phys. stat. sol. (b) 59, 241 (1973)

Subject classification: 6 and 20.1; 2; 22.1.1; 22.2.1; 22.2.2; 22.2.3

Max-Planck-Institut für Festkörperforschung, Stuttgart

Far-Infrared Absorption in Amorphous III–V Compound Semiconductors

By

W. PRETTL, N. J. SHEVCHIK, and M. CARDONA

The infrared spectra of amorphous films of GaP, GaAs, GaSb, InAs, and Ge prepared by sputtering have been measured from 10 to 4000 cm^{-1}. The absorption spectra in the region of the "optical" phonon frequencies show similarities to the phonon density of states as deduced from Raman scattering but the absorption becomes much smaller at low frequencies. It is shown that while the coupling constant for Raman scattering by an amorphous material varies as the square of the wave vector, it varies in the case of infrared absorption as its fourth power. The results are compared with those of Raman scattering and with the predictions of a simple model.

Amorphe Filme aus GaP, GaAs, GaSb, InAs und Ge wurden durch Kathodenzerstäubung hergestellt und ihre Infrarotspektren von 10 bis 4000 cm^{-1} gemessen. Im Frequenzbereich der optischen Phononen zeigen die Absorptionsspektren Ähnlichkeiten mit der Zustandsdichte der Phononen, die aus der Ramanstreuung folgt, jedoch ist die Absorption bei niedrigen Frequenzen wesentlich geringer. Während die Kopplungskonstante der Ramanstreuung an einem amorphen Material sich wie das Quadrat des Wellenvektors verhält, wird gezeigt, daß sie im Falle der Infrarotabsorption proportional zu seiner vierten Potenz ist. Die Ergebnisse werden mit den Vorhersagen eines einfachen Modells verglichen.

1. Introduction

It has been found that the relaxation of the k-selection rule in amorphous materials activates Raman scattering and infrared absorption of phonon modes which are usually forbidden in the corresponding crystalline materials [1 to 3]. This relaxation of the selection rules seems to be more complete for those compounds which lack a molecular unit [4], so that the Raman scattering intensity and the infrared absorption represent the phonon density of states multiplied by transition probabilities (i.e., matrix elements). If the short range order of the amorphous form is similar to that of the corresponding crystal, we may expect the Raman intensity and the infrared absorption to show some similarity to the phonon density of states of the crystal: essentially, the density of states in the amorphous form should be a broadened version of that of the crystalline phase [5].

The amorphous III–V compounds have been found to possess short range order similar to their crystalline forms [6, 7]. Raman scattering experiments on the materials have shown a striking similarity to the calculated density of phonon states [3, 8, 9]. We report here the first far-infrared measurements in amorphous III–V compounds. These results demonstrate that the infrared absorption resembles the phonon density of states less well than the Raman intensity, especially at low frequencies. We suggest that this result is due in part to the poor dipole coupling of the radiation to the low frequency modes in the long

wavelength limit: it is possible to show that the transition probabilities are proportional to the square of the phonon wave vector q^2 for Raman scattering [9] and to q^4 for infrared absorption.

2. Sample Preparation

The samples were prepared by rf sputtering of pressed powders of the compound material in a high purity (99.9999%) argon atmosphere at a pressure of 4×10^{-3} Torr. The base pressure of the vacuum chamber was 5×10^{-6} Torr before commencement of the sputtering. Silicon plates, 0.6 mm in thickness, were used as substrates because of their good optical transparency in the whole frequency range of interest. During sputtering the substrates were held at room temperature. The films were deposited to thicknesses ranging from 1.4 to 7 μm at rates of 1 to 2 μm/h. X-ray diffraction confirmed that the films were amorphous.

3. Experimental

The transmission spectra of the samples were measured in the frequency range from 10 to 4000 cm^{-1}. In the far-infrared region, up to 500 cm^{-1}, a Michelson type Fourier spectrometer (Polytec FIR 30) was used. At higher frequencies the measurements were performed with a grating spectrometer (Perkin Elmer 180).

