

Raman Effect in Cadmium Sulfide

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The Raman effect of cadmium sulfide has been measured under a high degree of polarization using photoelectric recording and the continuous helium-neon and ionized-argon lasers as sources. The frequency and symmetry character of the fundamentals have been determined. The results are: two E_2 vibrations at 44 and 252 cm^{-1} ; one transverse A_1 at 228 cm^{-1} and a transverse E_1 at 235 cm^{-1} ; one longitudinal A_1 and one longitudinal E_1 , both at 305 cm^{-1} .

INTRODUCTION

CONSIDERABLE work has been done on the lattice vibrational spectra of cadmium sulfide. First, the infrared reflectivity work of Collins determined the infrared active optical phonons.¹ There have also been several infrared absorption experiments² which are primarily concerned with two or more phonon processes. Furthermore, the longitudinal optical phonon has often been observed in fluorescence experiments.³ Finally, the Raman spectra of CdS were obtained⁴ using a mercury source. Because of our interest in wurtzite crystals, we decided to remeasure the Raman spectra of CdS, using a laser source and a high resolution spectrometer and performing the measurement under a high degree of polarization.

We have subsequently arrived at an interpretation for the "fundamental" (i.e., one-phonon processes near the center of the Brillouin zone) Raman active modes which is in disagreement with the previous Raman work.

EXPERIMENTAL

The experimental setup was identical to that used previously for ZnO.⁵ We have obtained data at two frequencies: 6328 Å from the He-Ne laser, and 5145 Å from the ionized argon laser. In the latter case, it was necessary to cool the crystal to liquid nitrogen temperature in order to obtain satisfactory transmission. (The room-temperature band gap is approximately 5100 Å.) The use of two frequencies was necessitated by the unusual relative magnitudes of the fundamentals, since only two of the expected phonons could be observed at 6328 Å and room temperature, while one of the fundamentals which was clearly observed at 6328 Å was observed only as a shoulder at 5145 Å. This was probably due to its proximity (44 cm^{-1}) to the exciting line, and our inability to separate it from

the accompanying direct scattering when the crystal was immersed in a bath of liquid nitrogen. Three of the fundamentals at 6328 Å appear only, if at all, as shoulders on a large line at 207 cm^{-1} which we attribute to a multiphonon process.

Preliminary data were taken on several crystals of various doping etc. Final data were taken on a 0.5-cm cube of CdS with the z or optic axis parallel to a cube edge. All data were taken with the incident and scattered light at right angles and directed along principal axes. The spectrometer slit width was approximately 8 cm^{-1} , and we estimate that the fundamental frequencies are reliable to within $\pm 3 \text{ cm}^{-1}$.

INTERPRETATION

Cadmium sulfide has C_{6v} symmetry with 4 atoms per unit cell. Group theory predicts, at the zone center, that of the 9 optical branches there is one A_1 and one doubly degenerate E_1 which are both Raman and infrared active, two doubly degenerate E_2 branches which are Raman active only, and two inactive B_1 branches. Furthermore, for the A_1 and B_1 branches, the ionic displacement (i.e., phonon polarization) is in the z direction, while for the doubly degenerate E_1 and E_2 branches the displacements are in the xy plane. For the infrared active A_1 and E_1 branches the anions move in opposite phase from the cations, while for the E_2 and B_1 branches the like ions move in opposite phase.

For infrared active modes, the macroscopic electric field associated with longitudinal phonons produces an additional stiffening and thereby lifts the degeneracy of transverse and longitudinal phonons. A generalization of the properties of long-wavelength optic vibrations to noncubic crystals results in a separate Lyddane-Sachs-Teller relationship for phonons polarized parallel and perpendicular to the z axis.⁶

In the limit where electric-field effects are large compared to anisotropy effects, the infrared active phonons are best described by their transverse or longitudinal character rather than by their group theoretical character. That is, a longitudinal phonon polarized along z (an A_1 longitudinal) will have a frequency only slightly different from a longitudinal phonon polarized in the xy plane (an E_1 longitudinal),

¹ R. J. Collins, *J. Appl. Phys.* **30**, 1135 (1959).

