PHYSICAL REVIEW B VOLUME 29, NUMBER 4 15 FEBRUARY 1984

Infrared phonons of $ZrS_{3-x}Se_x$

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(Received 31 May 1983)

Infrared transmission spectra of the pseudo-one-dimensional ZrS_3-$ZrSe_3$ solid solutions are reported. A mixed- (one-, two-, and three-) mode behavior is observed and a correspondence with the Raman phonons is established. It is shown that the conjugate-pair Raman and infrared phonons have the same type evolution in the mixed samples. It is also observed that the one-dimensional character is more important in ZrS_3 than in $ZrSe_3$.

I. INTRODUCTION

Lattice vibrations of the transition-metal trichalcogenides ZrS_3 and $ZrSe_3$ have been intensively studied in the last few years mainly in Raman and infrared spectroscopies.[1-7] The dimensionality of these materials and their atomic force constants have been tentatively analyzed. However, there still remains a lack in the detection and assignation of all the Raman and infrared phonons.

Both ZrS_3 and $ZrSe_3$ have a monoclinic unit cell [C_{2h}^2 ($P2_1/m$) space group] which contains eight atoms associated with two chains. Group analysis predicts 12 Raman-active modes (eight A_g and four B_g) and nine infrared-active modes (six B_u and three A_u). In the Raman modes the ZrS_3 or $ZrSe_3$ molecular units of the two chains within the unit cell vibrate out of phase while they vibrate in phase in the infrared modes. An association of conjugate modes is thus possible either parallel to the chains (B_g with A_u) or perpendicular to it (A_g with B_u).[5]

ZrS_3 and $ZrSe_3$ form a continuous series of solid solutions $ZrS_{3-x}Se_x$ with the same C_{2h} point-group symmetry.[8] The study of these ternary-phase infrared phonons is interesting in order to complement recent Raman works[1,2] which identified a complex mixed-mode behavior of this solid solution. Also such a study permits a better understanding of the lattice vibrations of ZrS_3 and $ZrSe_3$.

II. EXPERIMENTAL RESULTS

We used chemical transport with iodine to grow single crystals of $ZrS_{3-x}Se_x$. Their composition was verified by x-ray and gravimetric analysis. The latter method indicated a nonstoichiometry and a Se deficiency maximum in the midrange of composition (of the order of 10%). In order to reduce the Se deficiency an excess of Se was added in the growing process of $ZrS_{1.5}Se_{1.5}$.

Crystals of $ZrS_{3-x}Se_x$ have been used in polarized infrared transmission (Fig. 1) at 300 K, while unpolarized transmission was done using powdered samples on a polyethylene support at 50 and 300 K (Fig. 2). Spectra were recorded with a 180 Perkin-Elmer spectrophotometer.

Table I shows the regrouping of the results of both transmission in crystals and powders along with reflectivity measurements in the pure parents ZrS_3 and $ZrSe_3$; mode assignment in each compound and its evolution with composition x are listed. The average shift in frequency Δ (cm^{-1}) at low temperature is given for all modes except those of line 10 which were buried in a strong polyethylene absorption peak at 430 cm^{-1}. In Fig. 3 mode frequencies are plotted as a function of x.

III. DISCUSSION

The same mixed- (one-, two-, and newly designed three-) mode behavior[2] as in the Raman works[1,2] were observed. For the sake of comparison we reproduce in Fig. 4 the Raman results of Ref. 1, the different lines being identified by a number with an asterisk.

In Fig. 3, the three-mode behavior is represented by lines 6, 10, and 11 of B_u symmetry and can be easily associated with the Raman A_g lines 7*, 9* and 10* of Fig. 4. The frequency discrepancy between the infrared modes and the Raman ones does not exceed 3 cm^{-1}, and is within the experimental errors.

