Does the 8-N bonding rule break down in As$_2$Se$_3$ glass?

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Abstract – The coordination numbers in As$_2$Se$_3$ glass were determined by a combination of anomalous X-ray scattering experiments, reverse Monte Carlo modeling, and ab initio molecular dynamics simulations. We found that the well-known “8-N bonding rule” proposed by Mott breaks down around the As atoms, exceeding the rule by 7–26%. An experimental prediction based on mean-field theory agrees with the present experimental and theoretical results. The fourfold coordinated As atoms likely form As-As wrong bond chains rather than ethane-like configurations, which is identified as the origin for the breakdown of the “8-N bonding rule”.

It was widely believed that coordination numbers of covalent bonding glasses were governed by the “8-N bonding rule”, where $N$ is the total number of $s$ and $p$ electrons in the outmost shell of atoms. This rule was proposed by Mott [1], who emphasized that according to this rule, all electrons are situated in filled electronic bands so that large changes in the electrical conductivity do not occur in covalent glasses with a small change of composition [2], in contrast to crystalline semiconductors.

Street and Mott [3] proposed a model of dangling bond pairs in amorphous chalcogenide semiconductors to explain the pinning effect of the Fermi level. Subsequently, Kastner et al. [4] proposed another model of valence alternative pairs where threefold and dangling bond Se atoms appear as defect centers. These models showed a breakdown of the “8-N bonding rule”. However, these defects discussed there are in a negligible concentration regime undetectable by scattering experiments although they are very important for considering electronic states of glasses.

To our knowledge, only one group expressed their opposition to this rule experimentally by Boolchand and coworkers [5]. Their work was carried out on As$_{2-x}$Se$_{3-x}$ glasses using temperature-modulated differential calorimetry. It was found that non-reserving heat flow almost vanishes in the 0.29 < $x$ < 0.37 composition range, separating the floppy glasses from the stressed rigid ones within the framework of the rigidity percolation theory [6,7]. Since the ideal boundary should be $x = 0.40$ if the 8-N bonding rule was strictly valid, they proposed a breakdown of this rule and suggested that 28.6% of Se=As(Se$_{1/2}$)$_3$ quasi-tetrahedral units should exist in addition to the normal As(Se$_{1/2}$)$_3$ pyramidal units around the As atoms. This idea motivated diffraction and spectroscopic investigations of the local structures in these glasses. However, no experimental evidence could be achieved over the last ten years due to the experimental difficulties in determining local structures of glassy systems.

In this letter, we present an experimental evidence for the breakdown of the “8-N bonding rule” around the As atoms in the As$_2$Se$_3$ glass obtained from a combination of anomalous X-ray scattering (AXS) experiments and reverse Monte Carlo (RMC) modeling. This result is theoretically supported by an ab initio molecular dynamics (MD) simulation.

The bulk glass As$_2$Se$_3$ sample was obtained by quenching the melt in a quartz ampoule containing the mixed compound. The melt was homogenized at 600°C for at least 48 h before the sample was slowly quenched in air.

The AXS experiments were performed at two energies below each $K$ edge (20 and 200 eV below the As $K$
edge of 11868 eV and the Se K edge of 12658 eV) at the beamline BM20 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The diffraction measurements were carried out in reflectance geometry using a standard $\omega - 2\theta$ diffractometer installed at the beamline. For discriminating the elastic signal from the $K\beta$ fluorescence and Compton scattering contributions, a graphite crystal analyzer was mounted on an 1 m long detector arm. The feasibility of this detecting system was described in detail elsewhere [8,9]. Following the procedure given in ref. [10], differential structure factors, $\Delta k S(Q)$, were obtained from the difference between diffraction data with two different incident X-ray energies near each $K$ element.

