Brillouin scattering and elastic moduli of silver thiogallate (AgGaS₂)*

M. H. Grimsditch and G. D. Holah

Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 14 July 1975)

The room-temperature elastic moduli c_{ij} of AgGaS₂ have been determined using laser Brillouin scattering. This is the first determination of these moduli for any of the ternary compounds which crystallize with the chalcopyrite structure. From the Brillouin shifts the following values for the elastic moduli were obtained: $c_{11} = 8.79 \pm 0.05$, $c_{33} = 7.58 \pm 0.05$, $c_{44} = 2.41 \pm 0.05$, $c_{66} = 3.08 \pm 0.05$, $c_{12} = 5.84 \pm 0.05$, and $c_{13} = 5.92 \pm 0.06$, in units of 10^{11} dyn/cm².

I. INTRODUCTION

The electronic band structure,[1-5] lattice vibrational modes,[6-17] and nonlinear optical properties[18-22] of ternary semiconductors which crystallize in the chalcopyrite structure, with the general formulas I-III-VI₂ and II-IV-V₂, have been the subject of many recent investigations. Although some of these materials have been studied for possible use in heterojunctions, perhaps their most important potential lies in their application to nonlinear optical devices. The nonlinear susceptibilities of both groups of crystals have been calculated and discussed by Levine.[23-25] For a number of the chalcopyrites the nonlinear coefficient is greater than that of GaAs, which is often used as a standard for nonlinear optical properties. In addition, the chalcopyrites, being uniaxial, are birefringent and hence allow phase-matching possibilities which are not available in isotropic GaAs. These crystals are ternary isoelectronic analogs of the sphalerite binary systems II-VI and III-V, respectively. The greater degree of covalency of the II-IV-V₂ compounds compared to those of the I-III-VI₂ group suggests that the II-IV-V₂ will generally have smaller band gaps and less lattice vibrational absorption than the I-III-VI₂; because of this, the latter have been found to be more useful in the visible and near infrared, and the former in the far infrared. Of the I-III-VI₂ compounds, the nonlinear properties of AgGaS₂, with a direct gap[3] of 2.70 eV, have been the most widely investigated, and the compound has been used, for example, to generate tunable radiation from 4.6 to 12 μm by means of downconversion techniques.[22]
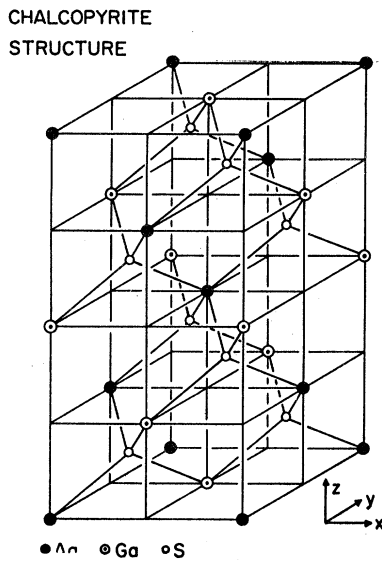
Because of the inherent interest in these materials, it is important to determine the elastic moduli c_{ij} of AgGaS₂. These moduli are also useful in lattice-dynamical calculations of phonon dispersion curves.

II. STRUCTURE AND LATTICE DYNAMICS OF CHALCOPYRITES

The body-centered tetragonal structure of AgGaS₂ is shown in Fig. 1. The primitive cell contains two formula units and the point group is $\overline{4}2m$ (D_{2d}). From Fig. 1 it is apparent that the structure is very closely related to that of sphalerite (zinc blende); as mentioned above, AgGaS₂ is an isoelectronic analog of ZnS. Both the binary and the ternary have tetrahedral coordination, and the zinc-blende structure is obtained from chalcopyrite if the two cations become indistinguishable. However, the structural correlation is not perfect, since chalcopyrites usually have tetragonal distortion, most often compression, along the c axis, i.e., $2 - c/a \geq 0$. The presence of two different cations, from different columns of the periodic table, gives rise to two anion-cation bonds, Ag–S and Ga–S. The Ga–S bond is more covalent[25] and hence is stiffer than the Ag–S bond, leading to a displacement of the anion relative to its equilibrium position in zinc blende. For AgGaS₂, $a = 5.75722$ Å, $2 - c/a = 0.2103$, and the anion free coordinate x_f, as defined below, is changed from 0.25 in ZnS to 0.304 in AgGaS₂.[26,27] The sulfur ions are therefore found at $(x_f, \frac{1}{4}, \frac{1}{8})$, $(\frac{3}{4}, \frac{1}{2} - x_f, \frac{3}{8})$, $(\frac{1}{4}, \frac{1}{2} + x_f, \frac{3}{8})$, and $(1 - x_f, \frac{3}{4}, \frac{1}{8})$, i.e., the anions are displaced towards the trivalent cation. The bond lengths are 2.276 (Ga–S) and 2.556 Å (Ag–S).[26]

