

Atomic structure and crystallization of $\text{As}_x\text{Te}_{1-x}$ glasses

M. Tenhover

*Department of Research and Development, Warrensville Research Center, The Standard Oil Company (Ohio),
4440 Warrensville Center Road, Warrensville Heights, Ohio 44128*

P. Boolchand and W. J. Bresser

Physics Department, University of Cincinnati, Cincinnati, Ohio 45221

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The results of a study of the atomic structure and crystallization behavior of As-Te glasses are reported. The primary tool of this investigation is Mössbauer-effect spectroscopy of the Te sites. Strikingly different behavior of the spectra is observed depending on whether the As content is above or below 40 at. %. In As-rich compositions, a well-defined Te site exists in which Te is twofold covalently bonded to As. For As-poor compositions, both twofold and threefold Te sites are observed. The poor glass-forming abilities of As-Te alloys (compared to As-Se or As-S) can be associated with the presence of these two types of Te environments.

I. INTRODUCTION

Information on the atomic structure of pnictide glasses ($\text{As}_x\text{X}_{1-x}$, $X=\text{S}$, Se , or Te) is very limited, despite the fact that they represent some of the most studied inorganic glasses. Raman and ir spectra of these glasses are devoid of the kind of sharp features that are observed in the spectra of tetrahedral glasses¹ ($\text{Ge}_x\text{X}_{1-x}$; $X=\text{S}$, Se). ^{75}As nuclear quadrupole resonance (NQR) spectra² of the pnictide glasses (As_2X_3) exhibit broad featureless unimodal distributions of quadrupole couplings. These observations have been attributed to the geometrical properties of the pyramidal $\text{AsX}_{3/2}$ units believed to dominate the atomic structure. This, of course, does not imply that the nature of chemical short- and medium-range order in pnictide glasses is so poorly defined as not to be amenable to experimental investigations. Experience has shown that in studying structurally disordered materials certain experimental observables are more suitable to measure than others. As an example, measurements of the asymmetry parameter of the ^{75}As electric field gradient (EFG) in As_2X_3 ($X=\text{S}$, Se , and Te) glasses³ have yielded more structural information than measurements of the NQR frequencies.²

A method that has been particularly successful in studying the network morphology of chalcogenide glasses is Mössbauer (^{129}I) emission⁴ and (^{125}Te) absorption spectroscopy.⁵ It was shown in an earlier paper through the use of ^{129}I emission spectroscopy that a breakdown in the $8-N$ coordination rule occurs in the glassy system $\text{As}_x\text{Te}_{1-x}$.⁶ These ^{129}I Mössbauer spectra exhibited a multimodal distribu-

tion of quadrupole couplings whose symmetry character (η) is directly accessible from the spectra. In this case the EFG's are well defined because they are largely determined by the near-neighbor coordination shell. Unlike NQR spectroscopy, quadrupolar line broadening due to relaxation and dipolar interactions is usually absent in the Mössbauer spectra of these materials. By combining the results of ^{125}Te absorption with those of ^{129}I emission spectroscopy, crucial information on both the nature of the chalcogen chemical order and the crystallization process of $\text{As}_x\text{Te}_{1-x}$ glasses is obtained.

Recently, Phillips has theoretically examined the topological properties of 3-2 (coordinated) glasses such as As-S and As-Se.⁷ According to him, a maximum in glass-forming tendency results when the number of constraints per atom in the network equals the number of degrees of freedom. For As-S and As-Se the optimum composition for glass formation is predicted to occur at $\text{As}_{0.40}(\text{S or Se})_{0.60}$. The case of As_2Te_3 is particularly interesting because of the weaker bond-bending forces associated with Te as compared to S or Se. The implications of this on the structure of As-Te glasses will be discussed.

