

Structural transitions in liquid $\text{Te}_{1-x}\text{Se}_x$ alloys

J. R. Magaña and J. S. Lannin

Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

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Polarized and depolarized Raman scattering measurements are reported in liquid $\text{Te}_{1-x}\text{Se}_x$ alloys near the melting point. The results provide the first direct evidence for a structural transition within the range $x=0.2-0.3$ from a twofold, chainlike bonding to a threefold, pyramidal As-like bonding. Higher-temperature polarized Raman measurements at $x=0.3$ do not indicate a twofold to threefold transition, as has been suggested, but rather indicate increased intrachain disorder.

I. INTRODUCTION

The $\text{Te}_{1-x}\text{Se}_x$ system is one of the most extensively studied liquid alloys. Detailed measurements have been performed on its electronic, thermodynamic, and structural properties.¹⁻⁷ These studies, which have also included variations of temperature as well as pressure and composition, indicate a progression from a nonmetallic to metalliclike state as temperature or pressure increase or x decreases. This electronic transition has generally been viewed as a consequence of a simultaneous change in local structure or coordination. Evidence for this is based in part upon radial distribution function (RDF) studies in semimetallic $l\text{-Te}$ which suggest a nearest-neighbor coordination that is approximately 3 near the melting point.^{4,8,9} This contrasts with the twofold coordination of insulating, chainlike $l\text{-Se}$ which suggests that a concentration in the Te-rich alloys exists for which the structure changes. Direct evidence for a change from twofold to threefold coordination in the alloys has been difficult to observe experimentally. In addition, recent RDF measurements¹⁰ in $l\text{-Te}$ suggest that the complexity of the spectrum may imply that the bond number may not equal the coordination number. While this result brings into question the threefold As-like bonding model proposed for $l\text{-Te}$ by Cabane and Friedel,¹¹ recent Raman scattering measurements¹² confirm this coordination.

In the present study Raman scattering measurements have been performed in the $l\text{-Te}_{1-x}\text{Se}_x$ system that allow, through the polarized and depolarized spectra, a means of more clearly determining the compositional dependence of Te and Se bonding and the character of the structural change than previously possible. In addition to structural changes with composition, a number of transport and thermodynamics studies^{5,7} have suggested that high temperature may also modify the bonding within the alloy series. Raman scattering measurements have thus been performed near the observed structural change in twofold-coordinated alloys. The results indicate that while a distinct bonding change occurs at the melting point with composition, the effect of temperature is qualitatively different from that suggested by a number of previous studies. In particular, the Raman spectra indicate that at elevated temperatures the twofold coordination of

an alloy with $x=0.3$ does not change to threefold coordination.

While extensive Raman scattering local-mode studies have been performed in crystalline semiconducting alloys¹³ as well as selected semimetallic¹⁴ and amorphous¹⁵ (a -) alloys, no comparable liquid studies have been performed. As in crystalline solid solutions, multimode behavior is expected due to statistically different atomic clusters. The Raman spectra of the Te-Se liquid system are shown below to indicate this behavior, in which both local- and resonant-mode character occurs.

II. EXPERIMENT

Raman scattering measurements were performed on $\text{Te}_{1-x}\text{Se}_x$ alloys near their melting points. The samples were sealed in quartz tubes after preheating in vacuum to remove oxides. Pseudo backscattering Raman measurements were performed at 5145 Å at incident powers of 120–150 mW. Local heating was avoided by employing a cylindrical focusing lens. A high-temperature furnace¹⁶ modified for reflectance measurements and reduced temperature gradients was employed. A Spex third monochromator system with microcomputer control was employed for obtaining the polarized HH , and depolarized VH spectra. V and H correspond to vertical and horizontal directions, respectively, in the laboratory frame. The Raman spectra have not, with the exception of pure $l\text{-Te}$ and the $x=0.2$ HH spectrum, been corrected for the SiO_2 cell Raman background. For the spectral range of interest here (70–260 cm^{-1}) this background decreases monotonically with phonon frequency and as such does not substantially modify the alloy peak positions.

III. RESULTS AND DISCUSSION

A. Compositional effects

Figure 1 compares the Raman spectra of pure $l\text{-Te}$ and that of higher Te concentration alloys at $x=0.2$ and 0.3 where evidence for a structural transition exists. These Raman spectra of $l\text{-Te}_{1-x}\text{Se}_x$ alloys exhibit a number of peaks in both the VH and HH configurations that correspond to features in the phonon density of states. The expected absence of any substantial intermediate-range structural order in the alloys implies that the VH spectra indicate the form of the phonon density weighted by

smoothly varying coupling parameters.¹⁷ In contrast, the *HH* spectra emphasize phase coherence of atomic motions within the first coordination sphere. A summary of the positions and polarization character of the alloy spectra is shown in Fig. 2. The open circles specify the positions of the primarily polarized peaks, i.e., the peaks for which the *HH* scattering is substantially greater than the *VH* com-

