

Transition of a one-mode to a two-mode behavior in the quasi-one-dimensional and quasi-two-dimensional solid solutions $ZrS_{3-x}Se_x$

J. Deslandes and S. Jandl

Centre de Recherche en Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

(Received 14 May 1984)

Infrared reflectivity of the fibrous solid solution $ZrS_{3-x}Se_x$ is studied. As predicted by the coherent-potential approximation and rescaling method, a switching from a one-mode-type to a two-mode-type phonon behavior is observed. Such behavior could also be the result of the transition from a quasi-one-dimensional to a quasi-two-dimensional system.

I. INTRODUCTION

Recent Raman^{1,2} and infrared transmission³ investigations of the solid solutions $ZrS_{3-x}Se_x$ have shown an interesting mixed- (one-, two-, and three-) mode behavior. Polarized infrared reflectivity allows the measurement of

longitudinal- and transverse-phonon frequencies with their damping. It also facilitates the impurity-mode identification. We report in this paper infrared reflectivity spectra of the mixed crystals $ZrS_{3-x}Se_x$ analyzed through

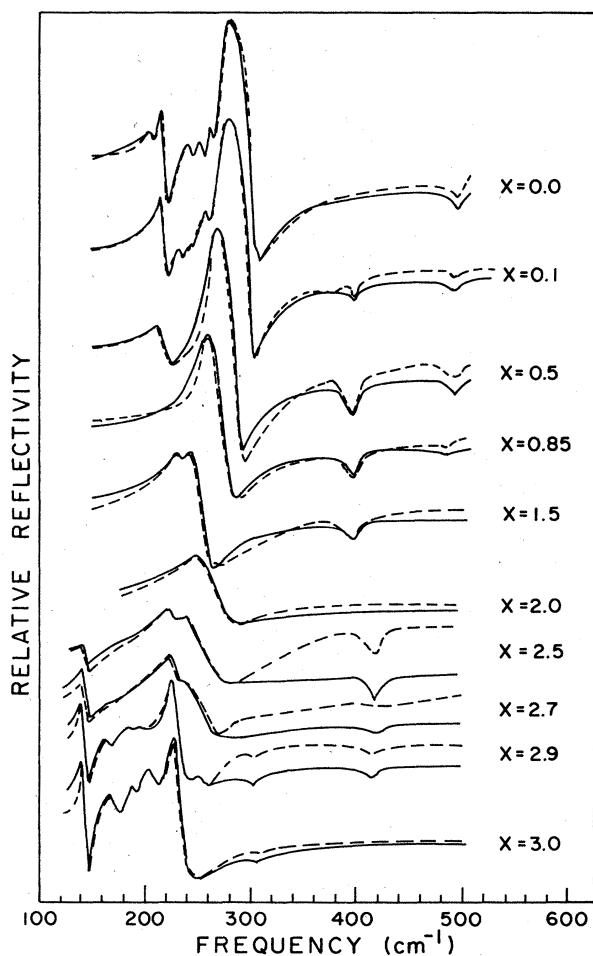


FIG. 1. Room-temperature measured (dashed lines) and calculated (solid lines) reflectance spectra of $ZrS_{3-x}Se_x$ polarized perpendicular to the chains.

