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BRILLOUIN SCATTERING DETERMINATION OF THE ELASTIC MODULI OF AgGaS_2 AND THEIR INFLUENCE ON THE ANALYSIS OF THE OPTICAL PHONON DATA (*)

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Résumé. — Les modules d'élasticité de AgGaS_2 ont été déterminés par diffusion Brillouin. On trouve qu'ils sont inférieurs à ceux de l'analogue binaire ZnS . Il est discuté en détail l'intérêt que peut avoir cette observation pour attribuer des coordonnées normales aux différents phonons optiques observés.

L'importance des électrons d de la configuration de Ag^+ dans l'analyse des phonons optiques est également prise en considération. Sur la base de ces discussions, on suggère que les attributions précédentes peuvent être erronées pour les modes de fréquences élevées et une nouvelle attribution est proposée.

Abstract. — The elastic moduli of AgGaS_2 have been determined using laser Brillouin scattering. It is found that they are lower than those of the binary analogue ZnS . The relevance of this overall decrease in helping to assign normal mode coordinates to observed optical phonon frequencies is discussed in detail. The importance of the d-electron configuration of the Ag^+ on the analysis of optical phonons is also considered. On the basis of the discussions it is proposed that the previous analyses may have been in error for high frequency modes and an alternative assignment is suggested.

1. Introduction. — The I-III-VI₂ and II-IV-V₂ ternary semiconductors, which form in the chalcopyrite structure, have been the subject of a number of recent investigations into their lattice vibrational modes [1-10]. With the exception of the results discussed here the data have been obtained using Raman scattering or infrared reflectivity, no previous determination of the elastic moduli for any chalcopyrite has been made. Although early work on ZnSiP_2 suggested that the main polar modes consisted of, for example, Zn vibrating in antiphase to P, with Si taking no part and Si against P with Zn taking no part, it is now generally accepted that the main polar mode should consist of the whole cation sublattice moving against the anion sublattice. It has been shown [6, 11] that due to the close similarity between the chalcopyrite and sphalerite (zincblende) lattice important relations between the two structures may be obtained which assist in the interpretation of the phonon spectra.

Due to the complexity of the optical phonon structure of the chalcopyrites, the assignment of specific atomic displacements to observed frequencies is not straightforward and for the I-III-VI₂ compounds additional ambiguities may arise due to the delocalized d-electron configuration of the Ag^+ ions. A complete analysis is further hindered by the conflicting data

which occurs for some modes. The present paper attempts to clarify some of the problems by making use of the consequences of the change in elastic constants of AgGaS_2 relative to ZnS . Some of the discussion will have relevance to the phonon spectra of II-IV-V₂ compounds, however the main emphasis will be on AgGaS_2 and to a lesser extent CuGaS_2 .

2. Experimental. — The structure of AgGaS_2 is shown in figure 1 and it can be seen that the tetrahedral coordination is very similar to zincblende. If the Ag and Ga sites were indistinguishable then the two structures would be identical. Since Ag and Ga belong to different columns in the periodic table their bondings to the sulfur ions are different, the more covalent Ga-S bond being stiffer. This moves the sulfur atoms away from a symmetric tetrahedral position to one nearer the trivalent Ga ions. Furthermore, there is tetragonal compression with $c/a = 1.789$ [11]. The point group for chalcopyrite is $\bar{4}2m$ and the character table is shown in table I. Since there are two molecular units per unit primitive cell there are 24 normal modes of vibration. Brillouin scattering from acoustic phonons of AgGaS_2 has been performed and the data analyzed to yield the elastic moduli, c_{11} , c_{33} , c_{44} , c_{66} , c_{12} and c_{13} . The scattering tensors appropriate to $\bar{4}2m$ have been given elsewhere [13] and will not be repeated here.

A Coherent Radiation argon laser with an etalon to produce a single axial mode was used as the exciting source. The scattered radiation, from both right-angle

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CHALCOPYRITE STRUCTURE

FIG. 1. — Structure of AgGaS₂.

and backscattering geometries, was analyzed using a triple-passed piezoelectrically-scanned Fabry-Pérot interferometer. An S-20 photomultiplier (RCA 7265) was used together with photon-counting electronics. For further discussion of the experimental details the reader is referred to reference [13]. Typical spectra are shown in figure 2.

