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Long wavelength optic phonons in WSe_2

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The first order Raman spectrum of the layer type semiconducting compound, WSe_2, has been investigated. The frequencies of the Raman active A_{1g}, $E_{2g}{}^1$, E_{1g}, and $E_{2g}{}^2$ modes have been determined to be 253, 250, 178, and 25 cm^{-1} respectively. Using a scaling relation the results have been compared to the values obtained previously for the isostructural compound 2H—MoS_2. The good agreement that is obtained between the measured and calculated values is taken as corroboration of the present assignments in WSe_2.

On a étudié le spectre Raman de premier ordre du composé semiconducteur WSe_2. Les fréquences des modes A_{1g}, $E_{2g}{}^1$, E_{1g} et $E_{2g}{}^2$ actifs en effet Raman ont été déterminées, et on a obtenu les valeurs 253, 250, 178 et 25 cm^{-1} respectivement. En utilisant une relation d'échelle, on a comparé les résultats aux valeurs obtenues antérieurement pour le composé isostructural 2H—MoS_2. Le bon accord qu'on obtient entre les valeurs mesurées et les valeurs calculées constitue une corroboration des attributions faites dans le présent travail pour WSe_2.
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Introduction

In recent years there has been a great deal of interest in the layered structure compounds. This interest has been generated by the approximate two dimensional nature of the compounds and by the many possible applications envisaged for the layer structure materials. WSe_2 is a member of the family of group VI dichalcogenides that crystallize in the form of a layer structure. MoS_2 is the best known compound in this group and it has been studied extensively (for example, see Wilson and Yoffe (1969), Wieting (1973), Chen and Wang (1974), and references cited in these papers). On the other hand very few investigations have been carried out on WSe_2. To the best of the authors' knowledge the far infrared experiments of Lucovsky *et al.* (1973) constitute the only previous investigation of the lattice vibrations of WSe_2. This paper presents a study of the first order Raman spectrum of WSe_2 and hence provides information complimentary to that of Lucovsky *et al.* (1973).

X-Ray work (Glemser *et al.* 1948) has shown that WSe_2 is isostructural to 2H—MoS_2 and thus the symmetry of WSe_2 can be described by the D_{6h}^4 space group. The unit cell spans two layers of the crystal and contains six atoms. There are 18 modes of vibration at the centre of the Brillouin zone and these can be represented by the irreducible representations of the D_{6h} point group (Verble and Wieting 1970):

$$\equiv A_{1g} + 2A_{2u} + B_{1u} + E_{1g} + 2E_{1u} + E_{2u} + 2E_{2g} + 2B_{2g}$$

There are two non-degenerate infrared active modes, $A_{2u}{}^2$ and $E_{1u}{}^2$; four non-degenerate Raman active modes, $E_{2g}{}^2$, $E_{2g}{}^1$, E_{1g}, and A_{1g}; three acoustic modes, $A_{2u}{}^1$ and $E_{1u}{}^1$ and the B_{1u} and B_{2g} modes are optically inactive.