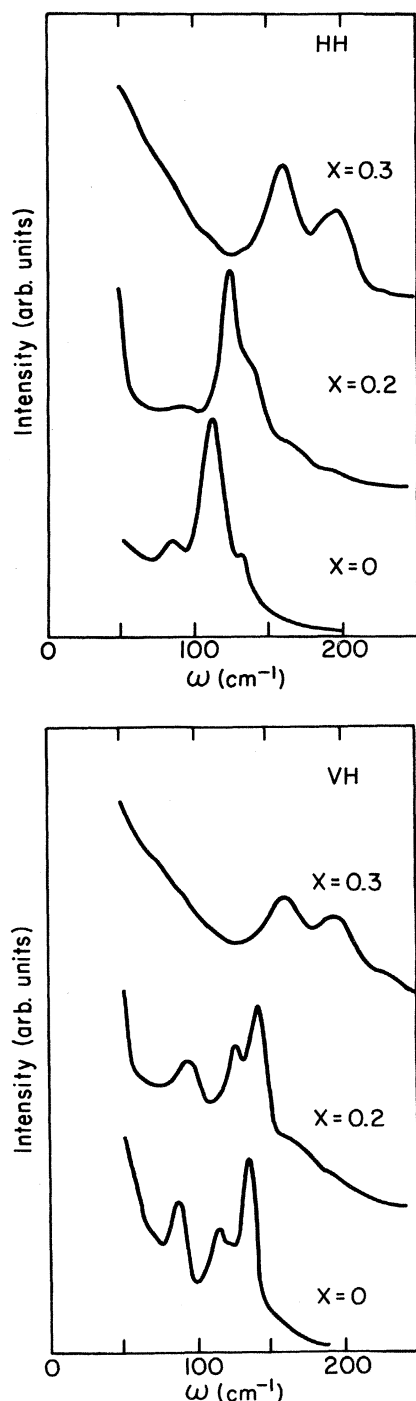


FIG. 1. Comparison of the *HH* (upper) and *VH* (lower) Raman spectra of Te-rich $l\text{-Te}_{1-x}\text{Se}_x$ alloys near their melting points. The cell background has been subtracted from the $x=0$ *VH* and *HH* spectra and the $x=0.2$ *HH* spectrum.

ponent. The closed symbols denote the positions of the depolarized peaks, while half-shaded symbols indicate the frequency of shoulder features.

In pure *l*-Te the Raman spectra exhibit three peaks, one of which is polarized. A comparison of the peak frequencies and polarization character with that of *a*-As and *a*-P indicates that *l*-Te is threefold coordinated.¹² With the addition of Se the *l*-Te derived peaks increase in frequency up to $x=0.2$. In addition, weak high-frequency shoulders are observed as noted in Fig. 2. At $x=0.3$ an abrupt change in the Raman spectra is observed as may be seen by the forms of Figs. 1 and 2. The considerable change in the Raman spectra is a reflection of a structural transition which involves modifications of short-range order. This corresponds to a threefold-to-twofold bonding transformation from predominantly pyramidal to chain configurations between $x=0.2-0.3$. Previous physical property measurements²⁻⁶ have indirectly implied a transition in the range between $x=0.2-0.4$.

In discussing the specific changes in the Raman spectra with alloying it is convenient to label the spectral features that appear separated from each other by similar symbols. For $x \geq 0.3$ the peaks or shoulders of Fig. 2 are labeled (1)–(5); the dashed curves are a visual aid only. Across the transition between $x=0.2-0.3$ designations (1), (1') and (2), (2') are employed for frequencies that appear not to change at the transition, although distinct peaks become shoulders. The curves labeled (a) and (b) do not, as Fig. 2 illustrates, have corresponding features at $x \geq 0.3$.

Feature (5) in Fig. 2 is derived from the polarized, primarily bond-stretching band in pure *l*-Se at $x=1$.¹⁸ At $x=0.6$ this peak decreases in frequency and then becomes a shoulder at lower x values. At higher Te concentrations this feature is associated with pairs or larger clusters with Se–Se bonds. As the probability of such clusters decreases with x the change in character and intensity follows. At $x=0.2$, beyond the structural transition, the Raman spectra do not exhibit any features near the 230 cm^{-1} frequency of this shoulder. The decrease in fre-

