Supplementary information for:

Binary alloys of Ge and Te: order, voids, and the eutectic composition

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DENSITIES

High energy γ-ray attenuation measurements of $Ge_{0.15}Te_{0.85}$ at 680 K yield a molar volume of 21.3 cm^3/mol (0.02827 atoms/Å^3) with an overall uncertainty of 0.3% [1]. The density of liquid GeTe used in both Ref. [2] and here (0.0335 atoms/Å^3, 5.59 g/cm^3) is based on Refs. [3] (error of $< 0.5\%$) and [4]. Grazing incidence x-ray reflectivity measurements of amorphous GeTe films report a density of 5.60 g/cm^3 [5].

An interpolation between the densities of amorphous GeTe (5.60 g/cm^3) and the extrapolated value for amorphous Te (ca. 5.72 g/cm^3) [6] gives a density estimate for 15:85 close to that of the liquid. We have optimized the structure of amorphous 15:85 to determine the effect of the pressure. The density at zero pressure is less than 1% lower than the one we adopted, where the calculated pressure is 0.96 kbar. This small value is of the same order of magnitude of the pressure in Ref. [2] (-0.8 ± 0.4 kbar).

BOND ANGLE DISTRIBUTIONS

Fig. 1 shows the distributions for a-$Ge_{0.15}Te_{0.85}$ of (a) the nine nearest-neighbors of Ge atoms and (b,c) bond angles. The first four distance distributions [Fig. 1(a), labels 1-4], which have double-peaked shapes, suggest that most of the atoms are fourfold coordinated. The assignment of maxima as “tetrahedral” (shorter) and “octahedral” (longer) is consistent with the bond angle distributions of Te-Ge-Te configurations [Fig. 1(b)]. Reduction of the bond cutoff distance (from 3.2 to 2.7 Å) leads to a gradual shift of the maximum towards the tetrahedral value (109.47°). The bond angle distributions of a-GeTe show a similar, if smaller, shift. The octahedral bonding angles of Te are illustrated in Fig. 1(c), where the Te-Te-Te distribution, in particular, shows maxima at 90° and 180°.

STRUCTURE FACTORS OF LIQUIDS

Fig. 2 shows the structure factors $S(Q)$ for liquid GeTe calculated by Fourier transforming the calculated partial pair correlation functions with weights appropriate to x-ray (xr) and neutron scattering (ns) [7]. Experimental curves are shown: xr and ns at 653 K from Ref. 8, ns at 773 K from Ref. 9. Structure factors of liquid $Ge_{0.15}Te_{0.85}$ are shown in Fig. 3. Measurements: ns(773 K) from Ref. 10, xr(653 K) and ns(653 K) from Ref. 11.

ORDER PARAMETERS

Order among atoms of types A (Ge) and B (Te) can be measured by the parameters α_x ($x =$Ge or Te, Table 1) [12]:

$$\alpha_x = \frac{1 - n_{AB}/[c_A c_B(n_A + n_B)]}{1 - n_x/[c_A c_B(n_A + n_B)]}, \tag{1}$$

where c_A and c_B are the concentrations of the atom types A and B, n_A and n_B are the total coordination numbers, and n_{AB} is the AB coordination number.

CAVITIES

The cavity analysis uses concepts illustrated for a 2D system in Fig. 4. A *vacancy domain* (I, red) is a region where the minimum distance to nearby atoms is larger than a given cutoff (here 85% of the bond length, in the simulations 2.8 Å, the average Ge-Te distance), and each domain is characterized by the point where the distance to all atoms is a maximum. If there are no maxima closer than the *divacancy cutoff* (2.4 Å in the simulations), we locate the center of the largest sphere that can be placed inside the cavity (dashed circle in Fig. 4) and use this point to calculate RDF, including vacancy-vacancy correlations. *Vacancy cells* (II, yellow in Fig. 4) are analogous to the Wigner-Seitz cell in crystals or Voronoi polyhedra in amorphous materials and were assigned using a mesh of 0.08 Å. This definition and the cutoffs are used consistently in all our work on Ge/Sb/Te alloys.