In order to take into account the absorption occurring in the silicon substrates, as background spectrum the transmission of a silicon plate of the same thickness as those used for substrates was measured. The film thicknesses were determined from the spacings of the interference fringes in the near-infrared using the refractive indices of the bulk crystalline materials, as given in the literature [10, 11]. In the far-infrared region, where the wavelength of the radiation is much larger than the thickness of the films the absorption coefficient may be determined to a good approximation in the usual way by dividing the sample transmission by the background transmission and assuming the reflections at the film surfaces to be frequency independent [12]. At shorter wavelengths this approach is not valid, thus for wavelengths less than 25 μm only transmission curves will be shown. The GaP sample was measured at various temperatures from 6 to 300 K; all other samples were measured at room temperature only. The frequency resolution of 1 cm^{-1} in the far-infrared and 2 to 3 cm^{-1} at higher frequencies was sufficient to resolve all structures observed in the absorption spectra.

4. Results

The absorption coefficient of all investigated samples is shown in Fig. 1 as a function of the frequency in the far-infrared region. The spectral range covers the phonon frequencies of the corresponding crystalline materials. The phonon frequencies at the X, L and Γ critical points of the Brillouin zone as obtained from [13 to 15] are indicated. The general features of the absorption curves are the same for all amorphous samples. One strong absorption band appears which is concentrated in the frequency range of the optical phonons of the corresponding crystalline material. Only modes whose frequencies correspond to that of the longitudinal acoustic phonons contribute to the absorption at the low frequency side of the bands. In the frequency region of the transverse acoustic phonons the absorption vanishes or is very low. In all cases the maximum of the absorption occurs at a frequency somewhat less than $\omega_{TO(\Gamma)}$, the frequency of the

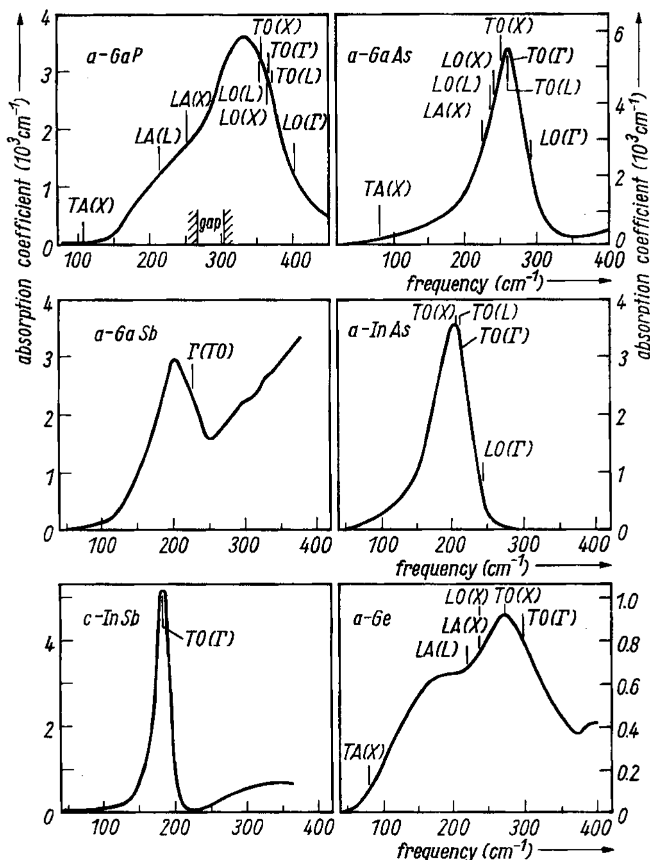

Fig. 1. Far-infrared absorption of a-GaP, a-GaAs, a-GaSb, a-InAs, c-InSb and a-Ge determined from transmission measurement of sputtered films on Si substrates. The film thicknesses varied between 1.4 and 7 μm. The resolution was 1 cm^{-1}. The a-Ge spectrum has also been measured by [21]

