HAL
open science

BRILLOUIN SCATTERING DETERMINATION OF THE ELASTIC MODULI OF AgGaS2 AND THEIR INFLUENCE ON THE ANALYSIS OF THE OPTICAL PHONON DATA

G. Holah, M. Grimsditch

To cite this version:

G. Holah, M. Grimsditch. BRILLOUIN SCATTERING DETERMINATION OF THE ELASTIC MODULI OF AgGaS2 AND THEIR INFLUENCE ON THE ANALYSIS OF THE OPTICAL PHONON DATA. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-185-C3-188. 10.1051/jphyscol:1975334 . jpa-00216304

HAL Id: jpa-00216304

https://hal.science/jpa-00216304

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

JOURNAL DE PHYSIQUE *Colloque* C3, *supplément au n°* 9, *Tome* 36, *Septembre* 1975, *page* C3-185

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

G. D. HOLAH (**) and M. GRIMSDITCH

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

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-VI_2 and II-IV-V_2 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 $ZnSiP_2^3$ 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-VI_2 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-V_2 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

(*) Supported by N. S. F. through Grant Nos. 32001-A1, GH-43409 and MRL Program GH 33574-A3.

(**) Address after Sept. 1st, Physics Dept., Heriot-Watt University, Edinburgh.

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:1975334

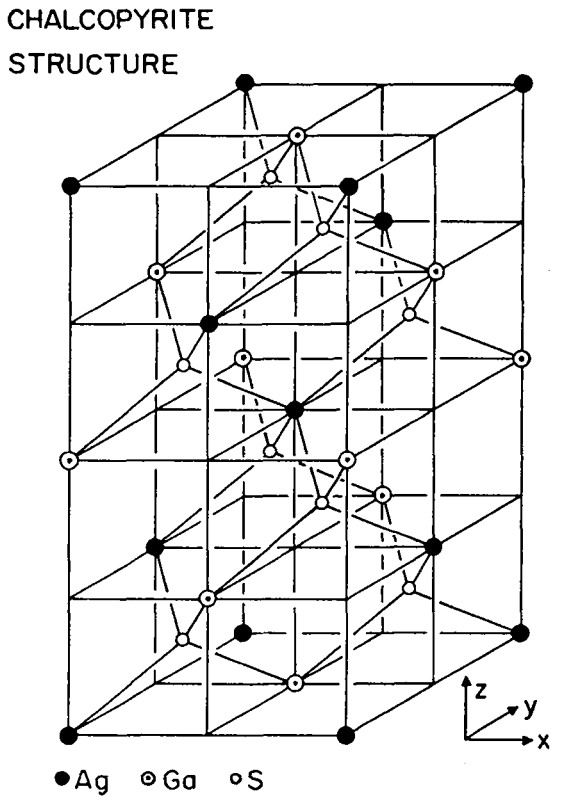

FIG. 1. — Structure of $AgGaS_2$.

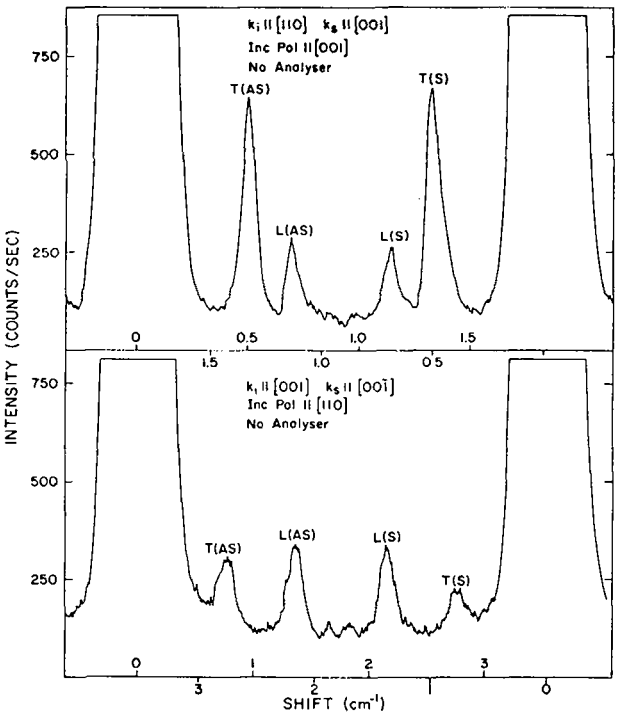

FIG. 2. — Brillouin Spectra of $AgGaS_2$. Upper curve right-angle scattering. Lower curve backscattering.

and backscattering geometries, was analyzed using a triple-passed piezoelectrically-scanned Fabry-Pèrot 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 wurzite 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 $CuGaS_2$ and $AgGaS_2$. 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 $CuGaS_2$. We may also expect some indications from ZnS to hold for $AgGaS_2$.

