Microscopic structure and dynamics of molten $\text{Se}_{50}\text{Te}_{50}$ alloys

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In this work we investigate the microscopic structure and dynamics of the molten equimolar alloy, $\text{Se}_{50}\text{Te}_{50}$ using a combination of neutron and x-ray diffraction experiments, reverse Monte Carlo analysis, and first principles molecular dynamics. The range of temperatures studied covers the semiconductor/metal transition. From our results it can be seen that the latter is associated with an increase in coordination numbers and a reduced tendency to heterocoordination. In agreement with previous inelastic neutron scattering experiments, our molecular dynamics calculation predict a certain widening of the stretching vibrational modes band in connection with the increase of coordination and the presence of longer bonds in the metallic phase. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790899]

I. INTRODUCTION

SeTe alloys have interesting electronic properties they share with elemental Se. In particular, the fact that increasing temperature induces a semiconductor/metal transition has motivated numerous experimental and theoretical investigations.^{1–6} In the case of alloys, this transition can also be tuned by changes in the composition, a feature that makes this system even more attractive from the technological point of view. However, despite the growing number of works concerned with the properties of elemental Se and Te, relatively few investigations have focused on the behavior of SeTe alloys. Some 20 years ago, Bellisent published a rather complete neutron diffraction study⁷ (in which, however, the different components of the structure factor could not be extracted) and some data for inelastic neutron scattering of SeTe glasses⁸ have only very recently been complemented by more detailed studies of the dynamic structure factor of equimolar SeTe .^{5,6} Additionally, Tsuchiya⁹ presented a study of the thermodynamics of isostructural transitions in liquid SeTe alloys from a careful determination of sound velocities and isothermal compressibilities. Some *ab initio* computer simulation results have also been recently published by

Lomba *et al.*¹⁰ focusing on the compositional dependence of the microscopic structure and dynamics.

In the solid phases, various Mössbauer spectroscopy analyses give contradictory results as to where the structure of the equimolar alloy $\text{Se}_{50}\text{Te}_{50}$ should be formed by alternating chains of Se–Te atoms,¹¹ or should present compositional disorder.¹² A recent study based on electron energy loss spectroscopy¹³ seems to rule out the presence of compositionally ordered chains in the trigonal structure of solid $\text{Se}_{50}\text{Te}_{50}$.

It is the main purpose of this work to complement the available experimental and computer simulation results for the molten equimolar alloy $\text{Se}_{50}\text{Te}_{50}$. To that aim, we have performed a series of neutron and x-ray diffraction (XRD) experiments, extracting the relevant structural information by means of a reverse Monte Carlo (RMC) analysis.¹⁴ Additionally, we have carried out extensive *ab initio* molecular dynamics (MD) calculations which yield both structural and dynamic informations. The latter has been checked against the inelastic neutron scattering results of Chiba *et al.*⁶

The rest of the paper is sketched as follows. In the next section we summarize the experimental details. Section III is devoted to a brief account of the RMC method as applied here. Technical details of the *ab initio* simulation and the key formulae for the analysis of the results are contained in Sec.

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FIG. 1. (Color online) Liquid $\text{Se}_{50}\text{Te}_{50}$ structure factors (top) and differential cross sections (bottom) as obtained from neutron diffraction and x-ray diffraction experiments in this work.

IV. Our most significant results and conclusions are to be found in Sec. V.

II. EXPERIMENT

Selenium-tellurium alloys were prepared by melting 99.9999% pure elemental Se and Te enclosed in vacuum-sealed quartz tubes with a length of 15 cm and a diameter of 11 mm. The samples were heated for 24 h at 773 K. Neutron diffraction was performed with the GEM diffractometer at ISIS.¹⁵ The sample was contained in a sealed cylindrical quartz tube with an outer diameter of 10 mm and wall thickness of 1 mm. The quartz tube was held by a thin vanadium tube in a furnace and measurements were performed at 700, 900, and 1100 K. This corresponds to the same points in the phase diagram measured by inelastic neutron scattering by Chiba *et al.*⁶ Background was subtracted and the data were normalized to a vanadium measurement. Corrections for absorption, extinction, and multiple scattering were performed with the GUDRUN package available at ISIS. Finally, corrected data from the different detector banks were merged to give the structure factors seen in Fig. 1.