The RMC simulations were performed using $\Delta_{\text{As}} S(Q)$, $\Delta_{\text{Se}} S(Q)$, and the total structure factor, $S(Q)$. The starting configurations of a system containing 2000 As and 3000 Se atoms with a number density of 35.74 nm$^{-3}$ were generated using hard-sphere Monte Carlo simulations, i.e., random configuration excluding short bonds. In order to avoid unphysical atomic configurations, three constraints were applied. Firstly, the cut-off values were determined to be 0.235, 0.230, and 0.225 nm for the As-As, As-Se, and Se-Se atomic pairs, respectively, to avoid physically unreasonable spikes in the partial pair-distribution functions, $g_{ij}(r)$, in the low $r$ range. Secondly, weak bond angle constraints were applied for each type to be about 100°. Finally, a constraint of a wrong Se-Se bond ratio was applied around the Se atoms. A ratio of 16.6% was chosen for this constraint, being determined from the result of the ab initio MD simulation.

The ab initio MD calculation was based on density functional theory with the generalized gradient approximation (GGA) [11] for the exchange-correlation energy. The projector augmented wave (PAW) potentials [12] were employed for the electron-ion interaction with valence electrons $4s^24p^54d^0$ and $4s^24p^64d^0$ for As and Se, respectively. The electronic wave functions and the electron density were expanded by plane wave basis sets with cutoff energies of 11 and 55 Ryd, respectively. In a previous ab initio MD study [13], a larger cutoff energy of 20 Ry was used for the norm conserving pseudopotentials. We have used a projector-augmented-wave method, which requires a rather small cutoff energy for the wave functions, in the same way as the ultrasoft pseudopotentials. For the current As-Se system, the cutoff energy of 11 Ry is enough to reproduce the structural and dynamic properties. The $\Gamma$ point was only used to sample the Brillouin zone of the MD supercell. We used 128 atoms (48 As and 72 Se) in a cubic MD cell with periodic boundary conditions. The side length of the MD cell was 1.48 nm. The constant-temperature MD simulation [14,15] was performed at 300 K for 30000 steps in time steps of 2.9 fs. The quantities of interest were obtained by taking average over ten simulations starting from different initial configurations taken from simulations for the liquid state at 800 K and different cooling rates, where only small differences were found in the results.

Circles in fig. 1 show $\Delta k S(Q)$ obtained from the present AXS measurements close to the As and Se K edges, together with $S(Q)$. $\Delta_{\text{As}} S(Q)$ has a distinct and sharp prepeak at about $Q = 12$ nm$^{-1}$, and the $Q$ position almost

![Fig. 1: (Color online) From top to bottom: $\Delta k S(Q)$ around the As and Se K edges, and $S(Q)$. Circles indicate those obtained from the AXS experiments, and solid curved denote (a) fits by the RMC modeling and (b) results calculated from the ab initio MD simulation.](image-url)
RMC modeling (solid curves) and the ab initio Sically obtained partial structure factors, MD simulation, which were calculated from theoret-initio coincide with that in S(Q), although the peak height of the latter is very small. Δ_{Se}S(Q) shows a shoulder at a higher Q value of about 14.5 nm\(^{-1}\). Solid curves in fig. 1(a) show the best fits of the RMC atomic modeling, which mostly coincide very well with each of the present experimental data.

Solid curves in fig. 1(b) indicate results of the ab initio MD simulation, which were calculated from theoretically obtained partial structure factors, S_{ij}(Q), by taking atomic form factors for X-ray scattering into account. The circles denote again the experimental data. Overall features of the theoretical spectra are in good agreement with the experimental results although the prepeaks and the shoulder in the low-Q region are slightly smaller.

Figure 2 shows S_{ij}(Q)'s obtained from the AXS+RMC (solid curves) and the ab initio MD simulation (circles). The S_{ij}(Q) results obtained from AXS+RMC and ab initio MD coincide quite well although the theoretical data are rather scattered. In S_{AsAs}(Q), a large and sharp prepeak locates at about 12 nm\(^{-1}\), indicating that the intermediate-range order in this glass is mainly due to the As–As correlation as was pointed out in ref. [16]. A small prepeak is also seen in S_{AsSe}(Q) at the same Q position, and a steep hump is observed near the first peak position in S(Q). In S_{SeSe}(Q), on the other hand, there is no indication for a prepeak. Instead, a shoulder is observed at about 14.5 nm\(^{-1}\). These features are very similar to those found in GeSe\(_2\) glass [17].