dispersion oscillator (reststrahlen) in the crystalline material. With a-GaAs and a-InAs an asymmetric absorption curve with no structures at all has been found. In a-GaSb, which shows the same type of a structureless band, the absorption further increases at higher frequencies. In a-GaP a weak shoulder at the low frequency side of the absorption band has been found which leads to an inflexion of the curve. This inflexion corresponds just to the band gap between the acoustic and optical phonons in the crystalline GaP [13]. The a-Ge sample shows a similar but more distinct low frequency shoulder. The frequency of the minimum in the absorption curve lies below the zone boundary longitudinal acoustic phonons. For the purpose of comparison we have measured the far-infrared absorption of a crystalline InSb thin film prepared by the same method as were the amorphous films. X-ray diffraction indicated that the film consisted of small zincblende structure polycrystals of about 30 Å in size, so that they do not have much more long range order than the amorphous films, which have "crystallite" sizes of about 10 Å. Nevertheless, the absorption curve is

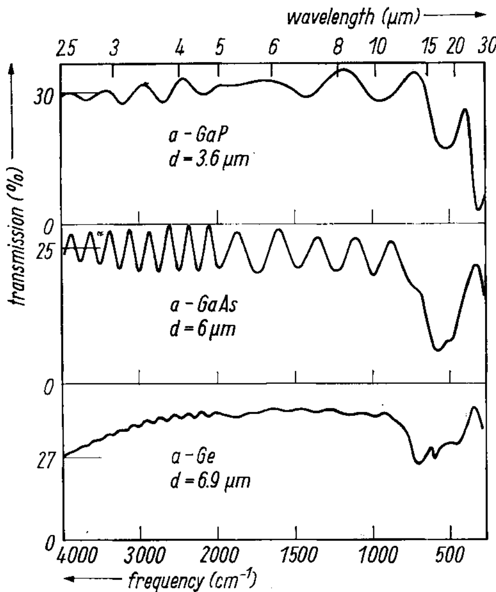

Fig. 2. Transmission spectra of a-GaP, a-GaAs, and a-Ge sputtered films on Si substrates. d is the film thickness. The resolution was 2 to 3 cm^{-1}

roughly of Lorentzian type, as expected for a crystalline film, and somewhat narrower than the absorption bands of the amorphous films. The maximum absorption occurs at the frequency $\omega_{TO(\Gamma)}$.

In Fig. 2 we have plotted the transmission of a-GaP, a-GaAs and a-Ge from 400 to 4000 cm^{-1}. At high wavenumbers these films show structures associated with interference fringes. In the region 500 to 700 cm^{-1} a dip occurred in all the transmission spectra which corresponded to a maximum absorption strength of 10^3 cm^{-1}. Although it is tempting to attribute this absorption to combination phonon bands, the absorption band in a-GaP did not show any temperature dependence down to 6 K and the magnitude of the absorption in all amorphous samples is about 100 times greater than that observed in the crystal [16]. We know of no disorder induced mechanism that could account for such an increase in the oscillator strength. It is more likely that these bands correspond to vibrations from oxygen impurities [18, 19].

No data exists for the amorphous III–V compounds relating the absorption bands to impurities. Some investigations have, however, been made for amorphous Ge. In our amorphous Ge film, the absorption band measured at 700 cm^{-1} is equal in strength to the bands measured in sputtered films by Tauc and Abraham [18]. They attributed this band to about a 5% oxygen impurity. Assuming that the dipole coupling of the oxygen defect in the III–V compounds is comparable to that of Ge, we estimate the oxygen content of our films to be about the same. We thus stress the importance of having an ultrapure background pressure, since even at deposition rates of about 10 Å/s, with a base pressure of 5×10^{-6} Torr, the flux of contaminants is equal to this rate. To obtain a film of sufficient purity it would be necessary to have a base pressure in the 10^{-8} Torr range and better.

5. Discussion

The far-infrared absorption as measured here may be attributed to the disorder of the amorphous materials, although some contribution of impurities to the violation of the k-selection rule, with conservation of oscillator strength may also exist.