² See, for example, M. Balkanski and J. M. Besson, *J. Appl. Phys.* **32**, 2293 (1961). R. Marshall and S. S. Mitra, *Phys. Rev.* **134**, A1019 (1964). M. Balkanski, J. M. Besson, and R. LeToullec, *International Conference on Semiconductors, Paris* (Academic Press Inc., New York, 1964), p. 1091.

³ See, for example, J. J. Hopfield, *J. Phys. Chem. Solids* **10**, 110 (1959).

⁴ H. Poulet and J. P. Mathieu, *Ann. Phys. (Paris)* **9**, 549 (1964).

⁵ T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.* **142**, 570 (1966).

⁶ R. Loudon, *Advan. Phys.* **13**, 423 (1964).

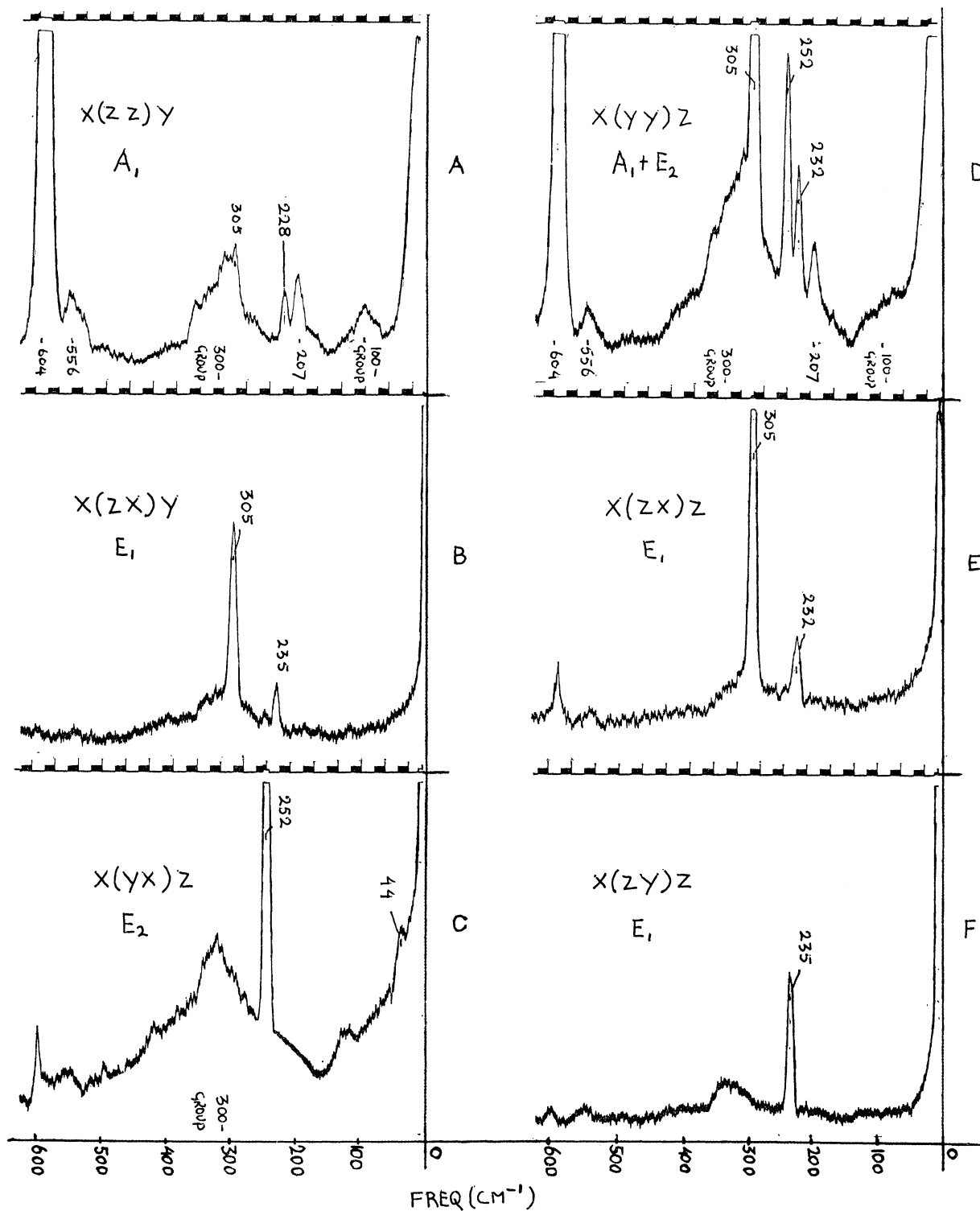


FIG. 1. Right angle Raman scattering for CdS at liquid nitrogen temperature and 5145 Å excitation for various polarization and propagation directions sufficient to define the symmetry character of the vibrations.

but considerably different from either an A_1 transverse or E_1 transverse. The E_1 degeneracy is therefore removed except for phonon propagation along the z axis. Furthermore, for phonon polarization in a general direction, the phonons remain predominantly transverse or longitudinal, (quasitransverse and quasilongitudinal) and have "mixed" group theoretical symmetry.⁶

Before presenting our results, it may be worthwhile to review the results of the infrared experiments and the previous Raman work. The reflectivity work of Collins¹ yielded the infrared active transverse and longitudinal optical frequencies at 241 and 305 cm^{-1} , respectively. Recently, Balkanski, Besson, and LeToullec² have determined an asymmetry in the transverse mode from transmittance studies of thin evaporated layers. They find an A_1 transverse at 234 cm^{-1} and an E_1 transverse at 242 cm^{-1} .