Synchrotron x-ray diffraction measurements at different temperatures were performed at the beam line 11-ID-C (Advanced Photon Source, Argonne National Laboratory) using synchrotron radiation of energy of 115.596 keV ($\lambda = 0.10726$ Å). The sample was loaded in a quartz capillary and sealed in helium gas environment. An electric furnace

was used to heat the sample to high temperature. A two-dimensional image plate detector (MAR345) was used to collect data over a wide Q range ($1\text{--}30$ Å⁻¹). Up to ten images were taken on the sample at $T=700$ K and $T=900$ K. X-ray diffraction data of an empty capillary were also collected at the same experimental condition for background corrections. The corresponding images/scans were combined, subjected to geometrical corrections, integrated, reduced to one-dimensional XRD patterns using the program FIT2D, which were further converted into absolute (electron) units, and reduced to the so-called structure functions using the program PDFGETX2.¹⁶ Data were successfully collected up to 900 K. But attempts to collect data at 1100 K failed because the sample seemed to react with the quartz capillary wall above 950 K. Also, the sample moved in the capillary making the control of the temperature difficult.

To get reliable x-ray measurements of the high temperature metallic phase, another set of experiments was performed at the wiggler beam line BW5 at HASYLAB in Hamburg, Germany. The energy of the monochromatic beam was 100 keV ($\lambda = 0.124$ Å⁻¹). The samples were contained within sealed quartz-glass capillaries with an inner diameter of 2 mm and a 0.02 mm wall thickness. The furnace is a self-made vacuum resistance heater, giving place for two samples. Both the heat shielding and the furnace chamber were equipped with Be windows to avoid background contributions. We performed two complete scans on each sample. The scattering angle reached from 1° to 17° (giving $Q_{\text{max}} = 15$ Å⁻¹). We divided the range into two parts, $1^\circ\text{--}10^\circ$ and $9^\circ\text{--}17^\circ$. The former was measured with an angle step of 0.02° , for 2 s at each point, with a Fe absorber applied in the primary beam, the latter with an angle step of 0.04° , for 4 s, and no absorber. Both scans were averaged, and the absorption of the attenuator was corrected making use of the overlap region, correction for geometry, and polarization.

With this setup, we managed to do the 1100 K measurement but in a smaller Q range (useful between 0.9 and 13 Å⁻¹). There are still some small features in $S(Q)$ at this high temperature which are probably due to some reactions with the tube. The two lower temperatures were also measured at HASYLAB and agree well with the measurements obtained at APS. In the following analysis, we have used data from APS for 700 and 900 K and data from HASYLAB for 1100 K. All x-ray structure factors can be seen in Fig. 1.

III. RMC MODELING

To extract the three partial structure factors for the SeTe system, we need three measurements; each measurement weighted with different scattering factors for Se and Te. Isotope substitution of atoms with different scattering length for neutrons is the most obvious way to do this.¹⁷ In our case, however, there are no available isotopes of Se or Te for such measurement. Instead, we are using a combination of neutron and x-ray diffraction measurements. According to Faber and Ziman¹⁸ the total neutron structure factor $S(Q)$ is a sum of the partial structure factors $S_{ij}(Q)$ weighted by the constant scattering length b and concentration c of each component,

TABLE I. Number density and distances of closest approach used in RMC simulations.

