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Amorphous Ge$_{15}$Te$_{85}$: density functional, high-energy x-ray and neutron diffraction study

J Kalikka$^1$, J Akola$^{1,2,3}$, R O Jones$^{3,4}$, S Kohara$^5$ and T Usuki$^6$

1 Nanoscience Center, Department of Physics, University of Jyväskylä, PO Box 35, FI-40014 Jyväskylä, Finland
2 Department of Physics, Tampere University of Technology, PO Box 692, FI-33101 Tampere, Finland
3 Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
4 German Research School for Simulation Sciences, FZ Jülich and RWTH Aachen University, D-52425 Jülich, Germany
5 Research and Utilization Division, JASRI/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan
6 Graduate School of Science and Engineering, Yamagata University, 1-4-12 Kojirakawa, Yamagata, 990-8560, Japan

E-mail: jaakko.akola@tut.fi

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Abstract

The structure and electronic properties of amorphous Ge$_{15}$Te$_{85}$ have been studied by combining density functional (DF) simulations with high-energy x-ray and neutron diffraction measurements. Three models with 560 atoms have been constructed using reverse Monte Carlo methods constrained to (1) agree with the experimental structure factors $S(Q)$, and have (2) energies close to the DF minimum and (3) a semiconducting band structure. The best structure is based on the melt-quenched DF structure and has a small number of Ge–Ge bonds. It shows interlocking networks of Te and GeTe with a significant fraction (22–24%) of voids (cavities). Ge occurs with both tetrahedral and 3+3 defective octahedral configurations, and the coordination of Te is slightly higher than indicated by the ‘8−N’ rule ($N$ is the number of valence electrons). The GeTe network includes clusters of ABAB squares ($A = Ge$, $B = Te$), and the bonding is characterized by the chemical bond orders.

Online supplementary data available from stacks.iop.org/JPhysCM/24/015802/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Germanium and tellurium provide prototypes of a large and interesting family of binary alloys of groups 14 and 16 (IV and VI). Ge and Te are components of many alloys whose rapid crystallization from the amorphous state is the basis of phase change memory materials with applications such as digital versatile disk-random access memory (DVD-RAM) and Blu-ray Discs [1]. Tellurium-rich Ge–Te alloys are often good glass formers, and liquids with compositions near the eutectic Ge$_{15}$Te$_{85}$ have remarkable thermodynamic properties, including extrema in the specific heat, compressibility, and thermal expansion coefficients. These have been interpreted as signs of structural changes [2], which can also be induced by pressure [3]. Ge/Se alloys are also members of the 14/16 family that have been studied on numerous occasions [4, 5].

The unusual properties of Ge$_{15}$Te$_{85}$ (sometimes called GeTe$_6$) have led to numerous studies of the structure of its amorphous phase. Reverse Monte Carlo (RMC) analysis of x-ray and neutron diffraction data, as well as extended x-ray absorption fine structure (EXAFS) data [6–9], has led to...
structural models that we discuss below, but we note here that the results of all RMC analyses depend on the constraints applied during refinement. There have also been combined density functional/molecular dynamics (DF/MD) simulations of a small sample (80 atoms in the unit cell) for a range of temperatures [10]. Such small simulations have led to finite size problems in other chalcogenide alloys, and the debate about the nature of the amorphous structure continues.

We study here the amorphous structure of Ge$_{15}$Te$_{85}$ by combining DF simulations with high-energy x-ray (XRD) and neutron diffraction (ND) measurements. The combination of large-scale DF/MD simulations with the RMC analysis of high-energy XRD data has been successful in unravelling details of the structures of amorphous Ge$_2$Sb$_2$Te$_5$ [11] and an Ag/In/Sb/Te alloy [12] and should give a reliable picture of the structure of Ge/Te alloys. Three 560-atom models have been constructed: (a) a structure based on DF simulations (melt-quench) and RMC refinement without Ge–Ge bonds, (b) RMC-generated geometry with DF relaxation without Ge–Ge bonds, and (c) DF–RMC structure with a small number of Ge–Ge bonds, as in the original DF structure. The system is much larger and the agreement between theory and experiment is much better than in our earlier DF study with a 216-atom sample [13], but the results of the two investigations are consistent.