The question must also be raised as to whether some of the absorption in Fig. 1 is not due to the impurities themselves (local or resonant modes). As discussed, we believe that the dominant impurity, introduced during the sputtering procedure, is oxygen. To settle this question we determined from our measurements

the integral absorption of the amorphous forms $A_a = \int \alpha(\omega)\, d\omega$, where α is the absorption coefficient. The integral absorption (f-sum rule) is a measure of the oscillator strength of the phonons. Further we calculated the same expression, A_c, for the crystalline materials from the known dielectric constants [20]. The results are given in Table 1. A comparison of A_a and A_c shows that within the accuracy of our measurements both values are comparable. Thus, we conclude that, in spite of the fact that impurities are present in our samples, they do not contribute significantly to the oscillator strength of the III–V compounds in the phonon region. The absorption may be described by

$$\alpha(\omega) \propto |\boldsymbol{M}(\omega)|^2 \varrho(\omega)\,, \tag{1}$$

where $\boldsymbol{M}(\omega)$ is a frequency dependent dipole moment and $\varrho(\omega)$ is the density of phonon states of the amorphous material. In a single crystal with one optical active phonon at $\omega_{TO(\Gamma)}$, $|\boldsymbol{M}(\omega)|^2$ is a Lorentzian type function centered at $\omega_{TO(\Gamma)}$, whose width is given by the damping constant resulting from the anharmonicity. In this case $|\boldsymbol{M}(\omega)|^2$ projects a narrow line out of the phonon density of the crystal contributing to the infrared absorption. This may be visualized from the absorption curve of c-InSb in Fig. 1.

Table 1

Integrated absorption: A_a experimental determined from amorphous materials, A_c calculated from the dielectric data of the crystalline materials

	GaP	GaAs	GaSb	InAs	InSb
A_a (10^5 cm^{-2})	5.9	5.8	2.8	3.5	1.5
A_c (10^5 cm^{-2})	7.8	4.5	1.7	3.8	1.6

In an amorphous material, where the translational symmetry is relaxed, in principle, all phonons are optically active and $\boldsymbol{M}(\omega)$ may be different from zero in the whole frequency range of the phonons. If $\boldsymbol{M}(\omega)$ were weakly dependent on the frequency ω, the absorption curve would resemble the density of states.

A comparison in Fig. 3 of the broadened density of GaAs (curve a) with the experimental absorption spectrum (curve c) shows that this is not the case: while $\boldsymbol{M}(\omega)$ is nearly constant between 250 and 300 cm^{-1}, it must decrease rapid-

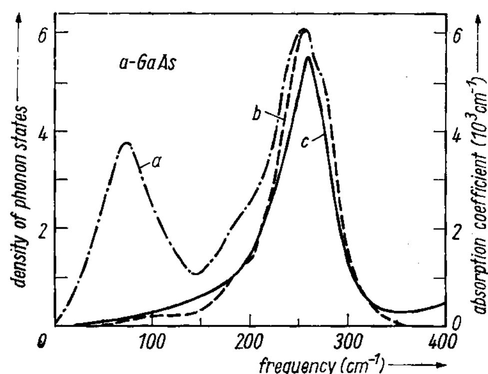

Fig. 3. Density of phonon states and absorption coefficient of amorphous GaAs: (a) broadened density of states after Smith et al. [3], (b) calculated absorption coefficient according to equation (7), (c) experimentally determined absorption coefficient

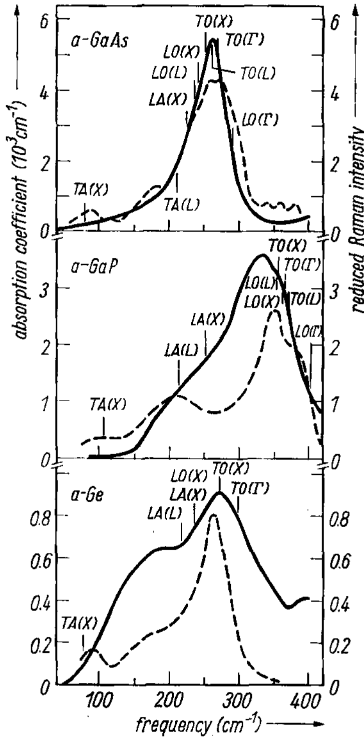

Fig. 4. Comparison between far-infrared absorption (solid lines) and Raman scattering intensity (dashed lines) of a-GaAs, a-GaP, and a-Ge. The Raman data are taken from Smith et al. [3] (GaAs) and from Wihl et al. [8] (GaP, Ge)

ly between 250 cm^{-1} and zero. A consequence of this fact is that the TA branch, which is actually seen in Raman scattering (see Fig. 4), does not appear in the infrared absorption.