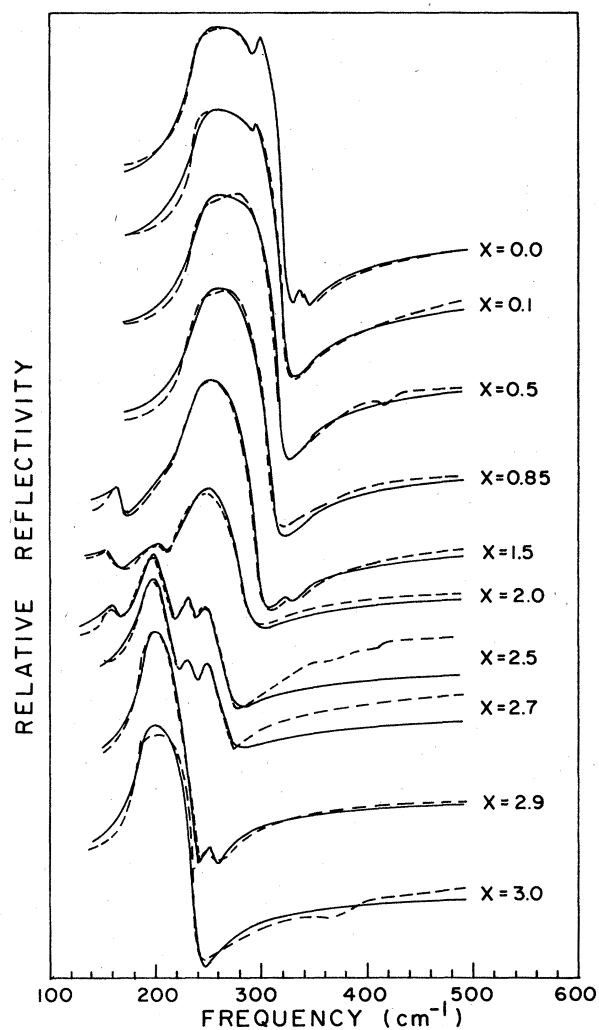


FIG. 2. Room-temperature measured (dashed lines) and calculated (solid lines) reflectance spectra of $ZrS_{3-x}Se_x$ polarized parallel to the chains.

TABLE I. Oscillator parameters fitting the three B_u stretching modes of the S—S, S—Se, and Se—Se pairs in the $ZrS_{3-x}Se_x$ reflectivity spectra. Frequencies and damping constants are in cm^{-1} .

| Composition x | Oscillator S—S | | | Oscillator S—Se | | | Oscillator Se—Se | | |
|--------------------|----------------------|------------|------------|----------------------|------------|------------|----------------------|------------|------------|
| | ω_T, ω_L | γ_T | γ_L | ω_T, ω_L | γ_T | γ_L | ω_T, ω_L | γ_T | γ_L |
| 0.0 | 528 | 15 | 11 | | | | | | |
| 0.1 | 527 | 17 | 14 | 431 | 12.5 | 10 | | | |
| 0.5 | 525 | 13 | 10 | 428.5 | 16 | 10 | | | |
| | | | | 423 | 11 | 10 | | | |
| 0.85 | 521 | 19 | 17 | 430 | 15 | 10 | | | |
| 1.1 | | | | 430 | 15 | 11.5 | | | |
| 1.25 | 521 | 19 | 17 | 429 | 15 | 12 | | | |
| 1.5 | | | | 429 | 16 | 12 | | | |
| 1.75 | | | | 428.5 | 15 | 12.5 | | | |
| 2.0 | | | | | | | | | |
| 2.25 | | | | 420 | 14 | 11.5 | | | |
| 2.5 | | | | 421 | 16 | 10 | | | |
| 2.7 | | | | 422 | 16 | 14 | | | |
| 2.9 | | | | 416.5 | 13 | 11 | 303 | 13.5 | 11 |
| 3.0 | | | | | | | 304 | 13.5 | 12 |

the entire composition range $0 \leq x \leq 3$.

ZrS_3 and $ZrSe_3$ form a continuous series of solid solutions with the same C_{2h} point-group symmetry.⁴ Group-theoretical analysis predicts twelve Raman-active modes (eight A_g and four B_g) and nine infrared-active modes (six B_u and three A_u). They correspond to atomic displacements either parallel (B_g and A_u) or perpendicular (A_g and B_u) to the chains.

II. EXPERIMENTAL RESULTS

We used chemical transport with iodine to grow single crystals of $ZrS_{3-x}Se_x$ typically 1.5 cm long, 5 mm wide,

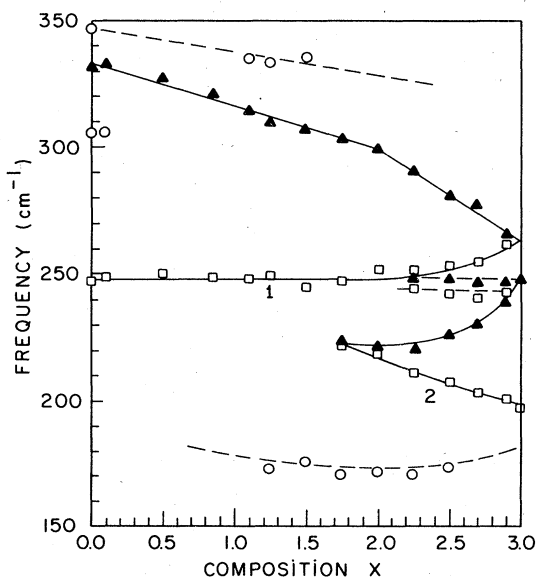


FIG. 3. Phonon frequencies of $ZrS_{3-x}Se_x$ as a function of composition x in A_u symmetry. \square and \blacktriangle represent ω_T and ω_L , respectively. \circ indicates the ω_T of weak-strength oscillators ($\omega_T \sim \omega_L$). Dashed lines are used to represent possible defect modes or zone-edge phonons activated by the structural disorder (Ref. 3).

and 0.3 mm thick. Their composition was verified by x rays. Since the gravimetric analysis of the first preparations indicated a Se-deficiency maximum in the midrange of composition, an excess of 10 at. % of Se was added in growing compounds with $1 \leq x \leq 2.5$.