The four Raman active modes have been

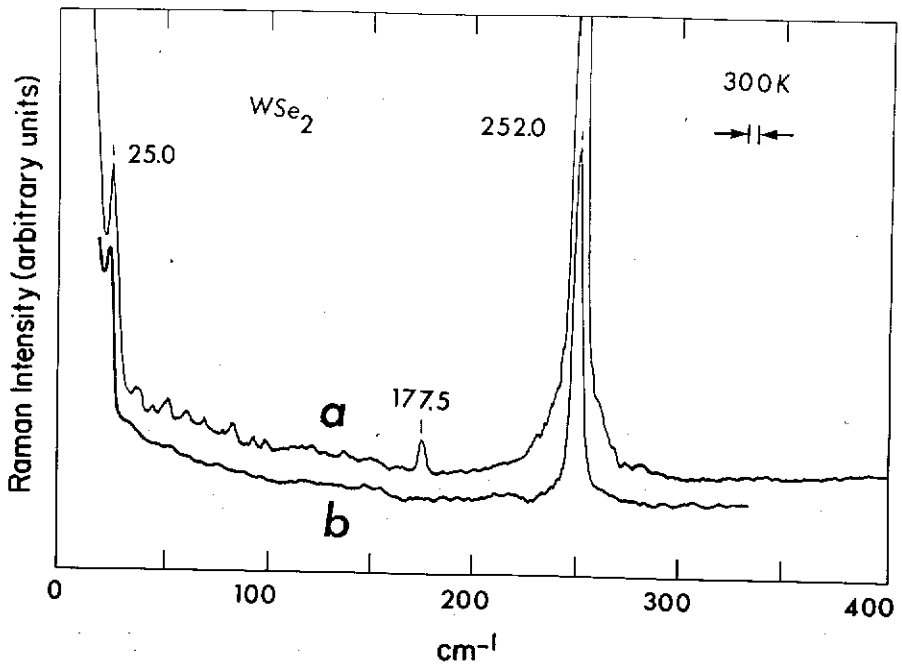

FIG. 1. The Raman spectrum of WSe_2 at 300 K. Trace *a* was obtained with the electric vector of the incident light in the plane of incidence (*p*-polarization) and trace *b* was obtained with the electric vector of the incident light perpendicular to the plane of incidence (*s*-polarization).

observed and assigned to an appropriate irreducible representation. These assignments have been made partially on the basis of the observed polarization selection rules and have been corroborated by using scaling laws to compare the observed frequencies to the well-known results in MoS_2 (Wieting and Verble 1971). In addition the $E_{2g}{}^2$ mode frequency has been compared to that of the $E_{1u}{}^2$ mode (Lucovsky *et al.* 1973) and the values are consistent with the two modes being conjugate (Wieting and Verble 1972).

Experimental

The crystals used in this work were provided by Dr. R. F. Frindt and Dr. F. Levy. All were grown by vapour transport and ranged in thickness from a few microns to approximately 0.1 mm with a surface area of approximately 0.5 cm^2. Back reflection Laue X-ray photographs enabled a crystal orientation to be carried out to within 2°. The Raman spectra were obtained using a Spex 1401 spectrometer with third monochromator attached, an ITT FW-130 photomultiplier, and standard photon counting techniques. The 488.0 and 514.5 nm lines of a Spectra Physics argon ion laser were used for excitation. Spectra were obtained with powers of less than 100 mW incident on the crystal. The surface of the crystals were tilted approximately 5° from a vertical plane and the incident light was directed vertically. This approximate right-angle scattering geometry was used throughout the work.

Results

A typical spectrum is shown in Fig. 1. The spectrum labelled *a* was obtained with the electric vector of the incident light in the plane of incidence (*p*-spectrum) and hence perpendicular to the layers. The *z*-axis of the crystal is perpendicular to the layers and hence features arising from the *zx* and *zy* components of the polarizability tensor, namely the E_{1g} mode, should be selected in the *p*-configuration. Spectrum *b* was obtained with the electric vector perpendicular to the plane of incidence (*s*-spectra) and the E_{2g} and A_{1g} modes should be selected in the *s*-spectra. As can be seen from Fig. 1 the spectra obtained in both orientations were very similar with the exception of the appearance of the relatively weak feature at 177.5 cm^{-1} in the *p*-spectrum. The similarity of the two spectra has been attributed to depolarization arising from the

deviation from a 90° geometry and from imperfections in the crystal surface.

The 177.5 cm^{-1} feature, however, appears in only the *p*-spectra and hence can be identified as the E_{1g} mode. This feature was found to be quite weak, similar to findings in MoS_2 (Wieting and Verble 1971; Wang and Chen 1974) where the E_{1g} mode was found to be two orders of magnitude weaker than the A_{1g} mode. The feature at 25 cm^{-1} has been identified as the rigid layer mode primarily on the basis of its small energy, and partly on the basis of its slightly greater relative strength in the *s*-spectra. The 252 cm^{-1} peak had roughly the same strength in both the *s* and *p* orientations and thus could not be immediately identified.

The lack of a fourth peak in the spectra was quite puzzling, particularly in view of the fact that the $E_{2g}{}^1$ and A_{1g} modes usually appear with approximately equal strength in similar structures (Wieting and Verble 1971; Wang and Chen 1974). This observation coupled with the lack of polarization dependence suggested a degeneracy and a careful investigation of the 252 cm^{-1} peak was carried out with higher resolution (≈ 1 cm^{-1} slit width). A portion of a spectrum taken with the sample at 80 K is shown in Fig. 2. The results indicated quite clearly that the 252 cm^{-1} peak was actually a doublet and enabled the assignment of frequencies to the $E_{2g}{}^1$ (250 cm^{-1}) and A_{1g} (253 cm^{-1}) modes. This assignment is further supported by comparison with the MoS_2 spectrum as discussed in the following section. It should be noted that the A_{1g} mode is forbidden in the scattering geometry of Fig. 2, and its appearance is attributed to depolarization arising from crystal surface imperfections.