2. Experimental details

The Ge$_{15}$Te$_{85}$ sample was prepared from the pure (99.999%) elements, sealed under vacuum in a silica ampoule, and heated in a furnace up to 1000°C for more than 50 h. The ampoule was quenched from 800°C in ice water. The sample for the neutron diffraction (ND) measurement was sealed under vacuum in a silica container (inner diameter 7.3 mm, wall thickness 0.5 mm), and the high-energy x-ray diffraction (XRD) sample was a pellet of 2 mm thickness. The time-of-flight ND measurement was carried out on the HIT-II instrument at the pulsed neutron source KENS at the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). Scattered neutrons were detected by 104 $^3$He counters covering scattering angles in the range 10° $\leq 2\theta \leq 157°$. Diffraction patterns were taken at room temperature for the sample, background, an empty container and a vanadium rod with the same dimensions as the sample. The XRD experiments were carried out in transition geometry at room temperature at the SPring-8 high-energy XRD beamline BL04B2 [14] using a two-axis diffractometer dedicated to glass, liquid and amorphous materials. The intensity of the incident x-rays (energy 113.5 keV) was monitored by an ionization chamber filled with Ar gas, and the scattered x-rays were measured in a Ge detector. Air scattering near the sample was suppressed by using a vacuum chamber, and the data were corrected using a standard program [14]. The corrected ND and XRD data were normalized to give the Faber–Ziman [15] total structure factors $S(Q)$.

The experimental $S(Q)$ for XRD and ND (figure 1) are very similar, apart from a prepeak (first sharp diffraction peak, FSDP) in ND at low $Q$ (∼1.1 Å$^{-1}$) that was also observed by Jóvári et al [6]. Although Te (atomic number 52) is a stronger scatterer of x-rays than Ge (atomic number 32), the reverse is true for neutrons, where the bound coherent scattering lengths are 5.68 and 8.185 fm, respectively [16]. This is clear evidence that the ND prepeak is related to the Ge atoms, and we return to this point in section 4.4.

3. Computational methods

3.1. DF simulations

We have used the CPMD program [17, 18], which combines the density functional theory of electronic structure with molecular dynamics. We use scalar-relativistic Troullier–Martins pseudopotentials [19] for the electron–ion interaction, periodic boundary conditions with a single point ($k = 0$) in the Brillouin zone, and a kinetic energy cutoff of 20 Ryd for the plane wave basis. We have chosen Born–Oppenheimer molecular dynamics (BO-MD) with a Nosé–Hoover thermostat (frequency 800 cm$^{-1}$, chain length 4) [20], a predictor–corrector algorithm [21], and a time step of 125 au (3.025 fs).

Figure 1. $S(Q)$ fits for samples (a) top, (b) middle, and (c) bottom. Red: calculation; blue: experimental. The x-ray $S(Q)$ has been shifted by 0.5 units.

For MD simulations (annealing, see below), the exchange–correlation energy was calculated using the PBEsol
approximation [22]. This has the same analytic form as that of Perdew, Burke, and Ernzerhof (PBE) [23], but the optimization of two parameters has led to improved lattice constants in solid semiconductors [11, 22]. This is important in chalcogenide materials, where overestimates of bond lengths using PBE have been reported [24–26]. Since PBEsol can lead to overcoordination in chalcogenides (especially Te), we have re-optimized our final geometries using the Tao–Perdew–Staroverov–Scuseria (TPSS) [27] functional, where the structures and energy differences are generally better [11, 27]. The orbital-dependent terms in TPSS increase the computing demands considerably.

The atomic coordinates of amorphous Ge15Te85 were generated by periodically repeating the melt-quenched 216-atom sample reported previously [13] and selecting a 560-atom sample. The box size was adjusted to satisfy periodic boundary conditions and the structure optimized. The final (cubic) unit cell of the 560-atom sample (side 27.08 Å) is consistent with the experimental number density (0.0282 Å−3 [13]). The optimized structure was then heated to 500 K (below the melting point of 680 K) and annealed in five steps of 20 ps at 500, 450, 400, 350 and 300 K. The total annealing time was 100 ps, after which the geometry was optimized with the TPSS functional and refined using the RMC++ program [28].

### 3.2. RMC refinement

The TPSS-optimized (annealed) structure, referred to below as ‘DF-opt’, was used as the basis of the first RMC refinement. A second (‘ideal’) structure was created by a long ‘hard sphere’ RMC run, followed by a long RMC fit to the experimental data and DF relaxation. Three schemes were used to fit the ND and XRD structure factors $S(Q)$, while requiring that the total DF energy remains near the calculated minimum value.

(a) Structures based on the DF-opt structure, refined with short RMC runs that used equal fitting weights for ND and XRD data. Ge–Ge bonds were forbidden.

(b) Structures based on short RMC refinements of the ‘ideal’ structure that used equal fitting weights for ND and XRD data. Ge–Ge bonds were forbidden.

(c) As in (a), but with added weight on ND data and allowing Ge–Ge bonds.

The minimum distances chosen for atom pairs were: Ge–Te, 2.55 Å; Te–Te, 2.70 Å; Ge–Ge, 3.50 Å (Ge–Ge bonds forbidden) or 2.50 Å (Ge–Ge bonds allowed). The ‘long’ hard sphere and RMC runs used for ‘ideal’ base structure generation were 10–100 times longer than the ‘short’ RMC refinement runs, which were constrained to give improved fits to the measured $S(Q)$ while having energies only 100 ± 6 meV/atom higher in energy than the minimum value. A typical ‘short’ RMC run had 15 000 accepted moves, but we used 10 000 moves for model (b), since the energy of the ‘ideal’ structure is 10.15 meV/atom higher than that of DF-opt, which relaxes on annealing. The maximum displacement was set to 0.05 Å for all RMC runs. Short RMC runs might favour particular structural types, so RMC refinement was iterated several times for each structure.