It has been shown that the zone points Γ (000), X (001), $W(01\frac{1}{2})$, and W $(10\frac{1}{2})$ of zinc blende become zone center points in chalcopyrites.[28,29] The two Brillouin zones are shown in Fig. 2, and it can be shown that the chalcopyrite Brillouin zone is one-quarter that of zinc blende. Using these relations, the electronic band structures of chalcopyrites have been interpreted,[3,4] and a set of symmetry coordinates for the lattice vibrational modes has been derived.[8] These would be exactly normal mode coordinates if there were exact correlations with zinc blende. Although the analysis of electronic band structure has been reasonably successful, a number of difficulties have arisen in the interpretation of the Raman and infrared reflectivity data of some of the I-III-VI₂ compounds. Figure 3 shows the dispersion curves of ZnS,[30] and also indicates the symmetry of certain zone points when they are transformed to zone-center points in chalcopyrite.

FIG. 1. Chalcopyrite structure of $AgGaS_2$.
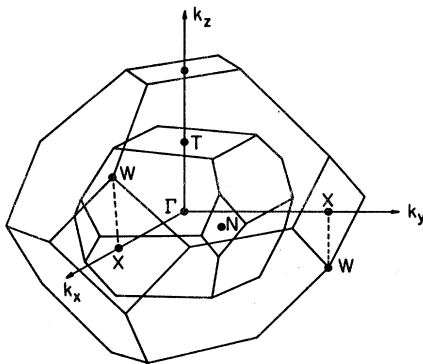

FIG. 2. Brillouin zones of zinc blende and chalcopyrite.
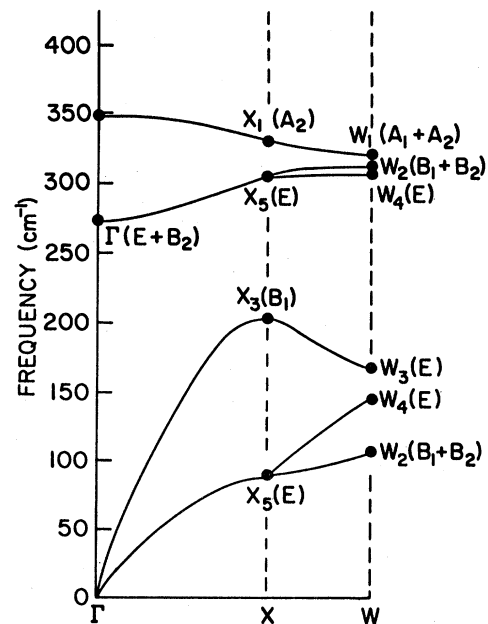

FIG. 3. Phonon dispersion curves of ZnS (see Ref. 30). Irreducible representations to which the phonons belong are indicated, and the designations in parentheses give the symmetry of these modes when they are folded back into the chalcopyrite structure.

However, the presence of two different cation-anion bonds having significantly different bonding strengths (force constants) may restrict the usefulness of zinc-blende–chalcopyrite correlations.

A group-theoretical analysis shows that $AgGaS_2$ has 21 zone-center optical modes which can be classified by their symmetry into one A_1, two A_2, three B_1, three B_2, and six E, the E modes being doubly degenerate. The elastic moduli that characterize the chalcopyrite structure are c_{11}, c_{33}, c_{44}, c_{66}, c_{12}, and c_{13}.