Figure 3 shows g_{ij}(r)'s obtained from the AXS+RMC (solid curves) and the ab initio MD simulation (circles). The first peak in the total pair-distribution function (not shown) mainly results from the As-Se heteropolar bonds centered at 0.237(1) nm (AXS+RMC) and 0.246(2) nm (ab initio MD), which are in good agreement with previous total diffraction works [18–20].

The As-As and Se-Se homopolar bonds, the so-called wrong bonds do exist at almost the same r position as the As-Se heteropolar bonds. To our knowledge, this is the first experimental proof of the existence of such wrong bonds in the As\(_2\)Se\(_3\) bulk glass. The peak heights of the first peaks in both the homo- and heteropolar bonds coincide well between experiment and theory, while the peak positions systematically shift by about 0.01 nm.

The partial coordination numbers, N_{ij}, were obtained from the g_{ij}(r) functions. Here, i and j indicate the central and neighboring elements, respectively. They were estimated by the integrals of 4πr^2g_{ij}(r) up to the minima of the theoretical g_{ij}(r) functions, i.e., 0.290, 0.280, and 0.260 nm for the As-As, As-Se, and Se-Se correlations, respectively. The results are given in table 1. N_{ij} show good agreement between experiment and theory, except for the As-As correlation.

The total coordination numbers, N_{i}, are also given in table 1. The N_{Se} values are two from both the experimental and theoretical results within the errors, indicating that the “8-N bonding rule” is strictly valid for the Se atoms. On the other hand, the N_{As} values exceed the octet rule value of three in experiment and theory although with a different extent: the AXS + RMC result indicates about 26% of fourfold coordinated As atoms on average, while the ab initio MD simulation shows about 7%.

To examine the effect of constraint on the ratio of homopolar Se-Se bonds around the Se atoms (16%) in the RMC modeling, we carried out several RMC calculations
Table 1: Partial and total coordination numbers obtained from experiment (AXS+RMC) and theory (ab initio MD simulation).

| Neighbor | Central | As       | Se       | Total    |
|----------|---------|----------|----------|----------|
| Experiment | As      | 0.73(1) | 2.53(1) | 3.26(2)  |
|           | Se      | 1.69(1) | 0.32(1) | 2.01(2)  |
| Theory   | As      | 0.53(2) | 2.54(1) | 3.07(3)  |
|           | Se      | 1.69(1) | 0.32(1) | 2.01(2)  |

with ratios from 0 to 50%. As a result, the same \( N_i \) values were obtained within the error bars given in table 1. Another RMC calculation was performed with a different constraint of no homopolar As-As wrong bonds, and the same \( N_i \) values were obtained producing As(Se\(_{1/2}\))\(_4\) tetrahedra, whereas the RMC fit functions largely deviated from the experimental structure factors.

We also examined the the initial configuration dependence by using fully random configurations or crystal structures. Consequently, the same results were obtained in \( S_{ij}(Q) \), \( g_{ij}(r) \), and \( N_{ij} \).

Another doubt arose about small discrepancies between \( \Delta k S(Q)'s \) and the RMC fits in the high-\( Q \) region shown in fig. 2(a). We suppose that these discrepancies originate from the errors in experimental data. As is well-known, atomic form factors in X-ray diffraction (XD) signals rapidly decrease with increasing \( Q \), and the experimental errors becomes large at the high \( Q \) values, in particular, in \( \Delta k S(Q)'s \), because they are contrasts of the XD data of several % with changing incident X-ray energies. As can be seen in fig. 1, experimental \( \Delta k S(Q)'s \) show more significant oscillations at high \( Q \) values than both the RMC and ab initio MD results, suggesting that both the RMC model and ab initio MD simulation underestimate the coordination number. Nevertheless, these results support the breakdown of the “8-\( N \) bonding rule”. Therefore, we are confident that our conclusion is not biased by experimental errors.

