Ge AND Mg<sub>2</sub>Sn.

Iowa State University of Science and Technology Ph.D., 1962 Physics, solid state

University Microfilms, Inc., Ann Arbor, Michigan

- -

INFRARED INDICES OF REFRACTION AND REFLECTIVITIES OF Mg<sub>2</sub>Si, Mg<sub>2</sub>Ge AND Mg<sub>2</sub>Sn

by

Donald Arthur McWilliams

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physics

### Approved:

Signature was redacted for privacy.

#### In Charge of Major Work

Signature was redacted for privacy.

## Head of Magor Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University Of Science and Technology Ames, Iowa

## TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	DETERMINATION OF THE INDEX OF REFRACTION IN THE INFRARED	8
III.	MEASUREMENT OF REFLECTIVITY	23
IV.	REFLECTIVITY RESULTS	30
V.	DISCUSSION	34
VI.	BIBLIOGRAPHY	47
VII.	ACKNOWLEDGMENTS	50
VIII.	APPENDIX A: LIST OF SYMBOLS	51
IX.	APPENDIX B: CLASSICAL OSCILLATOR EQUATIONS WITH FIGURES AND PRINTED COMPUTER SOLUTIONS	53
Х.	APPENDIX C: INDEX OF REFRACTION DETERMINATION DATA	60
XI.	APPENDIX D: REFLECTIVITY DETERMINATION DATA	63

.

# LIST OF FIGURES

Figure 1.	Apparatus for determining the index of refraction by minimum deviation	9
Figure 2.	Index of refraction versus wavelength for NaCl III prism	12
Figure 3.	Index of refraction versus wavelength for Si III prism	13
Figure 4.	Index of refraction versus wavelength for a Ge prism	14
Figure 5.	Index of refraction versus wavelength for Mg <sub>2</sub> Si III prism	15
Figure 6.	Index of refraction versus wavelength for Mg <sub>2</sub> Si III prism	16
Figure 7.	Index of refraction versus wavelength for Mg <sub>2</sub> Ge I prism	18
Figure 8.	Index of refraction versus wavelength for Mg <sub>2</sub> Sn I prism	20
Figure 9.	Summary of index of refraction measurements	21
Figure 10	Apparatus for the reflectivity determination	24
Figure 11	Reflectivity of NaCl	28
Figure 12	Reflectivity of Mg <sub>2</sub> Si	31
Figure 13	Reflectivity of Mg <sub>2</sub> Ge	32
Figure 14	Reflectivity of Mg <sub>2</sub> Sn with different	
	carrier concentrations	33
Figure 15	. Reflectivity of a classical oscillator compared to the reflectivity of Mg <sub>2</sub> Si II	35
Figure 16	Reflectivity of a classical oscillator compared with the reflectivity of Mg <sub>2</sub> Si II	36

-

iii

Figure 17.	Reflectivity of a classical oscillator compared with the reflectivity of Mg <sub>2</sub> Ge I	37
Figure 18.	Reflectivity versus wavelength for p-doped Mg <sub>2</sub> Ge and a classical oscillator with free carrier modifications	41
Figure 19.	Reflectivity of the Mg compounds versus energy	դդ
Figure 20.	Extinction coefficient versus wave- length for a classical oscillator	55
Figure 21.	Susceptibility versus wavelength for a classical oscillator	56
Figure 22.	Conductivity/frequency versus wave- length for a classical oscillator	57
Figure 23.	Index of refraction versus wavelength for a classical oscillator	<b>5</b> 8
Figure 24.	Approximate wavelength calibration for a 12° CsI prism in the Perkin-Elmer Model 160 monochromator	68

## LIST OF TABLES

Page

Table 1.	Refractive index of Mg <sub>2</sub> Si III	1 <b>7</b>
Table 2.	Refractive index of Mg <sub>2</sub> Ge I	19
Table 3.	Refractive index of Mg <sub>2</sub> Sn I	22
Table 4.	Wavelength ranges, prisms and filtering techniques	26
Table 5.	Computer solution for a classical oscillator	59
Table 6.	Sextant calibration	60
Table 7.	Minimum deviation data for Mg <sub>2</sub> Sn I	60
Table 8.	Minimum deviation data for Mg <sub>2</sub> Si III	61
Table 9.	Minimum deviation data for Mg <sub>2</sub> Ge I	62
Table 10.	Reflectivity data - CsI prism	64

#### I. INTRODUCTION

#### A. Purpose of This Experiment

This work was undertaken with the hope that some new light could be cast on the properties of Mg<sub>2</sub>Si, Mg<sub>2</sub>Ge and Mg<sub>2</sub>Sn. The optical properties of many semiconducting materials have been summarized by Moss (1). In semiconductors the optical properties have been very useful in determining, typically, the mechanisms of electrical conduction, the structure of the energy gap, the interatomic forces in the crystals, the surface properties of the materials, the effective masses of the carriers and the mechanisms of light absorption and photoconductivity.

The primary purpose of this experiment was to add to current knowledge of these Mg compounds. In particular, the effective mass of the carriers might be determined from the index of refraction or the reflectivity. Simultaneously, one might obtain the optical dielectric constant and the static dielectric constant, with the difference of these giving the ionicity. The optical data for the Mg compounds could be compared with other materials for similarities or differences. An indication of the effect of the atomic lattice on the reflectivity would give useful information to people studying the interatomic forces in the Mg compounds and other materials.

#### B. Previous Work

The preparation and electrical properties of  $Mg_2Si$  have been discussed by Morris (2) and Whitsett (3); of  $Mg_2Ge$  by Redin (4); of  $Mg_2Sn$  by Blunt <u>et al</u>. (5). The optical transmission of  $Mg_2Ge$  and  $Mg_2Si$  was discussed by Koenig <u>et al</u>. (6); of  $Mg_2Sn$  by Blunt <u>et al</u>. (5).

Several people have made Hall effect measurements on the Mg compounds and have obtained estimates for the effective masses of the carriers. Morris (2) reported the effective mass of electrons,  $m_e^*$ , in Mg<sub>2</sub>Si as 0.46 m, where m is the mass of the electron. He also reported  $m_h^* = 0.87$  m where  $m_h^*$  is the effective mass of the hole. His work differs from Winkler's (7) results, which were  $m_e^* = 0.36$  m and  $m_h^* = 0.72$  m. Redin (4) studied Mg<sub>2</sub>Ge and gave  $m_e^* = 0.18$  m and  $m_h^* = 0.31$  m. All of these people report a lack of confidence in the values reported due to the number of assumptions made. Blunt <u>et al</u>. (5) reported  $m_e^* = 1.17$  m and  $m_h^* = 1.28$  m for Mg<sub>2</sub>Sn.

Heller (8) studied the Seebeck effect in  $Mg_2Si$  and obtained  $m_e^* \approx 0.5 \text{ m}$  and  $m_h^* \approx 2 \text{ m}$ . There is also reason for uncertainty in these values.

There seems to be no previous reported work on the determination of the indices of refraction or the reflection spectra of these compounds in the infrared region. It is

possible, using an approximation given by Moss (9, p. 61), to arrive at an approximate value for the optical dielectric constant based on observations of the energy gap in different semiconducting materials. Moss notes that for many semiconducting materials the product of the dielectric constant squared and the energy gap is equal to a constant value. Madelung (10) obtained a value of 155 on an average of 8 values for different materials. Using Madelung's average, with an energy gap of 0.78 ev obtained by Morris (2) for Mg<sub>2</sub>Si, one obtains  $\mathcal{E} = 14$  for Mg<sub>2</sub>Si. Morris (2), using this value of  $\mathcal{E}$  in his analysis of the mobility of Mg<sub>2</sub>Si, obtained reasonable agreement between theory and experiment.

C. Remarks on the Theory of Optical Measurements

A general discussion of the optical properties of semiconductors is given by Moss (1); the notation in this paper agrees with his and is given in Appendix A. All expressions and data are in MKS units.

In vacuum the electric field of a light wave can be written in the form

$$E = E_{o} \exp i \omega (\frac{x}{c} - t)$$

where  $E_0$  is a constant called the amplitude,  $\frac{\omega}{2\pi}$  is the frequency, x is the displacement of the wave parallel to the

motion of the light wave, t is the time and c is the speed of light. Inside isotropic matter the light wave can be expressed as

$$E = E_o \exp i \omega (\frac{Nx}{c} - t)$$
.

Allowing for the possibility that  $\underline{N}$  is complex, one usually writes

$$\underline{N} = n - ik$$

where n is the index of refraction and k is the extinction coefficient.  $\underline{N}^2$ , of course, is complex and

$$\underline{N}^2 = n^2 - k^2 - 2 \operatorname{in} k \, .$$

Maxwell's equations for a conducting medium can be solved to show that the dielectric constant is  $n^2 - k^2$  and  $2nk = \frac{\sigma}{\omega E_o}$ , where  $\sigma$  is the conductivity [Moss (1, p. 1)].

The measurement of the index of refraction, n, of a material can yield the optical dielectric constant,  $\in$ , since, when the extinction coefficient, k, is small compared with n, as it must be in any transparent crystal,

$$\epsilon = n^2 - k^2 \approx n^2$$
.

In the transparent region k is quite small, as can be seen from the relationship between K, the absorption coefficient, and k.

$$K = \frac{4 \pi k}{\lambda} .$$

 $\lambda$  is the wavelength of the incident light. A crystal 1 millimeter thick transmitting 0.01 of the incident light would have a value of K = 4600 per meter. With  $\lambda$  = 5 microns, k = 1.83 x 10<sup>-3</sup>, which is quite small compared with typical values of n which are greater than 1.0.

Similarly, when  $k \ll n$ , n and  $\epsilon$  can be determined from the normal reflectivity, R, which is given by the expression [Moss (1, p. 6)]

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

In the region where changes in n and R are due only to free carriers, one can determine the effective mass,  $m^*$ , of the carriers by using the classical equations of motion of a particle under the influence of an oscillating field. The appropriate equation [Moss (1, p. 236)] is

$$n^2 - k^2 = \epsilon - \frac{Ne^2}{m^* \epsilon_e \omega^2}.$$

Here  $\in$  is the near infrared dielectric constant and  $\mathcal{E}_o$ is the dielectric constant of free space. A determination of the effective mass could not be made for the studied Mg compounds because the influence of the atomic lattice on the reflectivity was pronounced and the free carrier contribution could not be evaluated. In addition to the free carrier contribution to the optical properties of solids, one finds that electromagnetic radiation interacts with bound charges in the atomic lattice. In a classical sense the electric field of the light induces motion of the ions in the lattice. Kittel (11, p. 103) discusses the elementary arguments which lead to the possible ways (modes) in which these atoms may move with respect to one another. He shows how a local charge separation (electric dipole moment) can occur with which an incident electromagnetic wave can interact. Whitten (12) has studied  $Mg_2Si$  and gives for the modes with a dipole moment (optical mode) in the limit of long phonon wavelengths

$$\mathcal{M}\mathcal{W}^2 = \mathbf{f}$$

 $\mathcal{M}$  is the reduced mass of the unit cell,  $\frac{\omega}{2\pi}$  is the frequency of the mode and f is a function of the restoring forces in the crystal. f can have two values. One of these values corresponds to a transverse mode of vibration and the other to a longitudinal mode. Incident light, being a transverse wave, cannot interact with the longitudinal optical mode. However, Lyddane, Sachs and Teller [Fröhlich (13)] have derived a relation between the frequencies of the two modes.

$$\omega_{\rm L} = \left(\frac{\epsilon}{\epsilon_o}\right)^{1/2} \omega_{\rm r}$$

where  $\mathcal{E}_{o}$  is the static dielectric constant,  $\mathcal{E}$  the near

infrared dielectric constant,  $\omega_r$  the frequency of the transverse optical mode and  $\omega_L$  the frequency of the longitudinal optical mode.

The longitudinal optical mode cannot be detected with light, but it does interact with charges inside the lattice, and contributes to the electrical resistance of a crystal by interacting with the current carriers. The frequency of the longitudinal mode enters into the calculation of the optical mode scattering by polar crystals and is discussed by Ziman (14, p. 434).