II. EXPERIMENTAL

Alloys of $\text{As}_x\text{Te}_{1-x}$ ($x=0.30$, 0.50 , and 0.57) were prepared by melting 99.999%-pure elemental As and Te in sealed, evacuated (pressure less than 7×10^7 Torr), fused silica tubes. The materials were heated to 800°C , slowly cooled, and allowed to equilibrate at approximately 50°C above the melting

point for one hour. At this point the melts were quenched in ice-cold water. The typical size of the alloys was 200 mg, and the compositions reported here are the nominal ones. The crystallization of $x=0.30$ and 0.50 glasses was studied on samples which were subjected to a variety of heat treatments after quenching. In each case, a quantity of the appropriate composition was quenched as above and heat treated in the same sealed tube. As-prepared samples were characterized by x-ray diffraction (Cu $K\alpha$ radiation, scanning rate equal to $0.02^\circ/\text{min}$) and atomic density measurements.

Mössbauer-effect (ME) experiments utilizing the ^{125}Te and ^{129}I resonances were performed by moving the appropriate source in the constant acceleration mode relative to the absorber, with both the source and absorber cooled to 4.2 K. Details on the experimental techniques can be found in Refs. 4 and 5. Absorbers for the ^{125}Te ME experiments were prepared by finely powdering the as-quenched or heat-treated samples and sealing the powder with a filler (MgO) in an aluminum holder. For the ^{129}I ME experiments, a trace of neutron activation ^{128}Te metal⁴ was incorporated in the melts. The same procedure for quenching and preparing the samples was followed for these radioactive samples.

In ^{125}Te ME spectroscopy, the experimentally measured parameters are the quadrupole splitting (Δ), the isomer shift (δ), and the width of the resonant lines.⁵ In general, two resonant lines are observed for each distinct Te site in nonmagnetic materials. In ^{129}I ME spectroscopy, there are 12 possible resonant lines in nonmagnetic materials and in addition to δ and linewidths, the magnitude and sign of the electric field gradient (eV_{zz}) and the asymmetry parameter η [$= |(V_{xx} - V_{yy})/V_{zz}|$] can be determined. Standard means of spectral analysis were used to interpret the ME spectra.⁸

III. RESULTS

A. X-ray diffraction

The x-ray diffraction patterns of the quenched $x=0.30$, 0.50 , and 0.57 samples consisted of a

smooth featureless band, characteristic of amorphous materials. Previous investigators^{9,10} have shown that bulk glasses can be prepared by water quenching throughout the composition range $0.20 \leq x \leq 0.65$ for $\text{As}_x\text{Te}_{1-x}$. The measured values of atomic density are displayed in Table I and are in good agreement with those reported by Ref. 9.

B. ^{125}Te absorption spectroscopy

^{125}Te ME spectra of the as-quenched samples consisted of well-defined symmetric doublets. A typical spectrum for amorphous $\text{As}_{0.50}\text{Te}_{0.50}$ is shown in Fig. 1. The spectra were least-squares-fitted to a pair of Lorentzian lines from which the values of Δ , δ , and linewidth were obtained (Table I). The Δ and δ values for all these samples are characteristic of Te sites having a substantial degree of π bonding.⁵ Shown in Fig. 2, are the values for Δ versus composition (x) for the three bulk glass samples and the values for rf-sputtered films from Ref. 11. The good agreement between the values for films and glasses indicates that the short-range order about the Te atoms is not a function of the means of preparation, but that it is intrinsically related to the composition.

There are two very interesting features of the $\Delta(x)$ behavior. First, the value of Δ we obtain from a smooth extrapolation for amorphous Te is significantly lower than that obtained from the $\text{Ge}_x\text{Te}_{1-x}$ glassy system.⁵ This illustrates the importance of the minority species (As,Ge) in determining the short-range order of the Te sites. The second noteworthy feature of the $\Delta(x)$ systematics is the saturation at high As concentrations ($x \geq 0.50$).

A significant result of the present study is the measurement of the linewidths of the glasses. Because of saturation effects having to do with the thickness dependence of the resonant absorption cross section¹² the sputtered films, which are generally quite inhomogeneous in thickness, do not permit a detailed comparison of linewidth values. The ability to produce bulk glasses allows the fabrication of absorbers which have a well-defined thickness, thus permitting a useful comparison of the linewidth values.