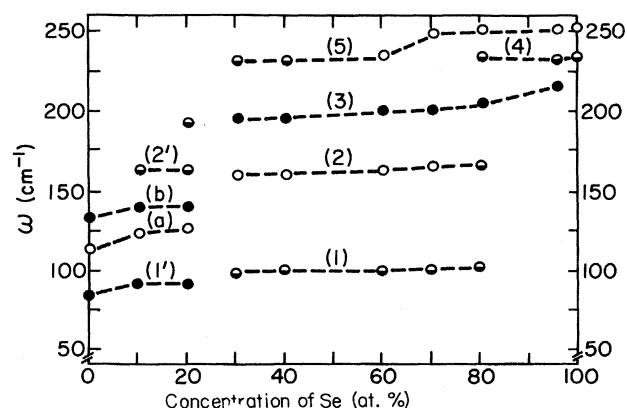


FIG. 2. Compositional variation of the polarized (open circles) and depolarized (closed circles) Raman peaks in $l\text{-Te}_{1-x}\text{Se}_x$ near their melting points. Half-shaded circles represent shoulder features. The dashed curves are visual aids.

quency of peak (5) between $x=0.6-0.7$ reflects a decrease in the Se-Se bond strength in the alloy.

Feature (4) corresponds to a shoulder in the Se-rich spectra which is not observable below $x=0.8$. Second-order Raman scattering measurements in α -Se suggest that the density of states of the higher opticlike band above 200 cm^{-1} may have a peak near this first-order shoulder as a consequence of coupling-parameter variations.¹⁹ The introduction of compositional and structural disorder with increasing Te concentration results in a loss of feature (4) at $x=0.7$.

The feature labeled (3) in Fig. 2 corresponds at large x to resonant modes of Te atoms in a Se matrix. A linear extrapolation of the peak positions yields a resonant mode as x approaches 1 at $\sim 200\text{ cm}^{-1}$. For $x=0.3-0.7$ the frequency of this peak is relatively constant. This is an indication that the Se-Te bond from which this peak is primarily derived does not change its character. For high Te-rich alloys this band corresponds to a local mode of Se in Te. The observation of local- and resonant-mode contributions to the phonon density of states in these binary liquid alloys parallels Raman observations of similar modes in amorphous and crystalline systems.^{15,20} At $x=0.2$, across the transition region, a rather weak high-frequency peak is observed that occurs near that of feature (3). This may imply a rather small number of twofold Se-Te configurations in the primarily threefold region. Alternatively, this weak feature might correspond to threefold Se-Se pairs whose frequency is reduced from the value in a twofold environment indicated by curve (5).

The polarized feature (2) in Fig. 2, which occurs between 150 and 166 cm^{-1} corresponds to Te-Te bonds in a twofold-disordered chain environment. This peak is near to that of the density of states of α -Te which occurs approximately 7% lower in frequency.^{21,22} This increase in the alloys represents a stronger Te-Te bonding. At high Se concentrations this feature is no longer observed, paralleling the behavior of the feature (5). At $x=0.1-0.2$ a weak shoulder (2) is observed that may indicate a small number of twofold Te-Te configurations. The relative intensity of this feature and that at 192 cm^{-1} for $x=0.2$ is roughly similar to that of features (2) and (3) at $x=0.3$. This further suggests a small number of twofold sites at $x=0.2$. An estimate of the fraction of twofold bonds from the relative areas and scattering intensities at $x=0.2$ and 0.3 yields less than 3.5% of such configurations at $x=0.2$. It is also possible, however, that feature (2) has contributions from local modes of Se atoms in threefold sites. An estimate of the local-mode frequency for Se-Te bonds obtained by scaling the densities of states of group-5 and group-6 systems^{23,24} yields a band between 160 and 170 cm^{-1} . It is thus difficult to unequivocally assign the weak higher-frequency features in the primarily threefold Te-rich alloys. The results do suggest a rather small fraction of twofold bonds for $x \leq 0.2$.

Peaks (a) and (b) of the primarily threefold alloy do not have corresponding features in the twofold region. As such, the Raman spectra further imply, within our signal-to-noise ratio, that for $x \geq 0.3$ the system is essentially twofold coordinated. The weaker l -Te-derived peak at 91 cm^{-1} , labeled (1), occurs near the shoulder (1')

across the transition region. This shoulder at 100 cm^{-1} is, however, relatively insensitive to the structural environment. This has been noted in the similar low-frequency peak positions of this band in the spectra of liquid, amorphous, and crystalline Te.¹² The difference in coordination between l -Te and amorphous and crystalline Te indicates the relative insensitivity of the low-frequency band to structural changes. As this mode is primarily bond bending determined, the spectra suggest to first order the relative constancy of this interaction with structure. In pure l -Se (Ref. 18) and l - $\text{Te}_{0.06}\text{Se}_{0.94}$ a low-frequency shoulder is observed at $\sim 140\text{ cm}^{-1}$ in the HH spectra alone. However, this weak feature is no longer observed at higher temperatures or Te concentrations and has thus not been indicated in Fig. 2.