The agreement between the various determinations [6, 7] of optical phonon energies and symmetries is, with the exception of the B_1 modes, quite good for $AgGaS_2$. Unfortunately there seems to be some discrepancies in the available data on $CuGaS_2$ [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 $AgGaS_2$ 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 $AgGaS_2$ and $CuGaS_2$.

TABLE II

Comparison of elastic moduli of cubic ZnS *and tetragonal* $AgGaS_2$, *units of* $10''$ dynes/cm^2

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 $AgGaS_2$ should prove useful in analyzing optical phonon data. The results for $AgGaS_2$ 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 $AgGaS_2$ 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 $AgGaS_2$ 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 W_1(LO) mode at 320 cm^{-1} [17] and for $AgGaS_2$ the corresponding mode is the A_1 at 295 cm^{-1}. This suggests a lower effective force constant. For $CuGaS_2$ the A_1 is at 312 cm^{-1}.

The ionicity of $AgGaS_2$ 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, $\varepsilon_s/\varepsilon_\infty$, as an indication of ionicity then again $AgGaS_2$ is higher than ZnS, at least for the E modes, $\varepsilon_s/\varepsilon_\infty$ (E modes) $= 1.7$ $\varepsilon_s/\varepsilon_\infty$ (B_2 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 $AgGaS_2$ mode.

If we examine the Raman and infrared data of $AgGaS_2$ the only E and B_2 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 B_2 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 B_2 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 Cu_2O. 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 tor RbClω_{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 ot $q = 0$ 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 $AgGaS_2$ 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 B_2 from W_2 and the E modes from W_3 and W_4.

Based upon these arguments we would tentatively suggest the assignments for the observed frequencies of $AgGaS_2$ and $CuGaS_2$ 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 $CuGaS_2$ B_1 phonon of the same energy. There is also no question of the A_1 modes coming from W_2 of ZnS at 320 cm^{-1}, being 312 cm^{-1} in $CuGaS_2$ and 295 cm^{-1}

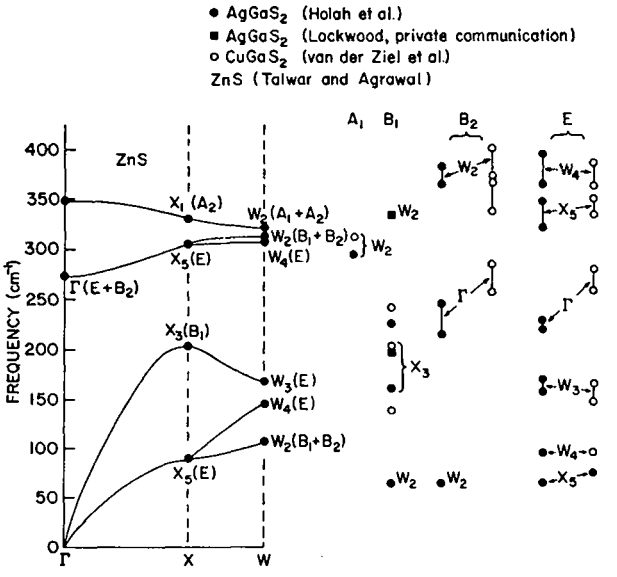

FIG. 3. — Phonon dispersion curves for ZnS and assignments. of phonon frequencies for $AgGaS_2$. Symmetry species of the $AgGaS_2$ modes are given in the brackets. Assignments for $CuGaS_2$ are also shown.

in $AgGaS_2$. This implies a lowering of force constants from ZnS to $CuGaS_2$ to $AgGaS_2$.