TABLE I. ^{125}Te ME data and atomic density values of $\text{As}_x\text{Te}_{1-x}$ alloys.

Sample	Δ (mm/sec)	δ (mm/sec)	Linewidth (mm/sec)	Atomic density (g/cm ³)
<i>a</i> - $\text{As}_{30}\text{Te}_{70}$	8.67(4)	0.27(8)	6.18(13)	5.54(2)
<i>a</i> - $\text{As}_{50}\text{Te}_{50}$	8.42(5)	0.26(5)	5.81(10)	5.39(3)
<i>a</i> - $\text{As}_{57}\text{Te}_{43}$	8.39(4)	0.22(4)	5.85(8)	5.34(3)
<i>c</i> - As_2Te_3	4.84(8)	0.36(8)	6.84(9)	6.25
<i>c</i> -Te	7.60(6)	0.50(4)	5.80(6)	6.24

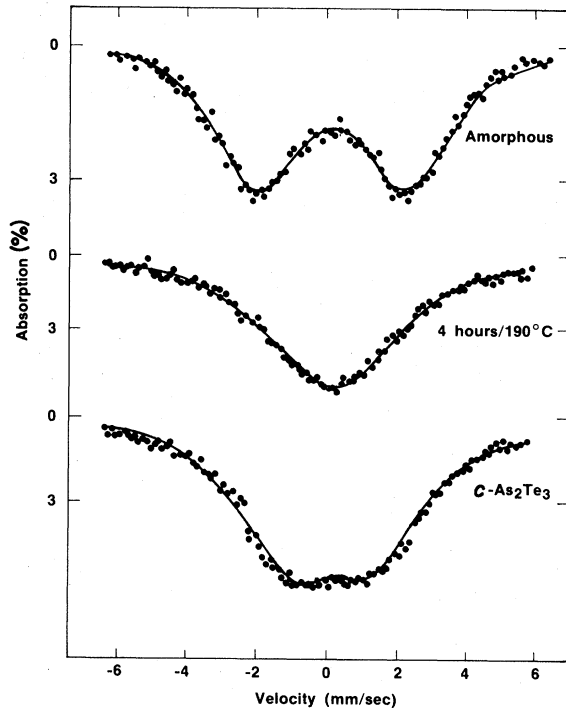


FIG. 1. ^{125}Te absorption Mössbauer spectra of as-quenched (amorphous) and heat-treated $\text{As}_{0.50}\text{Te}_{0.50}$ glasses. The dots are the actual data points and the smooth line is a fit of the spectra. All spectra were taken at 4.2 K.

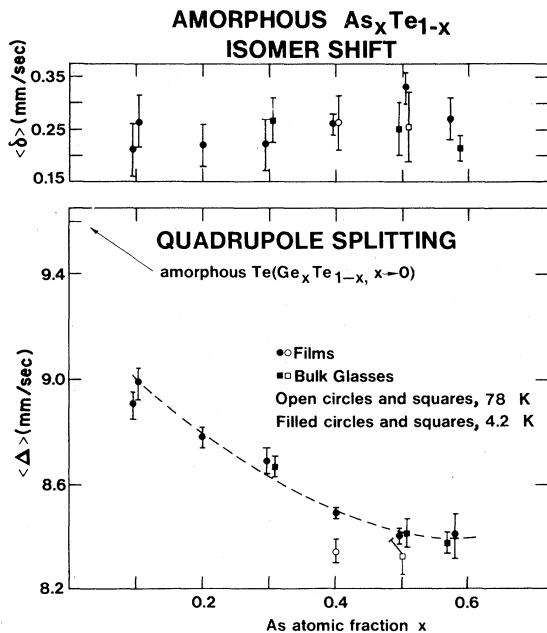


FIG. 2. Compositional dependence of the quadrupole splitting (Δ) and isomer shift (δ) of ^{125}Te in $\text{As}_x\text{Te}_{1-x}$ glasses. The value of Δ for amorphous Te is taken from Ref. 5.

