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Structure of Cu–As–Se glasses investigated by neutron diffraction with copper isotope substitution

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Neutron diffraction with copper isotope substitution was used to study the structure of glassy $Cu_5As_{46.25}Se_{48.75}$, which lies at $x=0.0513$ on the $(Cu_2Se)_x(AsSe)_{1-x}$ pseudobinary tie line. The results are consistent with fourfold coordination of copper to matrix (As or Se) atoms at a mean distance of 2.40(2) Å and with threefold coordination of arsenic to one As and two Se atoms at a mean distance of 2.43(2) Å. A comparison is made with the structure of glassy AsSe and with the structure of a high-Cu content glass with $x=0.25$. It is found that the short-range order of glassy AsSe is not changed when 5.13 mol % of Cu_2Se is added. However, the addition of 25 mol % leads to a disruption of the intermediate-range order and to an alteration of the short-range order, which is consistent [within a scenario where arsenic remains threefold coordinated by matrix atoms at a mean distance of 2.42(2) Å] with a substitution of As-As bonds by As-Se bonds. In the $x=0.25$ material, the Cu to matrix atom coordination number is $\simeq 3$ at 2.42(2) Å and the Cu-Cu nearest-neighbor coordination number is 1.0(3) at 2.70(4) Å. A comparison between (i) the measured structure of the glassy network formers AsSe and As_2Se_3 and (ii) the results obtained from first-principles molecular-dynamics methods points to a need for more accurate simulations in order to help elucidate the structure and properties of these materials.

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I. INTRODUCTION

The object of this paper is to apply the method of neutron diffraction with copper isotope substitution to give detailed information on the structure of glasses in the Cu–As–Se system, with attention focusing on the $(Cu_2Se)_x(AsSe)_{1-x}$ $(0 \leq x \leq 1)$ pseudobinary tie line. Motivation is provided by a desire to understand how the structure and properties of network forming *A*-*X* glasses, where *A* denotes an atom such as the pnictogen As and *X* denotes an atom such as the chalcogen Se, are affected by the incorporation of a metal atom *M* such as Cu or Ag. For example, the electrical conductivity changes from electronic to predominantly ionic along the $(Ag_2Se)_x(AsSe)_{1-x}$ tie line as *x* is increased from 0 to 0.25.[1–3] By contrast, glasses in the Cu–As–Se system remain semiconducting even when a large mole fraction of Cu is incorporated.[1,2] Also, the photodarkening effect, where a shift occurs in the optical-absorption edge of many chalcogenide glasses to a lower energy after illumination with light of band-gap energy, is destroyed when either 1 or 5 at. % of Cu is added to As_2S_3 or As_2Se_3, respectively.[4,5] Furthermore, Cu–As–Se glasses can be switched from a low- to a high-resistance state and the switching characteristics depend on the glass composition.[6–8] It is therefore important to gain information on the atomic scale structure of Cu–As–Se glasses in order to give insight into their basic physicochemical properties and to have a guide in making realistic models of these and other related materials.[9–11]

The structure of a high-Cu content glass with $x=0.25$, which corresponds to $Cu_2As_3Se_4$, has previously been studied by using the method of neutron diffraction with isotope substitution (NDIS) (Ref. 12) and the structure of glassy AsSe has also been investigated.[12] In the present paper, the NDIS method is applied to a low-Cu content glass $Cu_5As_{46.25}Se_{48.75}$, which lies at $x=0.0513$, thus, enabling a study of the effect of adding a small amount of modifying Cu compound to glassy AsSe and providing information that is complementary to that already obtained for the composition dependence of the structure of other glassy *M*-*A*-*X* systems. Indeed, the NDIS technique has been successfully used to gain detailed structural information on systems such as Ag-As-S,[13,14] Ag-As-Se,[12,15] Ag-As-Te,[16,17] Ag-P-S,[18] and Cu-As-Te (Ref. 17) in addition to the glassy chalcohalide CuI-Sb_2Se_3.[19] An important feature of the results is an overlap of the nearest-neighbor pair-distribution functions, which emphasizes the importance of using NDIS to separate the various contributions to the atomic ordering.[20] The $x=0.0513$ composition lies well within the glass forming region of the Cu–As–Se system[1,6] and the atomic fraction of Cu is sufficiently large to ensure a successful application of the isotopic substitution method.

The paper is organized as follows. The essential theory required to understand the neutron-diffraction results is given in Sec. II and the experimental method is outlined in Sec. III. The diffraction data are presented in Sec. IV and are discussed in Sec. V in reference to previous experimental results on the structure of glasses in the Cu–As–Se system and to the structural models that have been developed. Since density functional based methods provide a pathway for understanding the structure and other properties of these materials,[10,11] neutron-diffraction results for the network forming glasses AsSe and As_2Se_3 are also compared with the results obtained from the first-principles molecular-dynamics studies of Drabold and co-workers.[21–23] The main results from the present work are summarized in Sec. VI.

II. THEORY

In a neutron-diffraction experiment on a Cu–As–Se glass, the coherent scattered intensity can be represented by the total-structure factor[24]

$$F(k) = A[S_{\mathrm{AsAs}}(k) - 1] + B[S_{\mathrm{AsSe}}(k) - 1] + C[S_{\mathrm{SeSe}}(k) - 1] + D[S_{\mathrm{CuSe}}(k) - 1] + E[S_{\mathrm{CuAs}}(k) - 1] + F[S_{\mathrm{CuCu}}(k) - 1], \qquad (1)$$

where $A = c_{\mathrm{As}}^2 b_{\mathrm{As}}^2$, $B = 2c_{\mathrm{As}}c_{\mathrm{Se}}b_{\mathrm{As}}b_{\mathrm{Se}}$, $C = c_{\mathrm{Se}}^2 b_{\mathrm{Se}}^2$, $D = 2c_{\mathrm{Cu}}c_{\mathrm{Se}}b_{\mathrm{Cu}}b_{\mathrm{Se}}$, $E = 2c_{\mathrm{Cu}}c_{\mathrm{As}}b_{\mathrm{Cu}}b_{\mathrm{As}}$, and $F = c_{\mathrm{Cu}}^2 b_{\mathrm{Cu}}^2$. In these equations c_α and b_α denote the atomic fraction and coherent neutron-scattering length of chemical species α, respectively, $S_{\alpha\beta}(k)$ is a partial structure factor, and k is the scattering vector. If diffraction experiments are made on two glasses that are identical in every respect, except that the isotopic composition of copper is changed from ^{65}Cu (b_{Cu}) to ^{63}Cu (b'_{Cu}), then those correlations not involving copper can be eliminated by forming the difference function[14]