The $S(Q)$ fits of the three structures are shown in figure 1, and the $S(Q)$ fit quality ($\chi^2$) and DF energies are given in table 1. In the RMC++ software, the $\chi^2$ value is

$$\chi^2_i = \frac{1}{\delta_i^2} \sum_k (S_i^C(Q_k) - S_i^E(Q_k))^2,$$

where the superscripts E and C refer to the experimental and calculated $S(Q)$, respectively, and $\delta = 0.01$ was used. The average $\chi^2$ over all data points,

$$\langle \chi^2 \rangle = \frac{1}{N} \sum_i \chi^2_i,$$

measures the quality for the $S(Q)$ fits in table 1, which shows the properties of the three structures during iterative refinement.

Geometry optimization always resulted in a structure close to DF-opt, and the quality of the $S(Q)$ fits changed little on further refinement. The fit to the ND $S(Q)$ is slightly better (by ~0.1) for structure (b) than for structure (a), while the fit for structure (c) is better than (a) by ~0.5 units. All structures fit the x-ray $S(Q)$ well, but (b) is disfavoured by a small amount (~0.1 units). We were unable to improve the fit to XRD and ND data using structures (a) and (b) and varying the fitting weights. Although Raman spectra of Ge/Te alloys near the eutectic composition do not show the Ge–Ge vibrational mode at 275 cm−1 [29], we found satisfactory results only if Ge–Ge bonds were allowed (model (c)). They should not be excluded in the structure determination of such alloys.

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Structure (a)</th>
<th>Structure (b)</th>
<th>Structure (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ND ($\chi^2$)</td>
<td>XRD ($\chi^2$)</td>
<td>$\Delta E$</td>
</tr>
<tr>
<td>1</td>
<td>2.76</td>
<td>2.06</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>2.69</td>
<td>2.09</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>2.84</td>
<td>1.87</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>2.88</td>
<td>2.04</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>2.76</td>
<td>1.88</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 1. ND and XRD values of ($\chi^2$) and total energies during iterative refinement. Energies are in meV/atom with respect to the DF energy minimum.
Table 2. Distances and coordination numbers in a-Ge$_{15}$Te$_{85}$. $r_{\text{max}}^{\text{Ge-Te}}$ ($r_{\text{min}}^{\text{Ge-Te}}$): first PDF maximum (minimum); $N_{c}$: total coordination number; and $n_{X-Y}$: partial coordination number. $N_{c}$: chemical coordination numbers (see section 4.3). $N_{c}$ and $n_{X-Y}$ were determined with a bond cutoff of 3.0–3.3 Å (figure 4).

<table>
<thead>
<tr>
<th>Structure</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>DF-opt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{max}}^{\text{Ge-Te}}$ (Å)</td>
<td>2.58</td>
<td>2.58</td>
<td>2.58</td>
<td>2.65</td>
</tr>
<tr>
<td>$r_{\text{max}}^{\text{Te-Te}}$ (Å)</td>
<td>2.74</td>
<td>2.73</td>
<td>2.74</td>
<td>2.84</td>
</tr>
<tr>
<td>$r_{\text{min}}^{\text{Ge-Te}}$ (Å)</td>
<td>3.12</td>
<td>3.12</td>
<td>3.10</td>
<td>3.07</td>
</tr>
<tr>
<td>$r_{\text{min}}^{\text{Te-Te}}$ (Å)</td>
<td>3.12</td>
<td>3.12</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>$N_{c}$ (Ge)</td>
<td>3.63 ± 0.13</td>
<td>3.60 ± 0.10</td>
<td>3.71 ± 0.13</td>
<td>3.72 ± 0.28</td>
</tr>
<tr>
<td>$N_{c}$ (Te)</td>
<td>2.21 ± 0.14</td>
<td>2.22 ± 0.16</td>
<td>2.21 ± 0.13</td>
<td>2.32 ± 0.34</td>
</tr>
<tr>
<td>$n_{\text{Ge-Te}}$</td>
<td>3.63 ± 0.13</td>
<td>3.60 ± 0.10</td>
<td>3.58 ± 0.12</td>
<td>3.62 ± 0.27</td>
</tr>
<tr>
<td>$n_{\text{Te-Ge}}$</td>
<td>0.64 ± 0.02</td>
<td>0.64 ± 0.02</td>
<td>0.63 ± 0.02</td>
<td>0.64 ± 0.05</td>
</tr>
<tr>
<td>$n_{\text{Ge-Ge}}$</td>
<td>0</td>
<td>0</td>
<td>0.13 ± 0.01</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>$n_{\text{Te-Te}}$</td>
<td>1.57 ± 0.12</td>
<td>1.58 ± 0.13</td>
<td>1.58 ± 0.11</td>
<td>1.69 ± 0.30</td>
</tr>
<tr>
<td>$N_{c}$ (Ge)</td>
<td>3.44</td>
<td>3.50</td>
<td>3.55</td>
<td>3.53</td>
</tr>
<tr>
<td>$N_{c}$ (Te)</td>
<td>2.06</td>
<td>2.04</td>
<td>2.05</td>
<td>2.13</td>
</tr>
<tr>
<td>$n_{\text{chern}}^{\text{Ge-Te}}$</td>
<td>3.44</td>
<td>3.50</td>
<td>3.45</td>
<td>3.43</td>
</tr>
<tr>
<td>$n_{\text{chern}}^{\text{Te-Ge}}$</td>
<td>0.60</td>
<td>0.61</td>
<td>0.59</td>
<td>0.60</td>
</tr>
<tr>
<td>$n_{\text{chern}}^{\text{Ge-Ge}}$</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$n_{\text{chern}}^{\text{Te-Te}}$</td>
<td>1.46</td>
<td>1.43</td>
<td>1.46</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Figure 2. Partial distribution function of Te–Te for structures (a)–(c) and MD simulation at 300 K (annealing, PBEsol functional).