Temperature (K)	700	900	1100
Box side (Å)	71.806	72.091	71.446
Density (atoms/Å ³)	0.0270	0.0267	0.0274
	Se-Se	Se-Te	Te-Te
Min. separation	2.1	2.3	2.5

$$S(Q) = \frac{1}{\langle b \rangle^2} \sum_{i,j} c_i c_j b_i b_j S_{ij}(Q), \quad (1)$$

while the total x-ray structure factor contains Q -dependent form factors $f_i(Q)$ as

$$F(Q) = \frac{1}{\langle f(Q) \rangle^2} \sum_{i,j} c_i c_j f_i(Q) f_j(Q) S_{ij}(Q). \quad (2)$$

The simultaneous fit of neutron and x-ray structure factors by RMC (Ref. 14) has been successfully used to separate partial structure factors in binary alloys even when there are only two measurements available.¹⁹ In RMC, we can add constraints such as shortest distance between atoms and others, that we know in advance, should be able to make up for some of the lacking information when only two measurements are available. The final three-dimensional structure also corresponds to a topological structure that is consistent with the measured data and imposed constraints.

The configurations used for the RMC simulations consisted of 10 000 atoms randomly placed in a box and then separated to a minimum distance between the atoms, as given in Table I. A configuration was produced by first fitting to the partial pair correlation functions obtained from *ab initio* MD for this system. These configurations were then used as start configurations to RMC. This leads to very good fit to the experimental data. We have checked that the final results are independent on the initial guess configuration using various sets of particle coordinates generated by MD runs at different temperatures. Once the RMC cycles have converged, no discrepancies were found in the fits using different initial guesses, within statistical error.

As can be seen from Fig. 1, both the neutron and the x-ray differential cross sections (DCS) are relatively similar, this is probably the reason why a full separation of the partial functions was not possible using a totally random configuration as initial guess in the RMC procedure. In the upper part of Fig. 1 one can see the corresponding experimental structure factors that have been used as input for the RMC procedure. The resulting RMC structure factors are practically identical and are, thus, not represented in Fig. 1.

IV. SIMULATION DETAILS

As in Ref. 10, the *ab initio* molecular dynamics calculations in this work have been carried out using the Vienna *ab initio* simulation package (VASP).²⁰ We used ultrasoft Vanderbilt type pseudopotentials,²¹ as supplied by Kresse and Hafner.²² The density functional theory (DFT) calculations have been performed in the generalized gradient approximation using the PW91 exchange functional of Perdew and

Wang²³ with a Γ -point sampling and an energy cutoff of 150 eV.

Once the *ab initio* forces are evaluated, ionic positions are displaced according to the solution of the equations of motion, appropriately modified so as to keep a constant temperature using a Nosé-Hoover thermostat. This procedure is repeated using a time step of 5 fs. As a whole, we performed an equilibration run of 5 ps followed by a production run of 15 ps using samples of 256 particles.

The static structure factor is calculated by means of direct Fourier transformation of the partial pair distribution functions, $g_{\alpha\beta}(r)$, and by direct sampling. Since the sample is sufficiently large, the Fourier transformation of the $g_{\alpha\beta}$ yields reliable estimates even at relatively low Q vectors fully compatible with the direct sampling estimates, but is better behaved at medium and large Q vectors. In order to make a proper comparison with neutron scattering data, an average $g(r)$ is obtained from the partial distribution functions $g_{\alpha\beta}(r)$ weighted with the atomic neutron scattering lengths,

$$g(r) = \frac{1}{\langle b \rangle^2} (x^2 b_{\text{Se}}^2 g_{\text{SeSe}}(r) + (1-x)^2 b_{\text{Te}}^2 g_{\text{TeTe}}(r) + 2x(1-x)b_{\text{Se}}b_{\text{Te}}g_{\text{SeTe}}(r)), \quad (3)$$

with $\langle b \rangle = xb_{\text{Se}} + (1-x)b_{\text{Te}}$ x being the fraction of Se atoms, and the scattering lengths $b_{\text{Se}} = 0.797 \times 10^{-14}$ m and $b_{\text{Te}} = 0.58 \times 10^{-14}$ m. Fourier transformation of $h(r) = g(r) - 1$ from Eq. (3) leads to the Faber-Ziman structure factor,

$$S(Q) = 1 + \rho \tilde{h}(Q), \quad (4)$$

with $\tilde{h}(Q)$ determined from the Fourier transform of Eq. (3). Here, ρ is the total number density and the tilde denotes a Fourier transform. This is consistent with the definition of Eq. (1).