B. Thermal effects

The substantial changes in the character of the Raman spectra noted above very directly manifest the transition from twofold to threefold bonding that has been extensively discussed in the literature of this alloy. Thermodynamic and transport property measurements^{5,7} have also suggested that the effects of increasing pressure or temperature are similar to that of increasing Te concentration, i.e., a twofold-to-threefold transition occurs. However, Raman scattering measurements obtained at higher temperatures up to 600°C at $x=0.3$ do not support a thermally induced bonding transition. This is shown in Fig. 3, where the HH Raman spectra are shown as a function of temperature for $T=400-550^\circ\text{C}$. As is clear from this figure, the major effect of temperature is to broaden the melting-point spectra as well as to induce a small shift

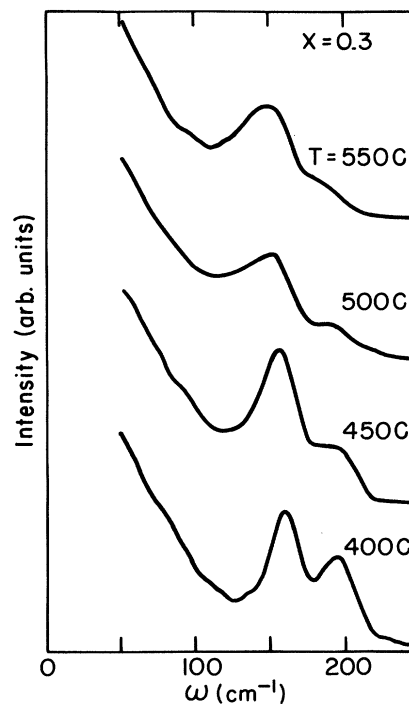


FIG. 3. Variation of the HH Raman spectra of l - $\text{Te}_{0.7}\text{Se}_{0.3}$ as a function of temperature.

to lower frequencies above 450°C. Similar effects are observed in *l*-Te with increasing temperature. It has also been suggested that Te atoms tend to transform to threefold configurations as temperature or their concentration increases. The Raman spectral features denoted in Fig. 2 as well as the high-temperature data at $x=0.3$ imply, however, that the Te coordination is relatively constant for $x \geq 0.3$. The distinct difference noted between predominantly twofold- and threefold-coordinated atoms indicated above emphasizes that the effect of temperature is not one of changing the structure, but rather of increasing disorder within chains. The observed peak shift to lower frequencies with temperature may be a consequence of increasing interchain coupling as intrachain bonding and chain length decrease. Anharmonic effects may also reduce the peak frequencies with temperature.

The range of temperatures studied at $x=0.3$ are $\sim 200^\circ\text{C}$ above the melting point and exceed those estimates for the bonding transition based on thermodynamic and transport measurements.^{5,7} This suggests that thermal effects on these properties as well as density² are not to be associated directly with major network short-range bonding changes as is often suggested. It is useful to note that for $x=0.2$, where the system is threefold coordinated, the conductivity at the melting point is indicative of semiconducting behavior. This implies that the coordination number may not be directly correlated with the transport regime in general. In the case of transport and susceptibility measurements the increased metallic character with temperature that parallels that of Te-rich alloys is logically a consequence of defect formation as noted in Se NMR studies at high temperature.²⁵ These chain scission defects may directly or indirectly be related to the disorder manifest in the spectra of Fig. 3 that are primarily intrachain in character. Thus while transport and thermodynamic measurements have implied a structural transition between $x=0.2-0.4$ at the melting point, in general agreement with the more direct Raman results, the effect of temperature is not consistent with a

network reordering.

Studies of the RDF in *l*-Te_{1-x}Se_x have suggested that the transition from threefold to twofold bonding is relatively smooth.⁴ This is based on variations of the area of the first RDF peak with composition. The Raman spectra, such as those shown in Fig. 1, indicate very weak high-frequency intensities that may imply a rather small number of twofold bonds in the predominantly threefold regime. In addition, there is no direct evidence for threefold bonding for $x \geq 0.3$. This suggests that the transition is more rapid with composition than that suggested by the RDF analysis. As the latter is complicated by an overlapping higher-frequency shoulder in Te-rich alloys, a straightforward estimate of coordination numbers is difficult.¹⁰ As such, this may explain the apparently smoother transition in the diffraction studies.

In summary, the present Raman spectra provide very direct evidence for a structural transition at the melting point from threefold to twofold coordination between $x=0.2-0.3$. Future measurements are planned to narrow this transition range. In contrast to other physical- and structural-property measurements, the vibrational states suggest a relatively abrupt transition as noted by changes in the peak positions, polarization character, and form of the Raman spectra. It was found that increasing temperature at $x=0.3$ does not result in a twofold-to-threefold bonding transition, as has been suggested, but rather indicates increasing intrachain disorder. The results imply that the alloy nonmetal-metal transition that occurs at higher temperatures does not in general require a network structural change. This transition may be associated with defect formation that arises concurrently with increasing intrachain disorder.

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