$$\Delta F_{\mathrm{Cu}}(k) \equiv {}^{65}F(k) - {}^{63}F(k) = D'[S_{\mathrm{CuSe}}(k) - 1] + E'[S_{\mathrm{CuAs}}(k) - 1] + F'[S_{\mathrm{CuCu}}(k) - 1], \qquad (2)$$

where $D' = 2c_{\mathrm{Cu}}c_{\mathrm{Se}}b_{\mathrm{Se}}(b_{\mathrm{Cu}} - b'_{\mathrm{Cu}})$, $E' = 2c_{\mathrm{Cu}}c_{\mathrm{As}}b_{\mathrm{As}}(b_{\mathrm{Cu}} - b'_{\mathrm{Cu}})$, and $F' = c_{\mathrm{Cu}}^2(b_{\mathrm{Cu}}^2 - b'^2_{\mathrm{Cu}})$. It is also possible to eliminate the Cu-μ correlations, where μ denotes a matrix atom (As or Se), by forming the difference function

$$\Delta F(k) \equiv {}^{65}F(k) - b_{\mathrm{Cu}}\Delta F_{\mathrm{Cu}}(k)/(b_{\mathrm{Cu}} - b'_{\mathrm{Cu}}) = A[S_{\mathrm{AsAs}}(k) - 1] + B[S_{\mathrm{AsSe}}(k) - 1] + C[S_{\mathrm{SeSe}}(k) - 1] + F''[S_{\mathrm{CuCu}}(k) - 1], \qquad (3)$$

where $F'' = -c_{\mathrm{Cu}}^2 b_{\mathrm{Cu}} b'_{\mathrm{Cu}}$. The real-space functions corresponding to $F(k)$, $\Delta F_{\mathrm{Cu}}(k)$, and $\Delta F(k)$ are denoted by $G(r)$, $\Delta G_{\mathrm{Cu}}(r)$, and $\Delta G(r)$, respectively, and are obtained from the above equations for the k-space functions by replacing each $S_{\alpha\beta}(k)$ by the corresponding partial pair-distribution function $g_{\alpha\beta}(r)$. The limiting values of these functions, namely $G(r=0)$, $\Delta G_{\mathrm{Cu}}(r=0)$, and $\Delta G(r=0)$, follow from setting $g_{\alpha\beta}(r) = 0$ in the relevant equations, e.g., $\Delta G_{\mathrm{Cu}}(r=0) = -(D' + E' + F')$ and $\Delta G(r=0) = -(A + B + C + F'')$.

The mean-coordination number of atoms of type β, contained in a volume defined by two concentric spheres of radii r_i and r_j centered on an atom of type α, is given by

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_i}^{r_j} dr\, g_{\alpha\beta}(r) r^2, \qquad (4)$$

where n_0 is the atomic number density of the material. Let ${}^{\max}\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$ denote the maximum Cu-Se coordination number, which is obtained by integrating over the first peak in $\Delta G_{\mathrm{Cu}}(r)$ and assuming that $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}} = \bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}} = 0$. Then for the case when $\bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}} = 0$ but $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}} \neq 0$, it follows [from consideration of Eqs. (2) and (4)] that $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}} = {}^{\max}\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}} - (c_{\mathrm{Se}}E'/c_{\mathrm{As}}D')\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$ such that,

$$\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}} = {}^{\max}\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}} - (b_{\mathrm{As}}/b_{\mathrm{Se}})\bar{n}_{\mathrm{Cu}}^{\mathrm{As}} \qquad (5)$$

and the maximum Cu-As coordination number corresponds to $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}} = 0$ such that ${}^{\max}\bar{n}_{\mathrm{Cu}}^{\mathrm{As}} = (b_{\mathrm{Se}}/b_{\mathrm{As}}){}^{\max}\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$. In the case of the matrix atom correlations, let ${}^{\max}\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$ denote the maximum As-Se coordination number, which is obtained by integrating over the first peak in $\Delta G(r)$ and assuming that $\bar{n}_{\mathrm{As}}^{\mathrm{As}} = \bar{n}_{\mathrm{Se}}^{\mathrm{Se}} = \bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}} = 0$. Then for the case when $\bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}} = \bar{n}_{\mathrm{Se}}^{\mathrm{Se}} = 0$ but $\bar{n}_{\mathrm{As}}^{\mathrm{As}} \neq 0$, it follows [from consideration of Eqs. (3) and (4)] that $\bar{n}_{\mathrm{As}}^{\mathrm{Se}} = {}^{\max}\bar{n}_{\mathrm{As}}^{\mathrm{Se}} - (c_{\mathrm{Se}}A/c_{\mathrm{As}}B)\bar{n}_{\mathrm{As}}^{\mathrm{As}}$ such that,

$$\bar{n}_{\mathrm{As}}^{\mathrm{Se}} = {}^{\max}\bar{n}_{\mathrm{As}}^{\mathrm{Se}} - (b_{\mathrm{As}}/2b_{\mathrm{Se}})\bar{n}_{\mathrm{As}}^{\mathrm{As}} \qquad (6)$$

and the maximum As-As coordination number corresponds to $\bar{n}_{\mathrm{As}}^{\mathrm{Se}} = 0$ such that ${}^{\max}\bar{n}_{\mathrm{As}}^{\mathrm{As}} = (2b_{\mathrm{Se}}/b_{\mathrm{As}}){}^{\max}\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$.

III. EXPERIMENT

The $\mathrm{Cu_5As_{46.25}Se_{48.75}}$ samples were prepared from As pieces (99.9999%), Se pellets (99.999+%), and highly enriched copper ^{65}Cu (99.73% ^{65}Cu and 0.27% ^{63}Cu) or ^{63}Cu (99.89% ^{63}Cu and 0.11% ^{65}Cu) isotopes. The elements were weighed in the correct proportions in a high-purity argon filled glove box using a balance of precision ±0.1 mg to give a total sample mass of $\gtrsim 3$ g. They were then sealed under vacuum ($\leq 10^{-5}$ torr) in cleaned silica ampoules (5 mm inner diameter and 1 mm wall thickness), heated slowly in a rocking furnace to 870 °C, maintained at this temperature for 6 h, and finally cooled to 500 °C before quenching in an ice/salt-water mixture. The samples were therefore processed in the same fashion in order to aid in the preparation of materials with an identical composition. The mass density of the glass was measured using pycnometry and gave $n_0 = 0.0354(14)$ Å^{-3}. The thermal properties of the samples were measured using a TA Instruments Thermal Analyst 2000 differential scanning calorimetry system with a scan rate of 10 °C min^{-1}, which gave a glass-transition temperature $T_g(\text{onset}) = 170(3)$ °C or $T_g(\text{mid-point}) = 183(3)$ °C, a crystallization temperature of 302(5) °C, and a melting temperature $T_{mp} = 386(3)$ °C with an enthalpy of melting $H_{mp} = 17(2)$ Jg^{-1}. The results for T_g compare with a value in the range of 164–174 °C for glassy AsSe (Refs. 1 and 25) and with a value of 165 °C for glassy $\mathrm{Cu_{4.76}As_{47.62}Se_{47.62}}$.[1]

