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Lattice dynamics of mixed crystals of TiSe_2

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We present the results of Raman scattering measurements on the mixed-crystal systems $\text{TiSe}_{2-x}\text{S}_x$, $\text{TiSe}_{2-x}\text{Te}_x$, and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$. At room temperature the pure compounds all have crystal structures represented by the D_{3d}^3 ($P\bar{3}m1$) space group with three atoms per unit cell. There are two Raman-active $\vec{k}=\vec{0}$ phonons, one of A_{1g} symmetry and one of E_g symmetry. In the $\text{TiSe}_{2-x}\text{Te}_x$ system, the A_{1g} - and E_g -phonon frequencies shift smoothly with concentration, and the shifts are well described by a simple virtual-crystal model. The other two systems exhibit a two-mode behavior for which the virtual-crystal model does not correctly predict the observed frequency shifts. A random element isodisplacement model, based on Jaswal's model for the pure-crystal lattice dynamics of TiSe_2 , is developed. This model correctly predicts several features of the observed Raman spectra with no adjustable parameters.

I. INTRODUCTION

The layered-structure transition-metal dichalcogenides have been extensively investigated because a number of them undergo phase transitions to structurally distorted states at low temperatures.¹⁻⁴ Since the phase transitions are to a large extent a result of the unusual Fermi-surface geometries of these compounds, most of the previous investigations have focused on their electronic properties. In particular, a considerable effort has gone into experiments in which the Fermi surface is modified through growth of doped or mixed crystals.^{1,5-12} In this paper, we also deal with mixed crystals of the layered compounds, but our primary concern is with their lattice-dynamical properties. The mixed-crystal systems investigated here include $\text{TiSe}_{2-x}\text{S}_x$, $\text{TiSe}_{2-x}\text{Te}_x$, and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$.

Single crystals of TiSe_2 , TiS_2 , TiTe_2 , and ZrSe_2 all grow as the 1T polytype, in which the metal ion is surrounded by six chalcogen ions in a nearly octahedral coordination. The space group for the structure is D_{3d}^3 ($P\bar{3}m1$), with one formula unit per crystalline unit cell. A group-theoretical analysis predicts two Raman-active phonons, corresponding to the A_{1g} and E_g irreducible representations of the D_{3d} point group, and two infrared-active phonons, of A_{2u} and E_u symmetries. Raman and infrared measurements of the $\vec{k}=\vec{0}$ phonons have been made on a number of 1T-structure layered compounds.¹³⁻²⁰ Pure TiSe_2 undergoes a phase transition to a structurally distorted state at 200 K, in which the unit-cell dimensions increase to $2a \times 2a \times 2c$.²¹ This phase transition persists in the mixed crystals for substantial doping levels [up to $x \sim 0.95$ in $\text{TiSe}_{2-x}\text{S}_x$ (Ref. 6) and $x \sim 0.14$ in $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ (Ref. 22)], and is responsible for the appearance of additional modes in the Raman spectra of these compounds. TiSe_2 and TiTe_2 are generally accepted to be small-band-overlap semimetals,^{23,24} whereas TiS_2 and ZrSe_2 are indirect-band-gap semiconductors with band gaps of ~ 0.2 and ~ 1.2 eV, respectively.^{25,26} Thus one expects that the mixed crystals of TiSe_2 with TiS_2 and ZrSe_2 will undergo a semimetal-semiconductor transfor-

mation as x is increased from 0. More will be said about this later in connection with the lattice dynamics of these compounds.

The lattice dynamics of many mixed-crystal systems have been investigated both experimentally and theoretically, and several review articles have been published.²⁷⁻²⁹ A large fraction of the mixed-crystal systems thus far studied have been derived from cubic crystals with two atoms per unit cell and composition $AB_{1-x}C_x$, with most of the work being done on the alkali halides³⁰ and the III-V (Refs. 31 and 32) and II-IV (Refs. 33 and 34) compounds. Two main types of mixed-crystal phonon behavior have been observed. The term "one-mode" behavior refers to a system in which the phonon frequency changes monotonically with mixed-crystal composition, with the appearance of no additional modes. "Two-mode" behavior refers to those cases where additional modes arising from impurity motion appear in the vicinity of the pure-crystal phonons. Some of these new modes remain fairly constant in frequency throughout the entire concentration range, while others are found to undergo considerable frequency shifts. These modes often become hard to trace at high mixing concentrations because of disorder-induced broadening.

Because of the difficulty of treating systems which do not have translational invariance, very few tractable models of mixed-crystal lattice dynamics have been developed.²⁷⁻²⁹ A number of numerical calculations on finite-model systems have been carried out, with much of this effort going into linear-chain models. Analytic models, including the virtual-crystal model, the more complicated isodisplacement models, and coherent-potential-approximation models have had some success in explaining the experimental results.

