

7. LYDDANE R. H., SACHS R. G. and TELLER E., *Phys. Rev.* **59**, 673 (1941).
8. LANDOLT-BERNSTEIN, II. Band, 6. Teil, Elektrische Eigenschaften, p. 449.
9. BRIDGMAN P. W., *Proc. Am. Acad. Sci. Paris* **67** 345/75, 351 (1932).
10. GÜNTERT O. J. und FAESSLER A., *Z. Kristallogr.* **107**, 357 (1956).
11. JACOBSON J. L. and NIXON E. R., *J. Phys. Chem. Solids* **29**, 967 (1968).

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Raman spectrum of hexagonal zinc sulfide at high pressures*

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THE PRESENT work was undertaken to investigate the possibility of a phase transformation of ZnS from wurtzite (hexagonal) to zinc blende (cubic) structure and to determine the pressure dependences of the Raman-active phonon frequencies of wurtzite. ZnS is unusual by virtue of the existence of two nearly identical solid phases at atmospheric pressure. In both phases, a given atom has the same four symmetrically-placed nearest neighbors, and even the second-nearest neighbors are identically situated in both structures. The first difference arises with the third-nearest neighbors; in wurtzite, the third-nearest neighbors are slightly closer than in the cubic zinc blende structure. It is the slight difference between the structures that leads to the many interesting properties of these materials that are discussed in detail in Berman's work[1] and in references cited therein.

The single crystal of wurtzite from which samples used in these experiments were cut, was obtained from Harshaw Chemical Co. Back-reflection Laue X-ray photographs of this crystal showed well-defined spots characteristic of a high-quality crystal. The crystal

was examined under a polarizing microscope for evidence of stacking faults, and a central section that showed colored bands was excluded from this study. Raman spectra were excited with an argon-ion laser at 488 and 514.5 nm, and the spectra were analyzed by means of a Spex double-monochromator with photon-counting detection. A modified Drickamer-type of high-pressure optical cell[2] was used to obtain spectra of samples under pressures up to 40 kbar at room temperature.

Wurtzite belongs to the space group $C_{6v}^4-P_{63mc}$ and all atoms occupy C_{3v} sites. The nine possible optic modes of the four-atom primitive cell have the following symmetries: $1A_1+2B_1+1E_1+2E_2$. The A_1 and E_1 branches are both Raman and i.r. active, the E_2 's are only Raman active, and the B_1 's are neither i.r. nor Raman active. Because the crystal is only slightly anisotropic, the A_1 and E_1 symmetry modes are accidentally degenerate within the resolution of this experiment[3] and are nearly degenerate with the corresponding F_2 -symmetry modes of the zinc blende structure of ZnS, if a slight correction is made for the different densities of the two phases. These modes are, however, split into longitudinal and transverse branches by the macroscopic electric field that elevates the frequency of the longitudinal branch.

The atmospheric-pressure frequencies and their pressure and volume dependences[4] obtained in this study are listed in Table 1. The assignments of the multi-phonon spectra listed in Table 1 are based upon an interpolation of the phonon dispersion curves determined by neutron scattering for the cubic phase[5]; however, the data are inadequate to assign unambiguously the critical points that contribute to this spectrum. Within experimental precision, the values of the frequencies and pressure derivatives were independent of the orientation of the crystal with respect to the spectrometer and to the high-pressure cell. The longitudinal and transverse optic branches of A_1 and E_1 symmetries are located at 350 and 276 cm^{-1} respectively in agreement