As to the dynamic quantities, the intermediate scattering function reads

$$F(\mathbf{Q}, t) = \frac{1}{N \langle b^2 \rangle} \left\langle \sum_{i,j} b_i b_j \exp[\mathbf{Q}(\mathbf{r}_i(t) - \mathbf{r}_j(0))] \right\rangle. \quad (5)$$

The temporal Fourier transform of Eq. (5) yields the dynamic structure factor,

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\omega t) F(\mathbf{Q}, t) dt. \quad (6)$$

with ω being the angular frequency. The dynamic structure factor can also be expressed in terms of frequency $\nu = \omega/2\pi$ or energy $E = h\omega/2\pi$ (h being Planck's constant). Following Chai *et al.*,²⁴ we calculate

$$S(\mathbf{Q}, \omega, t_1, t_2) = \frac{1}{\pi} \int_{t_1}^{t_2} \exp(i\omega t) F(\mathbf{Q}, t) dt, \quad (7)$$

for a sufficiently long t_2 so that

$$S(\mathbf{Q}, \omega, t_1) \approx S(\mathbf{Q}, \omega, t_1, t_2),$$

and then average over a correspondingly large number of time origins, N_{t_1} , to obtain

$$S(\mathbf{Q}, \omega) = \frac{1}{N_{t_1}} \sum_{t_1} S(\mathbf{Q}, \omega, t_1).$$

As in Ref. 10, we have set $t_2 = 15$ ps and averaged over 1000 time origins that span a time interval of 5 ps. The $\mathbf{Q}$ vector orientation has been sampled for a given $Q = |\mathbf{Q}|$, choosing a random orientation among those compatible with the periodic boundary conditions, i.e., $\mathbf{Q} = (n_1, n_2, n_3)2\pi/L$ (n_i being integer and L the side of the cubic simulation box) for each configuration. Then, an experimental resolution function is incorporated into the final dynamic structure factor,²⁴ such that

$$S(Q, \omega) = \int_{-\infty}^{\infty} R(\omega - \omega') S_{\text{raw}}(Q, \omega') d\omega', \quad (8)$$

where $S_{\text{raw}}(Q, \omega)$ represents the raw data as obtained from the sampling and averaging procedure. The resolution function is

$$R(\omega) = \frac{1}{\sqrt{\pi}\omega_0} \exp(-\omega^2/\omega_0^2), \quad (9)$$

and ω_0 is the experimental width of the resolution function, which we have set to 2.5 meV as in Ref. 24. Once this is done, we can get additional information on the vibrational properties of the sample^{6,10,24} using the relation between the longitudinal current correlation function $J_l(Q, \omega)$, which is related to the dynamic structure factor by²⁵

$$J_l(Q, \omega) = \frac{\omega^2}{Q^2} S(Q, \omega). \quad (10)$$

Information on the vibrational structure (and other collective excitations) can also be accessed via the velocity self-correlation function,

$$C(t) = \frac{1}{3N} \left\langle \sum_{i=1}^N \frac{\mathbf{v}_i(t) \mathbf{v}_i(0)}{v_i(0)^2} \right\rangle, \quad (11)$$

whose Fourier transform gives the frequency spectrum $Z(\omega)$. Additionally, the self-diffusion constant D is given by

$$D = \frac{k_B T}{M} Z(0), \quad (12)$$

where k_B is Boltzmann's constant and M is the particle mass. This quantity can also be obtained from Einstein's relation, which correlates the time dependent mean square displacement with the diffusion via

$$\langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle \rightarrow 6Dt + \text{constant} \quad (13)$$

in the long time limit.