Li and Drabold reported on the basis of ab initio MD simulation that the formation of wrong bonds, \( N_{\text{AsAs}} = 0.67 \) and \( N_{\text{SeSe}} = 0.43 \) [21]. Compared them with the present results, the former is in good agreement, and the latter is slightly larger. A discrepancy from the present result is seen in \( N_i \) that As and Se atoms have 3.01 and 1.99 neighbors on average in the first coordination shell, respectively, indicating the validity of the “8-\( N \) bonding rule” within the errors. They did not describe the explicit definition of \( N_{ij} \), and only wrote that all atoms in the first shell were distributed in the range 0.234–0.263 nm. If they calculated the \( N_{ij} \) values up to 0.263 nm, the obtained values \( N_{ij} \) may be underestimated, in particular, for \( N_{\text{AsAs}} \), since a large tail of the first peak is seen in \( g_{\text{AsAs}}(r) \) at \( r = 0.263 \) nm in fig. 3 of ref. [21].

Recently, another ab initio MD simulation was carried out by Bauchy et al. [13] on glassy and liquid As\(_2\)Se\(_3\) and other As-Se mixtures to clarify the relation between the structural and dynamical properties and the mean-field approaches of stiffness transition. They confirmed the existence of wrong bonds in As\(_2\)Se\(_3\) glass, \(~15%\) in \( N_{\text{AsAs}} \) and \(~18%\) in \( N_{\text{SeSe}} \), in good agreement with theories including the present one and the present experiment. A subsequent paper by Bauchy and Micoulaut [22] showed in detail that 9.2% of fourfold coordinated As atoms are found in the As\(_2\)Se\(_3\) glass, resulting in a number of constraints per atom to be 3.05, well exceeding three, the degree of freedom in a three-dimensional system.

Next, we discuss local atomic configurations or structural motifs in the As\(_2\)Se\(_3\) glass. Figure 4 shows a snapshot of the three-dimensional (3D) atomic configuration obtained from the ab initio MD simulation. Large purple and small green balls indicate the As and Se atoms, respectively. The As-As and Se-Se wrong bonds are given as dark red and blue bars, respectively. Both fourfold and threefold coordinated As atoms are observed. Of special interest is
that around the fourfold coordinated As atoms, the atomic configuration is not always Se$_3$-As-As-Se$_3$ ethan-like, but other As neighbors are frequently seen, i.e., As-As bond chains are formed.

Figure 5 shows an example of the spatial distribution of the electron charge density around a fourfold As atom in a As-As wrong bond chain. The central fourfold As atom has two Se and two As neighbors. Since the bond length with the As atom of the left-hand side is longer than the average, the bonding electrons are very few in number. Nevertheless, the existence of covalent electrons is confirmed for every bonds. From the further discussion using bond-overlap population (BOP) analysis [23], two As-Se bonds around the fourfold As atoms mostly form strong bonds with two covalent electrons, and are rarely broken during the MD simulation time. On the other hand, two As-As bonds have a tendency to share the remaining one covalent electron with each other, and the bonds are short-living with the lifetime of some ps. Note that the strengths of two As-As bonds are different depending on the environment surrounding the two bonds. Due to the change of the bond length caused by the lattice vibration, repeated switchings of the bonding electron are observed between the right and left As-As bonds in some hundred fs steps.

Figure 6 shows an example of 3D atomic configuration obtained from the AXS + RMC. The marks are the same as in fig. 4. As clearly seen in the figure, this experimental result also shows the existence of the As-As wrong bond chains, but longer than in the theoretical result, i.e., a five- or six-atoms chain was observed in the atomic configuration. From these findings, it is concluded that the fourfold coordinated As atoms likely form As-As wrong bond chains rather than ethan-like configurations.