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Figures

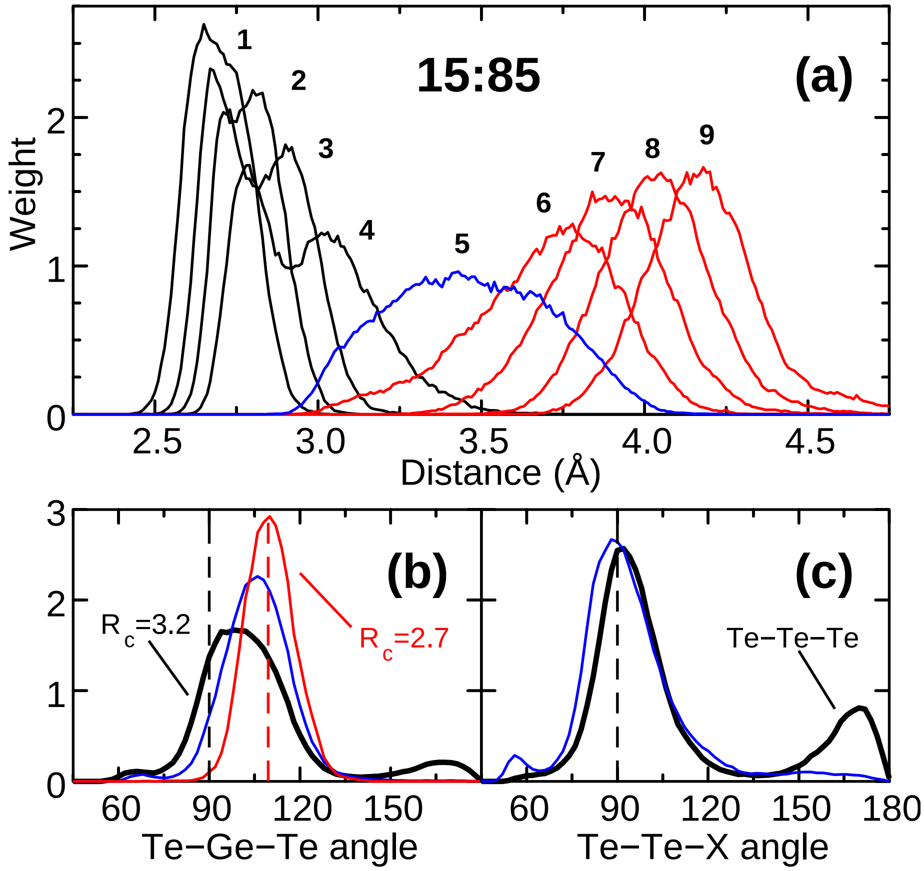

FIG. 1: Amorphous $Ge_{0.15}Te_{0.85}$ at 300 K. (a) Nearest-neighbor distributions of Ge atoms. (b) Te-Ge-Te bond angle distributions using cutoffs of 2.7 Å (red), 2.9 Å (blue), and 3.2 Å (black). Dashed vertical lines: black, octahedral; red, tetrahedral. (c) Te-Te-X bond angles (X=Te, black; X=Ge, blue) for cutoff of 3.2 Å.