Additionally, an estimate can be made of an upper limit to  $\epsilon_o$ , the static dielectric constant, by examining the reflectivity of a pure crystal on the long wavelength side of  $\omega_r$ . As is shown in Appendix B, k for a classical oscillator drops to a small value at long wavelengths. If the influence of free carriers is neglected, the index of refraction, determined from the limiting value of the reflectivity, should be close to  $\epsilon^{1/2}$ . With semiconductors, it is not possible to ignore the contribution of free carriers to the reflectivity since k for free carriers becomes larger as the frequency of the incident light decreases and may not be negligible in the reflectivity equations. A qualitative understanding of this conclusion is indicated by the equation relating n, k and  $\sigma$ , the conductivity, [Moss (1, p. 2)].

7a

$$2nk = \frac{\sigma}{\omega \mathcal{E}_o}$$

cr

$$k = \frac{\sigma}{2n \, \omega \, \varepsilon_o} \, .$$

This shows that k can get quite large as  $\omega$  decreases.

It is not yet possible to grow crystals of the Mg compounds pure enough to obtain even an approximation to  $\epsilon_o$ . It is only possible to establish an upper limit to  $\epsilon_o$ . The high conductivity also prevents the determination of  $\epsilon_o$  by electrical means.

# II. DETERMINATION OF THE INDEX OF REFRACTION IN THE INFRARED

#### A. Experimental Technique

This experiment obtained the indices of refraction of prisms of  $Mg_2Si$ ,  $Mg_2Ge$  and  $Mg_2Sn$  by the minimum deviation method. A diagram of the equipment is shown in Figure 1. A standard Perkin-Elmer monochromator was modified to accommodate a collimator, sample holder and movable detector. Light from a Globar was passed through a 13 cycles-per-second chopper and reflected from a flat mirror to a sourcefocusing mirror focused on the entrance slit of a NaCl monochromator. Light passing from the exit slit of the monochromator was incident on a focusing mirror called a receiving mirror. This mirror, in combination with the collimating mirror, caused the light beam from the exit slit to be collimated in the horizontal plane. The beam was then reflected to the sample by the small flat extraction mirror. Although the light did diverge vertically through the prism, the precision of the Si index of refraction determination indicates the curvature of the beam was negligible. After leaving the sample prism, which could be rotated to obtain minimum deviation, the light passed through two defining slits as shown in Figure 1 before being focused on the thermocouple detector by the detector mirror. The angle at which

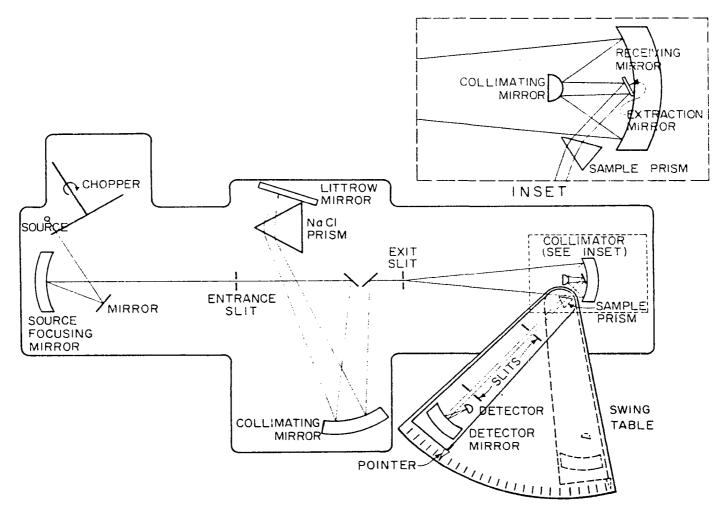


Figure 1. Apparatus for determining the index of refraction by minimum deviation

the refracted beam was detected was measured on the swing table and the point of maximum light was determined by the excursion of a Brown potentiometer driven by a Perkin-Elmer amplifier.

The sample was glued to a holder and ground with emery paper to the proper dimension (approximately 10°). The prism was then polished with  $Al_20_3$  on a nap cloth. The sample prism was mounted on a small brass table with clay and a standard spectrometer was used to determine the prism apex angle. A slit, illuminated with white light, was imaged in the eyepiece of the spectrometer by reflection from alternate sides of the mounted sample prism centered on the spectrometer table. The rotation angle of the spectrometer table could be read to 20 seconds of arc and the difference of the two readings obtained from opposite sides of the prism was used as the effective apex angle of the sample prism. This measurement gave the apex angle with an error of less than 1 minute. The prism and the prism table were then transferred to the monochromator swing table and a minimum deviation determination was done. The swing table arc was calibrated to ± 2 minutes of arc. The data thus obtained were substituted in the minimum deviation equation

$$n = \frac{\sin (\alpha + \delta)/2}{\sin \delta/2}$$

where  $\delta$  is the apex angle and  $\propto$  is the angle of minimum deviation. One can see that it is important to measure the effective apex angle accurately when it is small.

The equipment was tested by running various prisms of different materials. Prisms of NaCl, Si and Ge were made and measured with the same technique used for the prisms of Mg<sub>2</sub>Si, Mg<sub>2</sub>Ge and Mg<sub>2</sub>Sn.

Figure 2 shows the comparison of four datum points from NaCl prism III with the data of Coblentz (15). Several Si prisms were run. Silicon prism III is a prism made of Dow Corning hyper-pure p-type Si with 2500 Ohm-centimeters resistivity. The values for the index of refraction obtained on this equipment are compared in Figure 3 with the data of Salzberg and Villa (16). Similarly, a Ge prism of unknown purity is compared in Figure 4 with the data of Salzberg and Villa (16).

#### B. Experimental Results

The values obtained for the index of refraction of  $Mg_2Si$  III are given in Table 1. These values are plotted in Figure 5. The high absorption of the prism in the long wavelength region made it necessary to use wide slits. This decreased the precision of the determination because the beam was not collimated when wide slits were used. Figure 6 shows the data of  $Mg_2Si$  III in an expanded plot which gives a better

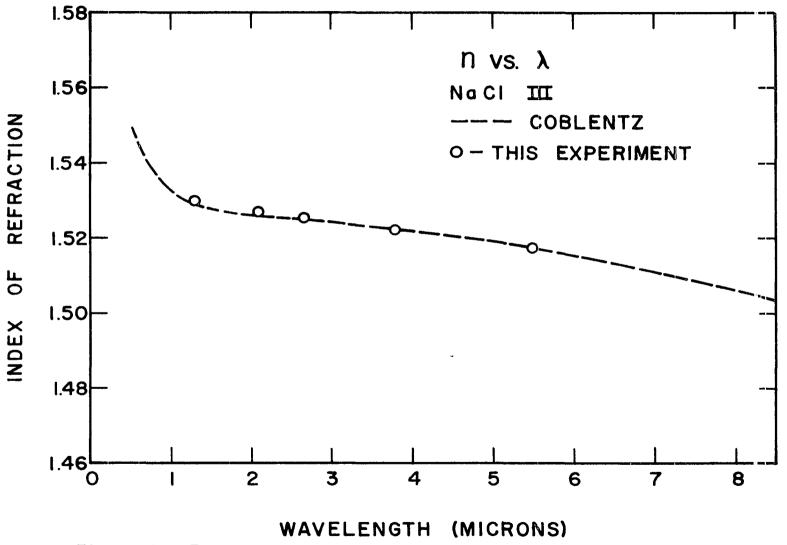
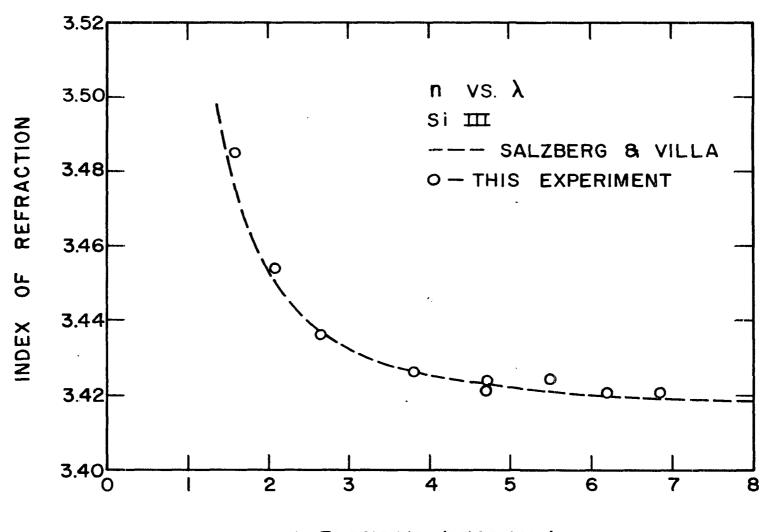


Figure 2. Index of refraction versus wavelength for NaCl III prism



WAVELENGTH, (MICRONS) Figure 3. Index of refraction versus wavelength for Si III prism

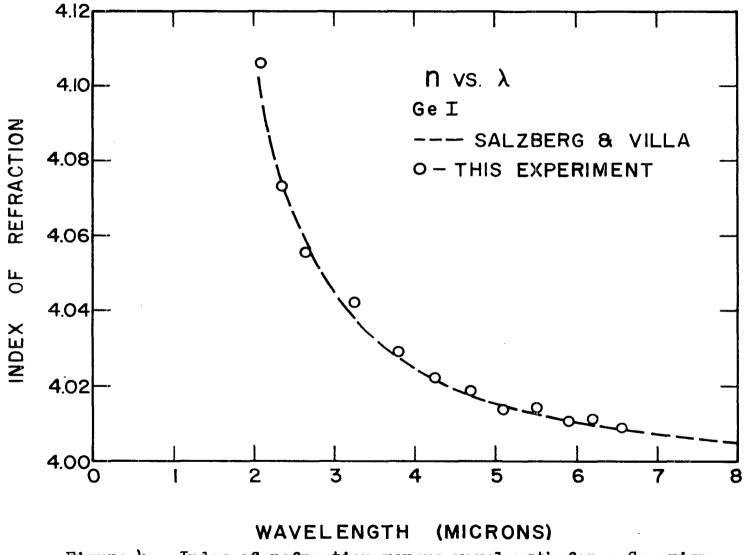


Figure 4. Index of refraction versus wavelength for a Ge prism

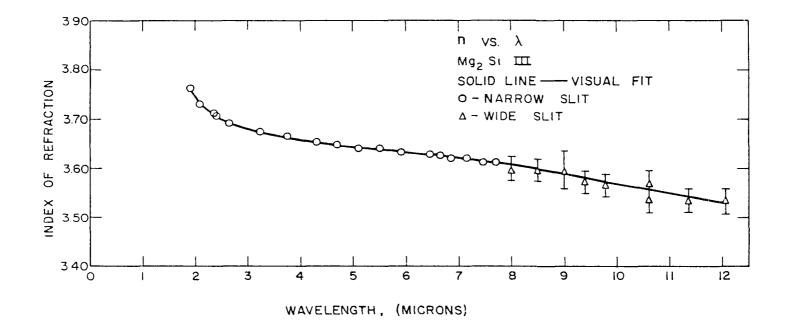
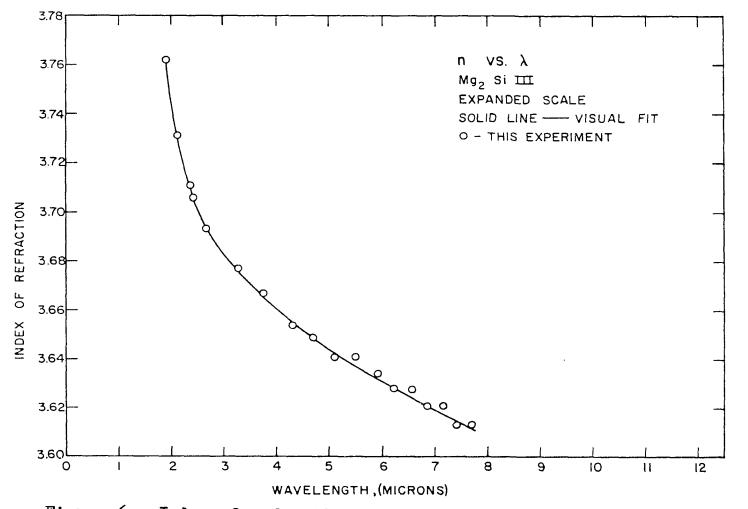


Figure 5. Index of refraction versus wavelength for Mg2Si III prism



.