Samples of glassy AsSe and $\mathrm{As_2Se_3}$ were also prepared from the same purity starting materials by bulk quenching the liquid, contained in a silica ampoule of 5 (AsSe) or 7 mm ($\mathrm{As_2Se_3}$) inner diameter and 1 mm wall thickness, from either 350 °C (AsSe) or 600 °C ($\mathrm{As_2Se_3}$) in an ice/salt-water mixture. For AsSe, the number density is given by $n_0 = 0.0354(2)$ Å^{-3} and a glass-transition temperature $T_g(\text{onset}) = 174(2)$ °C or $T_g(\text{midpoint}) = 182(2)$ °C was measured by using a DuPont Thermal Analyst 2200 differential scanning calorimeter operating at a scan rate of 10 °C min^{-1}.[25] For $\mathrm{As_2Se_3}$, $n_0 = 0.0354(1)$ Å^{-3} and temperatures of $T_g(\text{onset}) = 182(2)$ °C, $T_g(\text{midpoint}) = 191(2)$ °C, and $T_{mp} = 374(2)$ °C were measured by using a TA Instruments Thermal Analyst 2000 differential scanning calorimeter with a scan rate of 10 °C min^{-1}.[26]

The neutron-diffraction experiment was made using the SANDALS instrument at the ISIS pulsed neutron source. The samples were held in a cylindrical vanadium container of inner diameter of 6.8 ($\mathrm{Cu_5As_{46.25}Se_{48.75}}$ and AsSe) or 8.8 mm ($\mathrm{As_2Se_3}$) and wall thickness of 0.1 mm. The data analysis was made using the ATLAS suite of programs[27] and the neutron resonance of ^{74}Se at 27.1 eV was avoided by truncating the data sets for the different scattering angles at a suitable maximum k value. The reliability checks made on the data sets are described elsewhere.[18] The scattering lengths, calcu-

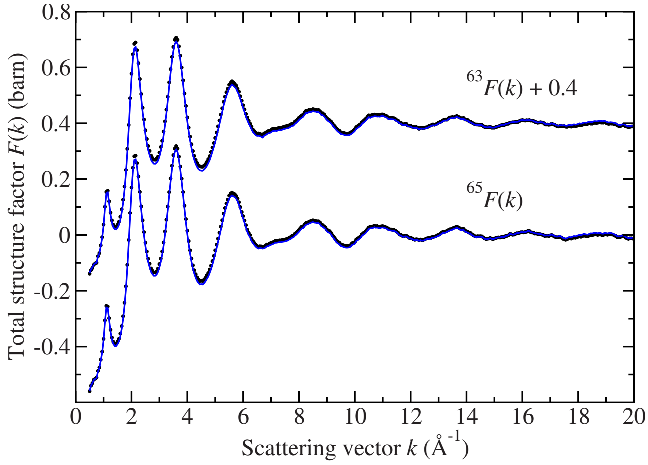

FIG. 1. (Color online) The measured total-structure factors ${}^{63}F(k)$ and ${}^{65}F(k)$ for glassy ${}^{63}Cu_5As_{46.25}Se_{48.75}$ and ${}^{65}Cu_5As_{46.25}Se_{48.75}$, respectively. The solid circles are the measured data points and the symbol size is larger than the statistical error. The solid curves are the Fourier back transforms of the corresponding total pair-distribution functions $G(r)$ after the unphysical oscillations at r values smaller than the distance of closest approach between the centers of two atoms are set to the calculated $G(r=0)$ limit.

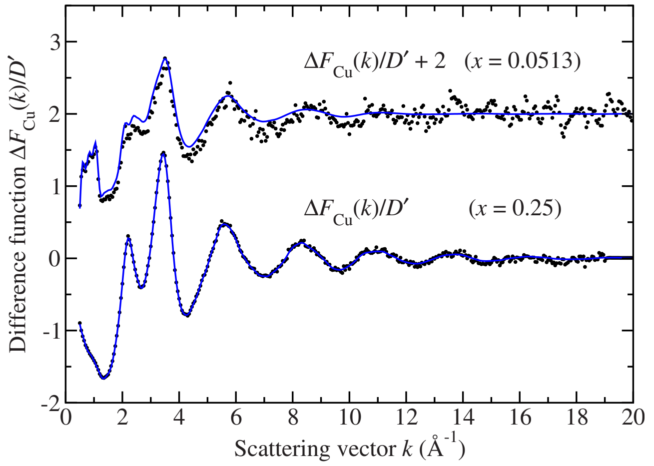

FIG. 2. (Color online) Comparison of the measured difference functions $\Delta F_{Cu}(k)/D'$ for glassy $(Cu_2Se)_x(AsSe)_{1-x}$ where $x=0.0513$ $(Cu_5As_{46.25}Se_{48.75})$ or $x=0.25$ $(Cu_2As_3Se_4)$ and $D'=2c_{Cu}c_{Se}b_{Se}(b_{Cu}-b'_{Cu})$. The solid circles are the measured data points and the solid curves show the MIN solutions. For the $x=0.25$ glass $D'=65.6(3.8)$, $E'=40.6(2.4)$, and $F'=35.1(2.2)$ mb.

lated for the enrichment of the Cu isotopes, are $b_{Cu}=10.61(19)$, $b'_{Cu}=6.43(15)$, $b_{As}=6.58(1)$, and $b_{Se}=7.970(9)$ fm (Ref. 28) and the coefficients in Eqs. (2) and (3) take values of $D'=16.24(94)$, $E'=12.72(74)$, $F'=1.78(11)$, $A=92.61(28)$, $B=236.48(45)$, $C=150.96(34)$, and $F''=-1.70(5)$ mb.