Figure 3. Ge–Te partial PDFs for structures (a)–(c) and MD simulation at 300 K (annealing, PBEsol functional). Inset: the first maxima.

4. Results

4.1. Pair distribution functions and coordination numbers

The partial pair distribution functions (PDFs, $g_{ij}(r)$) of structures (a)–(c) and DF-opt (the DF/MD result at 300 K after annealing) are shown in figures 2 and 3 for Te–Te and Ge–Te. The minimum distance in the PDF for this structure, not the position of the first peak, has been a constraint in our RMC fit. This strategy results in a very sharp peak near the minimum value chosen, as shown in table 2, where $r_{\text{max}}$ for all structures is within 0.05 Å of the RMC lower bound. While DF-opt overestimates bond lengths by 1–2%, the RMC-refined values are only slightly shorter than the EXAFS values (Ge–Te: 2.60 ± 0.02 Å; Te–Te: 2.79 ± 0.02 Å).

The calculated total and partial coordination numbers are given in table 2 using a cutoff range of 3.0–3.3 Å, which coincides with the first PDF minimum in each case. The dependence of coordination number on cutoff distance is also shown in figure 4. Our values for Ge–Te and Te–Ge deviate by less than 0.1 from the values of [6, 8] (Ge–Te: 3.63 and 3.56; Te–Ge: 0.64 and 0.62), and their Te–Te values are within our error bounds (1.71 and 1.66). More recent results of the same group [9] required coordination numbers to satisfy the $8-N$ rule of covalent networks ($N$ is the number of valence electrons) and gave a higher Ge–Te coordination (3.94) and lower Te–Te coordination than in the structures of related materials. Our results clearly support the earlier work [6, 8], where the $8-N$ rule was not imposed.
4.2. Bond angles

The bond angles (figure 5) were evaluated with a bond cutoff distance of 3.2 Å. The overall octahedral tendency is evident as increased weight near 90° and 180°. Bond angles from the DF structures were used as additional constraints during the RMC refinement. The constraints of 99° and 109° for Te–Te–Te and Te–Ge–Te bonds, respectively, mimic the helical chains in crystalline Te (former) and tetrahedral Ge (latter). The DF/MD calculations favour octahedral local environments, so that the bond angles are generally a little smaller than after RMC refinement. The bond angles in structures (a)–(c) agree very well, apart from Ge–Te–Ge, where a small number of Ge–Ge bonds in structure (c) introduces triangular configurations near 60°. The low concentration of Ge leads to significant fluctuations in the Ge–Te–Ge plot.
4.3. Short range order

The local environment of atoms has been studied with the aid of chemical bond orders (bond strengths, table 3), which have been analyzed by projecting the Kohn–Sham eigenfunctions onto atomic s- and p-orbitals (see section 4.6). The projection is 99.3% complete, and the results are shown in figure 6. A covalent single bond corresponds to the value 1 in this scheme, so that maxima in the Ge–Te and Te–Te distributions at 0.7–0.8 indicate nearly covalent bonding. There are no double bonds, and the increased weight near zero is due to non-bonded atoms (e.g. second-nearest neighbours). The Ge–Ge bond strengths in structure (c) deviate little from the Ge–Ge bonds in DF-opt, and the RMC refinement appears to enhance the division into bonded and non-bonded interactions (see the first sharp PDF peak in figures 2 and 3).