Figure 6. Index of refraction versus wavelength for Mg<sub>2</sub>Si III prism

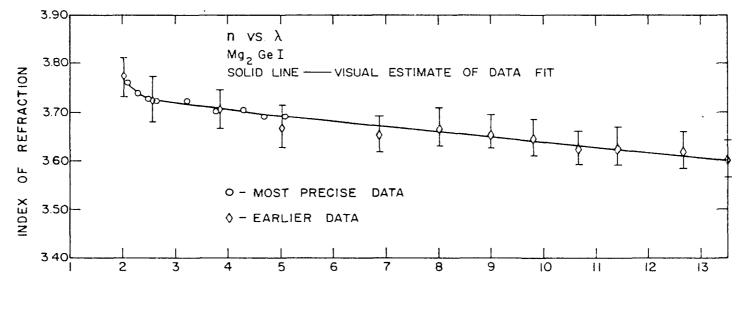
Wavelength (microns)	Index of refraction
$1.90 \pm 0.01$ $2.10 \pm 0.01$ $2.35 \pm 0.01$ $2.40 \pm 0.01$ $2.65 \pm 0.01$ $3.25 \pm 0.01$ $3.77 \pm 0.01$ $4.26 \pm 0.01$ $4.70 \pm 0.01$ $5.52 \pm 0.01$ $5.52 \pm 0.01$ $5.90 \pm 0.01$ $6.23 \pm 0.01$ $6.23 \pm 0.01$ $6.86 \pm 0.01$ $7.16 \pm 0.01$ $7.45 \pm 0.01$ $7.45 \pm 0.01$ $7.72 \pm 0.01$ $9.00 \pm 0.01$ $10.60 \pm 0.01$	$3.76 \pm 0.01$ $3.73 \pm 0.01$ $3.71 \pm 0.01$ $3.71 \pm 0.01$ $3.69 \pm 0.01$ $3.68 \pm 0.01$ $3.68 \pm 0.01$ $3.65 \pm 0.01$ $3.65 \pm 0.01$ $3.65 \pm 0.01$ $3.64 \pm 0.01$ $3.63 \pm 0.01$ $3.63 \pm 0.01$ $3.63 \pm 0.01$ $3.63 \pm 0.01$ $3.62 \pm 0.01$ $3.62 \pm 0.01$ $3.61 \pm 0.01$ $3.61 \pm 0.01$ $3.61 \pm 0.01$ $3.63 \pm 0.02$

Table 1. Refractive index of Mg2Si III

indication of the data scatter in a restricted region of 1-8 microns. Several other Mg<sub>2</sub>Si prisms gave the same results.

Figure 7 similarly shows a plot of the values for  $Mg_2Ge$  I given in Table 2. Here different prisms have been plotted with the precision indicated at each datum point. Where no error bar appears in the previous figures, the size of the data circle indicates the error of the determination, except for Figure 6.

All the available  $Mg_2Sn$  was highly absorbing and therefore required wide slits in order to make any determination



WAVELENGTH, (MICRONS)

Figure 7. Index of refraction versus wavelength for  $Mg_2Ge$  I prism

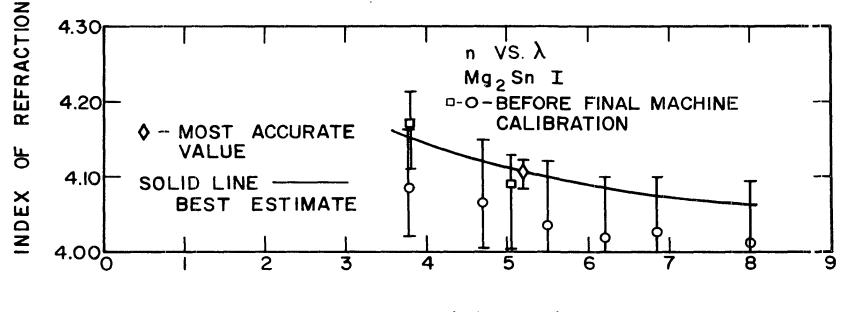
Wavelength (microns)	Index of refraction
$2.10 \pm 0.01$ $2.35 \pm 0.01$ $2.40 \pm 0.01$ $2.40 \pm 0.01$ $2.65 \pm 0.01$ $3.25 \pm 0.01$ $3.77 \pm 0.01$ $4.26 \pm 0.01$ $4.70 \pm 0.01$ $5.12 \pm 0.01$	$3.76 \pm 0.01$ $3.74 \pm 0.01$ $3.73 \pm 0.01$ $3.72 \pm 0.01$ $3.72 \pm 0.01$ $3.72 \pm 0.01$ $3.72 \pm 0.01$ $3.70 \pm 0.01$ $3.70 \pm 0.01$ $3.69 \pm 0.01$ $3.69 \pm 0.01$

Table 2. Refractive index of  $Mg_2Ge I$ 

at all. However, at the point of maximum transmission, approximately 5.2 microns, one measurement was made with a reasonably small error. This single value, combined with the data obtained with wider slits and the observation that widening the slits lowers the measured value of the index of refraction, led to the solid line plotted in Figure 8. These data are given in Table 3. The Mg<sub>2</sub>Sn was obtained from H. Guennoc of the Compagnie generale de. T.S.F., Paris, France.

Figure 9 is a summary of the data presented thus far.

The possible errors indicated in Tables 1, 2 and 3 are based on experimental observations of the values obtained for Si for different slit widths and the fact that the small sample prisms did not have perfectly flat faces. The lack of flatness was detectable in the determination of the apex



WAVELENGTH, (MICRONS)

Figure 8. Index of refraction versus wavelength for Mg2Sn I prism

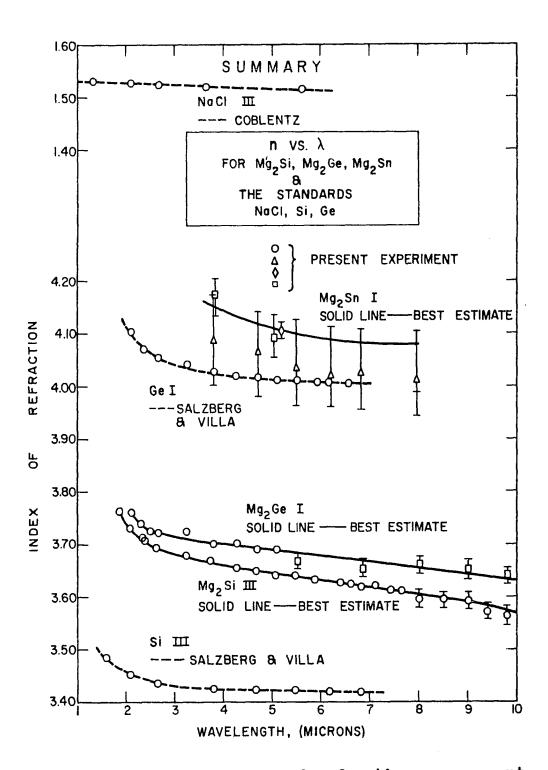


Figure 9. Summary of index of refraction measurements

	2					
Wavelength (microns)	Index of refraction					
	Slit 0.1 mm					
5.20 <u>+</u> 0.01	4.11 <u>+</u> 0.02					
	Slit 0.5 mm					
$\begin{array}{r} 3.77 \pm 0.01 \\ 4.70 \pm 0.01 \\ 5.52 \pm 0.01 \\ 6.23 \pm 0.01 \\ 6.86 \pm 0.01 \\ 8.00 \pm 0.01 \\ 3.77 \pm 0.01 \end{array}$	$\begin{array}{r} 4.07 \pm 0.07 \\ 4.07 \pm 0.07 \\ 4.07 \pm 0.07 \\ 4.02 \pm 0.07 \\ 4.03 \pm 0.07 \\ 4.01 \pm 0.07 \\ 4.09 \pm 0.07 \end{array}$					
	Slit 0.3 mm					
$3.77 \pm 0.01$ $5.05 \pm 0.01$	3.61 ± 0.03 3.57 ± 0.03					

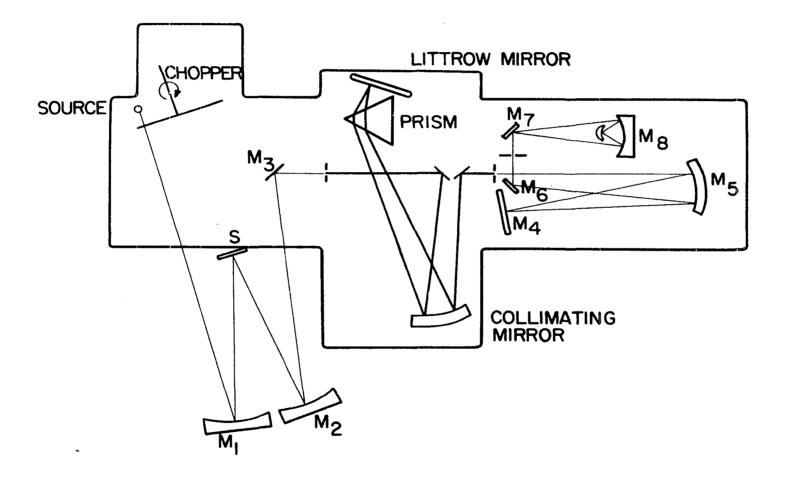
Table 3. Refractive index of Mg\_Sn I

angle. The slit image in these cases was broadened by the surface curvature of the prism face. The outside edges of the image were used to determine the range of possible values of the apex angle. In all cases this range was less than 1 minute of angle. The wavelength errors could have been easily reduced with more careful monochromator calibration. However, this did not seem necessary when the large possible error in the index of refraction measurement was considered.

#### III. MEASUREMENT OF REFLECTIVITY

Shown in Figure 10 is the optical arrangement used to determine the reflectivity of  $Mg_2Si$ ,  $Mg_2Sn$  and  $Mg_2Ge$  in the infrared. Light from the Globar passed through a 13 cyclesper-second chopper and was focused by the mirror  $M_1$  on the sample, S, at near normal incidence. The angle of incidence was approximately 12°. Reflected light from the sample was then focused by the mirror  $M_2$  on the entrance slit of a prism monochromator. This monochromator employed a NaCl prism for the wavelength range from 2 microns to 16 microns, a KBr prism for the wavelength range from 5 microns to 21 microns and a CsI prism for the wavelength range of 20 microns to 50 microns. The light exiting from the prism monochromator entered the grating monochromator used for wavelength calibration. After prism calibration, the grating was replaced with a plane mirror,  $M_{\mu}$ , which reflected light directly back to the collimating mirror,  $M_5$ , without dispersion. The beam was then focused by M<sub>R</sub> on a Reeder thermocouple detector with a CsI window.

The mirror, M7, could be replaced by a scatter plate or a reststrahlen reflection filter. In addition, a transmission filter of polyethylene sanded on both sides could be introduced into the beam at the entrance slit of the grating monochromator. Various combinations of filters and reflection



REFLECTIVITY APPARATUS Figure 10. Apparatus for the reflectivity determination filters were used to reduce unwanted radiation at the detector. Table 4 lists the wavelength ranges, prisms and various filtering techniques with the filter used to estimate the stray light contribution.

An electric motor and transmission were utilized to drive the prism Littrow mirror through the desired wavelength ranges. The detection and recording equipment were as previously described, with the output voltage continuously indicated on a strip chart.

