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Direct Evidence for Intrinsically Broken Chemical Ordering in Melt-Quenched Glasses

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The chalcogen site in bulk glasses of GeSe_2 and GeS_2 has been probed via nuclear quadrupole interactions with use of $^{129}\text{Te}^m$ impurity atoms as parent in ^{129}I Mössbauer emission spectroscopy. Two distinct types of chalcogen sites are observed and are shown to provide direct evidence for intrinsically broken chemical ordering in these network glasses. The composition dependence of the site parameters in pseudobinary-alloy glasses indicates the presence of characteristic large clusters rather than a continuous random network.

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Nuclear quadrupole resonance (NQR) experiments have recently provided detailed information on the atomic structure of alloy network¹ and metallic² glasses. The average electric field gradient (EFG) eV_{zz} and particularly the asymmetry parameter $\eta = |(V_{xx} - V_{yy})/V_{zz}|$ of the EFG tensor contain information characteristic of the atomic environment which can be interpreted quantitatively in terms of the same parameters in elemental solids. However, the application of NQR to chalcogenide glasses is restricted because there are no stable Se or Te isotopes that have a nonzero nuclear quadrupole moment eQ in the ground state. In this Letter we show that by means of a novel technique, ^{129}I Mössbauer emission spectroscopy, very precise nuclear quadrupole interaction (NQI) data are obtainable on chalcogen sites in these covalent glasses.

The basic idea of this technique is to measure the EFG, η , and electron charge density via the NQI of daughter ^{129}I nuclei at chalcogen sites by doping pseudobinary alloys such as $g\text{-GeSe}_{2-x}\text{Te}_x$

and $g\text{-GeS}_{2-x}\text{Te}_x$ with parent $^{129}\text{Te}^m$ atoms. The details of this technique and its application to elemental chalcogen glasses have been given previously.³ Purified elements were sealed in evacuated quartz ampules in stoichiometric ratios and alloyed at 900°C for 24 h before quenching in cold water. The glass transitions (T_g) of the $g\text{-GeSe}_{2-x}\text{Te}_x$ alloys were studied by differential scanning calorimetry. The T_g results were in quantitative agreement with the work of Sarrach, de Neufville, and Haworth,⁴ which indicated the absence of phase separation in this alloy system. Figure 1 shows some of the Mössbauer spectra obtained.

The central discovery of the present work is that in bulk melt-quenched alloy glasses of $\text{GeSe}_{2-x}\text{Te}_x$ and $\text{GeS}_{2-x}\text{Te}_x$ even as $x \rightarrow 0$ there are two inequivalent I sites A and B. For example, as can be seen in Fig. 1, a qualitative improvement in the fit to a $g\text{-GeS}_2$ spectrum results in going from a one-site to a two-site fit. The NQI parameters $e^2QV_{zz}^A$, $e^2QV_{zz}^B$, η^B , and η^A for $\text{GeSe}_{2-x}\text{Te}_x$ alloys are shown as a function of x in

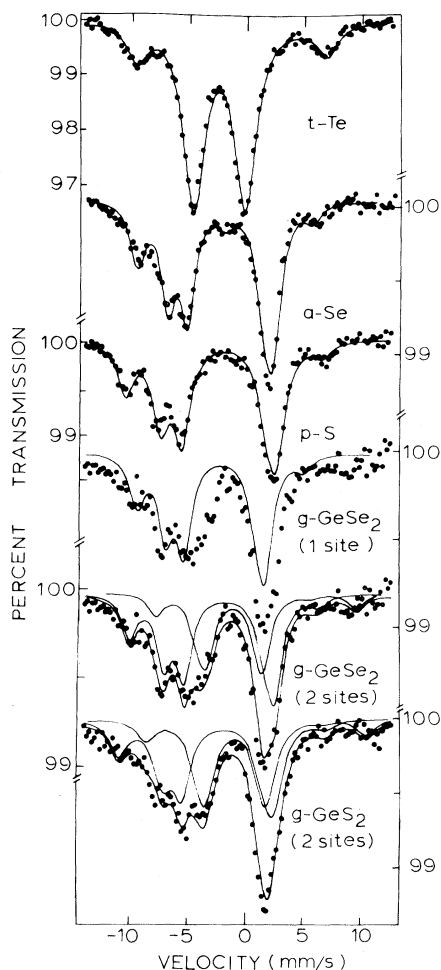


FIG. 1. Mössbauer spectra of $^{129}\text{Te}^m$ sources doped ($< \frac{1}{2}$ at.%) in indicated hosts. Spectra were taken at 4.2 K with use of a Na^{129}I absorber. A noticeable improvement in the fit to the spectra of $g\text{-GeSe}_2 - 2x\text{Te}_{2x}$ resulted in general in going from a one-site to a two-site fit. This is shown for $x = 0.005$, i.e., GeSe_2 in the figure.