IV. RESULTS

The measured total-structure factors for the $x=0.0513$ glass are shown in Fig. 1 and feature a so-called first sharp diffraction peak (FSDP) at $k=1.13(2)$ Å^{-1}, which is a signature of intermediate-range order.[29] The first-order difference function $\Delta F_{Cu}(k)$ is shown in Fig. 2 and the corresponding real-space function $\Delta G_{Cu}(r)$ is shown in Fig. 3. The latter was generated (i) by Fourier transforming $\Delta F_{Cu}(k)$ after a cosine window function was applied to the region beyond 2.5 Å^{-1} to suppress the effects of statistical noise at high k values and (ii) by using the minimum noise (MIN) reconstruction method.[30] The latter gives, essentially, a smoothed version of the Fourier transformed k-space function while ensuring that the $g_{\alpha\beta}(r)$ take physical values, i.e., $g_{\alpha\beta}(r)=0$ for $0\leq r\leq r_{\text{min}}$ and $g_{\alpha\beta}(r)\geq 0$ for $r>r_{\text{min}}$, where r_{min} is the distance of closest approach between two atomic centers. The first peak in $\Delta G_{Cu}(r)$ at 2.40(2) Å covers a range $2.02\leq r(\text{Å})\leq 3.2$ that encompasses typical Cu-Se, Cu-As, and Cu-Cu distances. For example, Cu has four nearest-neighbor Se atoms at 2.41–2.49 Å in crystalline $CuAsSe_2$ (Ref. 31) and has one As atom at 2.34–2.41 Å and three Se atoms at 2.37–2.41 Å in crystalline CuAsSe.[32] In glassy $Cu_2As_3Se_4$, copper has three nearest-neighbor matrix atoms at 2.42(2) Å and 1.0(3) nearest-neighbor Cu atom at 2.70(4) Å.[12] The coordination numbers obtained from the application of different analysis scenarios to the first peak in $\Delta G_{Cu}(r)$ are listed in Table I. Given the small fraction of Cu present in the glass and the small weighting factor for the Cu-Cu correlations in Eq. (2), it is likely that $\bar{n}_{Cu}^{Cu}=0$ and the overall mean Cu coordination number $\bar{n}_{Cu}=\bar{n}_{Cu}^{Cu}+\bar{n}_{Cu}^{As}+\bar{n}_{Cu}^{Se}\simeq 4$, provided that $\bar{n}_{Cu}^{Se}\neq 0$. The latter situation is not anticipated because As and Se are present in the glass in an almost identical proportion and Se has an affinity for Cu.

The difference function $\Delta F(k)$ is shown in Fig. 4 and, like the total-structure factors of Fig. 1, it features an FSDP at $k=1.14(2)$ Å^{-1}. The corresponding real-space function

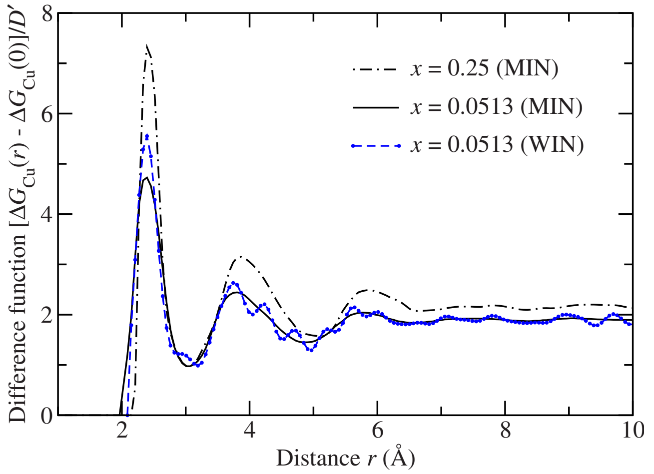

FIG. 3. (Color online) Comparison of the measured difference functions $[\Delta G_{Cu}(r)-\Delta G_{Cu}(0)]/D'$ for glassy $(Cu_2Se)_x(AsSe)_{1-x}$ where $x=0.0513$ $(Cu_5As_{46.25}Se_{48.75})$ or $x=0.25$ $(Cu_2As_3Se_4)$ and $D'=2c_{Cu}c_{Se}b_{Se}(b_{Cu}-b'_{Cu})$. In this representation the $g_{CuSe}(r)$ function is given the same weighting factor of unity for both glass compositions. The curves for $x=0.0513$ were obtained from $\Delta F_{Cu}(k)$ by using the MIN method and by Fourier transformation after the application of a cosine window function (WIN). The curve for $x=0.25$ was obtained from $\Delta F_{Cu}(k)$ by using the MIN method.

TABLE I. The mean-coordination numbers obtained from the first peak in $\Delta G_{\mathrm{Cu}}(r)$ for glassy $\mathrm{Cu_5As_{46.25}Se_{48.75}}$ ($x=0.0513$) by using different analysis scenarios and Eq. (5). The real-space function was obtained from $\Delta F_{\mathrm{Cu}}(k)$ by using either the cosine window function (W) or MIN (M) method (see the text) and the overall mean Cu coordination number $\bar{n}_{\mathrm{Cu}}=\bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}}+\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}+\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$.

$\bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}}$	$\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$	$\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$	$\bar{n}_{\mathrm{Cu}}$
		$4.0(2)^W$ or $3.7(2)^M$	3.9(2)
	1	$3.2(2)^W$ or $2.9(2)^M$	4.1(2)
	2	$2.3(2)^W$ or $2.0(2)^M$	4.2(2)
	$4.8(2)^W$ or $4.5(2)^M$		4.7(2)
1		$3.0(2)^W$ or $2.7(2)^M$	3.9(2)

$\Delta G(r)$ is shown in Fig. 5 and was generated by Fourier transforming $\Delta F(k)$ and by using the MIN method. The first peak in $\Delta G(r)$ at 2.43(2) Å covers the range $2.21 \leq r(\text{Å}) \leq 2.70$ and is likely to have contributions from both As-As and As-Se correlations. For example, arsenic has one As nearest neighbor at 2.56–2.58 Å and two Se nearest neighbors at 2.37–2.42 Å in crystalline AsSe (Refs. 33–35) and the average bond length found from a pair-distribution function analysis of x-ray diffraction data is 2.40 Å.[36] (A relatively short As-As distance of 2.44 Å reported for crystalline AsSe by Renninger and Averbach[37] is not supported by other work.[33–35]) Inspection of Eq. (3) shows that there may also be a contribution to the first peak from Cu-Cu correlations but the associated weighting factor is small and the first peak in $\Delta G(r)$ was therefore analyzed by assuming As-As and As-Se correlations alone. The coordination numbers obtained from the application of different analysis scenarios to the first peak in $\Delta G(r)$ are listed in Table II. We find that if the mean arsenic coordination number $\bar{n}_{\mathrm{As}}=\bar{n}_{\mathrm{As}}^{\mathrm{As}}+\bar{n}_{\mathrm{As}}^{\mathrm{Se}}+\bar{n}_{\mathrm{As}}^{\mathrm{Cu}}$ is to be at least three (a value that is anticipated on the basis of the "8-N" rule), then As-As bonds are a necessary feature of the glass structure. This observation is supported by nuclear quadrupole resonance (NQR) experiments made using the ^{75}As nucleus, which show that As-As bonds appear in glasses that lie on the As rich side of the $\mathrm{Cu_2Se}$-$\mathrm{As_2Se_3}$ pseudobinary tie line.[38]