One of the problems with producing a model is that there is considerable conflict in the B_2 modes of $CuGaS_2$, the Raman data suggests a mode at 259 cm^{-1}, whilst no such mode is given in the infrared data. If we accept the Raman data a trend appears which suggests that the Γ mode of ZnS at 273 cm^{-1}, becomes E modes at 260 cm^{-1} and 220 cm^{-1}, B_2 modes at 259 cm^{-1} and 214 cm^{-1} for $CuGaS_2$ and $AgGaS_2$ respectively. The main drawback to this assignment is the small Coulomb splitting of the 220 cm^{-1} E mode in $AgGaS_2$. The correlations between the remaining high frequency E and B_2 phonons would seem to be reasonable. The correlations for the B_1 modes for $AgGaS_2$ are also reasonable but not good for $CuGaS_2$. There is clearly a need for further work on $CuGaS_2$ to establish the Raman spectra and infrared spectra with a higher level of confidence.

4. **Summary.** — We have measured the elastic moduli of $AgGaS_2$ using Brillouin scattering. In all cases the magnitudes of the moduli were lower than those of the binary analogue ZnS. This suggests, along with other evidence, that the force constants are lower for $AgGaS_2$ and hence optical phonon energies should be lower for the modes corresponding to the Γ phonon of ZnS. It has been suggested therefore that the previous normal mode assignments may be in error. d-electron effects of the Ag^+ ion have been used to explain why the frequencies of the other polar modes are higher than the zone boundary modes of ZnS and why the Coulomb splitting of these modes is higher than may have been expected. No adequate explanation for the low Coulomb splitting of the E mode at 220 cm^{-1} is given, it remains for a detailed analysis to be made.

References

[1] MILLER, A., HOLAH, G. D., CLARK, W., *J. Phys. Chem. Solids* **35** (1974) 685.

[2] BETTINI, M., MILLER, A., *Phys. Stat. Sol.* b **66** (1974) 579.

[3] KAMINOW, I. P., BUEHLER, E., WERNICK, J. H., *Phys. Rev.* **B 2** (1970) 960.

[4] HOLAH, G. D., *J. Phys. C.* : Solid State **5** (1972) 1893.

[5] BETTINI, M., BAUHOFER, W., CARDONA, M., NITSCHE, R., *Phys. Stat. Sol.* b **63** (1974) 641.

[6] HOLAH, G. D., WEBB, J. S., MONTGOMERY, H., *J. Phys. C* : Solid State **7** (1974) 3875.

[7] VAN DER ZIEL, J. P., MEIXNER, A. E., KASPAR, H. M., DITZENBERGER, J. A., *Phys. Rev.* **B 9** (1974) 4286.

[8] BAARS, J., KOSCHEL, W. H., *Solid State Commun.* **11** (1972) 1513.

[9] KOSCHEL, W. H., HOHLER, V., RÄUBER, A., BAARS, J., *Solid State Commun.* **13** (1973) 1011.

[10] HOLAH, G. D., MONTGOMERY, H., WEBB, J. S., *Proc. Int. Conf. on Physics of Semiconductors* (Stuttgart) 1974, 316.

[11] KARAVAEV, G. F., POPLAVNOI, A. C., TYUTEREV, B. G., *Izv. Vuzov.* **10** (1970) 42.

[12] BRANDT, G., RÄUBER, A., SCHNEIDER, J., *Solid State Commun.* **12** (1973) 481.

[13] GRIMSDITCH, M., HOLAH, G. D., *Phys. Rev.* **B** to be published.

[14] ROWE, J. M., NICKLOW, R. M., PRICE, D. L., ZANIO, K., *Phys. Rev.* **B 10** (1974) 671.

[15] BERLINCOURT, D., JAFFE, H., SHIOZAWA, L. R., *Phys. Rev.* **129** (1963) 1009.

[16] LEVINE, B. F., *Phys. Rev.* **B 7** (1973) 2591.

[17] TALWAR, D. N., AGRAWAL, Bal. K., *Phys. Stat. Sol.* **B 64** (1974) 71.

[18] FISCHER, K., BILZ, H., HABERKORN, R., WEBER, W., *Phys. Stat. Sol.* (b) **54** (1972) 285.