The reflectivity was determined by comparing the output voltage with the sample in place with that obtained by reflection from Al at the sample position. A typical measurement in the 40 micron to 47 micron region began with the measurement of the signal obtained from Al at the sample position, followed by the measurement of the signal with an opaque filter in front of the entrance slit. Next a measurement was made of the signal with a NaCl window 6.5 millimeters thick in front of the entrance slit. The NaCl window did not transmit any light with wavelength longer than 23 microns, but transmitted a large fraction of all light with wavelength less than 20 microns. The sample was positioned in place of the Al and a determination made of the signal with and without the NaCl window before the entrance slit. Throughout these determinations the two thicknesses of polyethylene remained in the optical path. The NaCl window

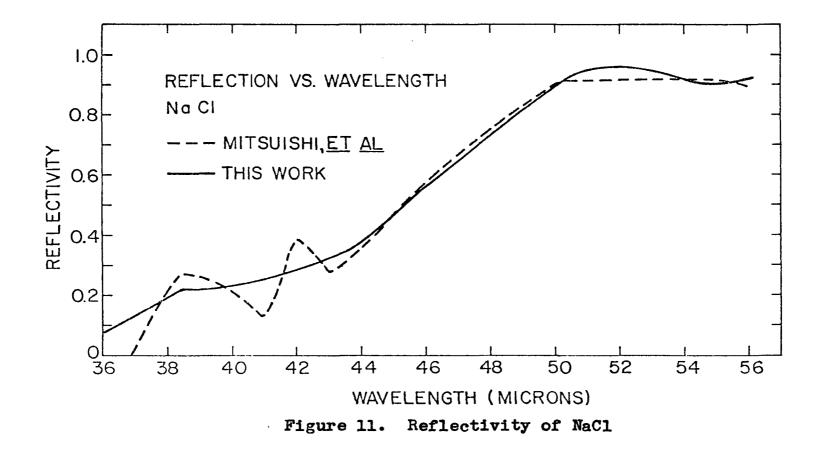
Wavelength (microns)	Prism	Filter	Filter for stray light determination	Stray light	Correction applied to zero
2 - 5	NaCl	None	None	Less than 0.1% (estimated)	No
5 <b>- 1</b> 0	NaCl	None	Glass 1 mm thick	Less than 0.5%	No
10 - 15	NaCl	Scatter plate	Fused SiO <sub>2</sub> 1 mm thick	Less than 1.0%	No
8 - 15	KBr	Scatter plate	Fused SiO <sub>2</sub> 1 mm thick	Less than 1.0%	No
15 - 20	KBr	Scatter plate	CaF <sub>2</sub> 5 mm thick	Less than 1.0%	No
20 - 30	CsI	Two thicknesses polyethylene sanded both sides	CaF <sub>2</sub> 5 mm thick	Less than 1.0%	No
30 - 40	CsI	Two thicknesses polyethylene sanded both sides	NaCl 6.5 mm thick	Less than 5.0%	Yes
40 - 47	CsI	Two thicknesses polyethylene sanded both sides	KBr 6.5 mm thick	Less than 25.0%	Yes
47 - 54	CsI	Two thicknesses polyethylene sanded both sides	KBr 6.5 mm thick	Less than 50.0%	Yes

Table 4. Wavelength ranges, prisms and filtering techniques

transmission was measured between 2.5 microns and 15 microns with a Beckman IR-7 monochromator. The transmission was close to 0.88 for the entire range. In order to correct for the stray light reflection by the NaCl window, all readings with the window in place were multiplied by 1.14. This value was subtracted from the readings without the window in place for both the sample and Al. The ratio of these two differences was recorded as the reflectivity. Where the stray light was small, no correction was needed. The alignment of the beam was done visually and was optimized for each run. The entire monochromator, sample and source volumes were swept with dry N<sub>2</sub>.

Figure 11 shows the reflectivity obtained from a freshly cleaved NaCl surface. Also pictured is the reflectivity of NaCl as determined by Mitsuishi <u>et al</u>. (17). The monochromator was operated in this range with 2 millimeter slits, which may be the reason the two humps on the left were not observed.

The reflectivity of a cleaved  $Mg_2Si$  surface was compared with the reflectivity of the same surface after light polishing with  $Al_2O_3$  on a nap cloth. The great differences in reflectivity led to the use of cleaved surfaces for the rest of the observations. In some cases, however, the samples were not perfect cleavage surfaces. There were many steps in the cleaved surface for some of the determinations.



28

÷

The faces of the steps were mostly parallel. It is believed that all samples used had reflectivities within 5 per cent of that which might have been obtained from a perfect face. All samples utilized in this experiment had been aged in air for a period of not less than thirty days. A surface film on the samples of  $Mg_2Si$  and  $Mg_2Ge$  was visually detectable, although slight. The sample of  $Mg_2Sn$  obtained from H. Guennoc was covered with a more obvious surface film.

#### IV. REFLECTIVITY RESULTS

The reflectivity obtained from a cleaved  $Mg_2Si$  surface is shown in Figure 12. The three x's on the left of the figure are reflectivities calculated from the index of refraction. The two datum points above the curve at 20 microns were not reproduced in subsequent determinations and are discounted. Figure 13 shows the reflectivity obtained from four samples of  $Mg_2Ge$ , three of which were doped with Al and Ag to yield the indicated carrier concentration determined by L. Lott from Hall data at room temperature. Figure 14 shows the reflectivity obtained for  $Mg_2Sn$ . Beyond 45 microns the CsI prism yielded a very small signal. As can be seen in Figure 12, where the actual datum points are included, the reflectivity beyond 45 microns is not precisely known. The small bump in Figure 14 falls in this region of uncertainty.

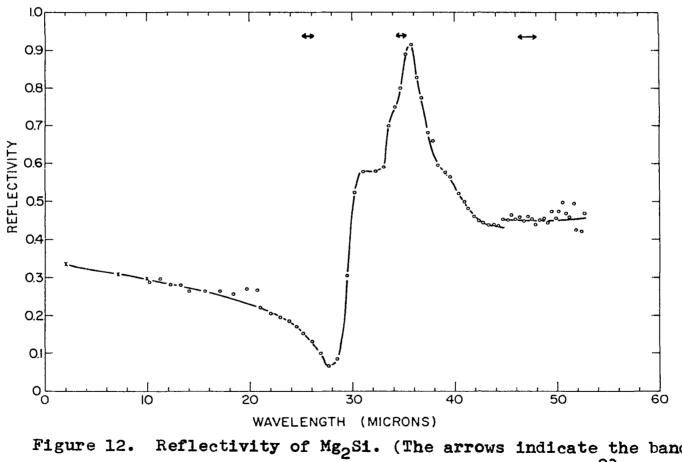
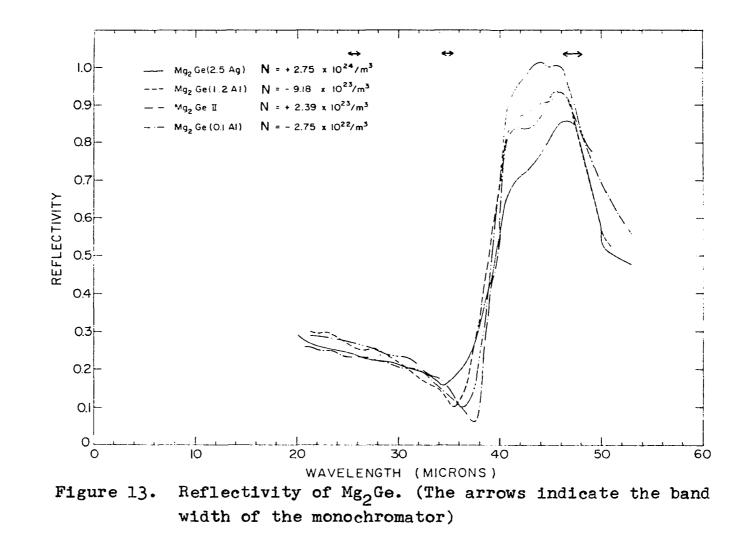


Figure 12. Reflectivity of Mg<sub>2</sub>Si. (The arrows indicate the band width of the monochromator.  $N = -1.0 \times 10^{23}$  per cubic meter)



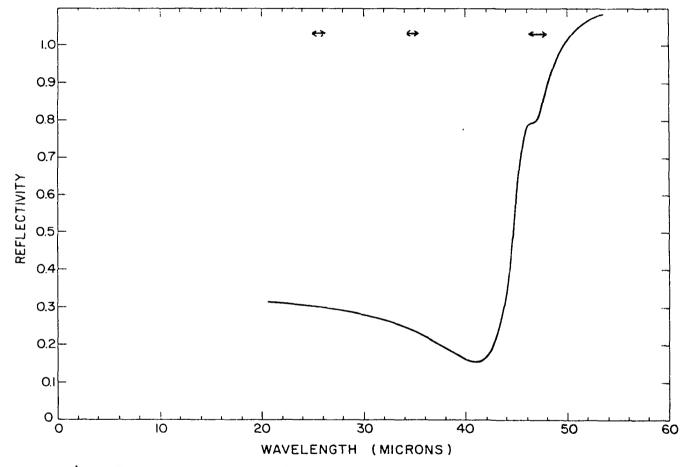


Figure 14. Reflectivity of  $Mg_2Sn$  with different carrier concentrations. (The arrows indicate the band width of the monochromator.  $N = -3.0 \times 10^{24}$  per cubic meter)

### V. DISCUSSION

Figure 15 shows the reflectivity of  $Mg_2Si$  II compared with the reflectivity of a classical oscillator as described in Appendix B. The classical oscillator curve shown in Figure 15 typifies the type of curve which can be said to approximate the data. This curve was one with  $\rho = 0.63$ ,  $\delta = 0.01$ ,  $\gamma_o = 8.00 \times 10^{12}$  per second, and  $\varepsilon = 12$ . Figure 16 shows another plot with different values of the parameters,  $\rho$ ,  $\delta$ and  $\varepsilon$ .  $\gamma_o$  is the reststrahlen frequency,  $\delta$  is called the strength of the oscillator,  $\rho$  is the width of the oscillator and  $\varepsilon$  is the short wavelength limiting value of the dielectric constant (see Appendix B).

Figure 17 is a classical oscillator approximation for  $Mg_2Ge$  reflectivity with  $\rho = 0.5$ ,  $\delta = 0.007$ ,  $\gamma_0 = 6.2 \times 10^{12}$  per second and  $\epsilon = 14$ .

The lack of a long wavelength limiting value of the reflectivity makes it difficult to fit a classical oscillator to the Mg<sub>2</sub>Ge data with any confidence in the values of  $\rho$ ,  $\gamma$  and  $\epsilon$ .  $\gamma_0$ , however, should be quite close to the real value. If the same curve shape is assumed for Mg<sub>2</sub>Sn, an approximate value for  $\gamma_0$  would be 5.6 x 10<sup>12</sup> per second.