III. EXPERIMENTAL PROCEDURE

A single-moded Coherent Radiation Ar^+ laser operating at a wavelength of 5145 Å was used as the exciting source. The laser power used ranged between 80 and 100 mW. The scattered radiation was analyzed using a triple-passed piezoelectrically scanned Fabry-Perot interferometer.[31] An RCA 7265 photomultiplier in conjunction with photon-counting electronics was used for detection. A narrow-band interference filter, half width ~ 10 Å, centered at 5145 Å was used to eliminate Raman lines and other unwanted radiation. Because the peak transmission of an interference filter shifts to shorter wavelengths when it is tilted, it was also used to identify the Stokes and the anti-Stokes components of the spectrum. In order to reduce the intensity of the parasitic laser radiation, an iodine-vapor cell was used in some of the experiments. The density ρ was calculated from the lattice constants to be 4.70 g/cm^3. The refractive indices n_o = 2.6676 and n_e = 2.6503 were obtained by a linear interpolation of the values of Boyd et al.[19] All the experiments in this investigation were performed at ~ 295 °K.

IV. THEORETICAL BACKGROUND

The theory of Brillouin scattering, i.e., light scattering by acoustic phonons, is well known[32,33] and only the important equations will be quoted here. The frequency shift of a Brillouin line is given by

$$\Delta \nu / \nu = \pm (v_s/c)(n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2}, \tag{1}$$

where $\Delta \nu$ is the frequency shift of the Brillouin line, i.e., the acoustic phonon frequency, ν is the fre-

TABLE I. Scattering tensor T, $X=v_s^2\,\rho$, and polarization vector $\vec{u}$ of phonons travelling along $\vec{q}$. The entries in the columns for $\vec{q}$ and $\vec{u}$ are their direction cosines. L, T, QL, and QT indicate longitudinal, transverse, quasilongitudinal, and quasitransverse, respectively. Notation of the p_{ij}'s conforms to the generalized theory of photoelasticity as given in Ref. a. Other than the changes introduced by the new symmetry of the elasto-optic constants, the tensors T agree with those of Ref. 31 except for a factor of 2, which arises because of the manner in which T is defined. In addition, the tensor for the phonon progapating along [001] and polarized along [100] is given incorrectly in Ref. 31.