Since the least-squares analysis of the spectra of the as-quenched samples is constrained to consist of a single pair of lines, the linewidth values are a measure of the Δ and δ distribution experienced by the Te atoms. As Fig. 2 clearly shows, δ is not a function of composition for the $\text{As}_x\text{Te}_{1-x}$ system. This implies that all Te sites have about the same value of δ and that the linewidth values give a direct measure of the Δ distribution. Examining the linewidth values of Table I, it is found that the $x=0.50$ and 0.57 samples have approximately the same values while the $x=0.30$ glass has a significantly higher linewidth than the other two.

C. ^{129}I emission spectroscopy

The ^{129}I spectra of $\text{As}_{30}\text{Te}_{70}$ and $\text{As}_{50}\text{Te}_{50}$ glasses have been reported in Ref. 6 by the authors. The spectra are shown in Fig. 3. In this work it was found that the spectra can best be understood as a superposition of at least two distinct Te sites. The parameters obtained by an analysis of the spectra are listed in Table II along with the values of crystalline As_2Te_3 and trigonal Te. As illustrated in Table II, the chemical identities of the two sites are not a function of composition. Instead, the changes in the spectra with composition can be attributed to a change in the relative amounts of each phase. In Ref. 6 the authors have asserted that site A results from a parent Te site having two As neighbors. Site B, on the other hand, represents a threefold-coordinated Te site similar to that of the Te site in crystalline As_2Te_3 .¹¹

D. Crystallization

The crystallization of $x=0.30$ and 0.50 glasses was studied by ME and x-ray diffraction experiments. Guided by the work of Cornet and Rossier,⁹ samples of $x=0.30$ were subjected to heat treatments of a 160°C anneal for 2 h and a 227°C anneal for 2 h. After the 160°C , 2-h anneal, the x-ray pattern showed that the sample consisted of an amorphous phase (presumably richer in As) and the Bragg reflections of crystalline Te. The Te peaks were very broad and slightly shifted to higher angles. This implies that the Te crystals are very small and that there is probably some As substitution in the Te structure. The ME spectrum for such a sample consisted of two very broad lines having $\Delta=8.20$ mm/sec and a linewidth of 6.4 mm/sec. Note that Δ is smaller than the starting amorphous value and larger than the value for crystalline Te ($\Delta=7.60$ mm/sec). The large linewidth suggests that the spectrum is a superposition of at least two Te sites, presumably Te in the amorphous phase (now richer in As) and Te in the form of crystalline Te with

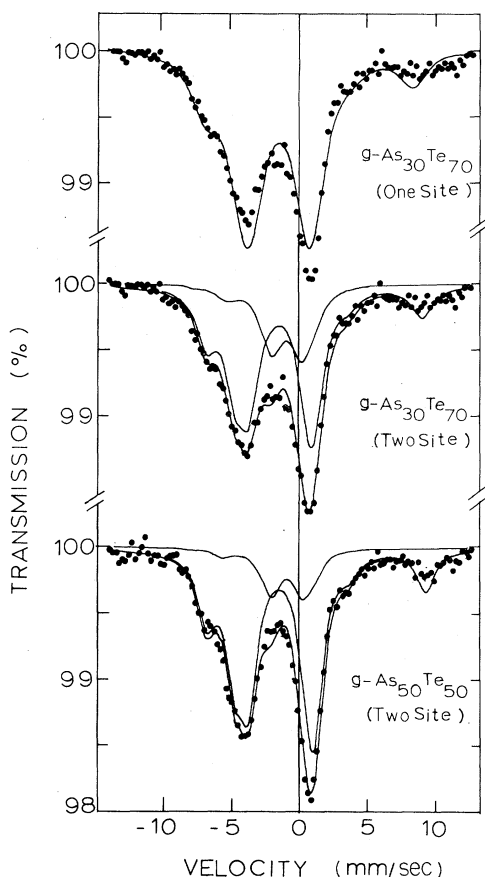


FIG. 3. Mössbauer spectra of ^{129m}Te sources in indicated hosts taken at 4.2 K using a Na^{129}I absorber. Note the qualitative improvement in the fit to the spectra of $g\text{-As}_{30}\text{Te}_{70}$ (as-quenched amorphous) in going from a one-site to a two-site fit. The spectra further reveal that the second site (site *B*) reduces in relative intensity as the As content of the glass increases.

some As substitutions. After the 227°C, 2-h annealing treatment, the x-ray diffraction pattern contained only the reflections of crystalline Te and crystalline As_2Te_3 . The corresponding ME spectrum could be well fit to a superposition of the lines of crystalline Te and As_2Te_3 . The fit yielded not only

TABLE II. ^{129}I ME parameters of $\text{As}_x\text{Te}_{1-x}$ glasses and crystals.