The infrared reflectivity spectra were recorded at room temperature with a 180 Perkin-Elmer spectrophotometer operated in the double-beam mode. The calibration was obtained with a front-surface aluminum mirror.

The spectra analysis was accomplished by finding the parameters in the factorized form⁵ for the damped oscillator,

$$\epsilon(\omega) = \epsilon_\infty \prod_{j=1}^M \frac{\omega_{Lj}^2 - \omega^2 - i\gamma_{Lj}\omega}{\omega_{Tj}^2 - \omega^2 - i\gamma_{Tj}\omega},$$

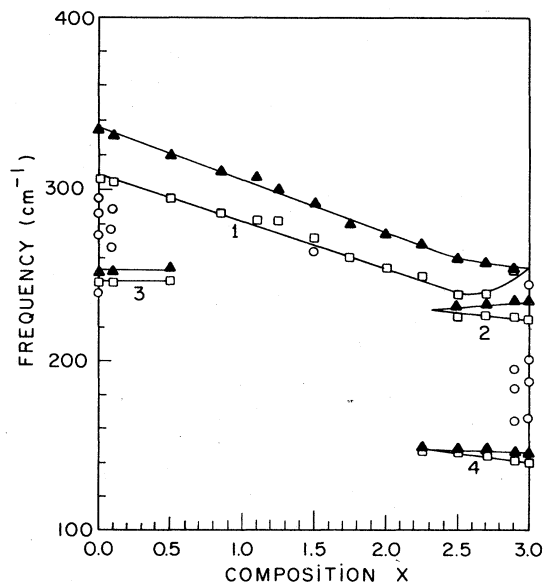


FIG. 4. Phonon frequencies of $ZrS_{3-x}Se_x$ as a function of composition x in B_u symmetry. \square and \blacktriangle represent ω_T and ω_L , respectively. \circ indicates the ω_T of weak-strength oscillators ($\omega_T \sim \omega_L$).

TABLE II. Oscillator parameters fitting the B_u vibrational modes of the $ZrS_{3-x}Se_x$ reflectivity spectra. Frequencies and damping constants are in cm^{-1} .

| Composition x | Oscillator 1 | | | Oscillator 2 | | | Oscillator 3 | | | Oscillator 4 | | | χ^2 (10^4) | | |
|--------------------|--------------|------------|------------|--------------|------------|------------|--------------|------------|------------|--------------|------------|------------|------------------------|------------|------------|
| | γ_T | ω_L | γ_L | ω_T | ω_L | γ_L | ω_T | ω_L | γ_T | γ_L | ω_T | ω_L | | γ_T | γ_L |
| 0.0 | 306 | 335 | 8 | | | | 246 | 251 | 7 | 4 | | | | | 2.7 |
| 0.1 | 304 | 331 | 6 | | | | 246 | 251 | 8 | 5 | | | | | 4.1 |
| 0.5 | 294 | 319.5 | 7 | 8.5 | | | 246 | 254 | 22 | 17 | | | | | 10.9 |
| 0.85 | 286 | 310.5 | 14 | 15 | | | | | | | | | | | 4.3 |
| 1.1 | 281 | 306 | 8.5 | 13.5 | | | | | | | | | | | 6.8 |
| 1.25 | 281 | 299 | 18 | 15 | | | | | | | | | | | 9 |
| 1.5 | 270.5 | 291 | 19 | 16 | | | | | | | | | | | 3.3 |
| 1.75 | 260 | 279.5 | 24 | 29 | | | | | | | | | | | 7.0 |
| 2.0 | 254 | 274 | 30 | 38 | | | | | | | 147 | 148 | 11 | 13 | 2.2 |
| 2.25 | 249 | 268 | 36 | 39 | | 226 | 232 | 23 | 17 | | 147 | 148 | 7 | 6 | 7 |
| 2.5 | 238.5 | 259 | 21.5 | 50 | | 226.5 | 235 | 23.5 | 15 | | 144 | 148 | 9 | 9 | 8 |
| 2.7 | 238.5 | 257 | 21 | 44 | | 226 | 235.5 | 9 | 15 | | 141.5 | 146 | 7 | 5 | 11 |
| 2.9 | 252 | 253 | 8.5 | 9.5 | | 224 | 235 | 10 | 11 | | 140 | 146 | 8 | 4 | 30.0 |
| 3.0 | | | | | | | | | | | | | | | 4.0 |