Ganesan and Srinivasan (18) have examined the three dimensional CaF<sub>2</sub> lattice to obtain a relationship

$$\mu w_r^2 = f$$

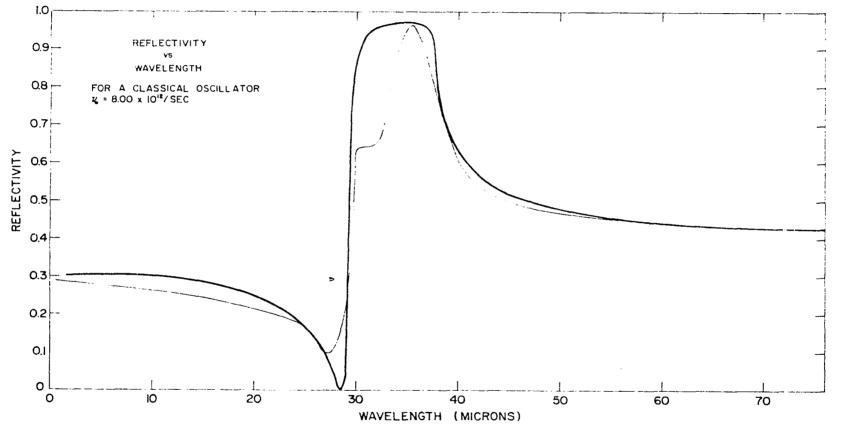
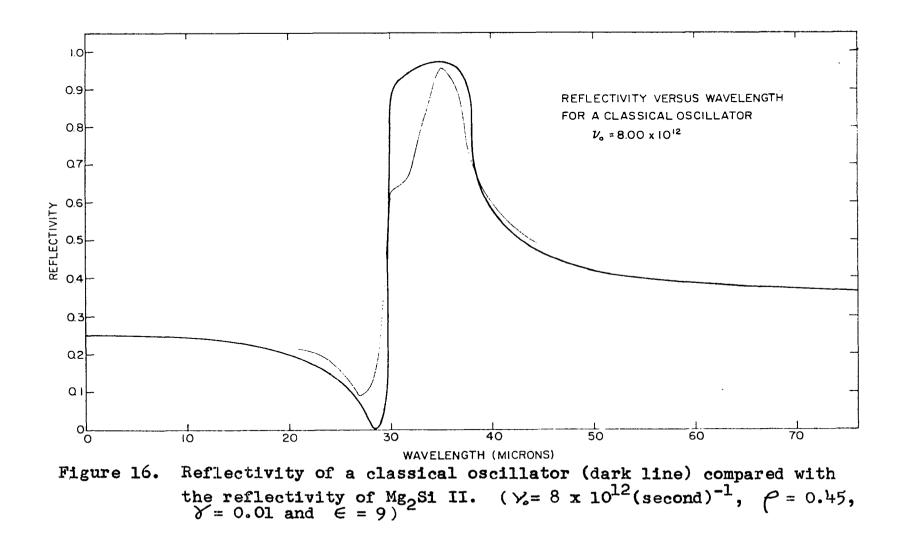
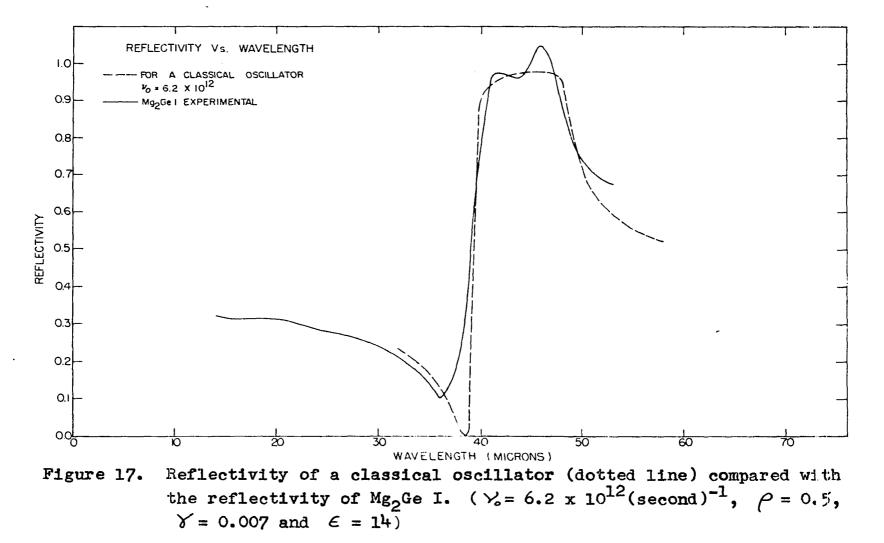


Figure 15. Reflectivity of a classical oscillator (dark line) compared to the reflectivity of Mg<sub>2</sub>Si II. ( $\gamma_{e} = 8 \ge 10^{12} (\text{seconds})^{-1}$ ,  $\rho = 0.63$ ,  $\gamma = 0.01$  and  $\epsilon = 12$ )





where  $\mathcal{M}$  is the reduced mass,  $\mathcal{W}_{r}$  is the reststrahlen frequency and f is a function including the Coulomb interaction and other terms pertaining to the lattice forces. Whitten (12) has made a similar solution for Mg<sub>2</sub>Si. It is interesting to examine the ratios of the experimental reststrahlen frequencies as given by the classical oscillator approximations. For Mg<sub>2</sub>Si

$$\mathcal{M}_{Mg_2Si} = \frac{m_{Si} m_{Mg}}{m_{Si} + 2m_{Mg}} = 1.47 \text{ x } 10^{-26} \text{ kilograms}$$

and

$$Mg_2Ge = 2.42 \times 10^{-26}$$
 kilograms

also

$$M_{g_2}Sn = 2.86 \times 10^{-26}$$
 kilograms.

Now

$$\sqrt{\frac{\mathcal{M}_{g_2}Si}{\mathcal{M}_{g_2}Ge}} = 0.78 \quad \text{and} \quad \sqrt{\frac{\mathcal{M}_{g_2}Si}{\mathcal{M}_{g_2}Sn}} = 0.72 .$$

From the previous estimates

$$\frac{\omega_{r_{Mg_2}Ge}}{\omega_{r_{Mg_2}Si}} = 0.78 \quad \text{and} \quad \frac{\omega_{r_{Mg_2}Sn}}{\omega_{r_{Mg_2}Si}} = 0.70$$

which implies that f is a constant for the three materials.

An examination of Figure 13 reveals a small shift in the

reflectivity minimum as the carrier concentration changes. For a specific carrier sign the minimum shifts to shorter wavelengths as the concentration increases. Simultaneously the maximum value of the reflectivity decreases. The change in the reststrahlen reflectivity is very much like that observed by Yoshinaga and Oetjen (19) in their observations of the temperature dependence of the reflectivity for pure samples of InSb. Their lattice reflectivity changed with increasing temperature in the same fashion as the Mg<sub>2</sub>Ge reflectivity changed with increasing carrier concentration.

It appears the changes in reflectivity are due to the free carriers and this is supported by an analysis suggested by Lynch<sup>1</sup>.

The equations for the susceptibility and the conductivity were modified by a free carrier term [Moss (1, p. 29)] and written as

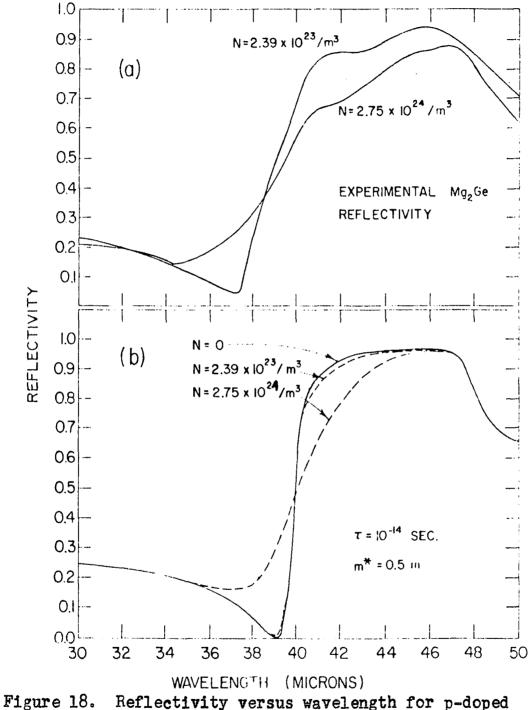
$$\begin{aligned} & \mathcal{X} = \mathcal{X}_{co} - \frac{Ne^2 \mathcal{Z}^2}{4 \pi \mathcal{E}_o (1 + \omega^2 \mathcal{Z}^2)m^*} \\ & \mathcal{T} = \mathcal{T}_{co} + \frac{Ne^2 \mathcal{T}}{m^*(1 + \omega^2 \mathcal{Z}^2)} . \end{aligned}$$

<sup>&</sup>lt;sup>1</sup>Lynch, D. W., Ames, Iowa. Influence of free carriers on the reflectivity of classical oscillators. Private communication. 1962.

The subscript co refers to the contribution of the classical oscillator as discussed in Appendix B.  $\tilde{\boldsymbol{\mathcal{U}}}$  is the collision time of the free carriers.

Figure 18 shows the influence of classical free carriers on the classical oscillator according to these equations. Figure 18 (a) gives the experimental reflectivity for two Ag doped Mg<sub>2</sub>Ge samples. Figure 18 (b) shows the classical oscillator without free carriers and with the addition of concentrations equal to the experimental concentrations for typical values of  $\mathcal{C}$  and m\*/m. The similarities in these curves are offered as additional evidence that the gross changes of reflectivity in Mg<sub>2</sub>Ge with doping are due to free carriers.

Many different combinations of  $\rho$ ,  $\chi$ ,  $\chi$ ,  $\epsilon$ ,  $\tau$ , and m\*/m were substituted into the equations, and Figure 18 gives the curves which came closest to the experimental results. The value of  $\tau$  which gave the best result is roughly in agreement with the collision time calculated from the resistivities reported by Redin (4) for Mg<sub>2</sub>Ge. From his values a typical value for holes would be 2 x 10<sup>-14</sup> seconds. Since the reflectivity measurements are a surface phenomenon, a shorter collision time would be expected. In the classical calculations reasonable results were obtained only for values of  $\tau$  between 5 x 10<sup>-15</sup> seconds and 10<sup>-14</sup> seconds. When  $\tau = 5 \times 10^{-15}$  seconds was used, m\* = 0.2 m provided a result



re 18. Reflectivity versus wavelength for p-doped Mg<sub>2</sub>Ge and a classical oscillator with free carrier modifications

similar to that shown in Figure 18 (b). On a reasonability basis the conclusion that  $m_h^* \ge 0.2$  seems proper.

The analysis for the Al doped samples was much less satisfactory. None of the combinations of constants tried gave results similar to the experiment.  $\mathcal{X}$  was varied from  $10^{-16}$  seconds to  $5 \times 10^{-14}$  seconds. m\*/m from 0.1 to 0.5 was tried. Both of these variations were matched with various values of  $\rho$ ,  $\mathcal{X}$ ,  $\mathcal{X}_o$  and  $\mathcal{E}$ . It was not possible to obtain a small shift in a sharp minimum when the minimum Was required to be near zero. No explanation can yet be offered about the small effect of n doping on the Mg<sub>2</sub>Ge reflectivity minimum.

Figure 19 shows the reflectivity data plotted against energy. The peak width decreases with increasing reduced mass. The decreasing width of the peak is similar to the observations of Lax and Burstein (20) on MgO, LiF, NaF, NaCl and KCl.

The cause of the bumps in the high reflectivity regions for these materials remains to be determined. There is a possibility that these bumps are due to multiple phonon effects as described by Lax and Burstein (20) and Kleinman (21) and observed by Turner and Reese (22) and others. Woods, <u>et al.</u> (23) have determined the energy-momentum relationships for phonons in KBr by neutron diffraction. With his values for energies of possible modes, one obtains several combina-

42-43

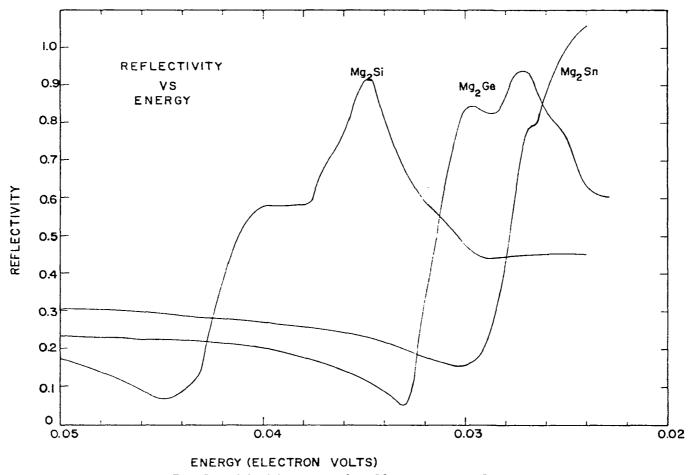


Figure 19. Reflectivity of the Mg compounds versus energy

tions of phonons which yield energies close enough together and at the correct wavelength to account for the small bump in the KBr reflectivity reported by Mitsuishi, <u>et al</u>. (17). The bumps observed in the Mg compound reflectivity are similar to those found in ionic crystals, particularly  $CaF_2$ and  $BaF_2$ , but need further study before deciding on their origin. Bumps of this nature are not found in the III-V compounds [Picus, <u>et al</u>. (24)].

Most recent work confirming multiple phonon effects in semiconductors has its basis in large changes in the absorption constant with wavelength Turner and Reese (22). The transmission of several  $Mg_2Si$  and  $Mg_2Ge$  crystals was examined between 1.5 microns and 40 microns. None of these determinations showed changes in transmission which could be attributed to multiple phonon effects.