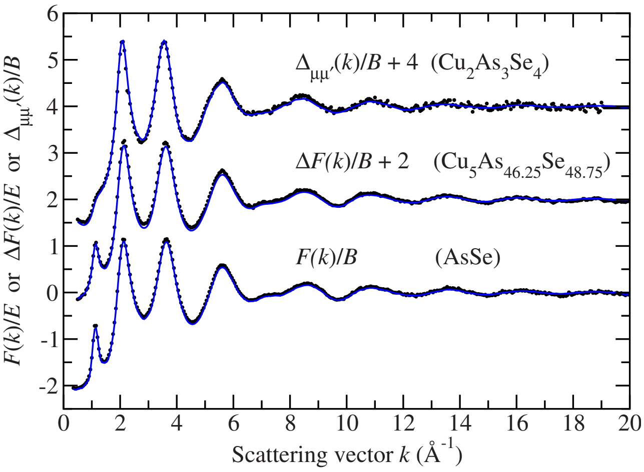

FIG. 4. (Color online) Comparison of the measured difference functions for glassy $(\mathrm{Cu_2Se})_x(\mathrm{AsSe})_{1-x}$, where $\Delta F(k)/B$ is shown for $x=0.0513$ ($\mathrm{Cu_5As_{46.25}Se_{48.75}}$) and $\Delta_{\mu\mu'}(k)/B$ is shown for $x=0.25$ ($\mathrm{Cu_2As_3Se_4}$), with the measured total-structure factor $F(k)/B$ for glassy AsSe. The solid circles are the measured data points, the solid curves show the MIN solutions, and $B=2c_{\mathrm{As}}c_{\mathrm{Se}}b_{\mathrm{As}}b_{\mathrm{Se}}$. For the $x=0.25$ glass, $A=48.1(1)$, $B=155.4(3)$, and $C=125.5(3)$ mb while for the AsSe glass, $A=108.2(3)$, $B=262.2(5)$, and $C=158.8(4)$ mb.

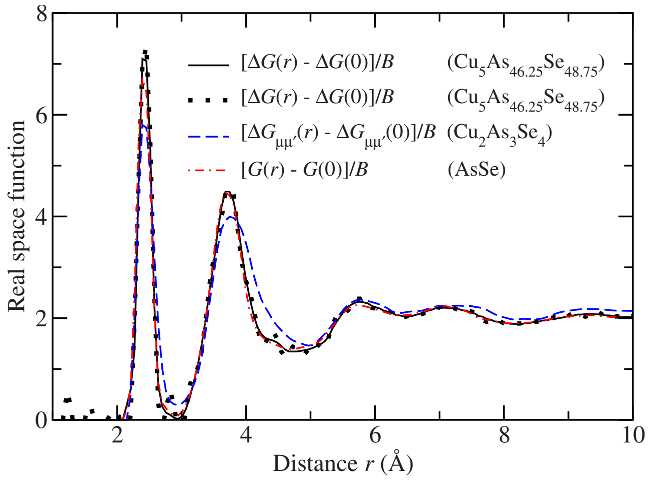

FIG. 5. (Color online) Comparison of the measured difference functions for glassy $(\mathrm{Cu_2Se})_x(\mathrm{AsSe})_{1-x}$, where $[\Delta G(r)-\Delta G(0)]/B$ is shown for $x=0.0513$ ($\mathrm{Cu_5As_{46.25}Se_{48.75}}$) and $[\Delta G_{\mu\mu'}(r)-\Delta G_{\mu\mu'}(0)]/B$ is shown for $x=0.25$ ($\mathrm{Cu_2As_3Se_4}$), with the measured total pair-distribution function $[G(r)-G(0)]/B$ for glassy AsSe. The coefficient $B=2c_{\mathrm{As}}c_{\mathrm{Se}}b_{\mathrm{As}}b_{\mathrm{Se}}$ so that in these representations the $g_{\mathrm{AsSe}}(r)$ function is given the same weighting factor of unity for all glass compositions. The dotted curve for $x=0.0513$ was obtained by Fourier transforming $\Delta F(k)$ shown by the circles in Fig. 4 while the other curves were obtained from MIN solutions (see Fig. 4).

V. DISCUSSION

A. Glasses on the $\mathrm{Cu_2Se}$-AsSe pseudobinary tie line

The difference functions $\Delta F_{\mathrm{Cu}}(k)$ for the $x=0.0513$ and 0.25 glasses are compared in Fig. 2 and the corresponding

TABLE II. The mean-coordination numbers $\bar{n}_{\mathrm{As}}^{\mathrm{As}}$ and $\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$ as obtained from the first peak in $\Delta G(r)$ for glassy $\mathrm{Cu_5As_{46.25}Se_{48.75}}$ ($x=0.0513$) by using different analysis scenarios and Eq. (6). The overall mean As coordination number is given by $\bar{n}_{\mathrm{As}}=\bar{n}_{\mathrm{As}}^{\mathrm{As}}+\bar{n}_{\mathrm{As}}^{\mathrm{Se}}+\bar{n}_{\mathrm{As}}^{\mathrm{Cu}}$, where $\bar{n}_{\mathrm{As}}^{\mathrm{Cu}}=(c_{\mathrm{Cu}}/c_{\mathrm{As}})\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$, and it is assumed that $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$ is in the range of 0–2 (see Table I).

$\bar{n}_{\mathrm{As}}^{\mathrm{As}}$	$\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$	$\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$	$\bar{n}_{\mathrm{As}}^{\mathrm{Cu}}$	$\bar{n}_{\mathrm{As}}$
	2.4(2)			2.4(2)
		1	0.1	2.5(2)
		2	0.2	2.6(2)
1	2.0(2)			3.0(2)
		1	0.1	3.1(2)
		2	0.2	3.2(2)

TABLE III. Parameters describing the first peak in (i) $G(r)$ for the network glasses AsSe and $\mathrm{As_2Se_3}$, (ii) $\Delta G(r)$ for glassy $\mathrm{Cu_5As_{46.25}Se_{48.75}}$ ($x=0.0513$), and (iii) $\Delta G_{\mu\mu'}(r)$ for glassy $\mathrm{Cu_2As_3Se_4}$ ($x=0.25$), where $\Delta G_{\mu\mu'}(r)$ is given by Eq. (3) after F'' is set to zero and the $S_{\alpha\beta}(k)$ are replaced by the corresponding $g_{\alpha\beta}(r)$ functions. The mean-coordination number of matrix atoms μ (As or Se) around As is given by $\bar{n}_{\mathrm{As}}^{\mu}=\bar{n}_{\mathrm{As}}^{\mathrm{As}}+\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$.