3. Discussion. — As indicated previously there are similarities between the zincblende and chalcopyrite structures which leads to a number of extremely useful correlations in their lattice vibrational spectra. It can easily be shown that modes corresponding to $\Gamma(0, 0, 0)$, $X(0, 0, 1)$, $W^a(1, 0, \frac{1}{2})$ and $W^b(0, 1, \frac{1}{2})$ of zincblende become zone center modes of chalcopyrite. This folding-back of zincblende dispersion curves is similar to the folding back along the $[111]$ direction of zincblende ZnS to give the dispersion curves of

FIG. 2. — Brillouin Spectra of AgGaS₂. Upper curve right-angle scattering. Lower curve backscattering.

wurztite ZnS. Immediately therefore, since the normal mode coordinates for zincblende are known, we have a good basis for the « normal mode » coordinates of chalcopyrite. Additionally since the force constants and reduced masses for the isoelectronic analogues may be similar, then judicious use of the phonon dispersion curves of zincblende should help to assign observed frequencies to the atomic displacements. The II-VI ZnS is the nearest binary analogue to CuGaS₂ and AgGaS₂. Since Cu and Ga lie each side of Zn in the periodic table their masses and electron configurations are similar, and we should expect the greatest correlation between ZnS and CuGaS₂. We may also expect some indications from ZnS to hold for AgGaS₂.

The agreement between the various determinations [6, 7] of optical phonon energies and symmetries is, with the exception of the B₁ modes, quite good for AgGaS₂. Unfortunately there seems to be some discrepancies in the available data on CuGaS₂ [7, 8].

TABLE I

Character table for point group $\bar{4}2m$

	E	2 S ₄	C ₂	2 C' ₂	2 σ _d	Symmetry	Activity	Optic	Acoustic
A ₁	1	1	1	1	1	x ² + y ² , z ²	R	1	
A ₂	1	1	1	-1	-1		inactive	2	
B ₁	1	-1	1	1	-1	x ² - y ²	R	3	
B ₂	1	-1	1	-1	1	xy; z	R; ir	3	1
E	2	0	-2	0	0	xz, yz; x, y	R; ir	6	1

The assignments for the polar modes of AgGaS₂ were mainly based on the Coulomb splitting of the modes and it is the intention on the paper to suggest that this argument may have been in error and to derive new assignments for AgGaS₂ and CuGaS₂.

TABLE II

Comparison of elastic moduli of cubic ZnS and tetragonal AgGaS₂, units of 10¹¹ dynes/cm²

Elastic moduli	ZnS [15]	AgGaS ₂
c^{11}	10.46	8.79 ± 0.05
c_{33}		7.58 ± 0.05
c_{44}	4.613	2.41 ± 0.05
c_{66}		3.08 ± 0.05
c_{12}	6.53	5.84 ± 0.05
c_{13}		5.92 ± 0.06

Since the same interatomic force constants are responsible for the elastic properties and the optical phonon properties of a given compound it is clear that a determination of the elastic moduli of AgGaS₂ should prove useful in analyzing optical phonon data. The results for AgGaS₂ are shown in table II along with those of ZnS, it is clear that in each case they are lower than the corresponding values for ZnS. If the two compounds had identical structures and reduced masses then it would be relatively straightforward to state that the lower elastic constants indicate lower optical phonon energies. This has been elegantly demonstrated by neutron scattering data on α -Sn, InSb and CdTe [14], an isoelectronic series of semiconductors with zincblende structure and almost equal reduced masses. As the ionicity of the bonding increases, i. e. α -Sn $\rightarrow$ CdTe, the elastic moduli and optical phonon frequencies decrease. Although there are mass differences between AgGaS₂ and ZnS, the lower elastic suggests that the force constants and hence the optical phonon energies should also be lower. An increase in ionicity is also suggested.