Because of the uncertainty in the long-wavelength reflectivity, it is not possible to determine a very reliable value for the ionicity by examining the differences in the dielectric constant. Szigeti (25) has derived an expression relating the optical dielectric constant, the static dielectric constant and the ionicity by assuming classical crystal fields. This relation essentially is the same as that given in Appendix B between Q and e\*.

 $\rho = \frac{2 \operatorname{Ne}^{*2}}{16 \pi^3 \mathcal{E}_{2} \mathcal{M} Y_{2}^{2}} \left[ \frac{\mathcal{E}_{3} + 2}{3} \right]^{2}$ 

where N is the concentration of ion triplets and  $\mu$  is the reduced mass. The unit volume is  $V - \frac{a^3}{4}$ . a, the lattice constant, is 6.338 x 10<sup>-10</sup> meters [Whitsett (3)].

For Mg<sub>2</sub>Si

$$\rho = 0.63$$
  
N = 1.57 x 10<sup>28</sup> per meter<sup>3</sup>

which gives  $e^* = 0.35 e$ .

This implies only that the ionicity exists, but is not very great.

1940 ye e e

#### VI. BIBLIOGRAPHY

- 1. Moss, T. S. Optical properties of semiconductors. London, Butterworths Scientific Publications. 1959.
- Morris, R. G. Semiconducting properties of Mg<sub>2</sub>Si. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.
- 3. Whitsett, C. R. Electrical properties of magnesium silicide and magnesium germanide. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.
- Redin, R. D. Semiconducting properties of Mg<sub>2</sub>Ge single crystals. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.
- Blunt, R. F., Frederikse, H. D. R. and Hosler, W. R. Electrical and optical properties of intermetallic compounds. IV. Magnesium stannide. Phys. Rev. 100: 663. 1955.
- Koenig, P. J., Lynch, D. W. and Danielson, G. C. Infrared absorption in magnesium silicide and magnesium germanide. J. Phys. Chem. Solids 20: 122-126. 1961.
- 7. Winkler, V. Die elektrischen Eigenschaften der intermetallischen Verbindungen Mg<sub>2</sub>Si, Mg<sub>2</sub>Ge, Mg<sub>2</sub>Sn, and Mg<sub>2</sub>Pb. Helv. Phys. Acta 28: 617. 1955.
- Heller, M. W. Seebeck effect in magnesium silicide. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.
- 9. Moss, T. S. Photoconductivity of the elements. London, Butterworths Scientific Publications. 1952.
- 10. Madelung, O. H. Handbuch der Physik 20: 1. 1957.
- 11. Kittel, C. Introduction to solid state physics. 2nd ed. New York, N. Y., John Wiley and Sons, Ltd. 1957.

- 12. Whitten, W. Lattice vibrations of Mg<sub>2</sub>Si. Unpublished paper. Typewritten. Ames, Iowa, Department of Physics, Iowa State University of Science and Technology. <u>ca</u>. 1962.
- 13. Fröhlich, H. Theory of dielectrics. London, Oxford University Press. 1949.
- 14. Ziman, J. M. Electrons and phonons. London, Oxford University Press. 1960.
- 15. Coblentz, W. W. Transmission and refraction data on standard lens and prism material with special reference to infra-red spectroradiometry. J. Opt. Soc. Am. 4: 432. 1920.
- 16. Salzberg, C. D. and Villa, J. J. Infrared refractive indexes of silicon germanium and modified selenium glass. J. Opt. Soc. Am. 47: 244. 1957.
- 17. Mitsuishi, A., Yamada, Y. and Yoshinaga, H. Reflection measurements on reststrahlen crystals in the farinfrared region. J. Opt. Soc. Am. 52: 14. 1962.
- 18. Ganesan, S. and Srinivasan, R. Lattice dynamics of calcium fluoride. I. Can. J. Phys. 40: 74. 1962.
- Yoshinaga, H. and Oetjen, R. A. Optical properties of indium antimonide in the region from 20 to 200 microns. Phys. Rev. 101: 526. 1956.
- Lax, M. and Burstein, E. Infrared lattice absorption in ionic and homopolar crystals. Phys. Rev. 97: 39. 1955.
- 21. Kleinman, D. A. Anharmonic forces in the GaP crystal. Phys. Rev. 118: 118. 1960.
- 22. Turner, W. J. and Reese, W. E. Infrared lattice bands in AlSb. Unpublished paper. Mimeographed. Yorktown Heights, New York, International Business Machines. 1962.
- 23. Woods, A. D. B., Brockhouse, B. N., Cochrane, W., Sakamoto, M. and Sinclair, R. N. Lattice vibrations of alkali halides. Bull. Am. Phys. Soc. Ser. 2, 5: 462. 1960.

- 24. Picus, G., Burstein, E., Henvis, B. W. and Hass, M. Infrared lattice vibration studies of polar character in compound semiconductors. J. Phys. Chem. Solids 8: 282. 1959.
- 25. Szigeti, B. Polarisability and dielectric constant of ionic crystals. Trans. Far. Soc. 45: 155. 1949.
- 26. Spitzer, W. G., Kleinman, D. and Walsh, D. Infrared properties of hexagonal silicon carbide. Phys. Rev. 113: 127. 1959.
- 27. Seitz, F. Modern theory of solids. New York, N. Y., McGraw-Hill Book Co., Inc. 1940.

# VII. ACKNOWLEDGMENTS

The author is grateful for the many pertinent remarks and continual encouragement given by Dr. G. C. Danielson and Dr. D. W. Lynch. He also wishes to thank Mr. W. B. Whitten for many enlightening discussions.

## VIII. APPENDIX A: LIST OF SYMBOLS

c = speed of lightE = electric intensity $E_{o}$  = amplitude of the electric intensity f = a function of the lattice forces  $i = \sqrt{-1}$  $K = \frac{\mu \pi k}{\lambda}$  = absorption coefficient k = imaginary part of the complex index of refraction called the extinction coefficient m = mass of the electron m\* = effective mass of electrons  $m_h^* = effective mass of holes$ N = magnitude of the carrier concentration  $\underline{N} = n - ik$  complex index of refraction  $\underline{N}^2 = n^2 - k^2 - 2 i n k = dielectric constant$ n = real part of the complex index of refraction R = reflectivityt = time $\mathbf{x} = displacement$  $\alpha$  = angle of minimum deviation X = height of the resonance of a classical oscillator  $\delta = apex angle$  $\mathcal{E}$  = optical dielectric constant  $\epsilon_{s}$  = static dielectric constant

E= dielectric constant of free space

 $\lambda$  = wavelength of light

 $\mu$  = reduced mass of a unit cell

 $V_{o}$  = reststrahlen frequency

-*T* = 3.14159....

 $\rho$  = width of the resonance of a classical oscillator

 $\mathcal{T} = \text{conductivity}$ 

$$\mathcal{O}_{co}$$
 = conductivity of a classical oscillator

$$\mathcal{C}$$
 = collision time of free carriers

 $\mathcal{X}$  = susceptibility

 $\mathcal{X}_{co}$  = susceptibility of a classical oscillator

 $\omega$  = angular frequency

- $\omega_r$  = reststrahlen angular frequency
- $\omega_{\rm L}$  = frequency of the longitudinal optical mode

## IX. APPENDIX B: CLASSICAL OSCILLATOR EQUATIONS

WITH FIGURES AND PRINTED COMPUTER SOLUTIONS

What follows is a quotation from the paper by Spitzer <u>et al.</u> (26) [CGS].

According to the classical dispersion theory of crystals [Seitz (27)], the susceptibility  $\approx$  and conductivity  $\sim$  in the neighborhood of a resonance frequency  $\neq_o$  are given by

and

$$\frac{\sigma}{\gamma} = 2\pi\rho \frac{\gamma}{(1-\gamma^2)^2 + \gamma^2 \gamma^2}, \qquad (2)$$

where  $\checkmark$  is the measured frequency divided by  $\checkmark_o$ ,  $\sim$  is the conductivity divided by  $\checkmark_o$ , and the dimensionless parameters  $\rho$  and  $\checkmark$  may be called the width and strength of the resonance, respectively. In the Lorentz theory,  $\rho$  is given by

$$\ell = \frac{\mathrm{Ne}^2}{4\pi^2 \mathrm{m}^* \ \gamma_o^2} , \qquad (3)$$

where N is the concentration of ion pairs and m is their reduced mass. The index of refraction, n, and extinction coefficient, k, are given by

$$n^{2} = \frac{1}{2} \left[ \left[ e^{2} + 4 \left( \sigma_{\gamma_{\gamma}} \right)^{2} \right]^{2} + e \right], \quad (4)$$

and

$$k^{2} = \frac{1}{2} \left\{ \left[ \epsilon^{2} + 4(\sigma/\gamma)^{2} \right]^{\frac{1}{2}} - \epsilon \right\}, \qquad (5)$$

where

$$\epsilon = \epsilon_{s} + 4\pi\chi, \qquad (6)$$

and  $\epsilon_o$  is the high-frequency ( $\checkmark$  >>1) dielectric constant.

According to Whitten (12) Equation 3 should read

$$\rho = \frac{2Nc^2}{4\pi^2 m^* \gamma_o^2} \tag{7}$$

for the Mg compounds.

. .

`

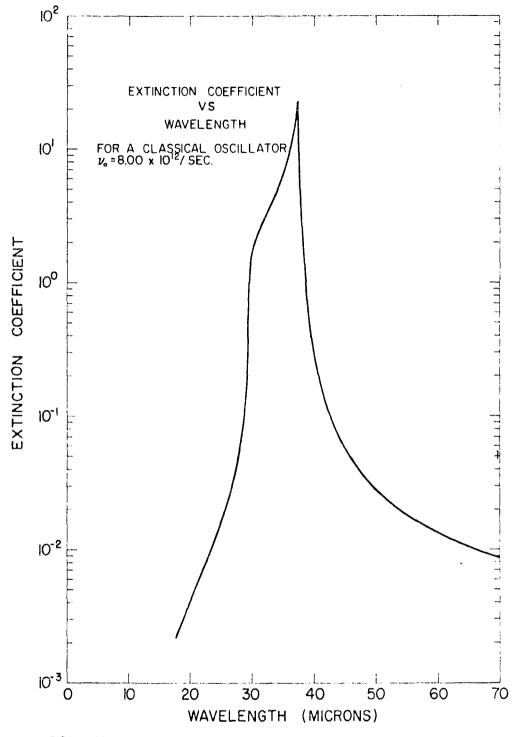
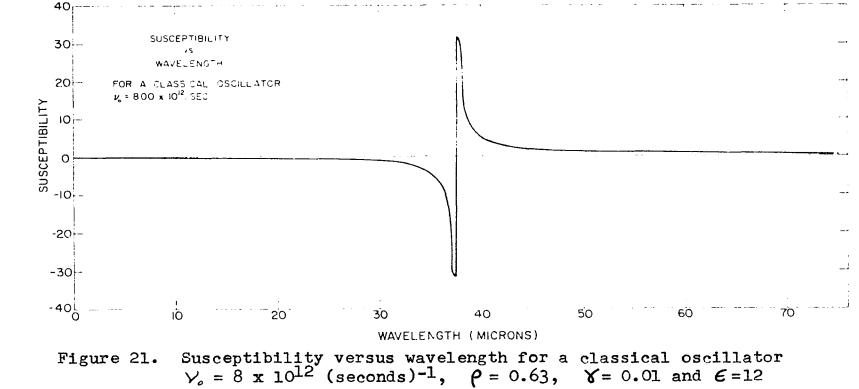


Figure 20. Extinction coefficient versus wavelength for a classical oscillator.  $\gamma_{\bullet} = 8 \times 10^{12} \text{ (seconds)-l}, \rho = 0.63, \gamma = 0.01 \text{ and } \epsilon = 12$ 



