PHYSICAL REVIEW B VOLUME 25, NUMBER 4 15 FEBRUARY 1982

Direct evidence for intrinsically broken 8 − N coordination rule in melt-quenched glasses by a novel method

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(Received 3 November 1981)

The sign of the electric field gradient at ^{129}I atoms formed from nuclear decay of ^{129m}Te parent atoms undergoes a change from positive to negative when the parent-atom coordination changes from 2 to 3. This provides a sensitive way to discriminate twofold from threefold Te sites in glasses by use of ^{129}I Mössbauer emission spectroscopy. Evidence for some threefold Te sites in As_xTe_{1-x} glasses is presented indicating the first clear breakdown of $8-N$ coordination rule intrinsic to a glass network.

The starting point for modeling atomic networks of the good glass formers Ge_xX_{1-x} and As_xX_{1-x}, where $X=S$, Se, and Te, has been the assumption that the $8-N$ coordination rule of valence is locally satisfied. This rule specifies that the chalcogen (X), As, and Ge atoms are, respectively, twofold, threefold, and fourfold coordinated. A breakdown in this rule, for impurity atoms incorporated in network glasses, first emerged when successful doping of amorphous SiH_n by As dopant was demonstrated.[1] In this work we provide direct microscopic evidence for a breakdown of this rule intrinsic to the host network of melt quenched As_xTe_{1-x} glasses. This evidence has been obtained by a novel method—^{129}I Mössbauer emission spectroscopy[2,3] which provides a simpler and more precise alternative to diffraction methods[4] to probe the chalcogen coordination in glasses.

The success of the present method rests on the experimental fact that the coordination number of ^{129m}Te atoms directly determines the sign of the electric field gradient (eV_{zz}) at the ^{129}I daughter atoms which are formed as a consequence of nuclear transmutation. When ^{129m}Te atoms are twofold coordinated (π bonded) as in the elemental chalcogens [see Fig. 1(a)], a bond rearrangement[3] accompanies the Te→I transformation; one of the Te π bonds breaks while the other π bond transforms into a σ bond leaving the ^{129}I daughter nominally onefold coordinated. I in such a configuration experiences a positive[5] eV_{zz}. On the other hand, when ^{129m}Te atoms are threefold coordinated (π bonded), there is overwhelming evidence[6] that the ^{129}I daughter continues to be threefold or twofold coordinated (π bonded) and experiences a negative[5] eV_{zz} [see Fig. 1(b)]. Thus the sign of eV_{zz}, which is directly accessible from ^{129}I Mössbauer emission spectra provides an elegant way to discriminate twofold from threefold coordinated Te sites.

High quality As_xTe_{1-x} bulk glasses of compositions $x=0.30$ and 0.50 were prepared as described in Ref. 7, and characterized by x-ray diffraction, electron microscopy, differential scanning calorimetry, and ^{125}Te Mössbauer absorption spectroscopy.[7] Detailed analysis of these data, to be published[8] elsewhere, indicates that the melt-quenched samples were homogenous glasses. The composition of the glasses was verified[7,8] independently by crystallizing and identifying the amounts of the two crystalline phases (c-Te, c-As_2Te_3) formed. In the present experiments, ^{129m}Te doping of the As_xTe_{1-x} glasses was carried out by incorporating traces of neutron activated ^{128}Te metal[3] in the melts. Figure 2 shows some of the spectra obtained.

The principal result to emerge from these spectra is that there are two types of chemically inequivalent ^{129}I sites. This is seen in Fig. 2 where a qualitative improvement in the fit to the spectra of the $As_{30}Te_{70}$ glass results in going from a one-site to a two-site fit. Nuclear-quadrupole-interaction (NQI) parameters (isomer-shift δ, quadrupole coupling e^2QV_{zz}) of the

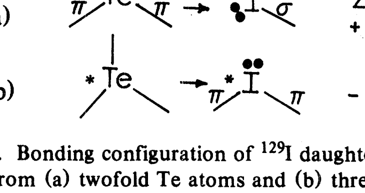

FIG. 1. Bonding configuration of ^{129}I daughter atoms formed from (a) twofold Te atoms and (b) threefold Te atoms. The filled circle and asterisk designate lone pair and antibonding electron states. Our usage of π and σ bonds here differs from the usual chemical language in that these are defined in the principal axes of the EFG tensor of Te or I. The sign of the I eV_{zz} on the right is derived in Ref. 5.