A further indication of force constant differences between AgGaS₂ and ZnS may be obtained from the frequency of the normal mode in which only the sulfur ion is vibrating. In ZnS this is the W₁(LO) mode at 320 cm⁻¹ [17] and for AgGaS₂ the corresponding mode is the A₁ at 295 cm⁻¹. This suggests a lower effective force constant. For CuGaS₂ the A₁ is at 312 cm⁻¹.

The ionicity of AgGaS₂ has been calculated using a bond charge model [16] to evaluate the bond ionicity of the two types of bonds. The average of the two bonds, $f_i = 0.719$ is greater than that of ZnS, $f_i = 0.621$. If we take the ratio of static dielectric constant to electronic dielectric constant, $\epsilon_s/\epsilon_\infty$, as an indication of ionicity then again AgGaS₂ is higher than ZnS, at least for the E modes, $\epsilon_s/\epsilon_\infty$ (E modes) = 1.7 $\epsilon_s/\epsilon_\infty$ (B₂ modes) = 1.5 and ZnS = 1.63.

The conclusion we tentatively draw from the above discussion is that the Γ_{15} mode of ZnS should be at a higher frequency than the corresponding AgGaS₂ mode.

If we examine the Raman and infrared data of AgGaS₂ the only E and B₂ modes which are almost equal and lower than Γ_{15} of ZnS (273 cm⁻¹) are the E mode at 223 cm⁻¹ and the B₂ at 214 cm⁻¹. Since Γ_{15} is the polar mode of ZnS we might expect the modes derived from this also to be most polar. This is found to be the case for the B₂ mode but not the E mode. The answer to the low Coulomb splitting of this E mode may perhaps lie with the d-electron configuration of the Ag⁺ ions. In the noble metals such as Ag and Cu the d-electrons are delocalized unlike the tightly bound d-electrons of Zn. This fact has been shown to have important consequences for the lattice vibrations.

Levine [16] has shown that it is necessary to include d-electron effects to calculate a reasonable value for the ionicity of Cu₂O. Also the same author has taken the number of valence electrons of Ag and Cu to be 11 and not 1 in his calculations for nonlinear susceptibilities and bond ionicity. Further evidence for the effect of d-electrons can be seen in a comparison of the phonon dispersion curves of AgCl and RbCl [18]. There are a number of important differences, the Ag halide is significantly more ionic with a large Coulomb splitting, although the force constants are not too dissimilar, ω_{LO} (AgCl) and ω_{TO} (AgCl) both show substantial dispersion over the Brillouin zone, whilst for RbCl ω_{TO} is almost dispersionless and ω_{LO} shows the usual decrease as the wavevector q approaches 1. Along [001] ω_{LO} (AgCl) has almost the same value of $q = 0$ as at $q = 1$, and ω_{TO} at $q = 1$ is more than 20 % higher than ω_{TO} at the zone center. Although these halides have rocksalt structure we may imagine that similar anomalies may occur for a zincblende compound containing Ag.

Another factor introduced by the d-electron configuration is that the effective charge of Ag⁺ is now 11 and since the Coulomb splitting of AgGaS₂ modes derived from zone boundary modes of zincblende is due to the differences in the cation effective charges we find the ΔZ for Ag-Ga is 11 - 3 = 8 instead of - 2. Therefore we might expect an anomalously large Coulomb splitting for modes in which Ag vibrates against Ga. From the symmetry coordinates of reference [6] these are the B₂ from W₂ and the E modes from W₃ and W₄.

Based upon these arguments we would tentatively suggest the assignments for the observed frequencies of AgGaS₂ and CuGaS₂ to be as shown in figure 3. It is clear that there is little problem in assigning the modes which correspond to the zone boundary acoustic phonons of ZnS. In each case the frequency of the chalcopyrite phonon is lower than ZnS with the exception of the LA(X) mode which corresponds to a CuGaS₂ B₁ phonon of the same energy. There is also no question of the A₁ modes coming from W₂ of ZnS at 320 cm⁻¹, being 312 cm⁻¹ in CuGaS₂ and 295 cm⁻¹