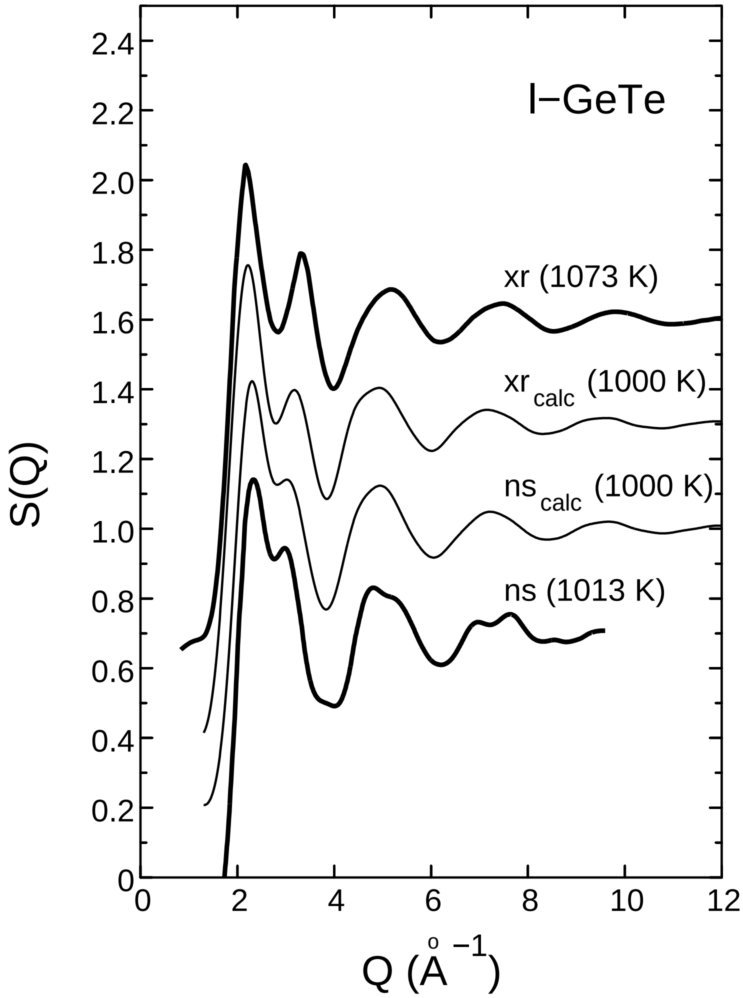

FIG. 2: Structure factor $S(Q)$ of liquid GeTe (see text).

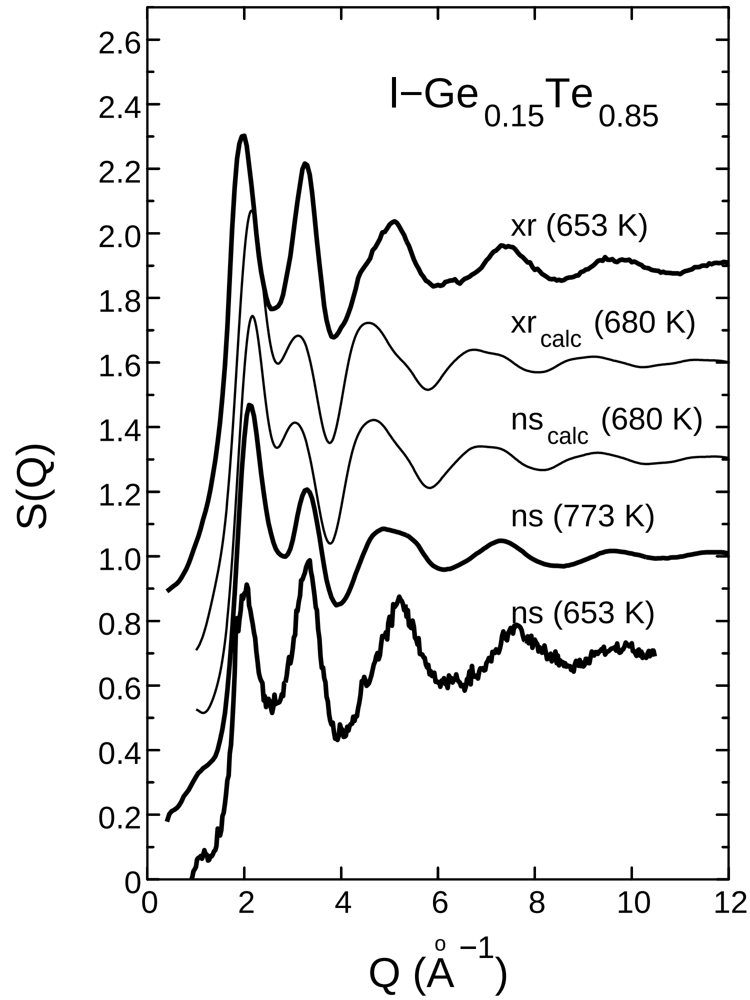

FIG. 3: Structure factor $S(Q)$ of liquid $Ge_{0.15}Te_{0.85}$ (see text).

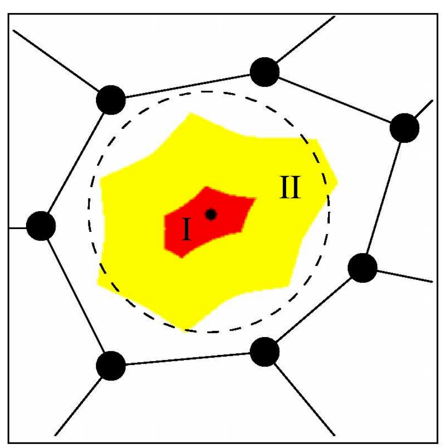

FIG. 4: Schematic form for 2D-vacancy.