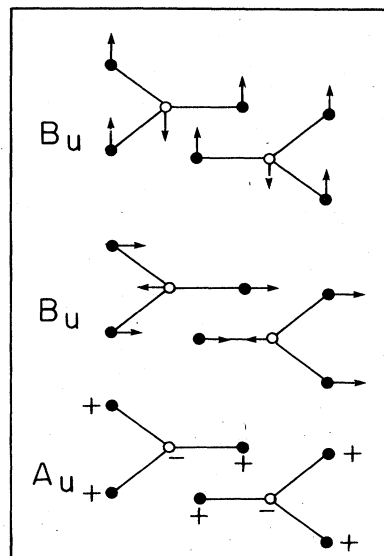


FIG. 5. Three infrared isodisplacement modes predicted by the group-theoretical analysis. In this picture, the two complex ZrX_3 (X denotes S or Se) of the unit cell are projected in the plane perpendicular to the chain axis.

which gave the theoretical reflectivity that best fitted the experimental spectra by minimizing the chi-square function χ^2 (Figs. 1 and 2). In the $\epsilon(\omega)$ function, the parameter ϵ_∞ is the high-frequency dielectric constant while ω_{Tj}, γ_{Tj} and ω_{Lj}, γ_{Lj} are the frequency and damping of the j th oscillator for the transverse and longitudinal phonon, respectively. Starting values of the oscillator parameters were obtained from the Kramers-Kronig analysis. TO-phonon frequencies ω_{Tj} were estimated from the position of the relative maxima in the imaginary part of the dielectric function, and LO-phonon frequencies ω_{Lj} were estimated from the position of the maxima in the energy-loss function $-\text{Im}(1/\epsilon^*)$.

The oscillator parameters of the most significant reststrahlen bands in the $ZrS_{3-x}Se_x$ spectra that gave the best fits are presented in Tables I and II for the B_u symmetry, and in Table III for the A_u symmetry. In Figs. 3 (A_u modes) and 4 (B_u modes) mode frequency is plotted as a function of x .

III. DISCUSSION

As shown in Table I, stretching modes ω_T of S-S, S-Se, and Se-Se are observed, in agreement with Ref. 3. Moreover, the fitted reflectivity spectra show a degeneracy of ω_T with ω_L due to the covalent nature of bonding within the pairs. Our reflectivity studies confirm also the transmission results³ in terms of an identification of transverse and defect modes. In this work the evolution of phonons as a function of composition is better resolved with the detection of the impurity modes, thus allowing the observation of a new feature.

In both Figs. 3 and 4 a transition from a one-mode to a two-mode behavior is observed for $x \sim 2$. In Fig. 4, although band 3 is not detected for the entire range of x , it could be correlated with band 4 in the same transition

TABLE III. Oscillator parameters fitting the A_u vibrational modes of the $ZrS_{3-x}Se_x$ reflectivity spectra. Frequencies and damping constants are in cm^{-1} .

