

SHORT COMMUNICATION

INFRARED ACTIVE TWO-PHONON PROCESSES IN CUBIC ZnS

By S. P. SRIVASTAVA*

[Manuscript received 20 November 1972]

Abstract

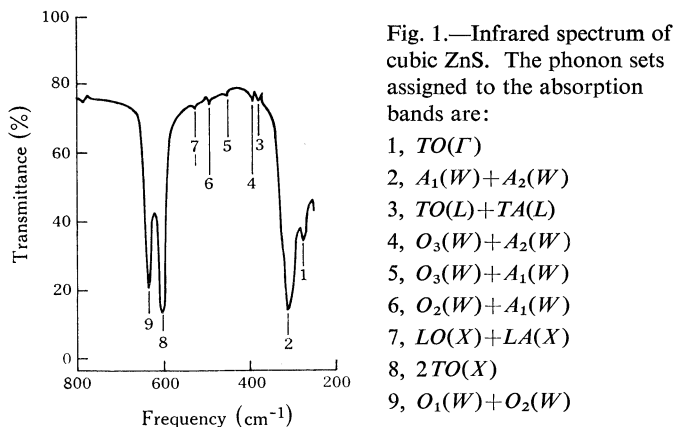
Results are presented of a study of the infrared transmission spectrum of cubic ZnS at room temperature. Besides the fundamental lattice absorption, a number of subsidiary bands due to the interaction of infrared radiation with more than one lattice phonon in the frequency range $250\text{--}800\text{ cm}^{-1}$ have been observed. These multiphonon bands are explained using inelastic neutron scattering data for the four characteristic phonon frequencies at various critical points and applying selection rules.

The infrared spectrum of cubic ZnS (space group Td^2) has previously been investigated both in transmission and reflection by a number of workers (Parodi 1937; Hass and Mathieu 1954; Mitsuishi *et al.* 1958; Deutsch 1962; Balkanski *et al.* 1964; Manabe *et al.* 1967; Le Toullec 1968). The Raman spectrum of this crystal has been reported by Couture-Mathieu and Mathieu (1953), Brafman and Mitra (1968), and recently by Nilsen (1969), while the lattice dynamics have been discussed by Kunc *et al.* (1970, 1971). The frequency of 310 or 312 cm^{-1} for the long wavelength transverse optical phonon as reported by the earlier workers (Deutsch 1962; Balkanski *et al.* 1964) was found to be in disagreement with the value of about 276 cm^{-1} obtained from inelastic neutron scattering (Bergsma 1970; Feldkamp *et al.* 1971) or Raman scattering measurements. The infrared spectrum of this crystal in the fundamental absorption region has recently been measured by Srivastava and Singh (1971) in an attempt to evaluate the effect of anharmonicity on the $q = 0$ modes. In this investigation it was found that besides the principal maximum at 310 cm^{-1} , as observed in many earlier cases, there was also a band at 275 cm^{-1} , although it was weak in intensity. There is, however, no evidence of a band around 310 cm^{-1} in the Raman spectrum, and Brafman and Mitra (1968) have concluded that this band may arise either from an infrared-active two-phonon process or from surface effects.

Besides the fundamental absorption band at the centre of the Brillouin zone, a number of subsidiary bands have also been observed in the infrared and Raman spectra of cubic ZnS. These bands are due to the interaction of the incident photon with two or more phonons in the crystal lattice. In all these interactions the energy and the wave vector of the incident photon are conserved. Such interactions take

* Department of Physics, Indian Institute of Technology, Kanpur, P.O. 11T, Kanpur-16, U.P., India.

place due to the anharmonicity terms in the potential function or in the series development of the transition moment (Szigeti 1959, 1960; Birman 1962, 1963). The maxima in the spectrum arise from the singularities in the phonon frequency distribution which are due to critical points where the frequency-wave-vector curves are flat. Since each of these critical-point phonons is related to one of the irreducible representations of the crystal space group, selection rules governing the infrared and Raman spectra can be enumerated allowing for the possibility of creation or annihilation of one or more critical-point phonons. The selection rules for the cubic ZnS and diamond structures have been given by Birman (1963). Interpretations of the observed infrared and Raman spectra of crystals belonging to these structures are then accurately possible in terms of critical-point phonons (at Γ , X , L , and W in cubic ZnS structure; Birman 1963) which are known from neutron scattering measurements. Such attempts have been made earlier, for example, in the cases of GaAs (zincblende structure) by Mitra (1964) and NaI and KI by Srivastava and Bist (1972). However, no comparable systematic studies have previously been made for cubic ZnS, and the results of such an analysis are presented here.