Sample	Site	e^2QV_z (MHz)	η	δ^a (mm/sec)
$a\text{-As}_{30}\text{Te}_{70}$	<i>A</i>	-868(4)	0.22(1)	1.13(1)
	<i>B</i>	+363(9)	0.10 ^b	1.13(4)
$a\text{-As}_{50}\text{Te}_{50}$	<i>A</i>	-889(3)	0.21(1)	1.13(1)
	<i>B</i>	+387(13)	0.10 ^b	1.22(5)
$c\text{-As}_2\text{Te}_3$		+186(4)	0.21(9)	1.14(1)
$c\text{-Te}$		-397(2)	0.70(1)	1.16(1)

^aRelative to Na^{129}I .

^bParameter kept fixed in fit.

the proper values of Δ and δ for the two sites, but also the proper relative intensities.

The more interesting results of the crystallization study concern the $x=0.50$ samples. Glasses of $x=0.50$ were heat-treated at 190°C for various times as described in Table III. The values for Δ and linewidth resulting from fitting the spectra to two lines are shown along with the x-ray diffraction and atomic density measurements. The identification of the crystalline phase that appears after 190°C anneal for 1 h in the x-ray patterns is somewhat tentative, being based on only six reflections yielding a lattice parameter $a_0=5.75\pm 0.30$ Å (assuming NaCl structure). A more complete analysis by Quinn¹⁰ has shown that this phase is AsTe having the NaCl structure with four As-Te units per cell and a lattice parameter of $a_0=5.778$ Å. Because this metastable phase can only be produced by heat treating the glass⁹ and because it exists together with the amorphous matrix the resulting Bragg peaks are weak and somewhat broad. The increase in atomic density observed for the heat-treated samples supports the notion of a high-density phase crystallizing from the glass.¹⁰ From the ^{125}Te ME spectra, the rapid drop in the average Δ as this cubic AsTe phase emerges demonstrates that it is characterized by a small value of Δ . Crystalline As_2Te_3 has a Δ of 4.84 mm/sec, so that the average value of Δ actually falls

TABLE III. Crystallization of $\text{As}_{50}\text{Te}_{50}$ glasses at 190°C for various time periods.

Time (h)	Δ (mm/sec)	Linewidth (mm/sec)	x ray	Atomic density (g/cm ³)
0	8.42(4)	5.81(10)	amorphous	5.39(3)
1	7.96(4)	6.44(9)	<i>A</i> + <i>c</i> -AsTe	5.50(3)
2	3.50(9)	6.88(16)		
3	3.33(10)	6.54(15)	<i>A</i> + <i>c</i> -AsTe	5.83(4)
4	3.03(10)	6.17(20)		
5	3.48(10)	7.12(16)	<i>A</i> + <i>c</i> -AsTe + <i>c</i> - As_2Te_3	

below this value for 190°C for 2-, 3-, or 4-h heat treatments. This fact is clearly illustrated in Fig. 1 and Table III. Heat treatments of 190°C for 5 h and beyond result in an increase in Δ as crystalline As_2Te_3 begins to form. The final products of crystallization are As and *c*- As_2Te_3 .