The interpretation by Poulet and Mathieu⁴ of their Raman data yielded two E_2 modes at 85 and 212 cm^{-1} which we attribute to multiphonon processes. (We apparently observed these lines at 97 and 207 cm^{-1} .) Furthermore, a 258 cm^{-1} line was interpreted by them as being the E_1 transverse mode, which probably corresponds to a line at 252 cm^{-1} observed in the present work. This mode appears to have E_2 symmetry as will be discussed below. Finally, the A_1 and E_1 longitudinal phonon in their work was probably obscured by a mercury emission line, although there is a line at 325 cm^{-1} which they attribute to this phonon.

We will follow the same notation used previously⁵ in that a spectrum is designated, for example, as $x(yz)y$ where the symbols to the left and to the right of the parentheses are the propagation directions of the incoming and scattered light, respectively, while the symbols inside are left to right the polarizations of the incoming and scattered light. The polarizability tensors for a C_{6v} crystal from which the symmetry character of the fundamentals is obtained are listed, for example, by Loudon.⁶ A complete explanation of the ensuing spectra is given in our previous work⁵ and by Loudon.⁶

The data presented were taken at liquid nitrogen temperature at 5145-Å and at room temperature with 6328-Å excitation. In Fig. 1 data taken at liquid nitrogen temperature are shown, and in Fig. 2 the room temperature data. The data of Fig. 1 are sufficient to determine unambiguously the symmetry character of the fundamental vibrations. In Fig. 1A, $x(zz)y$ the only fundamental excited is the A_1 transverse phonon at 228 cm^{-1} . In Fig. 1B, $x(zx)y$ both the E_1 transverse and E_1 longitudinal phonon are excited, the transverse at 235 cm^{-1} and the longitudinal at 305 cm^{-1} . In Fig. 1C, $x(yx)z$ only the E_2 's are excited. The 252 cm^{-1} line is well resolved, while the 44 cm^{-1} appears as a shoulder on the direct scattered light.