In this paper we present the results of Raman scattering measurements on the mixed crystals $\text{TiSe}_{2-x}\text{S}_x$, $\text{TiSe}_{2-x}\text{Te}_x$, and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$, and compare them with the predictions of the virtual-crystal model and the random element isodisplacement model. This latter model was developed by Verleur and Barker,³¹ and by Chen,

Shockley, and Pearson,³⁵ and it has enjoyed considerable success in describing the experimental results on several mixed-crystal systems, most notably $\text{GaAs}_{1-x}\text{P}_x$. In Sec. II we describe the growth and characterization of the crystals used in this investigation, and in Sec. III we present the Raman scattering data. These data show one-mode behavior for $\text{TiSe}_{2-x}\text{Te}_x$ and two-mode behavior for $\text{TiSe}_{2-x}\text{S}_x$ and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$. In Sec. IV we describe a virtual-crystal model that quite accurately predicts the frequencies observed experimentally in $\text{TiSe}_{2-x}\text{Te}_x$ but not in the other two systems. Next, we recast the lattice-dynamical model of Jaswal³⁶ for TiSe_2 into the random element isodisplacement approximation. With this model we obtain considerable agreement with the experimental results for $\text{TiSe}_{2-x}\text{S}_x$ and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$. We end in Sec. V by speculating on certain features of the data and discussing the applicability of the random element isodisplacement model to systems of this sort.

II. CRYSTAL GROWTH AND CHARACTERIZATION

Mixed crystals of $\text{TiSe}_{2-x}\text{S}_x$, $\text{TiSe}_{2-x}\text{Te}_x$, and $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ were grown at 600°C using the vapor-phase-transport method with iodine as the transporting agent. Single crystals of $\text{TiSe}_{2-x}\text{S}_x$ could be grown over the entire range of compositions ($0 < x < 2$). In order to determine the compositions of these crystals, we made accurate lattice-constant measurements using both an x-ray diffractometer and a Gandolfi rotating-crystal camera. The values of the c -axis lattice constants thus obtained agree with those of Rimmington and Balchin³⁷ to within 0.2%, with our measured values being consistently larger. This is to be expected since the relatively high growth temperatures used by Rimmington and Balchin should result in slightly metal-rich crystals, for which their data also show a decreasing c -lattice parameter as the amount of interstitial Ti increases. Thus we conclude that the actual compositions of our $\text{TiSe}_{2-x}\text{S}_x$ crystals are very close to the nominal compositions. This conclusion is also confirmed by electrical-resistivity measurements, which were in good agreement with the results reported by DiSalvo, Moncton, and Waszczak.⁶ Single crystals of $\text{TiSe}_{2-x}\text{Te}_x$ could only be grown with values of x near 0 or 2. These crystals were not analyzed for Te concentration, and the values of x assigned are the nominal values.

Single crystals of $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ could only be grown for $x < 0.21$, and the actual Zr concentrations were typically factors of 2–5 less than the intended concentrations, as determined by x-ray fluorescence measurements. Thermopower measurements by Gaby *et al.*¹² on crystals from the same growth batches showed a slight increase in the number of extrinsic carriers compared to pure TiSe_2 . Extended x-ray-absorption fine-structure (EXAFS) measurements by Davies and Brown,³⁸ also on crystals from the same growth batches as those studied here, indicated that essentially all of the Zr substituted for Ti.

For Raman scattering measurements the samples were glued to a copper substrate using General Electric 7031 varnish and cleaved with Scotch Tape immediately prior to mounting in an exchange-gas liquid-nitrogen cryostat. Although the nominal temperatures were 80 K, actual

sample temperatures were typically 40–60 K higher due to local heating by the incident laser beam.

The Raman scattering apparatus consisted of a Coherent Radiation, Inc. model-52 argon-ion laser, a Spex model-1401 double monochromator, and photon-counting electronics. Instrumental resolution for the data shown was typically 4 cm^{-1} . The Raman measurements were made employing a pseudo-Brewster-angle scattering geometry, with two cylindrical lenses (rotated by 90°) being used to focus the incident laser beam on the sample.³⁹ The spectrometer was advanced in 0.5-cm^{-1} increments and the data were recorded digitally using a Digital Equipment Corporation LSI-11 microcomputer system. Spectral calibration lines were included in each spectrum.

III. EXPERIMENTAL RESULTS

A. $\text{TiSe}_{2-x}\text{S}_x$

Figure 1 shows representative Raman spectra of the $\text{TiSe}_{2-x}\text{S}_x$ mixed-crystal system. For these spectra the incident laser beam was polarized in the plane of incidence, and the scattered light was unanalyzed, except for $x = 1.2$, where it was polarized in the plane of incidence. The

FIG. 1. Representative Raman spectra of the $\text{TiSe}_{2-x}\text{S}_x$ mixed-crystal system ($x = 0.0, 0.1, 0.2, 0.4, 0.76, 1.2, 1.4, 1.6$, and 2.0). These data were obtained using the 488-nm argon-laser line and an instrumental resolution of 4 cm^{-1} . The sample temperatures were approximately 125 K.