| Composition x | Oscillator 1 | | | | Oscillator 2 | | | | ϵ_∞ | χ^2 (10^4) |
|--------------------|--------------|------------|------------|------------|--------------|------------|------------|------------|-------------------|------------------------|
| | ω_T | ω_L | γ_T | γ_L | ω_T | ω_L | γ_T | γ_L | | |
| 0.0 | 247 | 332 | 11 | 7 | | | | | 8.5 | .6 |
| 0.1 | 249 | 332.5 | 12 | 12 | | | | | 12 | 2.9 |
| 0.5 | 250 | 327 | 15 | 9 | | | | | 11 | 3.0 |
| 0.85 | 248.5 | 320.5 | 17 | 14 | | | | | 9 | 5.2 |
| 1.1 | 248 | 314 | 15 | 13.5 | | | | | 8 | 2.1 |
| 1.25 | 249 | 309 | 27.5 | 15.5 | | | | | 6 | 4.1 |
| 1.5 | 245 | 306.5 | 17 | 16 | | | | | 9 | 1.8 |
| 1.75 | 247 | 302.5 | 28 | 21 | 222 | 223 | 22 | 16 | 5.5 | 17.7 |
| 2.0 | 252 | 300 | 30.5 | 28.5 | 219 | 220.5 | 17.5 | 14.5 | 5 | 2.6 |
| 2.25 | 251 | 290 | 25 | 22 | 211 | 220 | 23 | 22 | 4 | 27.2 |
| 2.5 | 253 | 280 | 20 | 23 | 207 | 226 | 19 | 22 | 5 | 47.1 |
| 2.7 | 255 | 277 | 20.5 | 27.5 | 203 | 230 | 18 | 22 | 5 | 24.4 |
| 2.9 | 261.5 | 265 | 13 | 10.5 | 201 | 238 | 10 | 16.5 | 11 | 1.1 |
| 3.0 | | | | | 197 | 248 | 11.5 | 11.5 | 11 | 5.7 |

process. One expects the phonon-damping constants to be affected at the transition. Actually they reach a maximum as observed in Tables II and III. Depending on the atomic displacement associated with the modes, we believe that two explanations could be invoked for the appearance of the Se impurity mode of band 2 (Figs. 3 and 4) and band 4 (Fig. 4) at $x \sim 2$. In the first explanation, as depicted in Fig. 5, the modes are characterized by isodisplacement-type of vibration where all the S or Se anions vibrate in phase against the cation Zr. The largest reststrahlen bands should result from this kind of vibration due to the induced dipolar moment. In such a case we can invoke the same mass parameters $\beta = M_B/M_A$ and $\epsilon = 1 - M_C/M_B$ defined for pseudobinary mixed crystals of the form AB_xC_{1-x} where $M_C < M_B$. Both the coherent potential approximation⁶ and the rescaling methods⁷ predict the one-mode-to-two-mode transition as a function of β , ϵ , and x for a one-dimensional chain. For $ZrS_{3-x}Se_x$ the transition is predicted to occur at $x \sim 1.5$ since $\beta = 2.6$ and $\epsilon = 0.6$. The discrepancy with the experimental observation could be explained by noting that the approximations of the model neglect the force-constant variation with composition.

The second explanation does not restrict the atomic vibrations to the isodisplacement type. Consequently, the same mass parameters β and ϵ cannot be invoked for the three modes. The impurity-mode appearance almost at the same composition implies more than one mass factor

in the process. In accordance with the analysis of the conjugate Raman-infrared modes of Ref. 3, the one-mode-to-two-mode behavior transition could be associated with a structural transition from a quasi-one-dimensional (ZrS_3) to a quasi-two-dimensional ($ZrSe_3$) system.

This interpretation supposes that for sulfur-rich compounds the interchain interactions are weak compared to the intrachain ones. The vibrational modes are not abruptly affected by the addition of the selenium impurity. The local modes of S occur at very high impurity concentrations of Se ($x \sim 3$), although they start to develop in compounds where $x > 2$, thus weakening the oscillator strength of normal modes.

On the other hand, the interchain interaction in selenium-rich materials is more important, and thus the vibrational modes are more perturbed by the impurities S located on adjacent chains and the gap modes of Se appear at a rather low impurity concentration of S ($x \sim 2$ instead of $x \sim 0$). At $x \sim 2$ general phonon behavior is clearly affected, thus pointing to a possible structural transition.

As a general conclusion, our infrared phonon studies with the observation for the first time of a one-mode-to-two-mode transition in a quasi-one-dimensional solid solution should stimulate the elaboration of theoretical models that include force constants varying with composition.

¹R. Provencher, S. Jandl, and C. Carlone, Phys. Rev. B 26, 7049 (1982).

²A. Zwick, G. Landa, R. Carles, M. A. Renucci, and A. Kjekshus, Solid State Commun. 45, 889 (1983).

³J. Deslandes and S. Jandl, Phys. Rev. B 29, 2088 (1984).

⁴L. Brattas and A. Kjekshus, Acta Chem. Scand. 26, 3441

(1972).

⁵D. W. Berreman and F. C. Unterwald, Phys. Rev. 174, 791 (1968).

⁶P. N. Sen and W. M. Hartmann, Phys. Rev. B 9, 367 (1974).

⁷A.-M. S. Tremblay and P. Breton, J. Appl. Phys. 55, 2389 (1984).