In Figs. 1D $x(yy)z$ and 1E $x(zx)z$, the quasitransverse and quasilongitudinal phonons of impure symmetry are excited at 232 and 305 cm^{-1} with the A_1 character observed in Fig. 1D and the E_1 in Fig. 1E. The line at

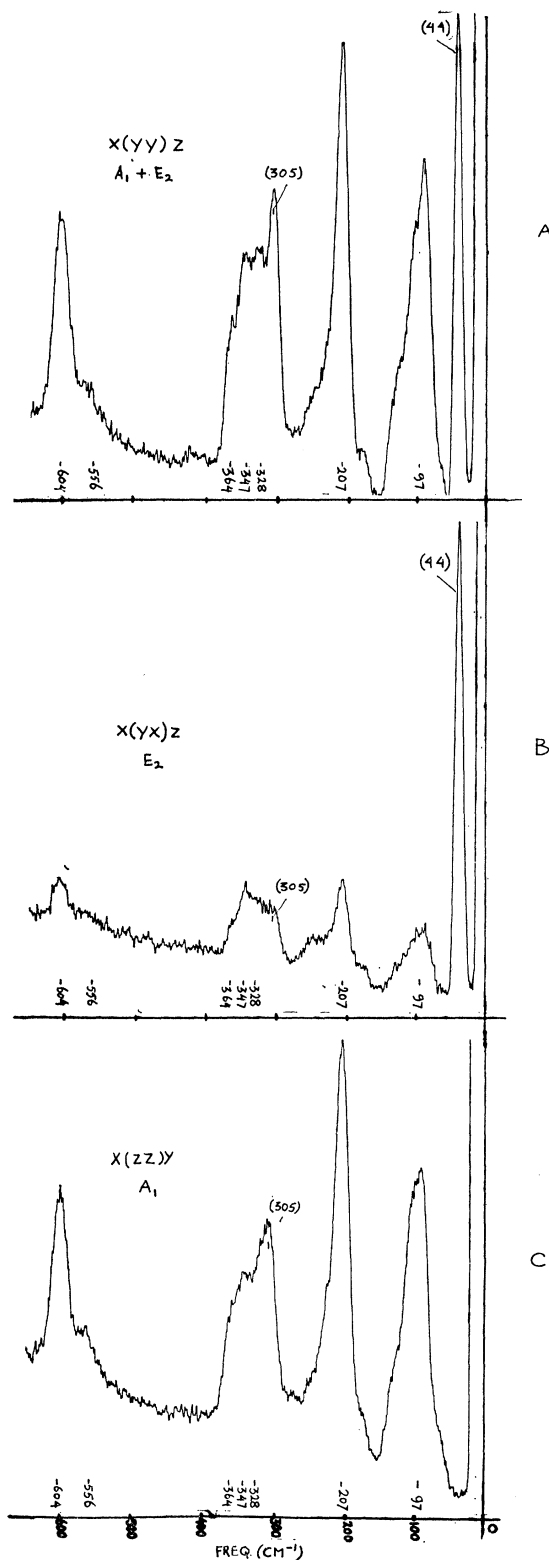


Fig. 2. Right-angle Raman scattering at room temperature and 6328 Å excitation for selected polarization and propagation directions.

TABLE I. Our results for the fundamental modes in CdS as compared with data obtained by other investigators. The previous Raman work and the infrared work were done at room temperature. The results of the present work were determined with 5145 Å excitation at liquid nitrogen temperature, with the exception of the 44 cm⁻¹ which was determined at room temperature and 6328 Å excitation. The fluorescence data were obtained at or below liquid-nitrogen temperature.

	Present work (cm ⁻¹)	Previous Raman work ^a (cm ⁻¹)	Infrared ^b (cm ⁻¹)	Fluorescence ^c (cm ⁻¹)
E_2	44	85		≈44
E_2	252	212		
E_1 (transverse)	235	256	242	
A_1 (transverse)	228		234	
E_1 (longitudinal)	305			
A_1 (longitudinal)	305	325	305	≈300

^a Reference 4.