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Table 1. Pressure dependencies of raman frequencies in ZnS (hexagonal) at 298K

| Frequency (cm ⁻¹) (1 atm) | Pressure dependence $\Delta\nu/\Delta P$ (cm ⁻¹ /k bar) | Mode Gruneisen (Volume dependence) | Assignment |
|--|---|---------------------------------------|--|
| 181 | -0.35 ± 0.05 | -1.8 ± 0.4 | 2TA |
| 219 | 0.63 ± 0.05 | 2.4 ± 0.1 | LA |
| 276 | 0.62 ± 0.01 | 1.8 ± 0.2 | A ₁ (TO), E ₁ (TO) |
| 350 | 0.43 ± 0.01 | 0.99 ± 0.16 | A ₁ (LO), E ₁ (LO) |
| 399 | 0.52 ± 0.08 | 1.1 ± 0.4 | TO+TA |
| 424 | 0.40 ± 0.02 | 0.75 ± 0.29 | LO+LA |
| 449 | 0.60 ± 0.07 | 1.1 ± 0.03 | 2LA |
| 617 | 1.06 ± 0.06 | 1.3 ± 0.4 | 2TO |
| 642 | 1.18 ± 0.05 | 1.5 ± 0.3 | TO+LA |
| 673 | 1.15 ± 0.08 | 1.4 ± 0.2 | 2LO |

with reported data[3, 5-9]. The vibrational frequencies increase with pressure with one exception, a zone-edge transverse acoustic mode (2TA). This negative pressure-dependence of the transverse acoustic branch at the zone edge is consistent with observations for ZnTe[10] and RbI[11]. No attempt was made to follow the weak E₂[6, 8].

The volume dependences of the frequencies are represented in Table 1 in terms of the equation:

$$\nu(P) = \nu_0 (V_0/V)^\gamma$$

where V_0 and ν_0 are the volume and frequency, respectively, at atmospheric pressure. The mode Gruneisen, γ , is defined as:

$$\gamma = - \frac{d \ln \nu}{d \ln V}$$

The difference between the γ 's for the transverse and the longitudinal mode is interesting:

$$\nu_{LO}(P) = 350 \text{ cm}^{-1} (V_0/V)^{0.99}$$

and

$$\nu_{TO}(P) = 276 \text{ cm}^{-1} (V_0/V)^{1.8}$$

The closeness in the magnitudes of these Gruneisen constants for the TO and LO modes in wurtzite (TO: 1.8; LO: 1.0) and in zinc blende (TO: 1.75[12]; LO: 0.99[9]) as determined by Mitra and coworkers reflects the similarity of the force constants in the two structures. The difference between the volume

dependences of the TO and LO phonons is not surprising; it represents the pressure dependence of the electrostatic interaction that splits these modes and is related to the dielectric constants of ZnS as discussed below. The available data from 1 atm to 40 kbar are inadequate to indicate whether the mode Gruneisen constants are volume dependent.

The effects of pressure on the phonon frequencies of wurtzite are related to the mixed ionic-covalent character of ZnS. In order to avoid confusion on the matter of different effective charges, the discussion of the pressure dependence of these phonon spectra will be restricted to a single model, involving Szigeti's effective charge[13], $sZ|e|$. This effective charge can be determined from the dielectric constants and phonon frequencies in terms of the following equation.

$$sZ|e| = \nu_{TO}(\epsilon_0 - \epsilon_\infty)^{1/2} \left(\frac{3}{\epsilon_\infty + 2} \right) (\pi\mu V_a)^{1/2}. \quad (1)$$

Here, ϵ_0 and ϵ_∞ are the low and high frequency dielectric constants respectively[14], μ is the reduced mass, V_a is the volume per ion pair, and s is the correction factor for the short-range interaction of atomic and electronic polarization. It should be noted that in an uniaxial crystal, s is not necessary unity since short range dipolar interaction does not vanish.