FIG. 2. Raman spectra of $\text{TiSe}_{2-x}\text{S}_x$ for $0.6 < x < 0.8$. These data were obtained using the 488-nm argon-laser line and an instrumental resolution of 4 cm^{-1} . The sample temperatures were approximately 125 K.

symmetries of the various scattering peaks were determined in separate polarized Raman scattering measurements. The spectra of the pure crystals agree well with the results of Smith *et al.*,¹³ Holy *et al.*,^{16,40} and Sugai *et al.*¹⁹ The sample temperatures, as determined by Stokes–anti-Stokes measurements, ranged from 134 to 155 K. Note the behavior of the A_{1g} (204 cm^{-1}) and E_g (136 cm^{-1}) phonons as x increases from zero. (Although it is not strictly correct to label the mixed-crystal phonons with the pure-crystal symmetry labels, we do so for ease of discussion.) At $x=0.1$, both the A_{1g} and E_g peak heights are reduced and the widths are somewhat increased. In addition, an impurity-induced mode is clearly in evidence at 217 cm^{-1} . The two-phonon peak at 316 cm^{-1} is still present in this scan. By $x=0.4$, the peak heights of all the modes are considerably reduced. By $x=0.76$, the E_g mode has become so weak and broad that it is scarcely observable. It should also be noted that a weak and broad peak at approximately 310 cm^{-1} starts to appear in the $x=0.76$ spectrum. Between $x=0.6$ and 0.8 , the spectrum changes from TiSe_2 -like to TiS_2 -like. This will be discussed in more detail later. Polarization measurements indicate that both of the peaks appearing in the spectra for x between 0.8 and 1.2 have A_{1g} -like symmetry. As x increases from 1.2 to 1.4 , the lower-frequency mode (242 cm^{-1}) changes from A_{1g} -like to E_g -like symmetry. By $x=1.6$, the lines have sharpened considerably and a large two-phonon tail can be observed on the A_{1g} (338 cm^{-1}) peak. The peak heights also become successively larger with increasing sulfur content.

Figure 2 shows in detail the change in the character of the Raman spectra from the selenide-like to the sulfide-

FIG. 3. Representative Raman spectra of the $\text{TiSe}_{2-x}\text{Te}_x$ mixed-crystal system ($x=0.0, 0.1, 0.2$, and 1.4). These data were obtained using the 488-nm argon-laser line and an instrumental resolution of 4 cm^{-1} . The sample temperatures were approximately 125 K.

like spectra for the region $100\text{--}330 \text{ cm}^{-1}$. Notice that as x increases from 0.6 , the TiSe_2 A_{1g} peak (at 195 cm^{-1}) decreases in intensity and disappears by $x=0.8$, and a new peak, as is evident from Fig. 1, continues to evolve at larger x to become the pure- TiS_2 A_{1g} phonon.

B. $\text{TiSe}_{2-x}\text{Te}_x$

Figures 3 and 4 show the Raman spectra obtained from the $\text{TiSe}_{2-x}\text{Te}_x$ mixed-crystal system for nominal concentrations of $x=0.1, 0.2, 1.4, 1.6, 1.8$, and 2.0 . First consider the spectrum of TiTe_2 , since it has not been previously reported in the literature. A Stokes–anti-Stokes determination of the temperature places it at 116 K . Polarization-analyzed scans reveal that the 101- and 146-cm^{-1} peaks have E_g and A_{1g} symmetries respectively. These peaks are quite narrow (the full width at half peak intensity is less than 4 cm^{-1}), unlike the corresponding peaks in TiSe_2 and TiS_2 . It seems reasonable to attribute the weak peak that is observed between the E_g and A_{1g} peaks to two-phonon scattering because resistivity measurements show no anomaly indicative of superlattice formation.

As x is decreased from 2.0 , both the A_{1g} and the E_g peaks increase in frequency and become very broad and weak by $x=1.6$. The weak two-phonon peak is also observable in these scans. For $x=0.2$ and 0.1 the spectra are very similar to the pure-selenide spectra above the transition temperature. The resistivity measurements of Kirby *et al.*²² show that the phase transition occurs at

FIG. 4. Representative Raman spectra of the $\text{TiSe}_{2-x}\text{Te}_x$ mixed-crystal system ($x=1.4, 1.6, 1.8$, and 2.0). These data were obtained using the 488-nm argon-laser line and an instrumental resolution of 4 cm^{-1} . The sample temperatures were approximately 125 K.

115 K for the $x=0.1$ sample, but show no evidence for a phase transition in the $x=0.2$ sample. Thus no superlattice-induced peaks would be expected in these Raman spectra.