System	Measured function	Peak position (Å)	$\bar{n}_{\mathrm{As}}^{\mathrm{As}}$	$\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$	$\bar{n}_{\mathrm{As}}^{\mu}$
AsSe	$G(r)$	2.42(2)		2.4(2)	2.4(2)
			1	2.0(2)	3.0(2)
$\mathrm{Cu_5As_{46.25}Se_{48.75}}$	$\Delta G(r)$	2.43(2)		2.4(2)	2.4(2)
			1	2.0(2)	3.0(2)
$\mathrm{Cu_2As_3Se_4}$	$\Delta G_{\mu\mu'}(r)$	2.42(2)		2.8(2)	2.8(2)
			0.5	2.6(2)	3.1(2)
			1	2.4(2)	3.4(2)
$\mathrm{As_2Se_3}$	$G(r)$	2.42(2)		3.0(2)	3.0(2)

real-space functions $\Delta G_{\mathrm{Cu}}(r)$ are compared in Fig. 3. In the case of the $x=0.25$ glass, the $g_{\mathrm{CuCu}}(r)$ function has been measured and the Cu coordination environment is described by $\bar{n}_{\mathrm{Cu}}^{\mathrm{Cu}}=1.0(3)$ at 2.70(4) Å and $\bar{n}_{\mathrm{Cu}}^{\mu}\simeq 3$ at a mean distance of 2.42(2) Å. For example, if $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}=0$ then ${}^{\mathrm{max}}\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}=2.9(2)$ and Eq. (5) is valid so that $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$ values of 2.1(2) and 1.2(2) are obtained by fixing $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}$ at 1 and 2, respectively.[12]

In Fig. 4, $\Delta F(k)$ for the $x=0.0513$ glass is compared with the measured $F(k)$ function for glassy AsSe (Ref. 12) and with the measured $\Delta_{\mu\mu'}(k)$ function for the $x=0.25$ glass, which has a number density $n_0=0.0425$ Å^{-3}.[12] The $\Delta_{\mu\mu'}(k)$ function *only* contains matrix atom correlations and is given by Eq. (3) after F'' is set equal to zero.[12,16,18,19] An FSDP at $k\approx 1.14$ Å^{-1} is a feature of $\Delta F(k)$ and $F(k)$ but not of $\Delta_{\mu\mu'}(k)$, i.e., the introduction of 25 mol % $\mathrm{Cu_2Se}$ disrupts the intermediate-range order of glassy AsSe whereas the introduction of 5.13 mol % has little apparent effect. The corresponding real-space functions are shown in Fig. 5 and the first-peak positions and associated coordination numbers are summarized in Table III. It appears that the basic structural motifs of AsSe are retained when 5.13 mol % of $\mathrm{Cu_2Se}$ is added but that the addition of 25 mol % results in a change of the short-range order. For the $x=0.25$ glass, the results in Table III show that there must be an increase in the number of As-Se bonds and an accompanying decrease in the number of As-As bonds relative to glassy AsSe if arsenic is to remain threefold coordinated by matrix atoms.

To further investigate the possible structural units, it is useful to consider the overall mean matrix atom coordination numbers $\bar{n}_{\mathrm{As}}$ and $\bar{n}_{\mathrm{Se}}=\bar{n}_{\mathrm{Se}}^{\mathrm{Se}}+\bar{n}_{\mathrm{Se}}^{\mathrm{As}}+\bar{n}_{\mathrm{Se}}^{\mathrm{Cu}}$, where $\bar{n}_{\mathrm{Se}}^{\mathrm{As}}=(c_{\mathrm{As}}/c_{\mathrm{Se}})\bar{n}_{\mathrm{As}}^{\mathrm{Se}}$, $\bar{n}_{\mathrm{Se}}^{\mathrm{Cu}}=(c_{\mathrm{Cu}}/c_{\mathrm{Se}})\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}$, and we have assumed that $\bar{n}_{\mathrm{Se}}^{\mathrm{Se}}=0$ since the glasses lie on the As rich side of the $\mathrm{Cu_2Se}$-$\mathrm{As_2Se_3}$ pseudobinary tie line. For the $x=0.0153$ glass, the results in Sec. IV demonstrate that threefold coordinated arsenic requires the presence of As-As bonds and Table II shows that if $\bar{n}_{\mathrm{As}}^{\mathrm{As}}=1$, then $\bar{n}_{\mathrm{As}}^{\mathrm{Se}}=2.0(2)$. Also, from Table I it follows that (i) $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}=3.9(2)$ if $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}=0$ or (ii) $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}=3.1(2)$ if $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}=1$, which leads to mean selenium coordination numbers $\bar{n}_{\mathrm{Se}}$ of 2.3(2) and 2.2(2), respectively. The latter are comparable to the value of $\bar{n}_{\mathrm{Se}}$ expected on the basis of the formal valence shell (FVS) model,[39] which is often used to interpret the structure of Cu–As–Se and other *M-A-X* glasses.[4,5,38,40] The model assumes that only *s* and *p* electrons are involved in the bonding, such that the "8-N" rule holds for each atomic species, and gives $\bar{n}_{\mathrm{Se}}=3c_{\mathrm{Cu}}/c_{\mathrm{Se}}+2$ for the case when $\bar{n}_{\mathrm{Cu}}=4$ and $\bar{n}_{\mathrm{As}}=3$, whereupon $\bar{n}_{\mathrm{Se}}=2.3$ for the $x=0.0513$ composition. In the case of the $x=0.25$ composition, $\bar{n}_{\mathrm{Cu}}^{\mathrm{Se}}=2.9(2)$ if $\bar{n}_{\mathrm{As}}^{\mathrm{Cu}}=(c_{\mathrm{Cu}}/c_{\mathrm{As}})\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}=0$ (see above) whereupon $\bar{n}_{\mathrm{As}}=\bar{n}_{\mathrm{As}}^{\mu}$. Also, for the analysis scenarios considered in Table III, we see that $\bar{n}_{\mathrm{As}}^{\mu}\simeq 3$ if either (i) $\bar{n}_{\mathrm{As}}^{\mathrm{As}}=0$ and $\bar{n}_{\mathrm{As}}^{\mathrm{Se}}=2.8(2)$ so that $\bar{n}_{\mathrm{Se}}=3.6(2)$ or (ii) $\bar{n}_{\mathrm{As}}^{\mathrm{As}}=0.5$ and $\bar{n}_{\mathrm{As}}^{\mathrm{Se}}=2.6(2)$ so that $\bar{n}_{\mathrm{Se}}=3.4(2)$. The FVS model for $\bar{n}_{\mathrm{Cu}}=4$ and $\bar{n}_{\mathrm{As}}=3$ gives $\bar{n}_{\mathrm{Se}}=3.5$ and therefore holds for the $x=0.25$ composition provided $\bar{n}_{\mathrm{Cu}}^{\mathrm{As}}\simeq 0$. On the other hand, other analysis scenarios give $\bar{n}_{\mathrm{As}}>3$ and it is not clear that the contribution to the bonding from *d* electrons can be ignored.[10,11] More detailed information at the partial pair-distribution function level is therefore required in order to provide a more rigorous examination of the local conformations.