It is now established that the frequencies of line 11 correspond to the stretching mode of the S-S pairs, whereas

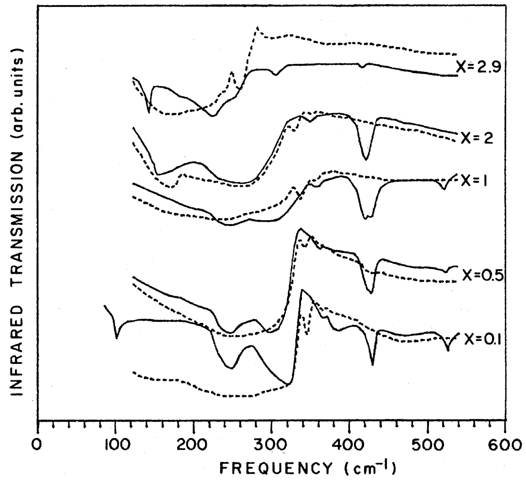

FIG. 1. Infrared crystal transmission spectra of $ZrS_{3-x}Se_x$ at 300 K. Solid lines and dashed lines stand, respectively, for B_u and A_u symmetry.

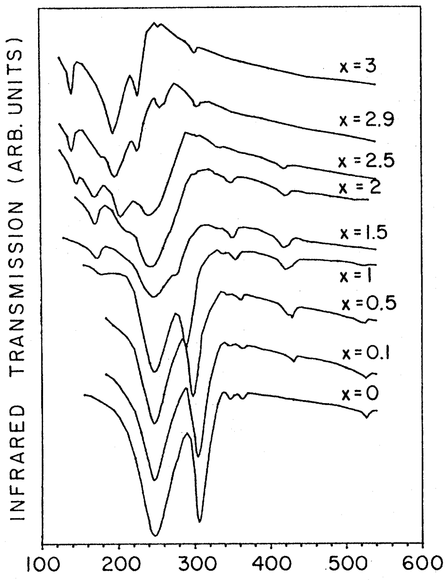

FIG. 2. Infared powder transmission spectra of $ZrS_{3-x}Se_x$ at 300 K.

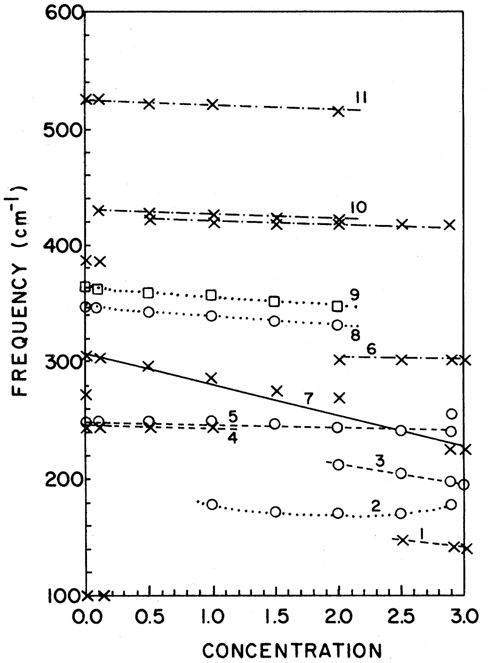

FIG. 3. TO frequencies of $ZrS_{3-x}Se_x$ as a function of composition x at 300 K. × and ○ represent B_u and A_u modes, respectively. □ represents mode appearing in both representations A_u and B_u.

the frequencies of line 6 are associated with the Se-Se pairs. Line 10 appears only in the ternary phases. As reported by Zwick *et al.*[9] it could be related to the S-Se pairs. Our transmission measurements showed that in the middle range concentration ($x = 0.5$, 1.0, 1.5, and 2.0), the absorption peak corresponding to the S-Se vibration is resolved into a doublet. While the highest-frequency component of the doublet dominates in intensity for $x = 0.5$, the lowest one supercedes it for $x \geq 1$. Such a doublet has been observed in the Raman measurements of Ref. 9 where a possibility of an isotropic effect ^{34}S-Se and ^{32}S-Se was invoked. However, as mentioned by the authors of Ref. 9, the relative intensity of the two components of the doublet does not reflect the relative natural abundance of the isotopes ^{32}S and ^{34}S. We interpret this doublet and its components' behavior as a result of the two possible configurations for the chalcogens of the trigonal prism in the ternary phase. Actually, the frequency of the S-Se pairing on the shortest side of the prism is affected by the nature of the atom (S or Se) located on the remaining summit of the prism. The high-frequency component of the doublet corresponds to a (S,S-Se) configuration, while the low-

TABLE I. Transmission infrared frequencies in cm^{-1} obtained from $ZrS_{3-x}Se_x$ powders and crystals. Crystal results are marked with an asterisk. Δ (cm^{-1}) gives the average shift at low temperature (50 K) of each mode. Line column refers to Fig. 3.