FIG. 5. Representative Raman spectra of the $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ mixed-crystal system ($x=0.02, 0.03, 0.10, 0.12$, and 0.15). These data were obtained using the 488-nm argon-laser line and an instrumental resolution of 4 cm^{-1} . The sample temperatures were approximately 125 K.

C. $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$

Figure 5 shows the Raman spectra of $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ for concentrations up to $x=0.21$. Sample temperatures determined by Stokes–anti-Stokes measurements were typically 110–120 K. The $x=0.02$ spectrum shows the E_g and A_{1g} phonons at 135 and 205 cm^{-1} , respectively. The lower-frequency peaks are due to superlattice formation, and they will be discussed in a separate publication. Some broadening of the A_{1g} phonon is evident in the $x=0.03$ spectrum, and by $x=0.10$, two modes (both of A_{1g} symmetry) are clearly resolved. As x is increased further, the lower-frequency mode shifts significantly downward in frequency, and the relative intensities of the two modes change markedly. The E_g phonon shows very little frequency shift with increasing concentration.

IV. MODEL CALCULATIONS

A. $\text{TiSe}_{2-x}\text{Te}_x$

Figure 6 shows the observed first-order Raman frequencies for the $\text{TiSe}_{2-x}\text{Te}_x$ mixed-crystal system as a function of x . The phonons of this system follow a one-mode behavior which can be discussed in terms of a simple model. In the Raman-active modes of the pure crystals, the metal atoms occupy inversion sites and remain at rest while the chalcogenide atoms oscillate with equal amplitudes in opposite directions around these fixed points.

FIG. 6. Virtual-crystal calculation for the A_{1g} - and E_g -phonon frequencies in $\text{TiSe}_{2-x}\text{Te}_x$. The symbols are the observed frequencies and the solid curves are the calculated frequencies.

Because the metal atoms remain at rest, the chalcogenides can be treated as simple harmonic oscillators whose frequency is given by

$$\omega = \sqrt{K/M}, \quad (1)$$

where K is the effective force constant and M is the chalcogenide mass. The simplest approach to the lattice dynamics of mixed crystals is the virtual-crystal approximation,²⁹ where the anion is replaced by an "average" anion whose mass and effective force constant depend linearly on the concentration. Thus, for $\text{TiSe}_{2-x}\text{Te}_x$, the mass and force constant in Eq. (1) become

$$M = (1-x/2)m_0 + m_2x/2, \quad (2)$$

$$K = (1-x/2)k_0 + k_2x/2, \quad (3)$$

where k_0 and k_2 are the force constants and m_0 and m_2 are the chalcogenide masses for the pure ($x=0$ and 2) compounds. The pure-crystal force constants k_{A_0} , k_{A_2} , k_{E_0} , and k_{E_2} for the A_{1g} and E_g modes can be determined from the observed Raman frequencies of the pure crystals. The results of these calculations are shown as the solid lines in Fig. 6. The agreement with experiment is quite good, with no adjustable parameters, indicating that more sophisticated calculations are not necessary. It should be noted that the force-constant changes between pure TiSe_2 and pure TiTe_2 amount to 12% for the E_g mode and 21% for the A_{1g} mode.

B. $\text{TiSe}_{2-x}\text{S}_x$

1. Virtual-crystal approximation

There is little point in applying the virtual-crystal approximation to the $\text{TiSe}_{2-x}\text{S}_x$ system, since it shows two-mode behavior. However, it is interesting to note that many other studies of mixed crystals involving sulfide-selenide combinations have revealed two-mode behavior. Examples of this are $\text{ZnSe}_{1-x}\text{S}_x$,³³ $\text{CdSe}_{1-x}\text{S}_x$,⁴¹ $\text{HfSe}_{2-x}\text{S}_x$,¹⁴ and amorphous $\text{As}_2\text{Se}_{3-x}\text{S}_x$.⁴² Chang and Mitra³³ and Verleur and Barker³¹ have been somewhat successful in describing the behavior of the $\text{ZnSe}_{1-x}\text{S}_x$ and $\text{CdSe}_{1-x}\text{S}_x$ mixed-crystal systems using the random element isodisplacement model. It therefore seems reasonable to try such an approach for the $\text{TiSe}_{2-x}\text{S}_x$ mixed crystals.

2. Random element isodisplacement model

The random element isodisplacement model was developed by Chen *et al.*³⁵ to describe two-mode behavior in $\text{GaAs}_{1-x}\text{P}_x$ and other anion-doped mixed crystals of the form $AB_{1-x}C_x$. Here we describe the fundamental concepts involved in the random element isodisplacement (REI) model. In the zone-center optic phonon of GaAs and GaP, the cation (Ga) sublattice beats against the anion (As or P) sublattice. In the REI model the anion sites throughout the crystal are assumed to be occupied randomly by one or the other of the two species of anions. Anions of like species are assumed to form rigid sublattices which vibrate as a unit. Thus, in this model, relative

motion is possible only between atoms of different species—thus the reason for the term "isodisplacement." The random occupation of the anion sites is taken into account by averaging the effects of the impurities over all the unit cells of the pure structure. To do this, a new unit cell is considered in which the actual anion is replaced by a weighted "average anion," composed of $1-x$ of the mass of the species B and x of the mass of species C . The unit cell for the $AB_{1-x}C_x$ crystal is thus composed of three particles. By considering the average anion to be composed of two particles, an extra degree of freedom is introduced into the equations of motion. It is from this extra degree of freedom that the two-mode behavior arises. In the equations of motion the concentration factors multiply the anion masses and the anion-cation force constants. These features will be common to any lattice-dynamical model reformulated in the REI approximation.