IV. DISCUSSION AND CONCLUSION

A. Te chemical order in $\text{As}_x\text{Te}_{1-x}$ glasses

A detailed study of various properties of As-Te glasses has been made by Cornet and Rossier^{9,13} via measurements of atomic density, microhardness, glass transition temperature, high-temperature heat capacity, and an analysis of the kinetics of crystallization. They concluded that these glasses fall into two distinct types depending on whether the As content is greater than or less than 0.40. Through electron, x-ray, and neutron diffraction studies of thin-film and bulk samples, they developed an elegant model for the local structure of $\text{As}_x\text{Te}_{1-x}$ glasses. The principal conclusions of their work are as follows: (1) For $x=0.40$, in contrast to the crystalline compound As_2Te_3 , the bonding is mainly covalent with As threefold and Te twofold coordinated. The first-order approximation to the glassy structure of $\text{As}_{0.40}\text{Te}_{0.60}$ is a random packing of $\text{AsTe}_{3/2}$ trigonal units. (2) For $x > 0.40$, the excess As is accommodated by the formation of $\text{As}_2\text{Te}_{4/2}$ molecular units in which As-As bonds form "arsenic-pair locks." In this region of composition, Te is coordinated to two As neighbors while As starts out at $x=0.40$ with three Te neighbors, and an additional As site emerges as x increases which has one As and two Te neighbors. (3) For $x < 0.40$, As atoms occupy the apex of a $\text{AsTe}_{3/2}$ pyramid unit. These units are unstable against a rotation about the $\text{As}_1\text{-Te}_2$ bond (see Fig. 4), which leads to the formation of

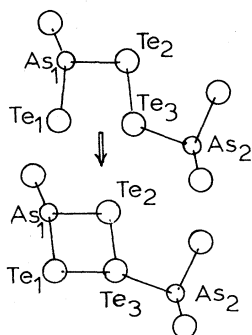


FIG. 4. Formation of a new $\text{Te}_3\text{-Te}_1$ bond and a threefold Te site (Te_3) by rotation of an $\text{AsTe}_{3/2}$ pyramidal unit about $\text{As}_1\text{-Te}_2$ bond. The figure is reproduced from Ref. 9.

threefold-coordinated Te sites. As the As content is decreased, Te clusters begin to develop, and as x approaches 0 the local structure evolves to that of amorphous Te. Thus the tellurium-rich glasses are more complex than the As-rich glasses due to the presence of at least two Te sites. At $x=0.25$, the simple mechanism described above predicts the formation of one threefold Te site for each pair of twofold Te sites. In terms of chemical environments the situation is quite complicated with the possible twofold Te sites having (As,As), (As,Te), or (Te,Te) neighbors and the possible threefold Te sites having (As,As,Te), (As,Te,Te), or (Te,Te,Te) neighbors.

The ME results of the present study provide strong evidence for the ideas above and additional insight into the local structure of the glasses. For $x > 0.40$, the narrow linewidths and constant values of Δ of the ^{125}Te spectra support the description given above, namely, that a single well-defined Te site exists in this composition range. In addition, the ^{129}I ME data show that the dominant Te site is one having two As neighbors. At $x=0.40$ the ^{125}Te ME parameters of the glass and corresponding crystal are significantly different. The ME parameters of the glass are characteristic of Te covalently bonded while the values of crystalline As_2Te_3 indicate a more metalliclike nature for Te.

In the Te-rich glasses ($x < 0.40$) the nature of the Te local environments becomes considerably more complex. This is reflected in the broader ^{125}Te linewidth of the $x=0.30$ glass compared to the $x=0.50$ and 0.57 glasses. At this point, a comment is necessary concerning the nature of the two sites observed in the ^{129}I ME of the glasses. Site A, which was described as a Te site having two As neighbors, needs to be generalized as representing Te sites having either (As,As) or (As,Te) neighbors. This ^{129}I site is an As-I σ bond⁶ that comes from a parent Te atom that was twofold-coordinated to (As,As) or (As,Te). The stronger affinity of I for As means that in both these cases the σ bond that is formed will be an As-I one. Which site a parent Te atom that has two Te neighbors contributes to in the ^{129}I ME spectra is not as clear as the cases above, although it is likely to add into site A. Site B is then made up of contributions from threefold Te sites having (As,As,Te), (As,Te,Te), and (Te,Te,Te) neighbors.