Line	Symmetry	$x = 0$	$x = 0.1$	$x = 0.5$	$x = 1.0$	$x = 1.5$	$x = 2.0$	$x = 2.5$	$x = 2.9$	$x = 3.0$	Δ (cm^{-1})
	B_u	101*	101*								
1	B_u							148	141.5	141	3
2	A_u				~178	172	171	171	~178		5
3	A_u						~212	205	197.5	195	3
4	B_u	245*	~245*	~245*	~245*						
5	A_u	247.5	247	247	247.5	247	244	241	~240*		4
	A_u								254		3.5
	B_u	275*									
6	B_u						~301.5	303.5	303.5	302	5
7	B_u	305.5	304	297	289	~275	~270		226.5	226.5	6
8	A_u	347	346	342	339	~334	331				4
9	A_u and B_u	363	362	359	356	351	347				4
	B_u	~388*	~386*								
10	B_u			~423	420	419	418	~418	~416*		
	B_u		430	427	~425	~423	~422				
11	B_u	527	526.5	523.5	~523		~517.5				2

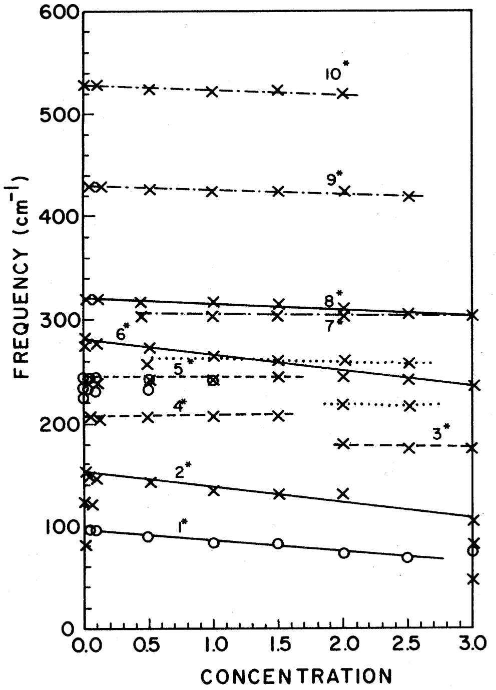

FIG. 4. Raman phonon frequencies of $ZrS_{3-x}Se_x$ as a function of composition x and 10 K. × and ○ represent A_g and B_g modes, respectively. This figure reproduces Fig. 2 of Ref. 1.

frequency component reflects the (Se,S-Se) configuration.

The two-mode behavior is represented by lines 3 and 5 in the A_u representation and lines 1 and 4 in the B_u representation. On one hand, we associate lines 1 (B_u) and 4 (B_u), respectively, with their conjugate Raman modes, lines 3* (A_g) and 5* (A_g) of Fig. 4, and, on the other hand, line 5 (A_u) with line 5*(B_g). Since some B_g modes are missing in the Raman works, mainly those of $ZrSe_3$, line 3 is not associable. Such a correspondence shows a small frequency difference between the Raman and infrared modes on the ZrS_3 side (~ 5 cm^{-1}) while the difference becomes more important on the $ZrSe_3$ side (~ 40 cm^{-1}).

The one-mode behavior appears with line 7 (B_u). Its Raman correspondent is line 8* (A_g). Again in this case the Raman infrared frequency difference increases from 15 cm^{-1} for ZrS_3 to 76 cm^{-1} for $ZrSe_3$.

The remaining lines 2, 8, and 9 cannot be easily identified. Lines 2 and 8 of A_u symmetry are not clearly affected at low temperatures; they could find their origin in some zone-edge phonon activation resulting from defects and disorder. Line 9 which is slightly stronger in the B_u symmetry does not disappear at low temperatures and could not be unequivocally assigned.

IV. CONCLUSION

The infrared measurements in $ZrS_{3-x}Se_x$ confirmed the previous infrared frequencies of the end parents and showed a mixed-mode behavior of one-, two-, and three-type. The behavior of an infrared mode is the same as its conjugate Raman mode. This indicates that the same interaction range, short for two-mode behavior and long for one-mode behavior, governs the conjugate modes. Finally, the one-dimensional character reflected in the values of the conjugate mode frequencies is more pronounced in ZrS_3 compared to $ZrSe_3$.

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