The REI approximation can also be applied to mixed crystals of the transition-metal dichalcogenides. The crystal structure appropriate for the systems investigated here is shown in Fig. 7. The pure crystals of these compounds have three atoms per unit cell, with one cation and two anion sublattices before doping. One anion sublattice is composed of all the anions at sites equivalent to those indicated by an open circle in Fig. 7; the other sublattice is composed of all the anions at sites equivalent to those indicated by a half-filled circle. Thus, within the REI approximation, anion doping will introduce two additional

FIG. 7. Crystal structure of undistorted TiSe_2 .

sublattices as described above.

Before the REI approximation can be applied, however, a good lattice-dynamical model is needed for the pure compounds. Jaswal³⁶ has developed a short-range force-constant model for the lattice dynamics of TiSe₂. He calculated dispersion curves for all nine phonon branches and his results are in good agreement with the neutron-scattering data reported by Wakabayashi *et al.*⁴³ The simplicity of Jaswal's model makes it an attractive one to reformulate in the REI approximation and this is done here for the TiSe_{2-x}S_x system. Figure 8(a) shows the force constants involved in Jaswal's model for the zone-center phonons.

The dynamical matrix for the $\vec{q}=\vec{0}$ pure-crystal phonons is 9×9 and, by symmetry, must take the form

$$\begin{pmatrix} A & \underline{0}_{3 \times 3} & \underline{0}_{3 \times 3} \\ \underline{0}_{3 \times 3} & A & \underline{0}_{3 \times 3} \\ \underline{0}_{3 \times 3} & \underline{0}_{3 \times 3} & C \end{pmatrix}, \quad (4)$$

where A and C are themselves 3×3 matrices of the form

$$\begin{pmatrix} \frac{2K}{M} & \frac{-K}{\sqrt{Mm}} & \frac{-K}{\sqrt{Mm}} \\ \frac{-K}{\sqrt{Mm}} & \frac{K+k}{m} & \frac{-k}{m} \\ \frac{-K}{\sqrt{Mm}} & \frac{-k}{m} & \frac{K+k}{m} \end{pmatrix}. \quad (5)$$

Here, M is the metal-ion mass and m is the chalcogenide mass (see Fig. 8 for the force-constant notation).

Away from the zone center along the higher-symmetry directions, three of the transverse-phonon branches have displacements only in the y direction, while the motion for the other six phonons couples the x and z displacements. Thus for $q \neq 0$, the form of the dynamical matrix and the matrices A and C is not the simple form indicated in Eqs. (4) and (5).

(a)

● METAL
□ ○ CHALCOGENS

$$k = k^l + k^g$$

(b)

FIG. 8. (a) Short-range force constants in Jaswal's model of the lattice dynamics of TiSe₂. (b) Force constants used in the random element isodisplacement adaptation of Jaswal's model.

When recast in the REI approximation, with appropriate concentration factors taken into account for both the masses and the force constants, A and C each become 5×5 matrices of the form

$$\begin{pmatrix} \frac{2K_1(1-x)+2K_2x}{M} & \frac{-K_1\sqrt{1-x}}{\sqrt{Mm_1}} & \frac{-K_1\sqrt{1-x}}{\sqrt{Mm_1}} & \frac{-K_2\sqrt{x}}{\sqrt{Mm_2}} & \frac{-K_2\sqrt{x}}{\sqrt{Mm_2}} \\ \frac{-K_1\sqrt{1-x}}{\sqrt{Mm_1}} & \frac{K_1+k_1(1-x)+k_{12}x}{m_1} & \frac{-k_1(1-x)}{m_1} & 0 & \frac{-k_{12}\sqrt{x(1-x)}}{\sqrt{m_1m_2}} \\ \frac{-K_1\sqrt{1-x}}{\sqrt{Mm_1}} & \frac{-k_1(1-x)}{m_1} & \frac{K_1+k_1(1-x)+k_{12}x}{m_1} & \frac{-k_{12}\sqrt{x(1-x)}}{\sqrt{m_1m_2}} & 0 \\ \frac{-K_2\sqrt{x}}{\sqrt{Mm_2}} & 0 & \frac{-k_{12}\sqrt{x(1-x)}}{\sqrt{m_1m_2}} & \frac{K_2+k_2x+k_{12}(1-x)}{m_2} & \frac{-k_2x}{m_2} \\ \frac{-K_2\sqrt{x}}{\sqrt{Mm_2}} & \frac{-k_{12}\sqrt{x(1-x)}}{\sqrt{m_1m_2}} & 0 & \frac{-k_2x}{m_2} & \frac{K_2+k_2x+k_{12}(1-x)}{m_2} \end{pmatrix}. \quad (6)$$