The increase in the intensity ratio (site B/site A) with Te content is then an accurate reflection of the emergence of threefold Te sites. To see how the threefold sites influence the $\Delta(x)$ behavior for the ^{125}Te experiments, it is useful to compare $\Delta(x)$ for $\text{As}_x\text{Te}_{1-x}$ glasses to that of the $\text{Ge}_x\text{Te}_{1-x}$ system.⁵ As Fig. 2 shows, the extrapolation of $\Delta(x)$ to amorphous Te for $\text{As}_x\text{Te}_{1-x}$ gives a significantly smaller value than that obtained from $\text{Ge}_x\text{Te}_{1-x}$.

B. Role of As and Ge impurities in amorphous Te

In the $\text{Ge}_x\text{Te}_{1-x}$ case, the addition of Ge to amorphous Te results in the formation of $\text{Ge}(\text{Te}_4)_{1/2}$ tetrahedral units which probably act as crossing points of Te chains or rings. Throughout the range $0 \leq x \leq 0.33$, the average coordination number of Ge is four, and that of Te is two. Extrapolating the $\Delta(x)$ values of $\text{Ge}_x\text{Te}_{1-x}$ should give a reliable estimate of Δ for amorphous Te. In contrast to this, the less restrictive nature of $\text{AsTe}_{3/2}$ units compared to $\text{Ge}(\text{Te}_4)_{1/2}$ tetrahedra permits the formation of threefold Te sites. These threefold Te sites, like the threefold-coordinated Te sites in $c\text{-As}_2\text{Te}_3$, are expected to have relatively low values of Δ . Starting from $x=0.40$ there are two principal contributions to $\Delta(x)$ as the Te content is increased. The first is an increase in $\Delta(x)$ as sites like that in amorphous Te having a large average value begin to emerge. This increase in $\Delta(x)$ is partially offset by the formation of threefold Te sites which reduce the average Δ . A rapid increase in $\Delta(x)$ is expected therefore as x approaches 0, due to the reduction of both the threefold Te sites and $\text{AsTe}_{3/2}$ units. Note that if threefold Te sites did not exist in the $\text{As}_x\text{Te}_{1-x}$ system, then $\Delta(x)$ would have been expected to extrapolate smoothly to amorphous Te like the $\text{Ge}_x\text{Te}_{1-x}$ alloys.

C. As_2X_3 glasses

Cornet and Rossier originally discussed the differences in atomic structure between As-Te and As-(S,Se) glasses in terms of valence bond angles. They

proposed that threefold Te sites are stabilized by a rotation of a given $\text{AsTe}_{3/2}$ pyramidal unit about an $\text{As}_1\text{-Te}_2$ bond as shown in Fig. 4. They asserted that this was most likely to occur when the chalcogen is Te since the valence angles are closer to 90° for this case. In the context of the ideas of Phillips,⁷ the differences in atomic structure between As-(S,Se) and As-Te can be understood in terms of the differences in bond-bending forces between As-(S,Se) and As-Te. Te is expected to be considerably more metallic than S or Se and in particular, the free-energy difference between twofold and threefold Te is expected to be small. The small bending force associated with Te (compared to S or Se) reduces the number of constraints of the network and results in a different local atomic structure. Furthermore, the simultaneous presence of twofold and threefold Te sites leads to the weak glass-forming tendency of As-Te alloys.⁷

D. Crystallization of $\text{As}_x\text{Te}_{1-x}$ glasses

The results of the crystallization studies of $x=0.30$ and 0.50 glasses are in agreement with previous investigations.^{9,10} For $x < 0.40$ the first step is the primary crystallization of Te followed by the eventual formation of $c\text{-As}_2\text{Te}_3$. On the As-rich side, the heat treatment of $x=0.50$ glasses leads first to the polymorphous crystallization of a metastable AsTe compound and finally to the equilibrium phases $c\text{-As}$ and $c\text{-As}_2\text{Te}_3$. The ability of ME spectroscopy to quantitatively measure the relative fractions of Te containing phases should be useful in kinetic studies of the crystallization process.

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