Then, two new questions arose. The first one is why the significant changes of the local environment around the As atoms do not affect the electronic states, in particular, isolated electron spins detectable with ESR experiment [24] or electron distributions observable by NMR measurement [25]. We believe that this may be solved by the above results of BOP analysis. The number of electrons belonging originally to the fourfold As atoms remains unchanged to be three. Each electron forms a pair with an electron from the neighboring As atom as a usual As(Se$_{1/2}$)$_3$ pyramid. Thus, no difference would be seen by the ESR and NMR measurements. The difference in the present fourfold As tetrahedron is that one electron is shared with two As-As bonds and a fast flickering of the electron positions occurs between two bonds. Also, this mechanism is the reason why the As-As wrong bond chains are preferable rather than ethan-like configurations with single As-As bond.

The second question is why there is a large discrepancy between the $N_{As}$ values in the experiment (26%) and the theory (7%), even though they exceed the “8-N bonding rule” value of three. The existence of wrong bond chains may explain it. Since the MD simulation box size is about five atoms, it acts as a constraint avoiding the longer As-As wrong bond chains even in the periodic boundary condition. A recent ab initio MD simulation by Bauchy and Micoulaut using a larger number of atoms of 200 showed more than 9% of fourfold coordinated As atoms.

The box size effect in ab initio MD simulations was examined by Micoulaut et al. [26] on liquid GeSe$_2$ by changing the size up to 480 atoms, and it was clearly found that the effect mostly modify the intermediate-range chemical orders. By taking the As-As chain length obtained from the AXS experiment with the RMC model into account, more than 2000 atoms would be necessary to reproduce the 26% of fourfold coordinated As atoms as obtained from the experiment. However, it is unrealistic at present.

Compared the present results with the prediction [5] based on the rigidity percolation theory, the portion of the fourfold coordinated As atoms, 28.6%, is in good agreement with the present AXS + RMC result of about 26%. However, they predicted the Se = As(Se$_{1/2}$)$_3$ quasi-tetrahedral units for the fourfold coordinated As atoms, while our experimental and theoretical data show the As-As wrong bonds in the network glass.

In summary, this is the first experimental proof for the breakdown of the “8-N bonding rule” proposed by Mott [1,2]. It was only seen around the As atoms, while the Se atoms strictly keep this rule. This experimental result could be confirmed by an ab initio MD simulation, where the dynamic properties such as the lifetime of the fourfold coordinated As atoms, i.e., a flickering motion of the As-As bonds around the fourfold coordinated As atoms, were discussed together with the corresponding electronic natures, which do not contradict the results of ESR [24] and NMR [25] measurements. The general picture of the averagely over-coordinated As atoms is valid in the As$_2$Se$_3$ glass.
However, we are still not confident the uniqueness of the experiment or the theory individually. For example, investigations of structures of non-crystalline materials have large ambiguities in the results although the accuracies of scattering techniques have recently been improved drastically by using intense synchrotron radiation or new spallation neutron sources. RMC modeling is only an example of atomic configurations of non-crystalline materials, even if the model fits properly to experimental data.

The box size for \textit{ab initio} MD simulations is always a subject of the criticisms, which cannot be overcome using a limited computer power at present. Moreover, too short simulation time of some ps does not correspond to the real relaxation time of glasses from melts of ms or longer. Atomic configurations obtained from \textit{ab initio} MD simulations are possible to be still those in melts. However, oneshould composedly judge how these limitations influence our final conclusion of the \textit{average} coordination number around the As exceeding the “8-N bonding rule” of three. On the experimental side, the intermediate-range atomic configurations are surely depend on the wrong bond ratio around the Se atoms, while the \(N_{\text{As}}\) value does not vary with such constraints in the RMC modeling. On the theoretical side, the density of the system already reaches the actual relaxed value under ambient conditions during the short time of some ps. The concentration of the wrong bonds may change by a longer and slower relaxations from melts to glasses. As regards the average coordination numbers, however, it is difficult at present to decide whether the values increase, decrease, or remain unchanged.

Here, we emphasize that a good agreement of the over-coordinate feature around the As atoms was obtained from two individual methods of experiment and theory, which is, we think, beyond an accidental coincidence, although both the methods have their own limitations. We could not find any failures against our conclusion of a breakdown of the “8-N bonding rule” around the As atoms in the \(\text{As}_2\text{Se}_3\) glass at present.

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