The matrices are 5×5 because in the random element isodisplacement model the anion doping introduces two additional particles per unit cell, which give rise to two additional equations of motion. Notice that if $x=0$, the

3×3 matrix in the upper left-hand corner reduces to Eq. (5). The interaction term k_{12} represents the interlayer and intralayer sulfur-selenium interactions. For simplicity in the calculations reported here it is taken to be

$$k_{12} = (k_1 + k_2)/2, \quad (7)$$

that is, an arithmetic average of the selenium-selenium and sulfur-sulfur interlayer and intralayer force constants.

The only quantities needed to perform these calculations are the infrared and Raman frequencies of the two pure compounds, the atomic masses of the constituent atoms, and the concentration factors x and $1-x$. The frequencies used in this calculation are listed in Table I. The A_{2u} modes are not well known because the samples are too thin parallel to the c axis for normal-incidence reflectivity measurements to be carried out. Thus the A_{2u} -mode frequencies used in the calculations require some justification. In simple lattice-dynamical models developed by Bromley⁴⁴ for $2H\text{-MoS}_2$ and Duffey and Kirby³⁹ for $1T\text{-TaS}_2$, the ratio of the A_{2u} to E_u frequencies is approximately 1.22. In Jaswal's model this ratio is not as simple to evaluate because it involves force constants which cannot be determined without knowing all the zone-center-mode frequencies. Since the E_u mode in TiSe_2 is known to be at 137 cm^{-1} in the normal state,¹⁶ multiplying this frequency by 1.22 would place the A_{2u} -mode frequency at 167 cm^{-1} . A shoulder at about 162 cm^{-1} appears on a large peak in the infrared data reported by Holy *et al.*¹⁶ This could be interpreted as the A_{2u} mode showing up in their spectra because of beam divergence. Wakabayashi *et al.*⁴³ also show a zone-center mode in this region on their experimentally determined dispersion curves. Nothing is known about the A_{2u} -mode frequency of TiS_2 , however. A value of 214 cm^{-1} (i.e., 1.22 times the 175-cm^{-1} E_u -mode frequency measured by Lucovsky *et al.*³²) is used in this calculation. Once the phonon frequencies used in the calculation are determined, the model contains no adjustable parameters.

The eigenvalues and eigenvectors of the matrices [Eq. (6)] were determined using standard matrix-diagonalization techniques. Figure 9 shows the calculated A_{1g} -like and A_{2u} -like (solid curves) and E_g -like and E_u -like (dashed curves) phonon frequencies as a function of concentration. Of the five eigenvalues determined by the matrix diagonalization for each coordinate direction, one is always zero and corresponds to the zone-center acoustic phonon.

The highest-frequency mode shown in Fig. 9 starts out at low x as an impurity mode. As x increases this mode eventually becomes the pure-crystal A_{1g} mode of TiS_2 . The agreement between the calculated and observed frequencies is quite good in the range $0.60 < x < 2.0$. How-

FIG. 9. Random element isodisplacement calculations for the phonons in $\text{TiSe}_{2-x}\text{S}_x$. The open symbols are the measured A_{1g} frequencies, the solid symbols are the measured E_g frequencies, the solid curves are the calculated frequencies for the A_{1g} and A_{2u} phonons, and the dashed curves are the calculated frequencies for the E_g and E_u phonons. imp indicates an impurity-induced mode. The dotted curve is explained in the text.

ever, there is a large discrepancy for $0 < x < 0.60$. In this region, it is almost as if the calculated curve must be rigidly shifted down by 47 cm^{-1} . The dotted curve in Fig. 9 is the upper curve shifted by this amount. Again the fit is quite good when this is done.

The lower-frequency A_{1g} mode, which originates at 204 cm^{-1} in pure TiSe_2 , and which decreases as x increases, is expected to become the selenium impurity mode in TiS_2 . However, it cannot be observed for $x=0.30$. For $0 < x < 0.40$, the agreement between the calculated and the observed values is good, but becomes increasingly worse as x increases to 0.80. The reason for the disappearance of this mode is not understood, but it may be related to the unusual jump in frequencies noted for the higher-frequency A_{1g} -like mode.