The variation of the effective charge with

volume can be expressed as:

$$\left[\frac{\partial \ln (sZe)}{\partial \ln V} \right]_T = \left[\frac{\partial \ln s}{\partial \ln V} \right]_T$$

$$= \frac{\partial \ln \nu_{TO}}{\partial \ln V} + \frac{1}{2} \frac{\partial \ln (\epsilon_0 - \epsilon_\infty)}{\partial \ln V}$$

$$+ \frac{1}{2} \frac{\partial \ln (\epsilon_\infty + 2)}{\partial \ln V}$$

A value of this derivative was calculated using the ratios $(\nu_{LO}/\nu_{TO})^2$ along with the Lyddane-Sachs-Teller relationship and published data on the change of refractive index with pressure [15]. The change of refractive index with pressure was computed for the ordinary direction since the principal contribution to the change in the ratio $(\nu_{LO}/\nu_{TO})^2$ [$= \epsilon_0/\epsilon_\infty$] arises from the change in the static dielectric constant and not from the change in high frequency dielectric constant. Thus, variations of latter contribution with crystallographic direction can be neglected. Details of this calculation are described in Table 2.

The effective charge was found to be 0.86 and 0.82|e| at 1 atm and 40 kbar pressure respectively. A value of 1.0 ± 0.3 was obtained for $\partial \ln s / \partial \ln V$. The contributions arising from the different terms are enumerated in Table 2. The largest contributions arise from change in frequency of the transverse mode and change in static dielectric constant.

The origins of the pressure dependence of the TO-LO splitting, from which this result was derived, can be understood in terms of this model by rearranging equation (1) to give:

$$\nu_{LO}^2(P) - \nu_{TO}^2(P) = \left[\frac{(Ze)^2}{9\mu\pi} \right] \left[\frac{(\epsilon_1 + 2)}{\epsilon_\infty} \frac{s^2}{V_a} \right]$$

and comparing this with the experimental data:

$$\nu_{LO}^2(P) - \nu_{TO}^2(P) = \left[9.2(\pm 0.4) \times 10^3 \right. \\ \left. + 3.86(\pm 0.30) \times 10^4 \frac{V}{V_0} \right] (\text{cm}^{-2}). \quad (2)$$

Table 2. Some properties of hexagonal ZnS at 298K

| Property | Value at: 1 atm | 40 kbar | Other |
|--|-----------------|-----------------|------------------|
| ϵ_0 | 8.29[a] | | |
| ϵ_∞ | 5.11[b] | [c] | [c] |
| $(\nu_{LO}/\nu_{TO})^2$ | 1.62 ± 0.01 | 1.50 ± 0.01 | |
| $sZ e $ | 0.86 e | 0.82 e | |
| $\frac{\partial \ln \nu_{TO}}{\partial \ln V} = \gamma_{TO}$ | | | -1.81 ± 0.19 |
| $\frac{1}{2} \frac{\partial \ln (\epsilon_0 - \epsilon_\infty)}{\partial \ln V}$ | | | 2.41 |
| $\frac{\partial \ln (\epsilon_\infty + 2)}{\partial \ln V}$ | | | -0.07 |

[a] Cubic value, SLACK G. A., ROBERTS S. and HAM F. S., *Phys. Rev.* **155**, 170 (1967).

[b] From refractive index of PIPER W. W., MARPLE D. T. F. and JOHNSON P. D., *Phys. Rev.* **110**, 323 (1958).

[c] Calculated from pressure dependence of refractive index (ordinary) as determined by VEDAM K. and DAVIS T. A., *Phys. Rev.* **181**, 1196 (1969).

This comparison indicates that the linear volume dependence of equation (2) arise mainly from the linear volume dependence of the effective charge.

Both the size and the sign of $\partial \ln s / \partial \ln V$ are of interest. The sign is consistent with Szigeti's explanation that as the pressure is increased and the ions are forced closer together, the short-range repulsive term or ionic distortion becomes more dominant and $\partial \ln s / \partial \ln V$ would be positive. The magnitude compares well with theoretical value of unity obtained for a deformation dipole model for KCl [16], although the numerical value may be fortuitous. The value of $\partial \ln s / \partial \ln V$ for ZnS is subject to many errors especially to the approximate nature of the Lyddane-Sachs-Teller relationship and to any anharmonicity of the phonons. The lack of independent measurements of low-frequency dielectric constants at high pressures is unfortunate; however, the calculated change of the static dielectric constant with pressure (-2×10^{-3} kbar⁻¹) is consistent in both sign and magni-

tude with values for MgO (-1.9×10^{-3} kbar $^{-1}$) [17] and RbCl (-9.7×10^{-3} kbar $^{-1}$) [18].