The bottom plots of figure 6 show the evolution of chemical bond strength as a function of bond distance in
Table 3. Nearest-neighbour analysis of Ge and Te (at.%) using a chemical bond strength cutoff of 0.4 for neighbour search (see figure 6).

<table>
<thead>
<tr>
<th>Atom Neighbours</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>DF-opt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>GeTe₃</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Te₂</td>
<td>45</td>
<td>52</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Te₀</td>
<td>54</td>
<td>45</td>
<td>41</td>
</tr>
<tr>
<td>Te</td>
<td>GeTe₂</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Te₁</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Ge₁</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Ge₀</td>
<td>31</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Te₂</td>
<td>47</td>
<td>45</td>
<td>46</td>
</tr>
</tbody>
</table>

DF-opt. For Ge–Te bonds, there are two distinct branches corresponding to threefold and fourfold (tetrahedral) Ge, which indicate differences in bond lengths (strengths) for the coexisting Ge coordinations; tetrahedral Ge–Te bonds are shorter and stronger than the bonds for threefold (defective octahedral) Ge. In addition, the scatter of bonds differs between the two types of Ge: tetrahedral Ge has a well-defined range of bond distances and a gap before the non-bonding distances. For threefold coordinated Ge, there is a continuous distribution from the nearest to the next nearest neighbours, as also found in Te–Te bonds (bottom right).

The chemical coordination numbers $N_c$ (table 2, average values) are obtained by counting the bonds with chemical strength stronger than 0.4 units for each atom. Comparison of $N_c$ with the coordination numbers calculated with a radial cutoff distance ($N_r$) shows that $N_c$ is lower, but within or near the error bounds in $N_r$. Most of the deviation in Ge (Te) total coordination numbers comes from the Ge–Te (Te–Te) partial PDFs. We have also evaluated the cutoff distances for PDFs that produce the same coordination numbers as the bond orders, and the results are (for DF-opt) Ge–Te: 3.03 Å; Te–Ge: 3.01 Å; Ge–Ge: 3.16 Å; and Te–Te: 3.06 Å. These values correspond to a bond strength $\sim 0.4$ (in figure 6) and provide an estimate for reasonable $N_r$ cutoff distances.

The environments of Te are very similar in all structures, while those of Ge differ slightly. Fourfold coordinated Ge is most common in structure (c), and this is reflected in the Ge coordination numbers in table 2. The existence of both threefold and fourfold coordinated Ge is also apparent in the nearest-neighbour distribution plots (figure 7), which show double maxima for neighbours 2–4. Some Ge atoms have four very close neighbours (peaks up to the fourth neighbour below 2.8 Å, top panel), while those corresponding to the second extend well beyond 3.0 Å. The shorter distances correspond to tetrahedral Ge atoms, and the secondary peaks in the range 2–4 Å, together with the broad shoulder in the fifth and the extended threshold in the sixth, indicate a distorted octahedral coordination for these Ge atoms. Tetrahedral Ge atoms are fourfold configurations where the average deviations of the six bond angles are more than 10° from the octahedral values of 90° and 180°, and all bond lengths are below 3.0 Å [11]. The fraction of such atoms for structures (a)–(c) (49–56%) is consistent with the ratio of fourfold Ge in table 3. Our findings for Ge coordination are similar to the ‘3–4–5’ model of Jovari et al [6].

The nearest-neighbour distances of Te atoms appear to be more uniform as there are no double peaks. This is consistent with table 3, which shows threefold coordination for only 14% of Te atoms. The shoulder in the first distance graph is due to the shorter Te–Ge bond lengths, in comparison to Te–Te bonds. The fourth distance (between 3–4 Å) is notably broader than the others, which is related to the fact that it no longer represents real chemical bonds. These intermediate neighbour distances (fourth and beyond) often span voids (cavities), which are abundant and predominantly surrounded by Te atoms.

4.4. Medium range order, rings

The low coordination number of chalcogen atoms means that medium range order (MRO) is prevalent in amorphous chalcogenide materials, many of which show a prepeak (or first sharp diffraction peak, FSDP) at a scattering vector $Q$ of $\sim 1$ Å⁻¹. This corresponds to a distance of order $2\pi/|Q|$ $\sim 6$ Å and indicates structural rearrangements of medium range [30]. We have noted above that the FSDP is apparent only in the ND structure factor, which is strong evidence that Ge atoms play the dominant role. The partial structure
factors $S_{ij}(Q)$ are given in the supplementary data (available at stacks.iop.org/JPhysCM/24/015802/mmedia), and show indeed pronounced peaks at low $Q$ for Ge–Te (near 1.1 Å$^{-1}$) and Ge–Ge (near 1.0 Å$^{-1}$).

The medium range order is also apparent in the distribution of irreducible rings (closed loops) in the bond network, using a bond cutoff distance of 3.2 Å. The ring statistics of the structures (figure 8) differ somewhat: (a) and (c) have maxima at five-membered rings, and structure (b) has more fourfold rings. Threefold rings are rare in all cases, as indicated by the small weight near bond angle 60°. There are numerous larger rings, even some with 18 or more atoms. This is related to the porous nature of the sample, and the presence of cavities allows large encircling rings [31, 32].