The Raman scattering cross section S of an amorphous material is given by [2]

$$S \propto \frac{1}{\omega} |\hat{m}_i C_{ij} \hat{n}_j|^2 \varrho(\omega) f\left(\frac{h\omega}{kT}\right), \quad (2)$$

where $|\hat{m}_i C_{ij} \hat{n}_j|^2$ is the coupling constant of the Raman tensor C_{ij} and the polarization vectors $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ of the incident and scattered field, and $f(x)$ the corresponding Bose-Einstein statistical factor. The coupling constant has been shown to vary like q^2 ($\boldsymbol{q}$ wave vector) both theoretically and experimentally [9, 17] in the quasi-continuum long wavelength limit. At higher frequencies $|\hat{m}_i C_{ij} \hat{n}_j|^2$ seems to become nearly constant. Thus the reduced Raman cross section $S \omega f^{-1}$ represents reasonably well the density of phonon states. The reduced cross sections of a-GaAs, a-GaP, and a-Ge are shown in Fig. 4 together with the corresponding infrared absorption spectra. All Raman spectra are stronger at low energies than the corresponding infrared spectra. We shall thus look for a mechanism which predicts for $|\boldsymbol{M}|^2$ (equation (1)) a dependence on wave vector stronger than the q^2 found for the coupling constant of Raman scattering. We consider the quasi-continuous limit in which plane waves of amplitude $\boldsymbol{u}$ propagate in the amorphous solid and expand the linear terms in $\boldsymbol{u}$ of the vector $\boldsymbol{M}$ and the Raman tensor C_{ij} in power series of q_i:

$$\left.\begin{aligned} M_i &= (M_{ik} + M_{ikj} q_j + M_{ikjl} q_j q_l + \cdots) u_k , \\ C_{ij} &= (C_{ijk} + C_{ijkl} q_l + C_{ijklm} q_l q_m + \cdots) u_k . \end{aligned}\right\} \quad (3)$$

If we now invoke the presence of macroscopic inversion symmetry in the amorphous material the tensors of odd rank in (3) must vanish. Besides, $M_{ij} = 0$ because it corresponds to a uniform translation of the solids. Thus, (3) reduces to

$$\left.\begin{aligned} M_i &= M_{ikjl} q_j q_l u_k , \\ C_{ij} &= C_{ijkl} q_l u_k . \end{aligned}\right\} \quad (4)$$

Equations (4) yield a proportionality of $|\boldsymbol{M}|^2$ to q^4 and of $|\hat{m}_i C_{ij} \hat{n}_j|^2$ to q^2 which, at least qualitatively, explains the experimental results.

In order for our reasoning to be valid we must understand the macroscopic inversion symmetry in the following sense: for q sufficiently small (long wavelength) we choose a piece A of amorphous material much smaller than λ but

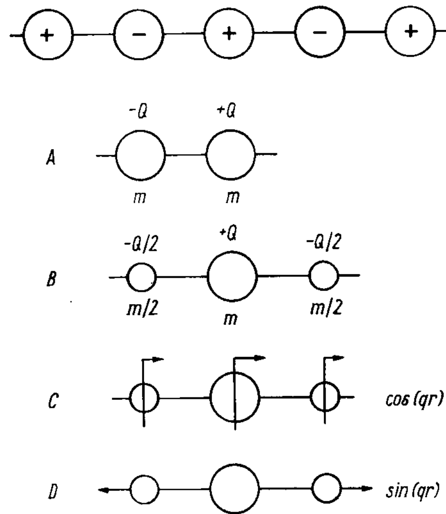

Fig. 5. One-dimensional ionic chain and its unit cell (A). B represents the symmetric unit cell used as a building block of an amorphous ionic chain. C is its infrared active and D its Raman active vibration

nevertheless a good statistical sampling. Within a distance small compared with λ we must be able to find with high probability a sample which is the inverse of A. We believe this criterion should be satisfied in the amorphous tetrahedral semiconductors.