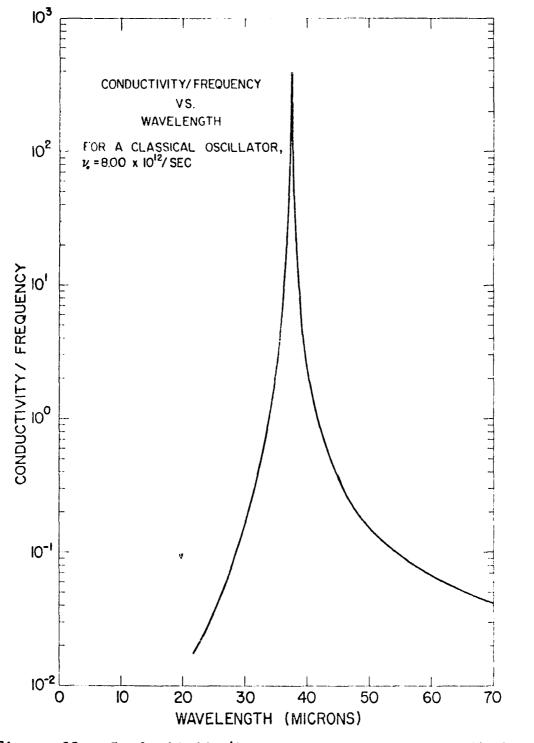


Figure 22. Conductivity/frequency versus wavelength for a classical oscillator.  $\gamma = 8 \times 10^{12} \text{ (seconds)}^{-1}$ ,  $\rho = 0.63$ ,  $\chi = 0.01$  and  $\epsilon = 12$ 

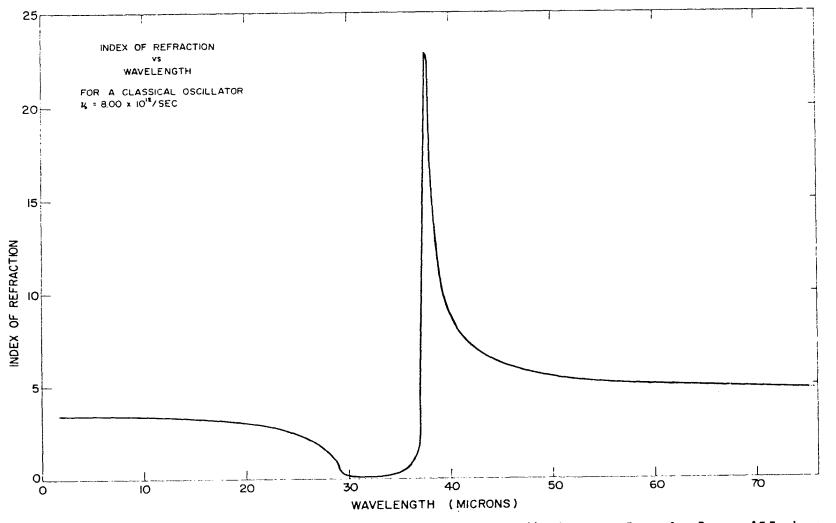


Figure 23. Index of refraction versus wavelength for a classical oscillator.  $V_o = 8 \times 10^{12} (\text{seconds})^{-1}, \ \rho = 0.63, \ \delta = 0.01 \text{ and } \epsilon = 12$ 

Table 5. Computer solution for a classical oscillator

		f = 0.63			
		x = 0.01			
		$\gamma_0 = 8.00 \text{ x}$	: 10 <sup>12</sup>		
		$\epsilon = 12$			
$\lambda$	$\sim$	<del>or</del> Y	k	n	R
2.00x10 <sup>0</sup>	-1.80x10 <sup>-3</sup>	6.04x10 <sup>-6</sup>	2.11x10 <sup>-4</sup>	3.46x10 <sup>0</sup>	3.04x10 <sup>-1</sup>
	$-1.66 \times 10^{-2}$	$1.71 \times 10^{-4}$	$2.11 \times 10^{-4}$	$3.43 \times 10^{0}$	3.01x10 <sup>-1</sup>
	-4.82x10 <sup>-2</sup>	$8.70 \times 10^{-4}$	2.11x10 <sup>-4</sup>	3.38x10 <sup>0</sup>	2.95x10 <sup>-1</sup>
	-1.02x10 <sup>-1</sup>	2.78x10 <sup>-3</sup>	8.46x10-4	$3.27 \times 10^{0}$	2.83x10 <sup>-1</sup>
	-1.89x10 <sup>-1</sup>	7.39x10 <sup>-3</sup>	2.38x10 <sup>-3</sup>	$3.10 \times 10^{\circ}$	$2.63 \times 10^{-1}$
	$-3.31 \times 10^{-1}$	$1.86 \times 10^{-2}$	$6.63 \times 10^{-3}$	$2.80 \times 10^{0}$	$2.25 \times 10^{-1}$
	-5.83x10 <sup>-1</sup>	4.89x10 <sup>-2</sup>	$2.26 \times 10^{-2}$	$2.16 \times 10^{0}$	$1.35 \times 10^{-1}$
	-1.12x10 <sup>0</sup>	$1.56 \times 10^{-1}$	$1.44 \times 10^{0}$	1.08x10 <sup>-1</sup>	•
$3.40 \times 10^{1}$	-2.90x10 <sup>0</sup>	9.29x10 <sup>-1</sup>	4.95x10 <sup>0</sup>	1.88x10 <sup>-1</sup>	9.71x10 <sup>-1</sup>
3.80x10 <sup>1</sup>	2.11x10 <sup>1</sup>	5.00x10 <sup>1</sup>	2.96x10 <sup>0</sup>	$1.69 \times 10^{1}$	$7.95 \times 10^{-1}$
4.20x10 <sup>1</sup>	3.10x10 <sup>0</sup>	8.58x10 <sup>-1</sup>	1.20x10 <sup>-1</sup>	7.14x10 <sup>0</sup>	$5.69 \times 10^{-1}$
$4.60 \times 10^{1}$	1.88x10 <sup>0</sup>	2.87x10 <sup>-1</sup>	4.80x10 <sup>-2</sup>	5.97x10 <sup>0</sup>	$5.08 \times 10^{-1}$
$5.00 \times 10^{1}$	$1.44 \times 10^{0}$	$1.55 \times 10^{-1}$	2.83x10 <sup>-2</sup>	$5.49 \times 10^{\circ}$	4.78x10 <sup>-1</sup>
$5.40 \times 10^{1}$	$1.22 \times 10^{0}$	$1.03 \times 10^{-1}$	1.96x10 <sup>-2</sup>	$5.22 \times 10^{0}$	4.61x10 <sup>-1</sup>
5.80x10 <sup>1</sup>	1.08x10 <sup>0</sup>	$7.56 \times 10^{-2}$	$1.49 \times 10^{-2}$	5.06x10 <sup>0</sup>	4.49x10 <sup>-1</sup>
6.20x10 <sup>1</sup>	9.93x10 <sup>-1</sup>	5.95x10 <sup>-2</sup>	$1.20 \times 10^{-2}$	4.95x10 <sup>0</sup>	4.41x10 <sup>-1</sup>
$1.10 \times 10^2$	7.13x10 <sup>-1</sup>	$1.73 \times 10^{-2}$	$3.77 \times 10^{-3}$	4.58x10 <sup>0</sup>	4.11x10 <sup>-1</sup>

# X. APPENDIX C: INDEX OF REFRACTION

## DETERMINATION DATA

Table 6	. Se	extant	calibr	ation
---------	------	--------	--------	-------

Sextant setting	Sextant angle
42.5°	+ 19° 53'
40 <b>.</b> 0°	+ 17° 25.5'
37•5°	+ 14° 50'
35.0°	+ 12° 26'
32 <b>.5</b> °	+ 9° 56'
30.0°	+ 7° 28'
27•5°	+ 4° 5 <b>4</b> 1
25.0°	+ 2° 26'
22.5°	- 0° 6'
20 <b>.</b> 0°	- 2° 33.5'
17.5°	- 5° 61
15.0°	- 7° 34!
12.5°	- 10° 7'
10.0°	- 12° 50.5'
7.5°	- 15° 6'
5.0°	- 17° 33'
2.5°	- 20° ॅ8.5'

Table 7. Minimum deviation data for Mg<sub>2</sub>Sn I

Prism <u>drive</u>	Sextant reading	$\frac{\alpha+\delta}{2}^{a}$	$\sin \frac{\alpha + \delta}{2}$	n <sup>b</sup>	$\lambda^{\mathbf{c}}$			
15.20	2.5(-9.1d) <sup>d</sup>	20° 23'	0.34830	4.105	5.2			
Sli	it = 0.1 millim	S = 9° 541						
Zer	$= 30.0^{\circ}(+3.)$	$\sin \frac{S}{2} = 0.08484$						

Table 8. Minimum deviation data for  $Mg_2Si$  III

$$\delta = 9^{\circ} 50^{\circ}$$
  
 $\sin \frac{\delta}{2} = 0.08571$   
 $zero = 30.0^{\circ}(+3.2d^{2}) = 8^{\circ} 19.2^{\circ}$   
 $slit = 0.1$  millimeters

Prism drive	Sextant reading	$\frac{\alpha+\delta}{2}^{b}$	$\sin \frac{\alpha + \delta}{2}$	n <sup>C</sup>	$\lambda^{d}$
13.25 13.50 13.75 14.2 14.2 14.55 15.25 15.50 15.50 16.250 16.60 16.60 16.75 17.25	$5.0^{\circ}(-1.4d)$ $5.0^{\circ}(-1.4d)$ $5.0^{\circ}(-1.7d)$ $5.0^{\circ}(-2.0d)$ $5.0^{\circ}(-2.0d)$ $5.0^{\circ}(-2.2d)$ $5.0^{\circ}(-2.5d)$ $5.0^{\circ}(-2.5d)$ $5.0^{\circ}(-2.5d)$ $5.0^{\circ}(-2.5d)$ $5.0^{\circ}(-2.5d)$ $5.0^{\circ}(-3.6d)$ $5.0^{\circ}(-3.6d)$ $5.0^{\circ}(-3.9d)$ $5.0^{\circ}(-5.2d)$ $5.0^{\circ}(-5.2d)$ $5.0^{\circ}(-6.0d)$ $5.0^{\circ}(-7.2d)$	18° 2.3' 18° 2.3' 18° 4.7' 18° 4.7' 18° 7.1' 18° 7.1' 18° 11.1' 18°11.1' 18°13.5' 18°15.1' 18°15.1' 18°22.3' 18°27.1' 18°31.1' 18°32.7' 18°39.1' 18°48.7'	0.30965 0.31032 0.31032 0.31098 0.31098 0.31143 0.31209 0.31209 0.31275 0.31275 0.31319 0.31430 0.31518 0.31651 0.31651 0.31982 0.31982 0.32247	3.613 3.621 3.621 3.628 3.628 3.628 3.628 3.628 3.641 3.641 3.649 3.654 3.654 3.667 3.693 3.706 3.731 3.731 3.762	7.456 6.555 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.466 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.467 7.477 7.467 7.477 7.4777 7.47777777777

<sup>a</sup>d = 16'. <sup>b</sup> $\propto$  = deviation angle;  $\delta$  = apex angle. <sup>c</sup>n = index of refraction. <sup>d</sup> $\lambda$  = wavelength in microns.

• •

Table 9. Minimum deviation data for  $Mg_2Ge I$ 

$$\delta = 10^{\circ} 00^{\circ}$$
  
 $\sin \frac{\delta}{2} = 0.08716$   
zero = 30.0°(+3.2d<sup>a</sup>) = 8° 19.2'  
slit = 0.1 millimeters

Prism drive	Sextant reading	$\frac{\alpha+\delta}{2}^{b}$	$\sin \frac{\alpha + \delta}{2}$	n <sup>c</sup>	$\lambda^{d}$
15.25 15.50 15.75 16.00 16.25 16.50 16.60 16.75 17.00	5.0°(-6.2d) 5.0°(-6.2d) 5.0°(-6.7d) 5.0°(-6.7d) 5.0°(-7.0d) 5.0°(-7.5d) 5.0°(-7.6d) 5.0°(-8.1d) 5.0°(-9.0d)	18° 45.7' 18° 45.7' 18° 49.7' 18° 49.7' 18° 52.1' 18° 56.1' 18° 56.9' 19° 0.9' 19° 8.1'	0.32164 0.32274 0.32274 0.32340 0.32450 0.32472 0.32582 0.32780	3.690 3.690 3.703 3.703 3.723 3.723 3.723 3.726 3.738 3.761	5.12 4.70 4.26 3.77 3.25 2.40 2.35 2.10
a <sub>c</sub>					

<sup>b</sup> $\propto$  = deviation angle; S = apex angle.