AB alternation (A: Ge; B: Te) is familiar from GeTe (50:50) and Ge$_2$Sb$_2$Te$_5$ [11, 13, 24–26], and ‘ABAB squares’ are essential features of the amorphous structure of Ge$_x$Te$_{1-x}$ alloys [13, 24]. In Ge$_{15}$Te$_{85}$, ABAB rings are less common in structures (a) and (b) than in structure (c), while DF-opt has the most (table 4). The last two structures also include homopolar Ge–Ge bonds, but this does not reduce the number of ABAB rings. The numbers of Ge and Te atoms in ABAB rings are the same, so that the Te percentages in table 4 are always $15/85 \sim 0.18$ times that of Ge.

Figure 9 shows the underlying structural motifs of DF-opt, where the atoms have been coloured according to

![Figure 8. Ring size statistics of structures (a)–(c).](image)

![Figure 9. DF-opt sample: (a) overview, (b)–(c) Te atoms not bonded to Ge (Te(II) and Te(III)) from front and right, (d)–(e) Ge and bonded Te atoms (Te(I)) from front and right, and (f) the largest cluster of ABAB rings. Red (thick): Ge atoms in ABAB rings; magenta: other Ge; yellow: Te(I); white: Te(II); blue: Te(III). Te(I)–Te(III) are defined in table 4.](image)

| Table 4. Distribution of types of Te(I–III) and percentages of Ge and Te in ABAB rings. Te(I) is directly bonded to germanium, Te(II) is not directly bonded to germanium but is bonded to Te(I), and Te(III) denotes all other configurations. |
|-----------------|-------|-------|-------|
|                 | (a)   | (b)   | (c)   | DF-opt |
| Te(I)           | 48    | 49    | 47    | 47     |
| Te(II)          | 26    | 26    | 25    | 27     |
| Te(III)         | 26    | 25    | 27    | 26     |
| Ge (ABAB)       | 15    | 14    | 20    | 27     |
| Te (ABAB)       | 3     | 3     | 4     | 5      |

7 The supplementary data contain plots of partial structure factors and a table of effective charges calculated for structures (a), (b), (c), and DF-opt.
Figure 10. Cavities in structure (c): (a) overview with cavity centres, (b) top face, (c) front face and (d) right face of the unit cell. Red: Ge; yellow: Te; cyan isosurfaces: cavities; magenta: cavity centres in (a).

type as well as element (table 4). The sample (figure 9(a)) shows Te-rich (Te(II) and Te(III)) and GeTe domains (figures 9(b)–(e)). Comparison of the Te(II)–Te(III) network (panels (b)–(c)) with the Ge tetrahedra network (panels (d)–(e)) shows that there are regions comprising mainly one of these structure types. This results in an increased Ge concentration (‘enrichment’) and the formation of Ge tetrahedra and ABAB rings with Te(I). These rings often fuse to form clusters (figure 9(f)) and contain both (defective) octahedral and tetrahedral Ge. Evidence of such clustering has been found in the analysis of ND data of liquid Ge_{15}Te_{85} [33]. Clustering results in Te networks (domains) outside GeTe units, and examples can be seen on the left sides of panels (b)–(e). Ge atoms, and particularly ABAB rings, are more pronounced on the right sides of these panels. Overall, there are no large Ge-free domains, but Te(II) and Te(III) form threads that entangle with the GeTe network [13].

4.5. Cavities

Figure 10 shows cavities in structure (c) from several perspectives. Empty space (‘free volume’) has been analysed by generating a 3D mesh with 0.1 Å grid spacing inside the unit cell and using test spheres of radius 2.8 Å [13, 24] within this mesh. Points farther than 2.8 Å from any atom form ‘cavity domains’, from which cavities are constructed in the spirit of atomic Wigner–Seitz cells in crystals or Voronoi polyhedra in amorphous structures. The large total volume of cavities (22–24% in structures (a)–(c), 21.5% for DF-opt) emphasizes the low overall coordination. The cavities in figure 10 display various shapes and sizes, and multivacancies are common. We found a pronounced $T$-dependence of the cavity volume distributions in earlier work on liquid Ge_{15}Te_{85} and Te [13, 31].