For the E_g -like and E_u -like modes, the agreement between the calculated and observed values is better than that found in the virtual-crystal calculation but certainly not as good as the agreement for the A_{1g} -like modes. Between $x=0.6$ and 0.80 , the observed values show a gradual increase, but the mode cannot be observed for $x=0.80$. For $1.4 < x < 2.0$, polarization measurements indicate the mode at 240 cm^{-1} has E_g -like character, but for $0.80 < x < 1.4$ the mode appearing at this frequency is observed to have A_{1g} -like character. The apparent polarization change of this mode is not predicted by the random element isodisplacement model. Although this could be interpreted as a new mode appearing in the spectra, it is

TABLE I. Phonon frequencies (in cm^{-1}) for the anion-doped mixed-crystal calculations.

	TiSe_2	TiS_2
$\omega(A_{1g})$	204	341
$\omega(E_g)$	136	242
$\omega(A_{2u})$	162 ^a	214 ^a
$\omega(E_u)$	137 ^b	175 ^c

^aEstimated frequencies.

^bFrom Holy *et al.*, Ref. 16.

^cFrom Lucovsky *et al.*, Ref. 32.

more likely a consequence of heavy doping relaxing the selection rules.

C. Zr_xTi_{1-x}Se₂

The Zr_xTi_{1-x}Se₂ family of mixed crystals shows a two-mode behavior for samples with $0.03 < x < 0.21$, which means that the virtual-crystal model will not agree with experiment. We have thus adapted Jaswal's model in the REI approximation in an attempt to explain the behavior of this system. Cation doping introduces only one additional degree of freedom because there is only one type of site involved in the substitution. The form of the matrices A and C in this case can thus be written as

$$\begin{pmatrix} \frac{2K_2}{M_2} & 0 & \frac{-K_2\sqrt{x}}{\sqrt{M_2m}} & \frac{-K_2\sqrt{x}}{\sqrt{M_2m}} \\ 0 & \frac{2K_1}{M_1} & \frac{-K_1\sqrt{1-x}}{\sqrt{M_1m}} & \frac{-K_1\sqrt{1-x}}{\sqrt{M_1m}} \\ \frac{-K_2\sqrt{x}}{\sqrt{M_2m}} & \frac{-K_1\sqrt{1-x}}{\sqrt{M_1m}} & \frac{K_1(1-x)+K_2x+k_1}{m} & \frac{-k_1}{m} \\ \frac{-K_2\sqrt{x}}{\sqrt{M_2m}} & \frac{-K_1\sqrt{1-x}}{\sqrt{M_1m}} & \frac{-k_1}{m} & \frac{K_1(1-x)+K_2x+k_1}{m} \end{pmatrix}, \quad (8)$$

FIG. 10. Random element isodisplacement calculations for the phonons in Zr_xTi_{1-x}Se₂. The open symbols are the measured A_{1g} frequencies, the solid symbols are the measured E_g frequencies, the solid curves are the calculated frequencies for the A_{1g} and A_{2u} phonons, and the dashed curves are the calculated frequencies for the E_g and E_u phonons. imp indicates an impurity-induced mode.

TABLE II. Phonon frequencies (in cm⁻¹) for the cation-doped mixed-crystal calculations.

	TiSe ₂	ZrSe ₂
$\omega(A_{1g})$	204	194 ^a
$\omega(E_g)$	136	148 ^a
$\omega(A_{2u})$	162 ^b	124 ^b
$\omega(E_u)$	137 ^c	102 ^d

^aFrom Smith *et al.*, Ref. 13.

^bEstimated frequencies.

^cFrom Holy *et al.*, Ref. 16.

^dFrom Ratajack *et al.*, Ref. 45.

where M_1 and M_2 are the cation masses and m is the chalcogen mass. Again notice that, if $x=0$, the 3×3 matrix in the lower right-hand corner reduces to Eq. (5).

The calculations are performed in a manner similar to those for anion doping. The results of these calculations are shown in Fig. 10 for the A_{1g} -like and A_{2u} -like modes (solid curves) and the E_g -like and E_u -like modes (dashed curves). Table II lists the pure-crystal phonon frequencies used as input parameters for these calculations. Again, the A_{2u} -mode frequencies are estimated as in the anion-doped case. The Zr_xTi_{1-x}Se₂ mixed-crystal system qualitatively behaves much the same as the TiSe_{2-x}S_x system. The room-temperature Raman data of Smith *et al.*¹³ reveal that the A_{1g} modes of TiSe₂ and ZrSe₂ differ by only 1 cm⁻¹, while the E_g modes differ by 12 cm⁻¹. The observed modes at 204 cm⁻¹ (A_{1g}) and 136 cm⁻¹ (E_g) in the Zr_xTi_{1-x}Se₂ mixed-crystal system are similar to those of pure TiSe₂ up to $x=0.21$, and the agreement between the observed frequencies and those calculated in the REI approximation for these modes is excellent. The additional A_{1g} mode observed in the spectra is an impurity mode. The calculation predicts two impurity modes at frequencies considerably lower than those observed.