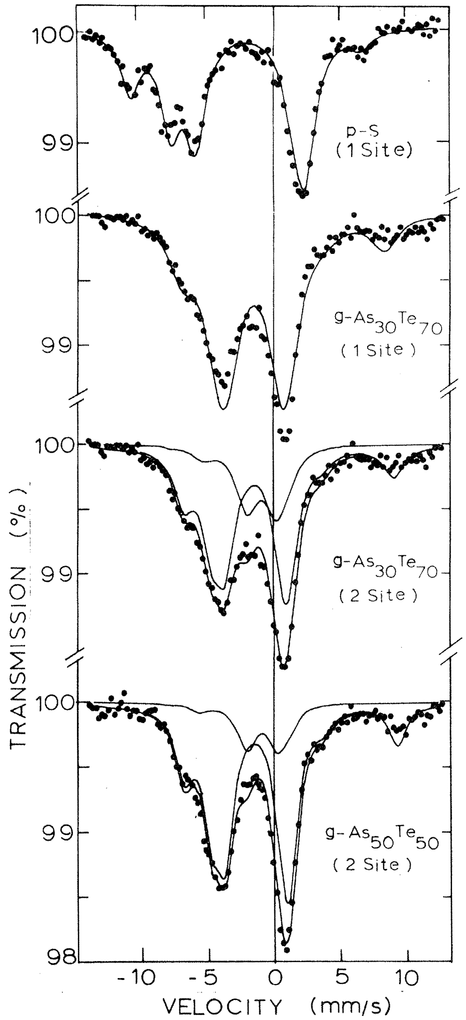

FIG. 2. Mössbauer spectra of ^{129m}Te sources in indicated hosts taken at 4.2 K using a Na^{129}I absorber. Note the qualitative improvement in the fit to the spectra of *g*-$As_{30}Te_{70}$ in going from a one-site to a two-site fit. The fits further reveal that the second site (site B) reduces in relative intensity as the As content of the glass increases.

two sites, which are henceforth labeled A (high $|e^2QV_{zz}|$) and B (low $|e^2QV_{zz}|$), were obtained by standard spectral analysis[3] and are summarized in Table I. We believe that these sites are the result of having two distinct ^{129m}Te sites in the glass network and that these are not formed[2] because of bond breaking caused by nuclear recoil in the transmutation $^{129m}\text{Te}\xrightarrow{\beta}{}^{129}\text{I}$. In contrast to the behavior of the present glasses, ^{129m}Te incorporated in plastic S or amorphous Se leads[3] to a single ^{129}I site (see Fig. 2).

In ^{129}I spectroscopy, a correlation of isomer shift (δ) with quadrupole coupling e^2QV_{zz} has been noted previously[9] (see Fig. 3) and this correlation provides a convenient way to identify the chemical nature of the sites A and B. On such a plot, nearly all available data lies in the region bounded by the π and σ line; these lines represent the two extreme cases of I bonding. On this plot we immediately recognize that site A, seen in both $As_{30}Te_{70}$ glass and $As_{50}Te_{50}$ glass, is closely related to the I site seen[10] in AsI_3 and $AsI_3 \cdot 3S_8$ crystals. These NQI data unambiguously show that site A represents an I—As σ bond that comes from a parent Te site that was twofold coordinated to As. In Fig. 3, the small systematic shift away from the σ line of the data point of AsI_3 and of site A is the result of increasing amounts of I bonding (π character) to a more distant second As neighbor and is a point which has been discussed earlier.[3] Thus site A, which is the dominant site in the spectra of the glasses, is also the site which conforms to the $8-N$ rule of Te coordination.