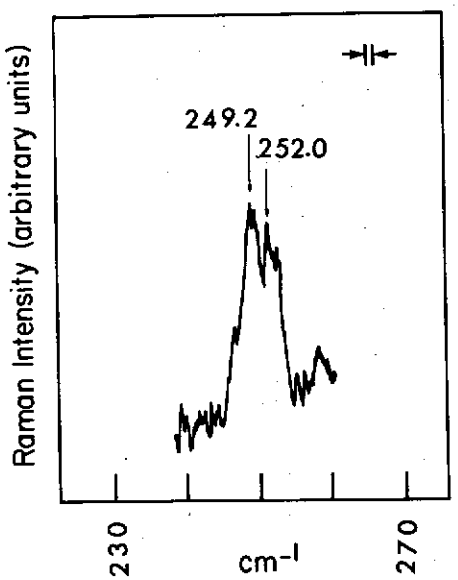

FIG. 2. A portion of the Raman spectrum of WSe_2 at 80 K, indicating the near degeneracy of the A_{1g} and $E_{2g}{}^1$ modes. The spectrum was obtained with a $y(xy)z$ scattering configuration (*z*-axis perpendicular to the layers of the crystal).

Discussion

The assignments made in the previous section can be corroborated by comparisons with similar compounds by means of a scaling rule. Keyes (1962) has introduced the concept of a characteristic optic mode frequency Ω_0 defined by

$$[1] \qquad \Omega_0{}^2 = \frac{e^2}{\mu r_0{}^3}$$

where μ is the reduced mass and r_0 is taken to be the nearest neighbour separation. A reduced frequency for the *j*th mode is then defined by $\overline{\omega j}^2 = \omega j^2/\Omega_0{}^2$. Lucovsky *et al.* (1973) have demonstrated that this relation holds extremely well for the infrared active modes of MoS_2, $MoSe_2$, WS_2, and WSe_2. Thus if [1] is used in a scaling format the frequencies of WSe_2 can be predicted on the basis of those found in MoS_2. In utilizing [1] r_0 is taken as the nearest neighbour separation (Gamble 1974) and $\mu^{-1} = (M_1)^{-1} + (2M_2)^{-2}$ for the E_{2g} modes. For the A_{1g} and E_{1g} modes where only the chalcogenide atoms are in motion $\mu = (2M_2)$. The results of this comparison are shown in Table 1 where the modes of WSe_2 have been scaled from the corresponding frequencies of MoS_2. As can be seen the results are in good agreement with the measured values and thus corroborate the previous assignments. The frequencies of WSe_2

TABLE 1. Raman frequencies

	Frequencies (cm^{-1})		
		WSe_2	
Mode	MoS_2[a]	Calcd.[b]	Obsd.[c]
A_{1g}	409	246.9	253
$E_{2g}{}^1$	384	244.5	250
E_{1g}	287	173.2	178
$E_{2g}{}^2$	33.7	21.5	25

[a] Wieting and Verble (1971).
[b] Values scaled from MoS_2 values using [1].
[c] This work; sample at 80 K; accurate to ± 2 cm^{-1}.

are slightly smaller than the measured values but the discrepancy is small and in fact is made smaller if the temperature dependence is taken into account.

The $E_{2g}{}^1$ assignment is also reinforced by the consideration of conjugate modes. Wieting and Verble (1972) have shown that the $E_{2g}{}^1$ mode should be almost degenerate with the $E_{1u}{}^1$ infrared active mode. Lucovsky *et al.* (1973) have found a room temperature frequency of 245 cm^{-1} for the $E_{1u}{}^1$ mode and a slightly higher value is expected for the conjugate $E_{2g}{}^1$ mode. The 80 K frequency of 250 cm^{-1} that has been measured in this work for the $E_{2g}{}^1$ mode is thus consistent with the infrared measurement of Lucovsky *et al.* (1973).

Summary

The four Raman active modes of WSe_2 have been observed and have been assigned to an appropriate irreducible representation on the basis of their observed energies and polarization dependence. A scaling law has been used to compare the measured frequencies to the values obtained previously in MoS_2. The good agreement between the calculated and measured values corroborated the assignments made in this work

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