V. DISCUSSION

A. TiSe_{2-x}S_x

As was discussed earlier and as can be clearly seen from the experimental data points in Fig. 9, the Raman spectrum of TiSe_{2-x}S_x changes abruptly in the vicinity of $x=0.80$. This is attributed to concentration-induced

changes in the electronic band structure. Band-structure calculations by Zunger and Freeman²³ indicate that TiS_2 is an indirect-gap semiconductor ($E_g = 0.23$ eV) and that TiSe_2 is an indirect-overlap semimetal ($E_g = -0.18$ eV). These calculations have been found to be in good agreement with the experimental optical and electronic data. In view of this, $\text{TiSe}_{2-x}\text{S}_x$ must, for some value of x , transform from a semimetal to a semiconductor as x is increased from zero. If the bands are assumed to shift rigidly with concentration, the energy gap can be approximated by

$$E_g(x) = (0.205x - 0.18) \text{ eV}, \quad (9)$$

which predicts that $E_g(0.88) = 0$.

There are other data to support this view. A careful look at the lattice constants measured by Rimmington and Balchin³⁷ for the $\text{TiSe}_{2-x}\text{S}_x$ mixed crystals reveals a kink (i.e., a change in the slope) in the lattice constants plotted as functions of concentration near $x = 0.80$. This may be an indication of the semimetal-semiconductor transformation. The resistivity data of DiSalvo and Waszczak⁷ show that the anomaly indicative of superlattice formation disappears at $x = 0.95 \pm 0.05$. This is also close to the estimate of the concentration at which the semimetal-to-semiconductor transformation is expected to occur. The observed resistivities for $1.0 < x < 2.0$ are metalliclike. Wilson⁴⁶ has attributed such behavior in pure TiS_2 to excess free carriers, introduced by nonstoichiometry, occupying the lowest conduction band. A similar behavior may be expected for the mixed crystals with $x = 1.0$.

The discontinuous changes in the Raman frequencies near $x = 0.80$ may result from the semimetal-to-semiconductor transformation. This is not likely to be due to a loss of screening electrons at the semimetal-to-semiconductor transformation because excess electrons are expected to be introduced by nonstoichiometry. However, the discontinuous change in the frequencies may mean that the screening length is smaller in the semimetal than in the semiconductor, although it can still be considered short range in both phases. Sulfur is certainly more electronegative than selenium, and the clustering of the sulfur atoms around the metal atoms and next to the selenium atoms at high concentrations may be responsible for a decrease in the screening. The bond angles determined from structure-refinement data reveal that TiS_2 has a structure that is closer to the ideal octahedral structure than that of TiSe_2 .^{47,48} This implies that subtle changes in the bonding or orbital hybridization might also be expected.

B. $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$

ZrSe_2 is an indirect-band-gap semiconductor ($E_g = 1.2$ eV), and, in the rigid-band approximation, the energy gap of $\text{Zr}_x\text{Ti}_{1-x}\text{Se}_2$ as a function of x can be expressed as

$$E_g(x) = (1.38x - 0.18) \text{ eV}. \quad (10)$$

This predicts $E_g(0.13) = 0$. Resistivity²² and thermopower¹² measurements reveal no anomaly indicative of superlattice formation in samples with $0.15 < x < 0.21$ at temperatures above 4.2 K. Since a similar behavior has been observed in the $\text{TiSe}_{2-x}\text{S}_x$ system near the semimetal-to-semiconductor transformation,⁶ this may indicate that the semimetal-to-semiconductor transformation and the suppression of the superlattice are related.

C. Comments on the random element isodisplacement model

The random element isodisplacement model used here has several drawbacks. First, this model forces the crystal to be translationally invariant, with a definite unit cell. This, of course, is unrealistic. Second, the effects of doping at low concentrations are not expected to be accurately described within this model because it fails to properly take into account local changes in the force constants. For extremely low concentrations, the impurity mode is expected to be a localized mode whose frequency need not be close to any of those of the host lattice, unlike the frequencies calculated in the random element isodisplacement calculation. Only at larger concentrations should the curves representing the frequencies calculated in the random element isodisplacement model and the frequencies of the localized modes become identical. In addition, at low concentrations the mass and force-constant changes are highly localized at the impurity sites, and it is not valid to average the effects of the doping over all the unit cells of the crystal as is done in this model.

In the case of $\text{TiSe}_{2-x}\text{S}_x$ the random element isodisplacement model cannot be expected to describe the discontinuous behavior of the phonon frequencies at the semimetal-to-semiconductor transition. The model assumes that the masses and force constants change monotonically and continuously as the crystal composition is varied between the two pure compounds.

In spite of the objectional features, for most of the modes the agreement between the calculated and observed frequencies is good, especially considering that there are no adjustable parameters in the model. Although there are still many gaps in the understanding of the lattice dynamics of these materials, the calculations presented here have been useful in providing a framework within which to discuss the data and in pointing out some of the unusual features of mixed crystals of TiSe_2 .

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