$\vec{q}$	X	T		$\vec{u}$	
(1,0,0)	c_{11}	2	$\begin{pmatrix} n_o^4 p_{11} & 0 & 0 \\ 0 & n_o^4 p_{12} & 0 \\ 0 & 0 & n_e^4 p_{31} \end{pmatrix}$	(1,0,0)	L
	c_{66}	2	$\begin{pmatrix} 0 & n_o^4 p_{66} & 0 \\ n_o^4 p_{66} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	(0,1,0)	T
	c_{44}	2	$\begin{pmatrix} 0 & 0 & n_o^2 n_e^2 p_{4\bar{4}} \\ 0 & 0 & 0 \\ n_o^2 n_e^2 p_{4\bar{4}} & 0 & 0 \end{pmatrix}$	(0,0,1)	T
(0,0,1)	c_{33}	2	$\begin{pmatrix} n_o^4 p_{13} & 0 & 0 \\ 0 & n_o^4 p_{13} & 0 \\ 0 & 0 & n_e^4 p_{33} \end{pmatrix}$	(0,0,1)	L
	c_{44}	2	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & n_o^2 n_e^2 p_{44} \\ 0 & n_o^2 n_e^2 p_{44} & 0 \end{pmatrix}$	(0,1,0)	T
	c_{44}	2	$\begin{pmatrix} 0 & 0 & n_o^2 n_e^2 p_{44} \\ 0 & 0 & 0 \\ n_o^2 n_e^2 p_{44} & 0 & 0 \end{pmatrix}$	(1,0,0)	T
(1/√2, 1/√2, 0)	$\tfrac12(c_{11}+c_{12}+2c_{66})$	2	$\begin{pmatrix} n_o^4(p_{11}+p_{12}) & n_o^4 2p_{66} & 0 \\ n_o^4 2p_{66} & n_o^4(p_{11}+p_{12}) & 0 \\ 0 & 0 & 2n_e^4 p_{31} \end{pmatrix}$	(1/√2, 1/√2, 0)	L
	$\tfrac12(c_{11}-c_{12})$		$\begin{pmatrix} n_o^4(p_{11}-p_{12}) & 0 & 0 \\ 0 & -n_o^4(p_{11}-p_{12}) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	(1/√2, −1/√2, 0)	T
	c_{44}	$\sqrt2$	$\begin{pmatrix} 0 & 0 & n_o^2 n_e^2 p_{4\bar{4}} \\ 0 & 0 & n_o^2 n_e^2 p_{4\bar{4}} \\ n_o^2 n_e^2 p_{4\bar{4}} & n_o^2 n_e^2 p_{4\bar{4}} & 0 \end{pmatrix}$	(0,0,1)	T
(1/√2, 0, 1/√2)	$\tfrac12(R+\sqrt L)^{\text{b}}$	c		c	QL
	$\tfrac12(R-\sqrt L)^{\text{b}}$	c		c	QT
	$\tfrac12(c_{66}+c_{44})$	$\sqrt2$	$\begin{pmatrix} 0 & n_o^4 p_{66} & 0 \\ n_o^4 p_{66} & 0 & n_o^2 n_e^2 p_{44} \\ 0 & n_o^2 n_e^2 p_{44} & 0 \end{pmatrix}$	(0,1,0)	T
(½, ½, 1/√2)	$\tfrac12(M+\sqrt N)^{\text{b}}$	c		c	QL
	$\tfrac12(M-\sqrt N)^{\text{b}}$	c		c	QT
	$\tfrac14(c_{11}+2c_{44}-c_{12})$		$\begin{pmatrix} n_o^4(p_{11}-p_{12})/\sqrt2 & 0 & n_o^2 n_e^2 p_{44} \\ 0 & -n_o^4(p_{11}-p_{12})/\sqrt2 & -n_o^2 n_e^2 p_{44} \\ n_o^2 n_e^2 p_{44} & -n_o^2 n_e^2 p_{44} & 0 \end{pmatrix}$	(1/√2, −1/√2, 0)	T

[a] D. F. Nelson and M. Lax, Phys. Rev. Lett. **24**, 379 (1970).