The infrared spectrum was recorded on a Perkin-Elmer 521 model double-beam grating spectrophotometer. The sampling technique and other experimental details were as reported by Srivastava and Singh (1971). The whole spectrum was standardized using thin films of polystyrene and spectroscopically pure indene. Under these conditions, the spectral resolution was approximately 2 cm^{-1} and the frequency was accurate to about $\pm 1 \text{ cm}^{-1}$.

The resulting spectrum is shown in Figure 1. It can be seen that many absorption bands are observed for cubic ZnS. In an earlier measurement of the infrared spectrum of this crystal on a Perkin-Elmer 112 spectrometer with a KBr prism, Deutsch (1962) found that the transmission was essentially constant from 1 to $14 \mu\text{m}$ but exhibited several absorption bands at longer wavelengths (up to $24 \mu\text{m}$). Three additional bands were observed by Balkanski *et al.* (1964) which were in the region found to be transparent by Deutsch. Further additional bands have been observed in the present experiment. However, one sharp band at 431 cm^{-1} which was observed by Deutsch has not been observed in the present work, and was also missing in the study by Balkanski *et al.*

In the absence of measured dispersion relations, Deutsch (1962) and Balkanski *et al.* (1964) explained the multiphonon bands by following the usual procedure, namely, assuming the values of the four characteristic phonons $LO = 379 \text{ cm}^{-1}$, $TO = 297 \text{ cm}^{-1}$, $LA = 263 \text{ cm}^{-1}$, and $TA = 228 \text{ cm}^{-1}$ at or near the zone edge. However, the band at 431 cm^{-1} observed by Deutsch remained unexplained with this set of phonon values. Later, Marshall and Mitra (1964) modified the phonon values, keeping in view the consistency of these values with the requirements of the Brout (1959) sum rule and the highly ionic nature of bonding in a ZnS crystal. They proposed two new sets of assignments that were only slightly different from each other and also explained the band observed at 431 cm^{-1} by Deutsch.

TABLE 1
INFRARED ACTIVE TWO-PHONON BANDS IN CUBIC ZnS

Present work	Observed band (cm^{-1})		Phonon assignments	Calculated frequency* (cm^{-1})
	Deutsch (1962)	Balkanski <i>et al.</i> (1964)		
275	312	310	$TO(\Gamma)$	276
310	—	—	$A_1(W) + A_2(W)$	295
375	—	—	$TO(L) + TA(L)$	372
390	—	—	$O_3(W) + A_2(W)$	385
—	431	—	$O_1(W) + A_2(W)(?)$	442
450	455	455	$O_3(W) + A_1(W)$	449
490	491	490	$O_2(W) + A_1(W)$	485
525	526	525	$LO(X) + LA(X)$	527
570	—	566	$O_2(W) + O_3(W)$	573
—	—	595	$O_1(W) + O_3(W)$	597
605	605	607	$2TO(X)$	600
635	642	642	$O_1(W) + O_2(W)$	632
—	677	677	$2LO(L)$	670

* From neutron scattering data.

It can be seen that the earlier procedures of adding frequencies and checking if they agree by chance with a measured line neither lead to a unique answer nor have any physical relevance. Such methods also do not give any idea about the origin of the phonons and of the critical points. With the availability of dispersion relations for ZnS, these multiphonon bands can now be explained by taking the values of the four phonon frequencies at Γ , X , L , and W critical points. Γ corresponds to the Brillouin zone centre at $\mathbf{q} = 0$, X at $(1, 0, 0)$, and L at $(\frac{1}{2}, \frac{1}{2}, 0)$. The assignment of the phonon frequencies belonging to these critical points from the dispersion curves is straightforward. W is located at $(1, \frac{1}{2}, 0)$ which thus presents some problems because the dispersion relations are generally measured in $[100]$, $[110]$, and $[111]$ directions. For reasons given by Phillips (1959) it will be a good approximation to assume $\nu(W) = \nu(\Sigma)$, where Σ denotes a critical point along the $[110]$ direction near $\mathbf{q} = (\frac{3}{4}, \frac{3}{4}, 0)$. With these values of the phonons at various critical points, the infrared active bands due to two-phonon processes, as observed in the present study, are listed in Table 1.