B. Structure of other Cu–As–Se glasses

The structure of glasses in the Cu–As–Se system has been extensively studied but there appears to be an absence of work on $\mathrm{Cu_2Se}$-AsSe glasses, which (like Cu-$\mathrm{As_2Se_3}$ glasses) lie on the As rich side of the $\mathrm{Cu_2Se}$-$\mathrm{As_2Se_3}$ pseudobinary tie line. Early investigations focused on vitreous $\mathrm{Cu}_y(\mathrm{As_2Se_3})_{1-y}$ $(0\leq y\leq 1)$ and a model was developed wherein $\bar{n}_{\mathrm{Cu}}=4$ for all compositions.[41,42] For this tie line, NQR experiments show that the fraction of arsenic atoms involved in As-As homopolar bonds increases with *y* (Ref. 38) while x-ray photoelectron and emission spectroscopy studies of the electronic structure indicate that Cu is bonded to both As and Se atoms.[43] An extended x-ray absorption fine structure (EXAFS) spectroscopy experiment on the $y=0.468\,75$ ($\mathrm{Cu_{15}As_{34}Se_{51}}$) glass[44] gave $\bar{n}_{\mathrm{Cu}}=4$, $\bar{n}_{\mathrm{As}}=3.44$, and $\bar{n}_{\mathrm{Se}}=2.61$ with Cu-μ distances of 2.35–2.37 Å and an As-Se distance of 2.42 Å, but the results were not interpreted by assuming As-As bonds and the reported Cu-Cu distance of 2.23 Å is much shorter than the distance of 2.70(4) Å observed for glassy $\mathrm{Cu_2As_3Se_4}$ (Ref. 12) or the distance of 2.56 Å found in metallic Cu.

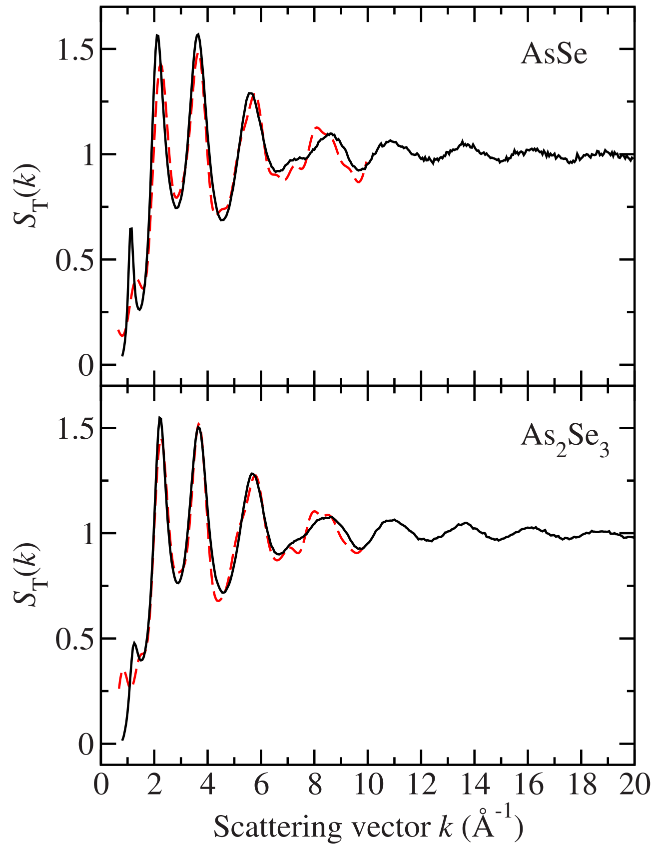

FIG. 6. (Color online) Comparison of the total-structure factor $S_T(k)\equiv[F(k)+\langle b\rangle^2]/\langle b\rangle^2$ for glassy AsSe and As_2Se_3 [solid (black) curve] as measured by using neutron diffraction with the functions calculated for these materials by using first-principles molecular-dynamics methods [broken (red) curves] (Refs. 21–23).

In the case of $(Cu_2Se)_y(As_2Se_3)_{1-y}$ glasses, NQR experiments show no As-As bonds at $y=0.3261$ ($Cu_{15}As_{31}Se_{54}$) (Ref. 38) and EXAFS experiments give $\bar{n}_{As}^{Se}=3$ at 2.42(1) Å for the composition range $y=0.1-0.5$.[45] Notably, the Cu-μ coordination number found from the EXAFS results is significantly less than four, with $\bar{n}_{Cu}^{Se}=3.1-3.2$ at 2.43(1) Å for all y values, while the mean Se coordination number $\bar{n}_{Se}$ is found to increase from 2.0 to 2.6 with increasing y. These results for $\bar{n}_{Se}$ are inconsistent with the FVS model, which gives $\bar{n}_{Se}=4c_{Cu}/c_{Se}+2$ if $\bar{n}_{Cu}=\bar{n}_{As}=3$, such that $\bar{n}_{Se}$ increases with y from 2.3 to 4.0, or $\bar{n}_{Se}=3c_{Cu}/c_{Se}+2$ if $\bar{n}_{Cu}=4$ and $\bar{n}_{As}=3$, such that $\bar{n}_{Se}$ increases with y from 2.2 to 3.5. The glasses $Cu_8As_{26}Se_{66}$ and $Cu_{26}As_{37}Se_{37}$ have also been studied by using EXAFS and x-ray diffraction.[46] The EXAFS results were interpreted to give $\bar{n}_{Cu}^{\mu}=3.96$ at 2.43 Å with $\bar{n}_{As}=2.97$ and $\bar{n}_{Se}=2.25$ for the low-Cu content glass and $\bar{n}_{Cu}^{\mu}=3.70$ at 2.39 Å with $\bar{n}_{Cu}^{Cu}=0.29$ at 2.50 Å, $\bar{n}_{As}=2.99$, and $\bar{n}_{Se}=3.83$ for the high-Cu content glass. These results are comparable to those predicted by the FVS model for $\bar{n}_{Cu}=4$ and $\bar{n}_{As}=3$, which gives $\bar{n}_{Se}$ values of 2.4 and 4.1 for the low- and high-Cu content glasses, respectively.