[b] $R=\tfrac12(c_{11}+c_{33})+c_{44}$; $L=\tfrac14(c_{11}-c_{33})^2+(c_{13}+c_{44})^2$; $\overline{M}=\tfrac14(c_{11}+2c_{33}+c_{12}+4c_{44}+2c_{66})$; $N=\tfrac{1}{16}(c_{11}-2c_{33}+c_{12}+2c_{66})^2+(c_{13}+c_{44})^2$.
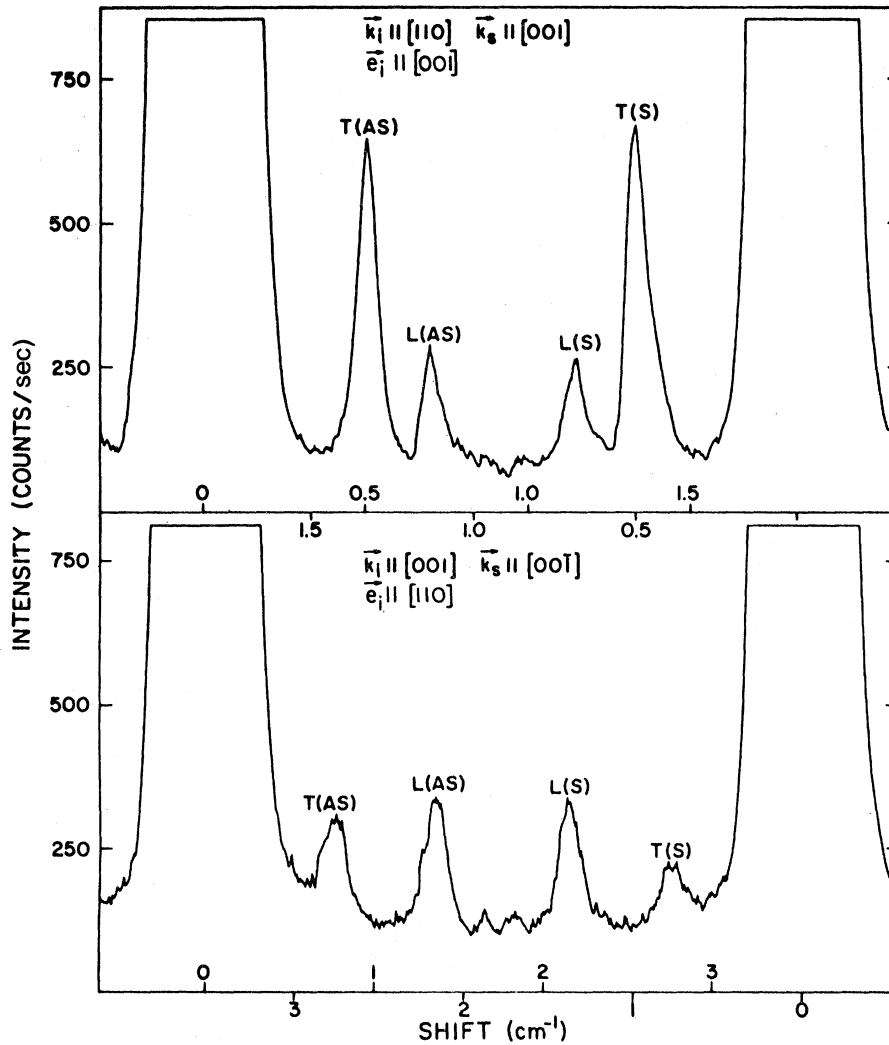
[c] Indicates that the vector or tensor depends on the c_{ij}'s.

FIG. 4. Brillouin spectra of AgGaS$_2$ observed with a triple-passed scanning Fabry-Perot interferometer using approximately 95 mW of 5145-Å radiation from an Ar$^+$ laser. The scales below and above the base line refer to the shifts of the Stokes (S) and anti-Stokes (AS) components, respectively. T (transverse) and L (longitudinal) give the polarization characteristics of the phonon responsible for the scattering. Upper part of the figure was obtained in the right-angle scattering geometry with the incident light along $\vec{k}_i \parallel$ [110] polarized along $\vec{e}_i \parallel$ [001], and the scattered light along $\vec{k}_s \parallel$ [001]. No analyzer was used. The lower part of the figure was obtained in the backscattering configuration with the incident and scattered light a few degrees from [001]. Incident light was polarized along [110] and no analyzer was used in the scattered light. An I$_2$ vapor cell was used to reduce the intensity of the scattered laser radiation. It should be noted that the transverse phonons have zero scattering intensity for light incident and scattered exactly along [001].

quency of the incident light, v_s is the sound velocity of the phonon responsible for the scattering, c is the velocity of light, n_i and n_s the refractive indices for the incident and scattered light, respectively, and θ is the angle through which the light is scattered.

The velocity of the acoustic phonon is related to the elastic moduli c_{ij} through $v_s = \sqrt{(X/\rho)}$, where ρ is the density and X is an appropriate combination of c_{ij}'s obtained by solving the equations of motion for a specific propagation direction. For a given direction of phonon propagation there will be generally three distinct solutions for X, corresponding to one quasilongitudinal and two quasitransverse phonons; for high-symmetry directions the two transverse phonons may be degenerate. Each phonon is characterized by a scattering tensor T such that the scattered intensity is given by

$$I \propto (\hat{e}_i \cdot T \cdot \hat{e}_s)^2 / X , \qquad (2)$$

where $\hat{e}_s$ and $\hat{e}_i$ are unit polarization vectors of the scattered and incident light, respectively. The effective elastic moduli and scattering tensors for the phonons studied in the present work are given in Table I.