V. RESULTS

In what follows, we summarize the key results of our experiments and *ab initio* simulations. The latter have been performed for the temperature and number densities indicated in Table I. These correspond to values interpolated from the experimental measures of Thurn and Ruska.²⁶

A. Microscopic structure

We will first focus on the pair structure of our equimolar molten alloy. A comparison of the structure factors obtained from x-ray and neutron diffraction measurements and those of *ab initio* simulation is presented in the upper part of Fig. 1. We see that both neutron scattering and x-ray structure factors exhibit the same qualitative temperature dependence. Actually, as mentioned before, they are quite similar which represents a handicap for a good partial structure factor separation using RMC simulation. Also, the MD estimates for $S(Q)$ agree qualitatively with the experimental results. There is some shift in the phase of long wave vector oscillations due to errors in the *ab initio* estimation of the equilibrium nearest neighbor distance, i.e., in the location of the first $g(r)$ maximum, a well known limitation of the DFT calculation when dealing with Te atoms.^{27,28} Despite this, we see that the temperature dependence of the height and location of the first and second maxima of $S(Q)$ is the same both in MD and in the experimental data. From Fig. 1, it is apparent that the MD somewhat underestimates the height of the second maxima. The analysis of the partial pair distribution functions below will point to a likely source for this discrepancy. The peculiar low Q behavior of the neutron data for the 900 K sample is most likely due to some errors in the experimental setup.

As mentioned before, the structure factors derived from the RMC modeling are practically indistinguishable from their experimental counterparts. The corresponding partial pair distribution functions are depicted in Fig. 2 together with the MD estimates. The location of maxima is well reproduced by the simulation results. As to the height of the maxima in the first coordination shell, MD data are in good agreement for SeSe and SeTe (except for the latter at 700 K), but there are substantial discrepancies as to the TeTe correlation, its maxima being clearly overestimated. This can be explained by the well documented failure of DFT treatments to properly account for bonding in solid and liquid tellurium.^{27,28} Additionally, these inaccuracies in the first TeTe coordination shell are likely to be responsible for the systematic underestimation of the second maximum of the total structure factor seen in Fig. 1. The other significant discrepancy is found in the height of the first maximum of g_{SeTe} at 700 K, which is much lower in the RMC results. This indicates that the strength of SeTe bonding (and hence the tendency to heterocoordination) is overestimated by the *ab initio* calculation. Below, we will see how this reflects in the coordination numbers as predicted by RMC and MD. Concerning the temperature dependence of the distribution functions, from Fig. 2, one sees that, except for the MD g_{SeTe} , the pair correlations are not too sensitive to changes in T . Aside from the decrease of the first maximum of g_{SeTe} when T rises, the only effect that can be appreciated is that the position of the first peak of the simulated g_{TeTe} is shifted from 2.8 Å at 700 K to 2.92 Å at 1100 K. In the case of the RMC results, the changes with temperature are less apparent (the shift in the first peak position of g_{TeTe} is from 2.8 Å at 700 K to 2.85 Å at 1100 K.).

If we turn now our attention to three particle correla-

FIG. 2. (Color online) Partial pair distribution functions for $\text{Se}_{50}\text{Te}_{50}$ at various temperatures, as calculated from *ab initio* MD (curves) and RMC fitting of the experimental structure factors.

tions, in Fig. 3, we have the most relevant bond angle distributions. At first sight we can say that the agreement between RMC and MD results is acceptable. Both techniques predict similar values for the principal maxima of the distribution, namely, 100° for g_{SeSeSe} and 98° for g_{TeSeTe} , and 94° and 95° for g_{TeTeTe} and g_{SeTeSe} , respectively. This indicates that the bond angles for Se atoms remain close to 100° and those of Te atoms close to 94° . This latter value is somewhat smaller than that the estimated experimental value in molten elemental Te ($\approx 100^\circ$, close to the value in the solid which is known to be preserved upon melting²⁹). As to the bond angle $X\text{Se}Y$ whose distribution peaks around 100° , is somewhat lower than the experimental and *ab initio* values³⁰ found in molten Se ($\approx 110^\circ$). It seems that the accurate *ab initio* description of Se atoms somewhat compensates the deficiencies in the treatment of Te atoms (note that the stability of the cubic structure is overestimated²⁸ in the DFT for Te and this tends to favor bond angles close to 90°) as found in Ref. 29.