The literature is confusing on the matter of the phase transformation. Cline and Stephens [4] state that hexagonal ZnS transformed to the cubic form under pressure; one can only conclude from their information that the transformation took place in the range 0–45 kbar. Bridgman [19] on the other hand reports that no pressure-induced transformation was observed in the absence of shearing force in the 0–50 kbar range. No spectral change indicating a first-order transition to the zinc blende structure was observed at any pressure for any sample orientation in this study. The atmospheric- and high-pressure spectra show a smooth shift of peak positions with pressure and no significant change in intensity of the 276-cm $^{-1}$ peak relative to that of the 350-cm $^{-1}$ peak, that would have been expected to accompany a phase transformation [7]. The absence of a phase transformation is not entirely surprising, however, in view of the fact that wurtzite is both denser [20] and more compressible [18] than zinc blende. The only known transformation of ZnS is that of zinc blende at 117 kbar [21].

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Department of Chemistry,*
University of California,
Los Angeles,
Calif. 90024, U.S.A.

Y. EBISUZAKI
M. NICOL

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REFERENCES

1. NUSIMOVICI M. A. and BIRMAN J. L., *Phys. Rev.* **156**, 925 (1967).
2. EBISUZAKI Y. and NICOL M., *Chem. Phys. Lett.* **3**, 480 (1969).
3. POULET H., KLEE W. E. and MATHIEU J. P., *Lattice Dynamics*, pp. 337–341, Proc. Intern. Conf., Copenhagen, 1963, Pergamon Press, New York (1965).
4. CLINE C. F. and STEPHENS D. R., *J. appl. Phys.* **36**, 2869 (1965).
5. BERGSMA J., *Phys. Lett.* **32A**, 324 (1970).
6. ARGUELLO C. A., ROUSSEAU D. L. and PORTO S. P. S., *Phys. Rev.* **181**, 1351 (1969).
7. NILSEN W. G., B. 6., *Light Scattering Spectra of Solids*, Proc. Intern. Conf., New York, 1968, Springer-Verlag, New York (1969).
8. BRAFMAN O. and MITRA S. S., *Phys. Rev.* **171**, 931 (1968).
9. MITRA S. S., BRAFMAN O., DANIELS W. B. and CRAWFORD R. K., *Phys. Rev.* **186**, 942 (1969).
10. VETELINO J. F., MITRA S. S. and NAMJOSHI K. V., *Phys. Rev.* **B 2**, 967 (1970).
11. SAUNDERSON D. H., *Phys. Rev. Lett.* **17**, 530 (1966).
12. MITRA S. S., POSTMUS C. and FERRARO J. R., *Phys. Rev. Lett.* **18**, 455 (1967).
13. SZIGETI B., *Trans. Faraday Soc.* **45**, 155 (1949).
14. In an uniaxial crystal such as ZnS, the above expression should be written for the two principal directions, however, it is not possible to differentiate between them with the available data.
15. VEDAM K. and DAVIS T. A., *Phys. Rev.* **181**, 1196 (1969).
16. BARRON T. H. K. and BATANA A., *Phil Mag.* **20**, 165 (1969).
17. BOSMAN A. J. and HAVINGA E. E., *Phys. Rev.* **129**, 1593 (1963).
18. SAMARA G. A., *Solid State Commun.* **4**, 279 (1966).
19. BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **74**, 21 (1940).
20. ROOYMANS C. J. M., *Structural Investigation on Some Oxides and Other Chalcogenides at Normal and Very High Pressures*, Thesis, University of Amsterdam (1967).
21. SMITH P. L. and MARTIN J. E., *Phys. Lett.* **19**, 541 (1965).