 $c_n = index$  of refraction.

 $^{d}\lambda$  = wavelength in microns.

XI. APPENDIX D: REFLECTIVITY DETERMINATION DATA

-	· · ·	A1			Mg	2Sn			Mg2	مسلم 10: الاردياسيتيورياسي	
PD	Z	V	D	Z	V	D	R	2	V	D	R
13.10	12.2	28.2	16.0	5.1	22.3	17.2	1.08	3.5	11.0	7.5	0.47
13.20	12.0	30.0	18.0	5.1	23.9	18.8	1.04	3.8	11.4	7.6	0.42
13.30	13.3	32.6	19.3	4.6	26.5	21.9 24.8	1.14	4.0	12.2	8.2	0.43
13.40	13.7	35.7	22.0	5.4	30.2	24.8	1.13	3.8	14.6	10.8	0.40
13.30 13.40 13.50 13.60 13.70	14.1	39.0	24.9	5.6	32.7	27.1	1.09	4 <b>.</b> 0	15.5	11.5	0.46
13.60	13.9 16.5 18.6	43.1	29.2 28.8	6.3	35.3	29.0	0.99	3.8 4.8	17.5	13.7	0.47
13.70	16.5	45.3 48.8	28.8	7.1	37.0	29.9	1.04	4.8	18.4	13.6	0.47
13.80	18.6	48.8	30.2	7.1 7.8 6.8	38.9	31.1	1.03	4.7	19.0	13.6 14.3 15.5	0.47
13.90	16.1	50.0	33•9 38•4	6.8	38.9 40.3 45.5	33.5 38.9 48.2	0.99	4.2	19.7	15.5	0.46
14.00	15.7	54.1	38.4	6.6	42.02	38.9	1.01	4.2	22.4	18.2	0.47
14.10	17.3 17.6	67•3 77•5	50.0 59.9 45.2	6.2 6.8	54 4 62.5	48.2	0.96	5.7	27.9	22.2	0.41.
14.20	17.0	57.2	29•9	0.0 4.0	46.0	55.7 42.0	0.93	4.8	32.0 24.4	27.2 20.4	0.45 0.45
14.30 14.40	12.0 12.2	68.8	49•2 54•6		<del>40.0</del> 54.0	42.0	0.93 0.91	4.0	24.4	20.4	0.43
14.50	12 2	79.7	67.5	4•3 14 2	62 2	47•/ 50 0	0.87	3.6 3.2	27.3 33.8 25.3	23.7 30.6	0.45
14.60	12.2 8.4 8.6	59.1	50.7	4.2 3.8	63.2 45.5	59.0 41.7 46.8	0.82	2.1	25.0	23.2	0.45 0.46
14.70	8.6	67.2	58.6	3.9	50.7	46.8	0.82	2.5	29.0	26.5	0.45
14,80	9.5	72.5	63.0	3.9 3.8	54.7	50.9	0.81	2.6	31.5	28.9	0.46
14.90 15.00 15.10	9.7	74.0	63.0 64.3 61.8	4.1	50.7 54.7 54.5 50.5 54.5 50.5 54.5 50.5 54.5 50.5 54.5 50.5 54.5 50.5 54.5 50.5 54.5 55.5 55	50.2	0.78	3.0	32.3	29.3	0.46
15.00	11.2	73.0	61.8	4.6	50.5	50.2 45.9	0.74	3.0 3.1 3.9	31.7	29.3 28.6 28.2	0.46
15.10	12.1	74.3	62.2	5.0	45.6	40.6	0.65	3.9	32.i	28.2	0.45
15.20	11.6	80.0	68.4	5.4	42.0	36.6	0.54	4.6	35.6	31.0	0.45
15.30	8.0	63.0	55.0	3.6	25.6	22.0	0.40	3.6	27.4	23.8	0.43
15.30 15.40	9.2	81.4	72.2	4.7	26.3	21.5	0.30	3.8 2.8	35.8	32.0	0.41
15.50 15.60	6.0	64.6	58.6	2.9	17.6	14.7	0.25	2.8	28.4	25.6	0.41+
15.60	6.3	75.0	68.7	3.j	17.5	14.4	0.21	3.1	33•7	30.6	0.45
15.70	7.4	83.2	75.8	3.6	17.2	13.6	0.18	3.1	37.2	34.1	0.45

Table 10. Reflectivity data - CsI prism (PD = prism drive; Z = corrected zero; V = maximum voltage reading; D = voltage difference; R = reflectivity)

		н	00000000000000000000000000000000000000
	2.5 Ag	۵	ϞͶϘϙΟͶϺϯϭͰͶϯϺͰͰϿϯͰϿϤϯϿϘϿϯΟͶϿͶͶ ϭͶͶͶϧϯϧϘϯϯϘͶΟϺϯͶϭͶϯͶϘϿϟϯͶͰϿϿϤ ϯͶͶͶϤϯͶϯͶϥͶͶͶϔϯͶϯͶϧϧϧϧϧϧ
	2 <sup>Ge</sup> (	Δ	и 8444 04 04 08 t 6 0 0 0 0 0 0 0 t 6 0 0 0 0 0 0 0 0 0
	Mg	Z	$   \mathcal{M} = \mathcal{M}$
	-	<b>£</b>	00000000000000000000000000000000000000
	2 <sup>Ge II</sup>	D	итыли 101000001/0/10/10/10/00000000/0/00/00/00
	Mg	Δ	илты ислововойной балана и илововов 1 илово - рогновни во во во во во во во во в 1 илово - рогновни во
	L. L.	2	00000000000000000000000000000000000000
(Continued)			
Table 10.		DA	

Table 10. (Continued)

- · · ·	· ·	A1		<u> </u>	Mg <sub>2</sub>	Sn		Mg <sub>2</sub> Si								
PD	Z	<b>V</b> .	D	Z	V	D	R	Z	V	D	R					
16.10	10.0	85.5	75.5	4.6	17.8	13.2	0.18	3.4	42.8	39.4	0.52					
16.20	~~~~	-	-	-	-		-	-			-					
16.30 16.40	6.8	75.5	68.7	3.2	14.6	11.4	0.17	2.4	41.2	38.8	0.57					
16.40	6.8	87.2	80.4	3.1 2.5	17.5	14.4	0.18	2.4	52.7	50.3	0.58					
16.50	4.7	66.5	61.8	2.5	17•5 13•5 15•1	11.0	0.18	1.9	38.7	36.8	0.60					
16.60	4.7	70.3	64.6	2.1	エシーエ	13.0	0.20	1.6	44.1	42.5	0.67					
16.70	0.0	45.0	45.0						- - -	- - -	~ <b>~</b> 0					
16.80 16.90	0.0	48.4	48.4					0.0	37.5	37.5	0.78					
17.00	0.0	24.5 32.8	32 8					0.0	20.3	20.3 30.0	0.83 0.92					
17.10	0.0	52.5	24.5 32.8 52.5					0.0	30.0 46.9	46.9	0.89					
17.20	0.0	70.0	70.0					0.0	56.0	56.0	0.80					
17.30	0.0	79.0	79.0					0.0	59.3	59.3	0.75					
17.40	0.0	62.0	62.0					0.0	59.3 43.4	59•3 43•4	0.70					
17.50	0.0	69.0	69.0					0.0	40.7	40.7	0.59					
17.60	0.0	75.0	75.0					0.0	43.2	43.2	0.58					
17.70	0.0	72.0	72.0						-	417	-					
17.80	0.0	79.5 65.0	79.5					0.0	46.0	46.0	0.58					
17.90	0.0	65.0	65.0 72.8					0.0	33.8	33.8	0.52					
18.00	0.0	72.8	72.8					0.0	22.0	22.0	0.30					
18.10	0.0	71.0	71.0					0.0	6.0	6.0 4.4	0.09					
18.20	0.0 0.0	66.5	66.5					0.0	4.4	4.4 7 0	0.07					
18.30 18.40	0.0	72.3 89.0	72.3 89.0					0.0	7.2 11.7	7.2 11.7	0.10 0.13					
18.50	0.0	64.3	64.3					0.0	10.0	10.0	0.16					
18.60	0.0	76.5	76.5					0.0	13.2	13.2	0.12					
18.70	0.0	64.3 76.5 87.5	64.3 76.5 87.5					0.0	16.3	16.3	0.19					
18.80	0.0	63.Ó	63.0					0.0	12.3	12.3	0.20					
18.90	0.0	71.0	71.0					0.0	14.6	14.6	0.2.					
19.00	0.0	94.5	94.5					0.0	21.0	21.0	0.22					

	(g	ш	0.63	ı í	₫.	4	ᠬ	ŗ.	<b>N</b>	2	0.21	2	4	-	4	H.		4	<u>م</u>	2	<b>N</b>	N.	2	1	<u>.</u>	2	~	2	2	4	0.26	2
	(2.5 A	Ω	47.9	1	ດ.	÷.	-	÷	•	•				, N	٠	N.	d.	÷.	+	2	'n	ທີ	9		9:	ċ	ហំ	ŵ	ູ່	<b>.</b>	18. J	•
	e C	Α	51.3	٤,	÷.	<b>.</b>	'n	'n		0		٠	\$	2	٠	<b>N</b>	d.		<u>+</u>	2	'n	s.	6		9	ċ	ហុំ	<b>∞</b>	<u>0</u>	6.	18•5	6
		7	<b>3.</b> 4	1	٠		٠		٠		0.0		•					۰					•	I		٠					0.0	
		щ	0.75	1	5	ņ	2	N.	-	•	0.10	H.	4	-	4	-	_	Ļ	ř.	Ñ.	Ň	N.	Ň	Ň	N.	0.23	2	2	N.		0.25	Ň
	e II	Ω	56.6	١,	<b>.</b>	٠	<b>.</b>	ů.	÷.	٠	2°‡	٠	•	٠	٠	0	ł	÷	÷	•	3	៶	ហំ	÷.	6.		÷	~			17.5	<b>.</b>
	82 G	Δ	60•0	1	<b>.</b>	'n	ω.	<b>ير</b>		'n	2.4		٠			0		'n		<b>°</b>	a.	م	s.	÷	9	20.2	÷	~	0		17• 5	<b>.</b>
		17	<b>з.</b> 4	1							0.0	•	•	•	•	٠	1			٠			٠			0.0			•	1	0.0	•
(Continued)																																
Table 10.		Qd	16.10		<u>ن</u> ،	<b>.</b>	<u>ئ</u>	$\dot{\mathbf{o}}$	<b>.</b>	<b>.</b>	$\dot{\mathbf{a}}$	~	~	~	~	~	~	r.	~	~	~	ŵ	ຕໍ	ໍ່	ຜ່	œ	ຜ	ໍ່	ŵ	ຜ່	ໍ່	6

67

!

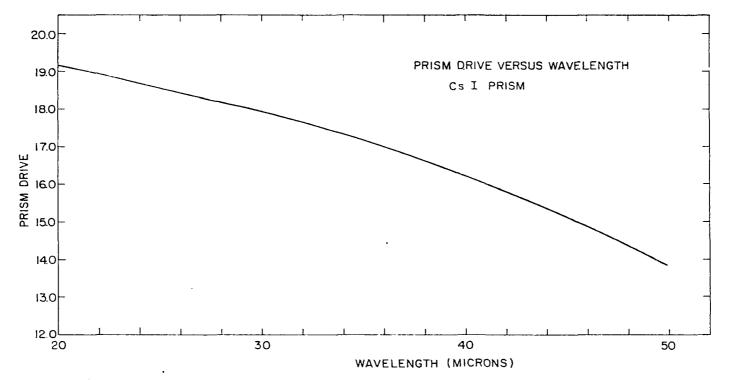


Figure 24. Approximate wavelength calibration for a 12° CsI prism in the Perkin-Elmer Model 160 monochromator. Hg green line at prism drive 23.0