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► **To cite this version:**

D. Lockwood, H. Montgomery. RAMAN SPECTRUM OF AgGaS<sub>2</sub>. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-183-C3-184. 10.1051/jphyscol:1975333 . jpa-00216303

**HAL Id: jpa-00216303**

**<https://hal.science/jpa-00216303>**

Submitted on 4 Feb 2008

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RAMAN SPECTRUM OF  $\text{AgGaS}_2$ 

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**Résumé.** — De nouvelles mesures des fréquences des modes optiques dans  $\text{AgGaS}_2$  sont présentées ; plusieurs raisons expliquant pourquoi les déterminations précédentes sont erronées sont suggérées. Nos résultats indiquent que la structure de  $\text{AgGaS}_2$  ne peut être considérée comme une perturbation faible de la structure blende, mais ils sont en accord avec les prédictions d'un modèle calculé récemment par Bettini.

**Abstract.** — We present new measurements of the optical mode frequencies in  $\text{AgGaS}_2$ , and suggest reasons why previous determinations are in error. The results indicate that  $\text{AgGaS}_2$  cannot be regarded as a small perturbation of a zincblende structure, but they are in accord with the predictions of a recent model calculation by Bettini.

Recently two papers have appeared reporting Raman measurements of optic mode frequencies in  $\text{AgGaS}_2$  [1, 2]. There is good agreement between the two determinations of the  $A_1$  and E modes, but serious disagreement in the case of the  $B_1$  and  $B_2$  modes. This suggests that the discrepancies arise from errors in the measurements rather than from imperfections in the crystals, and the sample used in reference [2] has now been re-examined under greatly improved experimental conditions. We believe that the true  $B_1$  modes have been observed for the first time, and that *both* the previous investigations gave erroneous values for their frequencies.

The new measurements were performed on two automated instruments, a Spex 1400 double monochromator and a Coderg T800 triple monochromator [3] ; all spectra were obtained using 5145 Å light from an argon laser, because effects due to the optical activity of  $\text{AgGaS}_2$  are negligible at this wavelength [4]. The interpretation of the spectra was complicated by two effects, the depolarisation of the scattered light [5], and the background produced by the second order scattering. The latter was fairly weak for off diagonal spectra in which the incident and scattered beams had different polarisations, and the  $B_2$  and E modes could be identified without much difficulty. But for diagonal spectra the second order background was found to be much stronger, and it completely obscured the  $B_1$  peaks in the usual  $z(xx)y$  scattering geometry. However, when the crystal was rotated about the  $z$  axis the  $B_1$  modes appeared in the off diagonal geometry  $z(y'x')y'$ , and the genuine peaks could be distinguished clearly by the fact that they rose to maximum height as the angle of rotation passed through 45°. The final results for all the modes are listed below.

Optic mode frequencies ( $\text{cm}^{-1}$ ) in  $\text{AgGaS}_2$ 

$A_1$	295
$B_1$	54, 190.5, 333.5
$B_2$	64, (212-237.5), (364-398.5)
E	84.5, 94.5, (159.5-160), (224-229.5), (321.5-346), (368-391).

These measurements cast considerable doubt on the validity of the *zincblende approximation* which was used to interpret the earlier data [2]. According to this approximation the highest  $B_1$  mode should have a similar frequency to the second highest  $B_2$  mode, because the corresponding modes in the zincblende structure are symmetry related. The discrepancy can be ascribed to the large mass difference between the two cations Ag and Ga ; but it is very surprising that in  $\text{CuAlS}_2$ , where the cation mass difference is even greater, the zincblende approximation seems to be much more successful [6].

The solution of this problem is probably contained in the recent model calculation by Bettini, which he has applied to the lattice dynamics of II-IV-V<sub>2</sub> compounds [7]. The present results on  $\text{AgGaS}_2$  show the same detailed structure as earlier data on the analogous compound  $\text{CdGeP}_2$  [8], and the only important difference between them is that the Coulomb splittings are larger for the sulphide than for the phosphide. Bettini's model implies that in  $\text{CdGeP}_2$  the mass and force constant differences are too great for the zincblende approximation to be valid, and the same is clearly true for  $\text{AgGaS}_2$ . A corresponding analogy can be drawn between  $\text{CuAlS}_2$  and  $\text{CdSiP}_2$  ; the measured phonon spectra are in fact very similar, and in both cases one of the three  $B_1$  modes has escaped observation [6, 9]. Bettini's model predicts that the missing mode in

$\text{CdSiP}_2$  is the highest  $B_1$  mode, and its frequency shows a very large deviation from the zincblende approximation. The same argument could well apply to  $\text{CuAlS}_2$ , and the apparent success of the zincblende approximation in these compounds probably arises from an

incorrect classification of the observed  $B_1$  modes. It would be very interesting to search for the predicted high frequency  $B_1$  mode in  $\text{CuAlS}_2$  and  $\text{CdSiP}_2$ , using the technique described above; discovery of this mode would add strong support to Bettini's model.

### References

- [1] VAN DER ZIEL, J. P., MEIXNER, A. E., KASPER, H. M. and DITZENBERGER, J. A., *Phys. Rev. B* **9** (1974) 4286.
- [2] HOLAH, G. D., WEBB, J. S. and MONTGOMERY, H., *J. Phys. C (Solid State Physics)* **7** (1974) 3875.
- [3] ARTHUR, J. W. and LOCKWOOD, D. J., *J. Raman Spectros.* **2** (1974) 53.
- [4] HOBDEN, M. V., *Acta Crystallogr. A* **24** (1968) 676.
- [5] PORTO, S. P. S., GIORDMAINE, J. A. and DAMEN, T. C., *Phys. Rev.* **147** (1966) 608.
- [6] KOSCHEL, W. H., HOHLER, V., RAUBER, A. and BAARS, J., *Solid State Commun.* **13** (1973) 1011.
- [7] BETTINI, M., *Phys. Stat. Sol.*, to be published.
- [8] BETTINI, M. and MILLER, A., *Phys. Stat. Sol. (b)* **66** (1974) 579.
- [9] BETTINI, M., BAUHOFFER, W., CARDONA, M. and NITSCHKE, R., *Phys. Stat. Sol. (b)* **63** (1974) 641.