As it was the case for the pair structure, the temperature dependence of the RMC bond angle distributions is very weak, whereas in the case of the *ab initio* results, all those functions that involve Se atoms (and very especially those in which there is direct SeTe bonding) have a much larger dependence. In the latter case, obviously, the heights of the

FIG. 3. (Color online) Bond angle distribution functions for $\text{Se}_{50}\text{Te}_{50}$ at various temperatures as calculated from *ab initio* MD (curves) and RMC fitting of the experimental structure factors.

bond angle distributions increase with decreasing temperature. Aside from this difference, in general, the RMC distributions are substantially more spread than their *ab initio* counterparts. This is likely a consequence of the tendency of the RMC method to lead to configurations with an excess of entropy (disorder).

In Fig. 4, we have plotted the global distribution of coordination numbers as obtained from the RMC and MD calculations, using as global cutoff distance of $3.2 \text{ \AA}$, which corresponds to the minimum of the TeTe pair distribution function. As a general trend, we observe that threefold and twofold coordination are dominant (in all cases, more than 75% of the atoms are either twofold or threefold coordinated). The MD somewhat overestimates the ratio of twofold coordinated atoms but, in any case, the agreement between MD and RMC is more than acceptable. Both techniques yield the same temperature dependence of the coordination numbers, namely, as temperature increases, twofold coordination decreases and the number of single, three, and fourfold coordinated atoms augments. This points to a destruction of the chains remnant from the solid trigonal structure. We can get a more precise picture analyzing the distributions of partial coordination numbers, which are plotted in Figs. 5 and 6 for RMC and MD configurations, respectively. The

FIG. 4. (Color online) Average distribution of coordination numbers evaluated from MD (striped bars) and RMC (shaded bars) configurations for $\text{Se}_{50}\text{Te}_{50}$ at various temperatures.

changes in this partial coordination numbers with temperature are less apparent than those of the global coordination, but one can see, for instance, that the percentage of Se atoms surrounded by two Te atoms and the percentage of Se an Te

FIG. 5. (Color online) Average of the partial distribution of coordination numbers evaluated from RMC configurations for $\text{Se}_{50}\text{Te}_{50}$ at various temperatures. $\%(X)Y$ denotes the percentage of atoms of type X surrounded by N_c atoms of type Y .

FIG. 6. (Color online) Same as Fig. 5 computed from MD configurations.

atoms with no other Se or Te atom around (i.e., heterocoordinated) decreases. The increase in the global coordination number is parallel to a decrease in the tendency to heterocoordination. This implies that the increase in entropy compensates the fact that the SeTe bonds are energetically favored with respect to SeSe and TeTe bonds.^{11,13} This trends are summarized in Table II in which the partial averaged coordination numbers are collected. Here, one can also appreciate that, as temperature rises, the global coordination number increases slightly whereas the tendency to heterocoordination diminishes. These effects are enhanced in the *ab initio* results.

B. Electronic structure and dynamics

The thermodynamic states studied in this paper span the semiconductor/metal transition.⁵ Thus, the 700 K sample is a semiconductor and, at 1100 K, the alloy becomes metallic.

TABLE II. Coordination numbers calculated from the pair distribution functions from MD and RMC. The atom in parenthesis is the atom of reference.

T (K)	$N_{(\text{Se})\text{Se}}$		$N_{(\text{Se})\text{Te}}$		$N_{(\text{Te})\text{Te}}$	
	MD	RMC	MC	RMC	MC	RMC
700	0.6	0.8	1.6	1.3	1.1	1.1
900	0.8	0.8	1.5	1.2	1.4	1.3
1100	0.8	0.8	1.5	1.2	1.6	1.3

FIG. 7. (Color online) Temperature dependence of the electronic density of states (DOS) of molten $\text{Se}_{50}\text{Te}_{50}$. The increase in conductivity is correlated with a larger DoS at the Fermi energy (≈ 2.1 meV).