4.6. Electronic structure

Figure 11 shows the electronic density of states (DOS) of DF-opt and the RMC-refined structure (c) (top panel). The DOS profiles are similar and show clear separations between the two s-bands and a p-band (see the projections in the bottom panel), particularly the gap at $-6$ eV between the upper s-band and the valence p-band. Unless constrained by bond angles and the need to reproduce features of DF calculations [11], RMC-based structures generally have broader bands and ‘metallic’ DOS for known semiconductors. Structure (c) has a distinct minimum at the Fermi energy $\epsilon_F$, but the band gap is very small (<0.1 eV), and there are several states nearby. The same applies to structure (a) and to DF-opt (the basis of models (a) and (c)), which shows a small peak in the middle of the 0.35 eV band gap with two ‘impurity states’. We note that standard DF exchange–correlation functionals,
including PBE, severely underestimate band gaps for solids. The appearance of impurity states in DF-opt may result from the details of the simulation, and other simulations with different initial and cooling conditions may lead to clearly defined band gaps. This view is supported by structure (b), which is independent of the other structure models and has a band gap of $\sim 0.1$ eV.

The degree of localization of a single-particle Kohn–Sham eigenfunction $\psi(r)$ can be measured by the inverse participation ratio

$$\text{IPR} = \frac{\int \! |\psi(r)|^4 \, dr}{\left(\int \! |\psi(r)|^2 \, dr\right)^2}. \quad (3)$$

A small value corresponds to a delocalized function, and a large value indicates localization around specific (covalent) bond(s) [34]. We have calculated the IPRs in figure 11 (lower panel) from the projections of $\psi(r)$ onto an atomic basis set (see bond orders below), and used the atomic orbital coefficients in the integral. The results emphasize the localized nature of the functions near the region of Te 5s character (between $-13$ and $-9$ eV), and particularly in the band of Ge 4s character around $-8$ eV. The states in the valence p-band are considerably less localized (note the logarithmic scale), and the states near $\epsilon_F$, especially the impurity states, are more localized than the states below or above the band gap. Figure 12 shows ‘impurity states’ in DF-opt structure (c) (lowest unoccupied molecular orbital, LUMO, and the next highest LUMO+1) and the neighbouring highest occupied molecular orbital (HOMO) and LUMO + 2 at the valence and conduction band edges. These states are localized in isolated parts of the unit cell and are not clearly related to particular structural units.

4.7. Charges

One can also compare $N_{\text{c}}$ (the valence) with the effective charges (Bader, Voronoi, and Mulliken prescriptions (see footnote 7)) by subtracting the values from the nominal valence of each element (Ge: 4; Te: 2). The resulting values (Ge: +0.5; Te: −0.1) are close to those evaluated with the Bader method from the electron density [35].

5. Conclusions

We have studied the structure and electronic properties of amorphous Ge$_{15}$Te$_{85}$ by combining DF simulations with high-energy XRD and neutron scattering measurements. Three models with 560 atoms have been constructed: (a) structure based on DF simulations and RMC refinement without Ge–Ge bonds (DF–RMC), (b) RMC-generated geometry with DF relaxation (+ RMC refinement) and no Ge–Ge bonds, and (c) DF–RMC structure with a small number of Ge–Ge bonds, as in the melt-quenched parent structure. Since RMC tends to produce the most disordered structure that is consistent with the experimental data, we have used either an annealed/melt-quenched sample (structures (a) and (c)) or a DF-optimized configuration (structure (b)) as starting points for RMC refinement. The energy is constrained to be within $\sim 100$ meV/atom of that of DF-opt [11]. Bond angle constraints are essential to limit band broadening and prevent a metallic electronic structure with no band gap. All structures considered here have small band gaps at the Fermi energy, which is consistent with the DF-optimized structure (figure 11). We emphasize again that we seek a balanced description of the electronic structure and the scattering data. Focus on the latter to the exclusion of the electronic properties would probably lead to a different structure with higher energy.

Structure (c) satisfies our criteria best: $S(Q)$ is reproduced well for both XRD and ND, the total energy of DF-opt (on which it is based) is lower by 10 meV/atom than that of the ‘ideal’ base structure (b) (effect of gradual cooling), and the electronic structure shows a small (semiconducting) band gap at the Fermi energy. A small number of Ge–Ge bonds should be allowed.

The structure of amorphous Ge$_{15}$Te$_{85}$ can be characterized by its short and medium range order. The picture is very similar to that found in an earlier study with a 216-atom sample [13], while improving greatly the agreement between theory and experiment. Although the Ge concentration is small for the 15:85 composition, it affects the properties of...
Te significantly. Approximately half of the Te atoms are in contact with Ge (type I) and form a GeTe network throughout the sample (figure 9) [13]. This network is interlocked with Te domains (types II and III) that form a similar network and cannot grow locally. Due to the high Te content, the concentration of cavities (22–24% of the total volume) is high [31].

The GeTe network itself comprises ABAB squares, which are the basic structural units of amorphous GeTe and combine occasionally to form ABAB clusters [24, 36]. Tetrahedral fourfold and defective octahedral (3 + 3) coordinations coexist in Ge, as found previously in GeTe and Ge2Sb2Te5 [24–26, 34], and occur with equal likelihood. The calculated bond orders (figure 6) show that the two types of Ge coordination bind differently, and the bond strengths vary as a function of distance. The Ge–Te and Te–Te bonds are nearly covalent, and a reasonable cutoff distance for counting bonds is around 3.0–3.2 Å for this class of chalcogenide materials.