V. RESULTS AND DISCUSSION

Figure 4 shows typical spectra for both right-angle and backscattering geometries from which Brillouin frequencies were obtained. As can be seen from the scattering tensors, the transverse modes observed in backscattering should have zero intensity. However, for geometries where the incident and scattered light are not exactly collinear, the selection rules are modified sufficiently to make the transverse modes observable. Table II contains the experimental values for combinations of the c_{ij}'s determined in this study. A least-squares fit was made to the first eleven expressions to determine

TABLE II. Elastic moduli of $AgGaS_2$ obtained from Brillouin scattering (units 10^{11} dyn/cm^2). Direction cosines of the incident and scattered light are given in the columns for $\vec{k}_i$ and $\vec{k}_s$, respectively.

Scattering geometry			Phonon		X		
$\vec{k}_i$	$\vec{k}_s$	$\vec{q}$	Polarization	Theory	Experiment	Least-squares fit
(0, 0, −1)	(0, 0, 1)	(0, 0, 1)	L	c_{33}	7.57 ± 0.05	7.58
(0, 0, −1)	(0, 0, 1)	(0, 0, 1)	T	c_{44}	2.38 ± 0.06	2.41
(−1, 0, 0)	(1, 0, 0)	(1, 0, 0)	L	c_{11}	8.83 ± 0.05	8.79
(−1, 0, 0)	(1, 0, 0)	(1, 0, 0)	L	c_{11}	8.83 ± 0.05	8.79
(−1, 0, 0)	(1, 0, 0)	(1, 0, 0)	T	c_{44}	2.30 ± 0.07	2.41
(−1/√2, −1/√2, 0)	(1/√2, 1/√2, 0)	(1/√2, 1/√2, 0)	L	$\frac{1}{2}(c_{11}+2c_{66}+c_{12})$	10.37 ± 0.03	10.40
(−1/√2, −1/√2, 0)	(1/√2, 1/√2, 0)	(1/√2, 1/√2, 0)	T	$\frac{1}{2}(c_{11}-c_{12})$	1.45 ± 0.03	1.47
(−1/√2, −1/√2, 0)	(0, 0, 1)	($\frac{1}{2}$, $\frac{1}{2}$, 1/√2)	T	$\frac{1}{2}(c_{11}-c_{12}+2c_{44})$	1.94 ± 0.02	1.94
(−1, 0, 0)	(0, 0, 1)	(1/√2, 0, 1/√2)	T	$\frac{1}{2}(c_{44}+c_{66})$	2.75 ± 0.01	2.75
(−1, 0, 0)	(0, 0, 1)	(1/√2, 0, 1/√2)	T	$\frac{1}{2}(c_{44}+c_{66})$	2.77 ± 0.02	2.75
(−1, 0, 0)	(0, 0, 1)	(1/√2, 0, 1/√2)		$X_{QL}+X_{QT}=R^a$	10.60 ± 0.02	10.60
(−1, 0, 0)	(0, 0, 1)	(1/√2, 0, 1/√2)		$X_{QL}-X_{QT}=\sqrt{L}^a$	8.29 ± 0.02	8.36
(−1/√2, −1/√2, 0)	(0, 0, 1)	($\frac{1}{2}$, $\frac{1}{2}$, 1/√2)	QL	$\frac{1}{2}(M+\sqrt{N})^a$	9.96 ± 0.04	9.93

^{a}Expressions for R, L, M, and N are given in Reference b of Table I.

c_{11}, c_{33}, c_{44}, c_{66}, and c_{12}; c_{13} was calculated using the last two expressions and the other constants. The results of the above computation are given in Table III, together with the elastic moduli of ZnS.[34] The errors given in this table are estimates based on the accuracy with which the scattering angle and the frequency shift are determined. The combinations of c_{ij}'s appearing in Table II have been recalculated using the least-squares results given in Table III. The difference between the calculated and experimental values shows the consistency of the determinations and gives an indication of the accuracy of the results.