The more profound result to emerge from the spectra is the existence of site B in the glasses which is characterized by a positive e^2QV_{zz}. We arrive at the sign of e^2QV_{zz} as follows. For $As_{30}Te_{70}$ glass, we recognize that when a negative sign is chosen for e^2QV_{zz}, the δ of the B site is anomalous; i.e., it is low and it lies below the σ line in the plot of Fig. 3. This is unexpected. Interestingly, if a positive sign is chosen for e^2QV_{zz}, then the plot reveals that not only does the δ of site B appear physically plausible, but in

TABLE I. ^{129}I quadrupole coupling (e^2QV_{zz}), asymmetry parameter $\eta = |(V_{xx} - V_{yy})/V_{zz}|$, and isomer-shift ($\delta$) in indicated hosts. The NQI parameters of sites seen in the glasses differ qualitatively from the ones known in the crystals.

Host	Site	e^2QV_{zz} (MHz)	η	δ^a (mm/s)
$As_{30}Te_{70}$	A	−868(4)	0.22(1)	1.13(1)
	B	+363(9)	0.10^b	1.13(4)
$As_{50}Te_{50}$	A	−889(3)	0.21(1)	1.13(1)
	B	+387(13)	0.10^b	1.22(5)
c-As_2Te_3		+186(4)	0.21(9)	1.14(1)
c-Te		−397(2)	0.70(1)	1.16(1)

[a] Quoted relative to Na ^{129}I.

[b] Parameter kept fixed in fit.

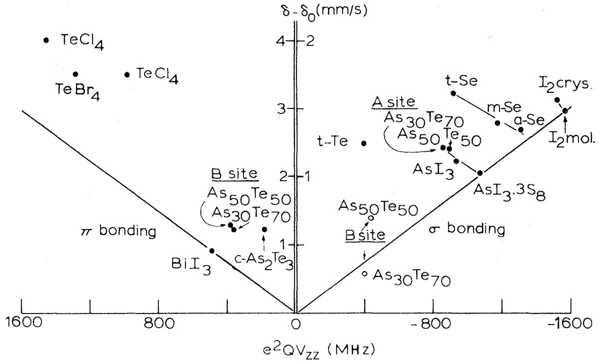

FIG. 3. Correlation of ^{129}I isomer shift $(\delta - \delta_0)$ with quadrupole coupling e^2QV_{zz} (see Ref. 9). Site A is related to the I site in AsI_3 (see text). For site B, note that the δ for $As_{30}Te_{70}$ glass lies below the σ line when a negative sign is chosen for e^2QV_{zz} (open circle). When a positive sign is chosen for e^2QV_{zz} (filled circles) at site B, the nature of this site seen in $As_{30}Te_{70}$ glass and $As_{50}Te_{50}$ glass becomes the same.

fact, the nature of site B seen in $As_{30}Te_{70}$ glass and the one seen in $As_{50}Te_{50}$ glass actually become the same. The effect of increasing the As content of the glass in the composition range $0.30 \leq x \leq 0.50$ then has a fairly simple interpretation; it merely consists of decreasing the site intensity ratio I_B/I_A (see Fig. 2 and Table I) and this is a point we discuss later. The positive sign of e^2QV_{zz} at site B is reminiscent of the positive sign of e^2QV_{zz} observed in the threefold coordinated Te compounds c-As_2Te_3 (Table I) and Te tetrahalides.[6] By analogy we conclude that site B must also represent a threefold Te site, i.e., the $8-N$ rule of Te coordination must be intrinsically broken in As_xTe_{1-x} glasses.