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References

[16] Landolt-Börnstein 2000 New Series I/16A ed H Schopper (Berlin: Springer) chapter 6
Supplementary information for:

**Amorphous Ge$_{15}$Te$_{85}$: Density functional, high-energy x-ray and neutron diffraction study**

J Kalikka$^1$, J Akola$^{1,2,3}$, R O Jones$^{3,4}$, S Kohara$^5$ and T Usuki$^6$

$^1$ Nanoscience Center, Department of Physics, University of Jyväskylä, P.O. Box 35, FI-40014 University of Jyväskylä, Finland
$^2$ Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland
$^3$ Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
$^4$ German Research School for Simulation Sciences, FZ Jülich and RWTH Aachen University, D-52425 Jülich, Germany
$^5$ Research & Utilization Division, JASRI/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan
$^6$ Graduate School of Science and Engineering, Yamagata University, 1-4-12 Kojirakawa, Yamagata, 990-8560, Japan

**PARTIAL STRUCTURE FACTORS**

The partial structure factors $S_{ij}(Q)$ can be calculated by Fourier transform from the partial pair distribution functions $g_{ij}(r)$:

$$S_{ij}(Q) = 1 + \frac{4\pi \rho}{Q} \int_0^\infty dr \ r \sin(Qr) \ g_{ij}(r),$$  \hspace{1cm} (1)

where $\rho$ is the number density of the sample. In Figure 1 we show $S_{ij}(Q)$ for the pairs Ge-Ge, Ge-Te, and Te-Te. The contribution of Te-Te correlations to the prepeak is weak.
BADER, VORONOI, AND MULLIKEN CHARGES

Table I shows the average partial charges of the elements calculated with the Bader, Voronoi, and Mulliken prescriptions [1]. Bader and Voronoi charges have been evaluated from the electron density (and its gradient) within an atomic volume, and the Mulliken charges from the overlap of projected atomic orbitals. The Bader charges indicate positively charged Ge, Voronoi values are negative, and the Mulliken analysis gives very small values for both elements. The discrepancy between Bader and Voronoi can be explained by the larger atomic volume in the latter. The Bader atom is bounded by the surface where the gradient of the electron density changes its sign, whereas the Voronoi cell is defined in purely geometrical terms by planes normal to the bonds and passing through their midpoints. The integrated charge for the corresponding Ge atom is smaller in the Bader analysis, and there is a net positive charge. The difference between the electronegativities also suggests that Te should attract charge when bonding to Ge.

FIG. 1: Partial structure factors $S_{ij}(Q)$ for structure (c): Red: Ge-Ge, blue: Ge-Te, black: Te-Te.
TABLE I: Calculated Bader, Voronoi, and Mulliken charges for structures (a), (b), and (c), and for DF-opt.

<table>
<thead>
<tr>
<th>Structure/element</th>
<th>Bader</th>
<th>Voronoi</th>
<th>Mulliken</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ge</td>
<td>0.56 ± 0.11</td>
<td>−0.26 ± 0.08</td>
<td>−0.00 ± 0.06</td>
</tr>
<tr>
<td>(b) Ge</td>
<td>0.53 ± 0.10</td>
<td>−0.27 ± 0.09</td>
<td>−0.01 ± 0.06</td>
</tr>
<tr>
<td>(c) Ge</td>
<td>0.54 ± 0.11</td>
<td>−0.27 ± 0.09</td>
<td>−0.01 ± 0.05</td>
</tr>
<tr>
<td>DF-opt. Ge</td>
<td>0.51 ± 0.10</td>
<td>−0.20 ± 0.08</td>
<td>0.04 ± 0.03</td>
</tr>
<tr>
<td>DF-opt. 3-coord. Ge</td>
<td>0.48 ± 0.10</td>
<td>−0.17 ± 0.08</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td>DF-opt. 4-coord. Ge</td>
<td>0.53 ± 0.09</td>
<td>−0.23 ± 0.07</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>(a) Te</td>
<td>−0.10 ± 0.19</td>
<td>0.05 ± 0.13</td>
<td>0.00 ± 0.09</td>
</tr>
<tr>
<td>(b) Te</td>
<td>−0.09 ± 0.20</td>
<td>0.05 ± 0.14</td>
<td>0.00 ± 0.09</td>
</tr>
<tr>
<td>(c) Te</td>
<td>−0.10 ± 0.20</td>
<td>0.05 ± 0.13</td>
<td>0.00 ± 0.09</td>
</tr>
<tr>
<td>DF-opt. Te</td>
<td>−0.09 ± 0.18</td>
<td>0.04 ± 0.11</td>
<td>−0.01 ± 0.07</td>
</tr>
</tbody>
</table>