Fig. 2. These parameters were obtained by standard Mössbauer spectra analysis³ and for $x \rightarrow 0$ they are compared in Table I with the elemental solute parameters.³ There is compelling evidence that the two sites seen in the present glasses do not originate from a nuclear aftereffect, i.e., bond breaking following nuclear transmutation. To date, such an effect has not been observed in any metallic or semiconducting host. Our observation of a unique and static NQI in the elemental glasses (S and Se) (see Fig. 1 and Table I) follows this pattern and it strongly suggests the absence of a nuclear aftereffect in these semiconducting glasses.

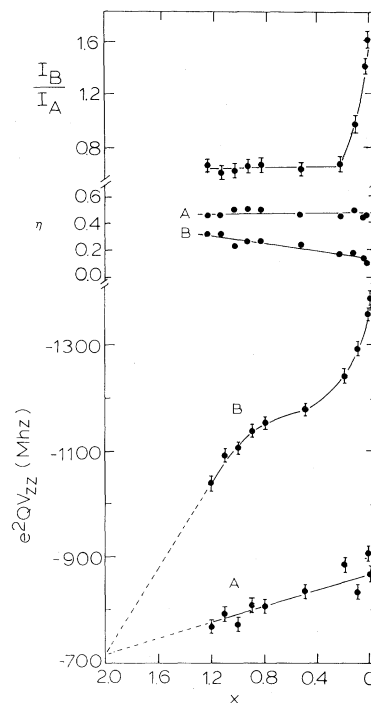


FIG. 2. The observed variation of the quadrupole couplings (e^2QV_{zz}), intensity ratio I_B/I_A , and asymmetry parameter (η) for the two sites (A and B) in $g\text{-GeSe}_{2-x}\text{Te}_x$ alloys plotted as a function of Te content (x) of the glass.

Most recent workers have assumed^{5,6} that the atomic structure of chalcogenide glasses can be described in terms of a chemically ordered continuous random network (COCRN), as originally proposed by Zachariasen.⁷ Our data provide the first direct evidence that this is not the case. Specifically, let us suppose that chalcogen sites are of two types, a chemically ordered site A bonded to two Ge atoms, and site B bonded to a Ge atom and a chalcogen atom. Let the probabili-

TABLE I. ^{129}I quadrupole coupling (e^2QV_{zz}), asymmetry parameter (η), and isomer shift (δ) deduced from spectra of Fig. 1. δ is quoted relative to Na^{129}I .

Host	e^2QV_{zz} (MHz)	η	δ (mm/s)
t-Te	-397(2)	0.70(1)	1.16(1)
a-Se	-1314(10)	0.11(2)	1.26(4)
p-S	-1453(6)	0.13(2)	1.26(2)
GeSe ₂ A	-860(12)	0.49(6)	0.76(3)
GeSe ₂ B	-1360(9)	0.15(6)	1.28(4)
GeS ₂ A	-936(15)	0.57(6)	0.62(4)
GeS ₂ B	-1432(10)	0.25(6)	1.29(4)

ty that a Te atom occupies an A or B site be p_A or p_B and let the branching probabilities that B site daughter I atoms will choose to attach themselves to their Ge or chalcogen neighbors be f_G or f_C . Then the probabilities $p_{G,C}$ that ^{129}I will be bonded to Ge or the chalcogen are given by

$$p_G = p_A + p_B f_G, \quad (1)$$

$$p_C = p_B f_C. \quad (2)$$

Returning to Table I, we see by comparison with the elemental chalcogen parameters (e^2QV_{zz} , η , and isomer shift δ) that for $x \rightarrow 0$, i.e., GeSe_2 (and also GeS_2), the B site definitely corresponds to an I-chalcogen bond.⁸ Further, we note by comparing A -site parameters in GeS_2 with the A -site parameters in GeSe_2 that these are really the same site, and identify it with an I-Ge bond.⁸ Regardless of the transmutational branching probabilities f_G and f_C , Eq. (2) tells us that there must be a substantial probability p_B of the type- B Te sites in the glass, i.e., the chemical ordering must be intrinsically broken.