It is clear from Table III that there is an overall decrease in the elastic moduli of $AgGaS_2$ compared to those of ZnS. This lowering of elastic moduli is consistent with the fact that $AgGaS_2$ has been shown to have a larger average ionicity than ZnS,[25] and for similar structures an increase in ionicity is usually associated with lower force constants[35] and hence lower elastic moduli. The lowering of elastic moduli can also be related to the frequency change of the A_1 mode. The A_1 mode, which in ZnS corresponds to a vibration of only the sulfur atoms in the xy plane,[8] can be expected to depend on some average of the Ga-S and Ag-S force constants. In ZnS,[30] the frequency of this mode is 320 cm^{-1}, as compared to 295 cm^{-1} in $AgGaS_2$.[8] This implies a decrease of ~17% in the effective force constant, which is of the same order of magnitude as the observed decreases in elastic moduli. In contrast to the above decreases it is interesting

to note that the E and B_2 modes at 367 and 365 cm^{-1} in $AgGaS_2$ have been correlated[8] with the $F_2(\Gamma_{15})$ mode at 271 cm^{-1} in ZnS.[36] This correlation implies an increase in the effective force constant for this mode of vibration.

It would seem, therefore, that some of the optical phonon energies in chalcopyrites are determined substantially by the higher force constant of the Ga–S bond,[25] rather than by an average of the two bonds, whereas the acoustic phonon energies are primarily determined by the lower force constant of the Ag–S bond.

Bettini's[37] calculations show that the optical phonon energies in the II-IV-V$_2$ chalcopyrites are higher than in the III-V binary analogs. More specifically, some preliminary calculations by Bettini[38] for $AgGaS_2$ give values of elastic moduli similar to those reported in this paper while at the same time showing high optical-phonon frequencies.

Before leaving this discussion, we wish to com-

TABLE III. Comparison of elastic moduli of cubic ZnS and tetragonal $AgGaS_2$ (units 10^{11} dyn/cm^2).

Elastic moduli	ZnS (Ref. 34)	AgGaS$_2$
c_{11}	10.46	8.79 ± 0.05
c_{33}	10.46	7.58 ± 0.05
c_{44}	4.613	2.41 ± 0.05
c_{66}	4.613	3.08 ± 0.05
c_{12}	6.53	5.84 ± 0.05
c_{13}	6.53	5.92 ± 0.06

ment on the effect that the d-electron configuration of the Ag ion may have on optical properties. In elements like Ag and Cu, the d electrons are loosely bound, unlike the tightly bound d-electron configuration of the elements from column II, e.g., Zn. Levine[25] has shown that d-electron effects have to be included to account for the nonlinear susceptibilities of the chalcopyrites containing these elements. The increase of the frequencies for modes derived from zone-boundary modes in ZnS may in part be due to the influence of d electrons, since these have been shown[39] to account for higher frequencies at the zone boundary than at the zone center for AgCl as contrasted to its analog RbCl. However, care must be taken with this proposed analogy, because these two materials crystallize in the rock salt and not in the zinc-blende structure. It has also been shown[25] that in order to obtain a reasonable value of ionicity for Cu_2O it is necessary to include all the d electrons of Cu and give Cu an effective charge of 11. Consider the B_2

mode of[8] $AgGaS_2$ at 213.6 cm^{-1}, which corresponds to W_2 of zinc blende, and consists of the Ag ions moving against the Ga ions; if the effective charge of Ag were ~ 11, the difference in the effective charges of Ag and Ga would be much larger than if Ag had a charge of 1. This may explain the relatively large Coulomb splitting of this mode. Similar arguments can be made for the E mode derived from from W_4.

ACKNOWLEDGMENTS

*Work supported by the NSF Grant Nos. GH 32001-A1 and GH 43409 and Materials Research Laboratory Program-No. GH33574A3.

[1]B. Tell, J. L. Shay, and H. M. Kasper, Phys. Rev. B 6, 3008 (1972).

[2]J. L. Shay and E. Buehler, Phys. Rev. B 3, 2598 (1971).

[3]J. L. Shay and B. Tell, Surf. Sci. 37, 748 (1973).

[4]A. Shileika, Surf. Sci. 37, 730 (1973).

[5]S. E. Stokowski, Phys. Rev. B 6, 1294 (1972).

[6]G. D. Holah, Opt. Commun. 5, 10 (1972).

[7]G. D. Holah, J. Phys. C 5, 1893 (1972).