C. Structure of glassy AsSe and As_2Se_3

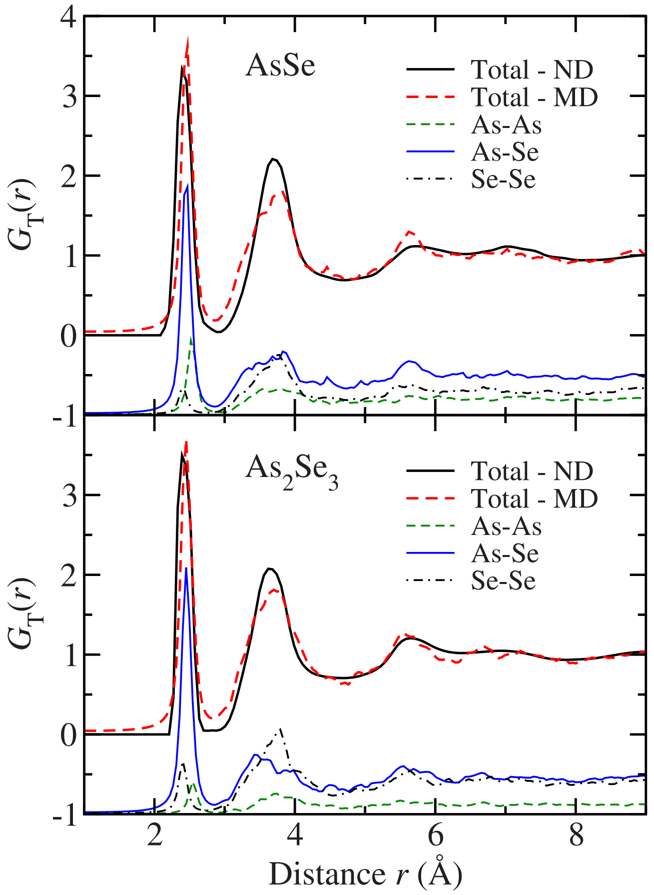

FIG. 7. (Color online) Comparison of the total pair-distribution function $G_T(r)\equiv[G(r)+\langle b\rangle^2]/\langle b\rangle^2$ for glassy AsSe and As_2Se_3 as measured using neutron diffraction (ND) [solid (black) curves] with the functions calculated for these materials by using first-principles molecular-dynamics (MD) methods [broken (red) curves] (Refs. 21–23). Also shown are the contributions to the molecular-dynamics results from the weighted As-As [broken (green) curve], As-Se [solid (blue) curve], and Se-Se [chained (black) curve] pair-correlation functions, which are displaced downward by unity. The measured $G_T(r)$ functions were obtained from the $S_T(k)$ functions shown in Fig. 6 by using the MIN method.

It is worthwhile examining in greater detail the structure of network formers in the Cu–As–Se system since amorphous AsSe and As_2Se_3 have been studied by using first-principles molecular dynamics[21–23] and this type of method provides a pathway for understanding the structure and other properties of the modified Cu–As–Se materials.[10,11] The total-structure factor is given by $S_T(k)\equiv[F(k)+\langle b\rangle^2]/\langle b\rangle^2=[c_{As}^2b_{As}^2S_{AsAs}(k)+2c_{As}c_{Se}b_{As}b_{Se}S_{AsSe}(k)+c_{Se}^2b_{Se}^2S_{SeSe}(k)]/\langle b\rangle^2$, where $\langle b\rangle=c_{As}b_{As}+c_{Se}b_{Se}$, and the functions measured by using neutron diffraction for glassy AsSe (Ref. 12) and As_2Se_3 (Ref. 26) are compared with the simulated functions in Fig. 6. The corresponding real-space functions $G_T(r)\equiv[G(r)+\langle b\rangle^2]/\langle b\rangle^2=[c_{As}^2b_{As}^2g_{AsAs}(r)+2c_{As}c_{Se}b_{As}b_{Se}g_{AsSe}(r)+c_{Se}^2b_{Se}^2g_{SeSe}(r)]/\langle b\rangle^2$ are shown in Fig. 7 where each simulated $G_T(r)$ is broken down into its contributions from the weighted partial pair-distribution functions.

The mean nearest-neighbor distance and coordination numbers obtained from the neutron-diffraction measurements for glassy AsSe and As_2Se_3 are compared in Table III.

The results show that, unlike the case of glassy AsSe, there is no need to invoke homopolar bonds in order to interpret the data for As_2Se_3 in terms of threefold coordinated As. By comparison, the first-principles results show the presence of homopolar bonds for both AsSe and As_2Se_3, although the mean-bond distance given by the position of the first peak in $G_T(r)$ is too large relative to the experiment and the second peak in the measured $G_T(r)$ is not reproduced (see Fig. 7). Also, the intermediate-range order, as manifested by the appearance in the measured $S_T(k)$ of an FSDP at $k = 1.13(2)$ Å^{-1} for AsSe or at $k = 1.26(2)$ Å^{-1} for As_2Se_3, is not reproduced for either glass (see Fig. 6). It is therefore desirable to improve on the molecular-dynamics models that have been developed for glassy AsSe and As_2Se_3 (Refs. 21–23) in order to make further progress in understanding the structure and properties of these materials. It would also be interesting to examine in more detail the effect of different quench rates and thermal histories on the nature of the local structural motifs and their relative arrangement.[47]

VI. CONCLUSIONS

The complexity of correlations associated with a single neutron-diffraction experiment on the three-component glass $(Cu_2Se)_x(AsSe)_{1-x}$ with $x = 0.0513$ has been simplified by use of the isotopic substitution method. The results are consistent with $\bar{n}_{Cu}^{\mu} \simeq 4$ at a mean distance of 2.40(2) Å and the short-range order associated with glassy AsSe is not substantially changed; the results for both materials are consistent with threefold coordinated arsenic with $\bar{n}_{As}^{As} = 1$ and $\bar{n}_{As}^{Se} = 1.9(2)$ at a mean distance of 2.43(2) Å. When the Cu_2Se content is increased to $x = 0.25$, the Cu-μ coordination number reduces to $\bar{n}_{Cu}^{\mu} \simeq 3$ at 2.42(2) Å and Cu-Cu close neighbors appear with $\bar{n}_{Cu}^{Cu} = 1.0(3)$ at 2.70(4) Å.[12] The short- and intermediate-range order of the network former is also altered and, if arsenic is to remain threefold coordinated by matrix atoms, there is a substitution of As-As bonds by As-Se bonds relative to glassy AsSe.

Overall, a picture emerges for the structure of Cu–As–Se glasses where usually $\bar{n}_{Cu} \simeq 4$. Short Cu-Cu distances can occur such that $\bar{n}_{Cu}^{Cu} = 1$ and $\bar{n}_{Cu}^{\mu} \simeq 3$ for glasses such as $Cu_2As_3Se_4$, i.e., Cu is not always exclusively bound to matrix (As or Se) atoms. As-As bonds feature in glasses on the As-rich side of the Cu_2Se-As_2Se_3 pseudobinary tie line and many of the results are consistent with threefold coordinated arsenic where As-Cu bonds are a possibility. The FVS model[39] can provide a guide to the structure of several Cu–As–Se glasses but the model is based on an assumption that *d* electrons do not participate in the bonding and does not account for all of the experimental results. Density functional based methods will prove useful in further elucidating the structure and properties of these materials,[10,11] including the network formers AsSe and As_2Se_3 after improvements are made to the models.[21–23]

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