According to Fig. 2, $I_B(x) > I_A(x)$, i.e., $p_C(x) > p_G(x)$, at $x = 0$ and further $p_C(x)$, $e^2QV_{zz}^B$, and η^B all sharply change with increasing x , especially p_C which is already halved at $x = 0.2$. This suggests several interpretations of the chalcogen environments and the physical mechanism responsible for the transmutational branching ratio. Because $p_C(0) > p_G(0)$, we conclude that f_G/f_C is small and is probably close to zero, i.e., I prefers to form I-Se(S) rather than I-Ge bonds in the glass. This result is somewhat surprising, because according to Pauling⁹ the ionic contribution to the heat of formation of I-Ge bonds should be almost fifty times greater than that of I-Se(S) bonds. We must remember, however, that these bonds are not formed in the vapor or in dilute solution. Instead they are formed in the melt-quenched glass which is 90% as dense as the crystal.¹⁰ In dense covalent networks the van der Waals repulsive energy between nonbonded lone-pair electrons can be quite large, as is shown by the near equality of bonded and nonbonded interatomic spacings in elemental S and Se crystals. Thus at B sites, I-Se(S) bonds are formed in preference to I-Ge bonds, apparently because in the latter case the repulsive or steric hindrance nonbonded I-Se(S) interactions overwhelm the ionic energy difference.

The sharp increase in $p_C(x)$ as $x \rightarrow 0$ is reminiscent of the very rapid variation of the scattering strength of the anomalous companion A_1 Raman

line with x in $\text{Ge}_{1-x}\text{Se}_{2+x}$ alloys which has been discussed by several workers.¹¹⁻¹³ Nemanich and Solin¹² were the first to emphasize that according to the law of mass action this rapid variation requires the presence of large clusters in the glass. However, in their model [see Fig. 3(a)] these clusters, which are twelve-atom rings similar to the basic rings in crystalline As_2S_3 , are chemically ordered and are presumably embedded in a perfectly chemically ordered network.^{5,6} More recently Bridenbaugh *et al.*¹⁴ have proposed that chemical ordering is intrinsically broken in chalcogenide glasses, in accord with the present results. They suggest that in stoichiometric chalcogenide glasses such as $g\text{-GeSe}_2$ two kinds of partially polymerized clusters are present which are either cation rich or chalcogen rich. The latter are raftlike fragments of the high-temperature crystalline form [see Fig. 3(b)] and they are laterally bordered by chalcogen-chalcogen bonds. These chalcogen edge sites, called outrigger units by Bridenbaugh *et al.*, are excellent candidates for our B sites. We have constructed a simple statistical model based on outrigger rafts

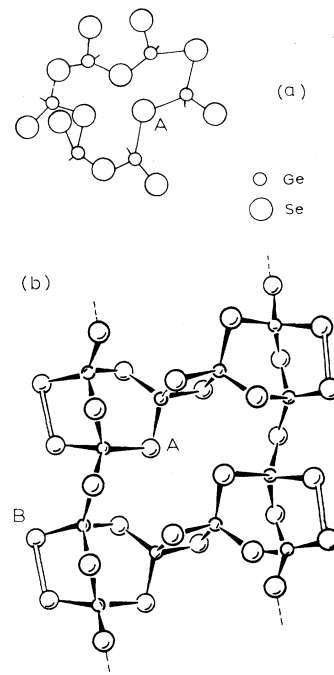


FIG. 3. Elements of medium range order in $g\text{-GeSe}_2$ according to (a) COCRN model (Ref. 12) and (b) outrigger-raft model (Refs. 14 and 16). (a) shows a Ge_6Se_6 ring cluster providing for one (A) Se site, while (b) shows a $\text{Ge}_6\text{Se}_{14}$ outrigger-raft cluster providing for two chemically inequivalent A and B Se sites.

which accounts quantitatively for the sharp increase in $p_c(x)$ as $x \rightarrow 0$ which will be published elsewhere.¹⁵

Further evidence for the distinctive role played by these large clusters in the glass-forming tendency which is strong⁴ in GeSe₂ (large $T_x - T_g$) and weak in GeTe₂ (small $T_x - T_g$) is as follows. A linear extrapolation of the A - and B -site e^2QV_{zz} and η in Fig. 1 for $x > 1$ shows that the two sites merge as $x \rightarrow 2$. This means that the poor glass-former GeTe₂ is close to being a COCRN. The same situation apparently prevails with the good (poor) glass-formers As₂Se₃ (Te₃) as well.^{1,16}

In conclusion, we have discussed NQI data which demonstrate that ¹²⁹I Mössbauer emission spectroscopy with use of ¹²⁹Te^m parent is a novel and particularly successful tool for probing the atomic structure of network glasses. We have shown directly and specifically that chemical order is intrinsically broken even in stoichiometric chalcogenide glasses. This specific kind of broken topological symmetry has been shown to arise from the formation of large clusters which correlate well with chemical trends in the glass-forming tendency. According to our data, these large clusters provide a much more suitable basis for describing the atomic structure of chalcogenide glasses than does the traditional random-network model.

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