Inspite of the generality of the proof given above, it is useful to derive the wavelength behavior of M and C_{ij} on the basis of simple models. Let us consider the simplest model of ionic solid, namely the linear chain of atoms of the same mass and charges $\pm Q$ (Fig. 5). The chain becomes amorphous by repeating the unit cells A in a disordered manner. These unit cells, however, do not have the inversion symmetry of which we made use in our formal proof. We thus use instead of A the symmetry unit cells B, with atoms of masses $m/2$ at both ends. We chose the ion of mass m as the center of coordinates and examine the dipole moment M induced by plane waves $\cos \boldsymbol{q}\,\boldsymbol{r}$ and $\sin \boldsymbol{q}\,\boldsymbol{r}$. The cosine wave induces the dipole moment

$$M \propto \frac{1}{2}(1 - \cos q\,a) = \sin^2 \frac{1}{2} q\,a\,, \tag{5}$$

while for the sine wave $M \equiv 0$. The vibration produced by $\sin \boldsymbol{q}\,\boldsymbol{r}$ (Fig. 5, D), however, is Raman active while the odd parity vibration produced by $\cos \boldsymbol{q}\,\boldsymbol{r}$ (Fig. 5, C) is Raman inactive. The contribution of Fig. 5, D to the Raman tensor thus is

$$C_{ij} \propto \sin q\,a\,. \tag{6}$$

Here a is the nearest neighbor distance between the ions. An expansion of (5) and (6) for small q yields, respectively, the q^4 and q^2 dependence of the infrared absorption and the scattering cross section found earlier.

The model just treated is actually not as far removed from the tetrahedral array under consideration in this paper. In fact, a building block very similar to Fig. 5, C is obtained by placing an atom of charge $+Q$ and mass m at the center of a tetrahedron and atoms of charge $-Q/4$ and mass $m/4$ at the corners in order

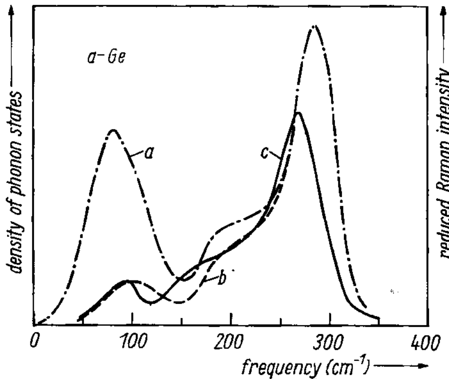

Fig. 6. Density of phonon states and reduced Raman cross section of a-Ge: (a) broadened density of states after Smith et al. [3], (b) calculated reduced Raman cross section according to equation (7), (c) experimental Raman cross section after Wihl et al. [8]

to take care of the fact that the corner atoms are shared by four tetrahedra. For waves along [001] and [111] results analogous to (5) and (6) are found. These equations are, in principle, only valid in the quasi-continuous limit ($q\,a \ll 1$) in which the sines become equal to the arguments. It is, however, interesting to test by comparison with the experimental results whether (5) and (6) have any validity beyond the small q region. The first difficulty arises with (6) which predicts zero Raman cross section for the Raman active optical modes which occur, in the extended zone, for $q = \pi/a$. Actually the coupling constant should be nearly frequency independent throughout the optical branches since these branches are nearly flat. We must therefore abandon the hope of using (5) and (6) throughout the whole extended zone. Our next, more modest effort will be to test whether they can be used throughout the first Brillouin zone. We replace, with the spirit of the Debye model, q by ω/c. We then determine the "average" speed of sound c so as to place the first maximum of $\sin \omega\, a/c$ at the peak ω_M of the density of optical phonons shown in Fig. 3 and 6 (it is also possible to use a different velocity for each phonon branch. We do not do it for the sake of simplicity, and in view of the qualitative nature of our considerations). This peak occurs at the edge of the first Brillouin zone. Above ω_M we take the $|\hat{m}_i\, C_{ij}\, \hat{n}_j|^2$ and $|\boldsymbol{M}|^2$ to be independent of frequency. Below ω_M they are taken to be

$$\left.\begin{aligned} |\boldsymbol{M}|^2 &\propto \sin^4\left(\frac{\pi\,\omega}{4\,\omega_M}\right), \\ |\hat{m}_i\, C_{ij}\, \hat{n}_j|^2 &\propto \sin^2\left(\frac{\pi\,\omega}{2\,\omega_M}\right). \end{aligned}\right\} \tag{7}$$

