

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 298 K

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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