Cornet and Rossier[11,12] were the first to propose the existence of threefold Te sites in As_xTe_{1-x} glasses on the basis of their diffraction results. In their electron RDF's, the area of the first neighbor peak containing contributions from As-As, As-Te, and Te-Te pairs showed a systematic reduction as a function of x, and this was taken as evidence of a reduced fraction of threefold Te sites. In the Te-rich phase $(x < 0.40)$, where presumably some Te—Te bonds occur, these authors suggested[11] that the threefold sites are stabilized by a rotation of a given $AsTe_{3/2}$ pyramidal unit about an As_1—Te_2 bond as shown in Fig. 4. This leads to a more efficiently packed network (of $As_{25}Te_{75}$ stoichiometry) in which for each threefold Te site, two twofold ones occur, and this is in reasonable agreement with the observed site intensity ratio $I_B/I_A = \text{Te(threefold)}/\text{Te(twofold)} = 1/2.8(4)$ for a $As_{30}Te_{70}$ glass. In the As-rich phase $(x > 0.40)$, these authors further pointed out that some As—As bonds must occur, which, owing to their small length, hinder free rotation of the $AsTe_{3/2}$ units and the formation of threefold Te sites. The reduced value of the site intensity ratio $I_B/I_A = \text{Te(threefold)}/\text{Te(twofold)} = 1/4.8(1.2)$ found for the $As_{50}Te_{50}$ glass is again in general accord with this idea.

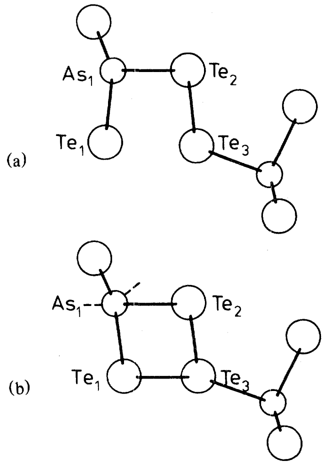

FIG. 4. Formation of a new Te_3—Te_1 bond and a threefold Te site (Te_3) by rotation of $AsTe_{3/2}$ pyramidal unit about As_1—Te_2 bond. The figure is reproduced from Cornet's work, Ref. 12.

The crystal structure[13] of As_2Te_3 is unique in that it has only threefold Te sites and an equal number of both threefold and sixfold As sites. The observation of threefold Te sites in the corresponding $As_{40}Te_{60}$ glass, which is 89% as dense as the crystal,[11] we believe has an origin in the presence of van der Waals interactions.[14] These interactions mediated by lone pairs in these glasses apparently overwhelm the local twofold bonding requirements of Te and lead to a more efficiently packed network with some threefold Te. These results confirm Phillips's conjecture[14] that the weak glass-forming tendency of Te (compared to S or Se) is a consequence of its failure to satisfy the coordination constraint of the $8-N$ rule. The As sites in these glasses are threefold coordinated as shown by extended x-ray absorption fine structure.[4]

In conclusion, by use of a novel method, we have demonstrated that both twofold and threefold Te sites occur in As_xTe_{1-x} network glasses. This result is shown to be in harmony with the existing diffraction data, density measurements, and understandings of the glass-forming ability of this binary. The present method is likely to provide important clues in understanding the structure, since it is the chalcogen site that appears to display a variety of unique bonding configurations in these technologically important materials.

ACKNOWLEDGMENTS

We acknowledge valuable correspondence with Dr. J. Cornet, Dr. J. C. Phillips, and Dr. J. P. deNeufville.

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[5] The sign of the EFG in covalent glasses is determined by the population of $5p$ orbitals of I, since

$$\langle p_{x,y}|eV_{zz}|p_{x,y}\rangle = -\tfrac{1}{2}\langle p_z|eV_{zz}|p_z\rangle = 2e/5\langle r^3\rangle \ .$$

For onefold I, such as in a I_2 dimer, the EFG is because of σ bonding of a p_z hole. This gives a positive $eV_{zz} = 4e/5\langle r^3\rangle$ and a negative e^2QV_{zz} since the ^{129}I nuclear moment $eQ = -0.55$ b. For site B, we conjecture that I is twofold coordinated [see Fig. 1(b)] as in BiI_3 (see Ref. 10). This requires two electrons to be in nonbonding lone pairs $|p_z\rangle$, two electrons in bonding $|p_x\rangle$ and $|p_y\rangle$ and one electron in antibonding $|p_x\rangle$ or $|p_y\rangle$. This results in a negative $eV_{zz} = -2e/5\langle r^3\rangle$ and a positive e^2QV_{zz}.

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