[8]G. D. Holah, J. S. Webb, and H. Montgomery, J. Phys. C 7, 3875 (1974).

[9]G. D. Holah, H. Montgomery, and J. S. Webb, in *Proceedings of the Twelfth International Conference on Physics of Semiconductors*, Stuttgart, 1974, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 316.

[10]I. P. Kaminow, E. Buehler, and J. H. Wernick, Phys. Rev. B 2, 960 (1970).

[11]A. Miller, G. D. Holah, and W. C. Clark, J. Phys. Chem. Solids 35, 685 (1974).

[12]M. Bettini and A. Miller, Phys. Status Solidi B 66, 579 (1974).

[13]M. Bettini, W. Bauhofer, M. Cardona, and R. Nitsche, Phys. Status Solidi B 63, 641 (1974).

[14]J. P. van der Ziel, A. E. Meixner, H. M. Kasper, and J. A. Ditzenberger, Phys. Rev. B 9, 4286 (1974).

[15]W. H. Koschel, F. Sorger, and J. Baars, Solid State Commun. 15, 719 (1974).

[16]W. H. Koschel, V. Hohler, A. Räuber, and J. Baars, Solid State Commun. 13, 1011 (1973).

[17]J. Baars and W. H. Koschel, Solid State Commun. 11, 1513 (1972).

[18]D. S. Chemla, P. J. Kupecek, D. S. Robertson, and R. C. Smith, Opt. Commun. 3, 29 (1971).

[19]G. D. Boyd, H. M. Kasper, and J. H. McFee, IEEE J. Quantum Electron. QE-7, 563 (1971).

[20]G. D. Boyd, H. M. Kasper, J. H. McFee, and F. G. Storz, IEEE J. Quantum Electron. QE-8, 900 (1 IEEE

[21]G. D. Boyd, T. J. Bridges, C. K. N. Patel, and E. Buehler, Appl. Phys. Lett. 21, 553 (1972).

[22]D. C. Hanna, V. V. Rampal, and R. C. Smith, Opt. Commun. 8, 151 (1973).

[23]B. F. Levine, Phys. Rev. B 7, 2600 (1973).

[24]B. F. Levine, J. Chem. Phys. 59, 1463 (1973).

[25]B. F. Levine, Phys. Rev. B 7, 2591 (1973).

[26]S. C. Abrahams and J. L. Bernstein, J. Chem. Phys. 59, 1625 (1973).

[27]G. Brandt, A. Räuber and J. Schneider, Solid State Commun. 12, 481 (1973).

[28]A. S. Borshchevskii, N. A. Goryunova, F. P. Kesamanly, and D. N. Nasledov, Phys. Status Solidi 21, 9 (1967).

[29]G. F. Karavaev, A. S. Poplavnoi, and V. G. Tyuterev, Izv. Vuzov, Fiz. 10, 43 (1970) [J. Sov. Phys. 13, 1292 (1970)]; see, for example, J. L. Shay and B. Tell, Surf. Sic. 37, 748 (1973); A. Shileika, *ibid.* 37, 730 (1973); G. D. Holah, J. S. Webb, and H. J. Montgomery, J. Phys. C 7, 3875 (1974).

[30]D. N. Talwar and B. K. Agrawal, Phys. Status Solidi 64, 71 (1974).

[31]Model FP-100 Fabry-Perot interferometer, Tropel Inc., 52 West Ave., Fairport, N. Y. 14450.

[32]H. Z. Cummins and P. E. Schoen, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam, 1972).

[33]V. Chandrasekharan, Proc. Indian. Acad. Sci. A 33, 183 (1951).

[34]D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. 129, 1009 (1963).

[35]J. M. Rowe, R. M. Nicklow, D. L. Price, and K. Zanio, Phys. Rev. B 10, 671 (1974).

[36]W. G. Nilsen, Phys. Rev. 182, 838 (1969).

[37]M. Bettini, Phys. Status Solidi B 69, 201 (1975).

[38]M. Bettini (private communication).

[39]K. Fischer, H. Bilz, R. Haberkorn, and W. Weber, Phys. Status Solidi B 54, 285 (1972).