^b References 1 and 2.

^c References 3 and 7.

252 cm⁻¹ appears in the $x(yy)z$ figure while the 44 cm⁻¹ is apparently obscured by direct scattering. Since the 252 cm⁻¹ line appears only with (xy) and (yy) polarizations, the use of the polarizability tensors for 90° Raman scattering establishes the E_2 symmetry and not E_1 as stated by Poulet and Mathieu. Finally, Fig. 1F $x(zy)z$ gives only the E_1 transverse at 235 cm⁻¹.

In Fig. 2 (A-C) are shown the $x(yy)z$, $x(yx)z$, and $x(zz)y$ orientations at room temperature with 6328-Å excitation. The 44-cm⁻¹ line has E_2 symmetry since it appears with considerable magnitude in (yy) and (yx) polarizations and with negligible magnitude in (zz) and (zx) (not shown) polarizations.⁷ It also appears to approximately follow an $(n+1)$ temperature dependence of a fundamental Stokes-Raman line, where

$$n = \left[\exp \frac{h\nu}{kT} - 1 \right]^{-1}$$

is the thermal occupation number for a phonon of energy $h\nu$. (This was determined at 6328 Å from a comparison of room temperature data and preliminary data at liquid nitrogen temperature.) The lines at 97

TABLE II. The frequency of various Raman active multiphonon processes in CdS (in cm⁻¹).

97
207
328
347
364
556
604

⁷ The E_2 mode at 44 cm⁻¹ appears to have been observed in fluorescence studies [K. Colbow, Phys. Rev. **141**, 742 (1966)].

and 207 cm⁻¹ which at room temperature have intensities larger than fundamentals are attributed to multiphonon processes, primarily because their temperature dependence is considerably larger than expected for a fundamental. This can be seen from a comparison of Figs. 1 and 2, and also from preliminary measurements at 6328 Å and liquid nitrogen temperature. These lines have predominantly A_1 symmetry which is in disagreement with the E_2 symmetry designation of Poulet and Mathieu. Furthermore, it is interesting to note that the 607 cm⁻¹ line (present experiment at 604 cm⁻¹), which was the strongest observed by Poulet and Mathieu, is considerably enhanced at 5145 Å from its value at 6328 Å. (Poulet and Mathieu used 5461-Å excitation at room temperature.)

In sum, we find two E_2 modes at 44 and 252 cm⁻¹, and A_1 transverse at 228 cm⁻¹ and an E_1 transverse at 235 cm⁻¹, and the A_1 and E_1 longitudinal at 305 cm⁻¹. The results are summarized in Table I along with the results of other investigators. Several multiphonon processes have been observed, and the most prominent are listed in Table II.

CONCLUSIONS

We have made a careful polarization study of the right angle Raman scattering in CdS similar to our previous work on ZnO.⁵ We have found all the expected modes as given by the theory of Loudon.⁶ We also find a small but definite asymmetry between the A_1 and E_1 transverse optical phonons. No frequency shift could be detected between the A_1 and E_1 longitudinal phonon.

In comparing the present results with previous workers, there are several discrepancies. We agree with Balkanski *et al.*, that the frequency of the E_1 transverse mode is around 8 cm⁻¹ larger than the A_1 , but there appears to be a slight discrepancy in the absolute frequencies. Our value for the 305 cm⁻¹ longitudinal optical mode is in good agreement with the accepted value. The most serious disagreement then appears to be with the previous Raman work, particularly in regard to the E_2 modes since they cannot be determined from infrared work. The lines that Poulet and Mathieu attribute to E_2 modes we attribute to multiphonon processes. On the other hand, the 44-cm⁻¹ line which we attribute to an E_2 was not previously seen because of its proximity to the exciting line, and the 252 cm⁻¹ line was previously interpreted as an E_1 mode.

ACKNOWLEDGMENTS

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