The dashed curves b of Fig. 3 and 6 represent the broadened density of phonons (curves a) multiplied by the corresponding coupling constant of equation (7). The agreement with the experimental curves c is quite good in view of the crudeness of the model and the experimental uncertainty.

Acknowledgements

The able assistance of J. Tejeda and A. Barynin in the film preparation are gratefully acknowledged. The authors wish to thank Prof. M. Thorpe and Prof. H. Bilz and Dr. J. S. Lannin, Dr. B. Gliss, Dr. A. Martin, Dr. T. P. Martin, and Dr. L. v. Heimendahl for their helpful comments.

References

[1] F. ANGRESS, S. D. SMITH, and K. F. RENK, Proc. Internat. Conf. Lattice Dynamics, Copenhagen 1963, Pergamon Press, Oxford 1964 (p. 467).
[2] R. SHUKER and R. W. GAMMON, Phys. Rev. Letters **25**, 222 (1970).
[3] J. E. SMITH, M. H. BRODSKY, B. L. CROWDER, and M. I. NATHAN, Proc. II. Internat. Conf. Light Scattering in Solids, Ed. M. BALKANSKI, Flammarion, Paris 1971 (p. 330).
[4] G. LUCOVSKY, Phys. Rev. B **6**, 1480 (1972).
[5] D. WEAIRE and R. ALBEN, Phys. Rev. Letters **29**, 1505 (1972).
[6] N. J. SHEVCHIK, Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass., Technical Report HP 29 and ARPA-44, 1972.
[7] N. W. SHEVCHIK and W. PAUL, J. non-cryst. Solids, in the press.
[8] M. WIHL, M. CARDONA, and G. TAUC, J. non-cryst. Solids **8–10**, 172 (1972).
[9] J. S. LANNIN, Solid State Commun. **11**, 1573 (1972).
[10] B. O. SERAPHIN and H. E. BENNETT, in: Semiconductors and Semimetals, Vol. 3, Ed. R. K. WILLARDSON and A. C. BEER, Academic Press, New York/London 1967 (p. 499).
[11] C. D. SALZBERG and J. J. VILLA, J. Opt. Soc. Amer. **47**, 244 (1957).
[12] E. E. BELL, Handbuch der Physik, Vol. XXX/2a, Ed. L. GENZEL, Springer Verlag, Berlin/Göttingen/Heidelberg/New York 1967 (p. 1).
[13] J. L. YARNELL, J. L. WARREN, R. G. WENZEL, and P. J. DEAN, IV. I.A.E.A. Symp. Neutron Inelastic Scattering, Vol. I, I.A.E.A., Vienna 1968 (p. 301).
[14] G. NELIN and G. NILSSON, Phys. Rev. B **5**, 3151 (1972).
[15] G. L. T. WAUGH and G. DOLLING, Phys. Rev. **132**, 2410 (1963).
[16] W. G. SPITZER, in: Semiconductors and Semimetals, Vol. 3, Ed. R. K. WILLARDSON and A. C. BEER, Academic Press, New York/London 1967 (p. 176).
[17] J. S. LANNIN, Solid State Commun., to be published.
[18] J. TAUC and A. ABRAHAM, J. non-cryst. Solids **4**, 279 (1970).
[19] A. S. BARKER, R. BERMAN, and H. W. VERLEUR, J. Phys. Chem. Solids **34**, 123 (1973).
[20] M. HASS, in: Semiconductors and Semimetals, Vol. 3, Ed. R. K. WILLARDSON and A. C. BEER, Academic Press, New York/London 1967 (p. 3).
[21] A. LURIO and M. H. BRODSKI, private communication.

(Received May 29, 1973)