From Table 1 we see that there are two bands at 375 and 390 cm^{-1} . Neither of these bands has been observed by Deutsch (1962) or by Balkanski *et al.* (1964). No combinations or overtones of the phonons at the four critical points are found to be active at 431 cm^{-1} , the band observed by Deutsch only. However, there is one combination (sum) band of $O_1(W)$ and $A_2(W)$ phonons at 442 cm^{-1} . Towards the high frequency side of the spectrum (Fig. 1) we further observe three bands at 450, 490, and 525 cm^{-1} ; these bands are common in all the studies. There is one band at 570 cm^{-1} which has also been observed by Balkanski *et al.* The band at 595 cm^{-1} , which has not been observed here or by Deutsch, is due to the combination of O_1 and O_3 phonons at the W critical point. The two bands at 605 and 635 cm^{-1} have been observed in all the studies. The former is an overtone of a TO phonon at the X critical point while the latter is a combination band at the W critical point. One more overtone of an LO phonon at the L critical point has been observed at 677 cm^{-1} by Deutsch and by Balkanski *et al.*

Beyond a frequency of 677 cm^{-1} there are a few more bands that have been observed in the present study (not shown in Fig. 1) as well as in the studies of Deutsch (1962) and Balkanski *et al.* (1964). These bands could be due to three- or higher phonon processes.

References

- BALKANSKI, M., NUSIMOVICI, M., and LE TOULLEC, R. (1964).—*J. Phys., Paris* **25**, 305.
 BERGSMAN, J. (1970).—*Phys. Lett. A* **32**, 324.
 BIRMAN, J. L. (1962).—*Phys. Rev.* **127**, 1093.
 BIRMAN, J. L. (1963).—*Phys. Rev.* **131**, 1489.
 BRAFMAN, O., and MITRA, S. S. (1968).—*Phys. Rev.* **171**, 931.
 BROUT, R. (1959).—*Phys. Rev.* **113**, 43.
 COUTURE-MATHIEU, L., and MATHIEU, J. P. (1953).—*C. r. hebdom. Séanc. Acad. Sci., Paris* **236**, 371.
 DEUTSCH, T. (1962).—*Proc. Int. Conf. on Physics of Semiconductors*, Exeter, p. 505.
 FELDKAMP, L. A., STEINMAN, D. K., VAGELATOS, N., KING, J. S., and VENKATARAMAN, G. (1971).—*J. Phys. Chem. Solids* **32**, 1573.
 HASS, C., and MATHIEU, J. P. (1954).—*J. Phys. Radium, Paris* **15**, 492.
 KUNC, K., BALKANSKI, M., and NUSIMOVICI, M. (1970).—*Phys. Status Solidi* **41**, 491.
 KUNC, K., BALKANSKI, M., and NUSIMOVICI, M. (1971).—*Proc. Int. Conf. on Phonons*, Rennes, p. 109.
 LE TOULLEC, R. (1968).—Ph.D. Thesis, University of Paris.
 MANABE, A., MITSUISHI, A., and YOSHINAGA, H. (1967).—*Jap. J. appl. Phys.* **6**, 593.
 MARSHALL, R., and MITRA, S. S. (1964).—*Phys. Rev.* **134**, A1019.
 MITRA, S. S. (1964).—*Phys. Lett.* **11**, 119.
 MITSUISHI, A., YOSHINAGA, H., and FUJITA, S. (1958).—*J. phys. Soc., Japan* **13**, 1235.
 NILSEN, W. G. (1969).—*Phys. Rev.* **182**, 838.
 PARODI, M. M. (1937).—*C. r. hebdom. Séanc. Acad. Sci., Paris* **205**, 1224.
 PHILLIPS, J. C. (1959).—*Phys. Rev.* **113**, 147.
 SRIVASTAVA, S. P., and BIST, H. D. (1972).—*Phys. Status Solidi* **51**, 85.
 SRIVASTAVA, S. P., and SINGH, R. D. (1971).—*Phys. Status Solidi* **45**, 99.
 SZIGETI, B. (1959).—*Proc. R. Soc. A* **252**, 217.
 SZIGETI, B. (1960).—*Proc. R. Soc. A* **258**, 337.