The fact that our *ab initio* model qualitatively reproduces this transition is illustrated in Fig. 7 where we have plotted the total density of electronic states (DOS). The gap in the region of -7 eV and -5 eV corresponds to the separation between the low lying s states and the p band. In the latter one can still observe the three-peaked structure typical of chalcogens, which corresponds to bonding π states, nonbonding (or lone-pair) p states, and the conduction band, formed by antibonding π^* states. The Fermi energy is located at around 2.1 eV, where at the lowest T there is a clear pseudogap which is completely closed at 1100 K. The increase in the DOS at the Fermi energy is correlated with the corresponding increase in the conductivity when going from semiconductor to metal. An explicit calculation could be carried out in the framework of the one electron approximation, which might be expected to yield reasonable values for the metallic states.³¹ This issue will be addressed in future works.

As far as the dynamics are concerned, the first property to consider is the diffusion coefficient, whose values are collected in Table III, as calculated from Einstein's relation [Eq. (13)] and the velocity autocorrelation, Eq. (12). Both Se and Te have similar diffusion constants, and the value of these substantially increases in the metallic phase. For the sake of comparison, the diffusion constant of Te at 743 K is^{32,33} $(1.5\text{--}2.6) \times 10^{-9}$ m/s², and for Se at 570 K (semiconductor regime) 0.4×10^{-9} m/s² and 5.4×10^{-9} m/s² at 1370 K, in the metallic regime.³⁴ Clearly the presence of Te atoms enhances the mobility with respect to the elemental Se, mainly by destabilization of the covalent chains responsible for the semiconducting character of molten Se. As to what extent

TABLE III. Diffusion constants (units of 10^{-9} m²) calculated from Einstein's relation (MSD) and the velocity autocorrelation function (VACF).

Temperature (K)	Se		Te	
	MSD	VACF	MSD	VACF
700	3.16(2)	3.0(2)	3.05(2)	2.1(3)
900	7.47(3)	9.3(5)	7.74(2)	7.6(3)
1100	11.20(2)	12.1(4)	10.42(1)	9.0(4)

FIG. 8. (Color online) Partial atomic contributions to the frequency spectra of molten $\text{Se}_{50}\text{Te}_{50}$ as obtained from *ab initio* MD simulations.

our calculations reproduce the experimental values for the alloy, unfortunately, to our knowledge, the only experimental diffusion coefficient available⁶ corresponds to 1100 K, namely, $D=6.1 \times 10^{-9}$ m/s² somewhat lower than our estimates. This might be connected with the fact, already commented above, that the *ab initio* calculations tends to overestimate bonding, in particular, SeTe bonds, at least when comparing RMC and MD structural results.

If we turn now to the vibrational structure, in Fig. 8, we have plotted the partial contributions to the frequency spectra calculated from the velocity autocorrelation functions. No excitations are visible beyond 30 meV. The bond stretching band in the range of 17–30 meV corresponds to excitations in which Se atoms are involved. As mentioned in Ref. 10, this band is somewhat redshifted with respect to elemental Se, since the presence of Te atoms weakens the Se–Se covalent bonds. The torsion modes are located in the range of 3–5 meV and the bending modes in the range of 10–15 meV (in elemental Te at 10 meV and in Se at 15 meV). In any case, as expected, most of the features are smeared out as temperature is increased. At the highest temperature, only the bending mode associated to Te atoms can be clearly assigned at 9 meV (somewhat redshifted due to the decrease of bonding strength). Finally, in Fig. 9, we have

FIG. 9. (Color online) Frequency spectra and apparent density of vibrational states of molten $\text{Se}_{50}\text{Te}_{50}$ as obtained from *ab initio* MD simulations and experimental data from Ref. 6. The longitudinal current correlation function has been obtained averaging the results in the Q range from 1 to $3 \text{ \AA}^{-1}$.

plotted the apparent density of vibrational states as calculated from the longitudinal current correlation function, Eq. (10), i.e., from the dynamic structure factor. The result of our calculation is compared with the experimental results of Chiba *et al.*⁶ From the figure, we observe that the locations of the vibrational excitations obtained from the dynamic structure factor and the velocity autocorrelation function are consistent. A comparison with the experimental data can only be carried out as to the temperature dependence of the stretching band, since other vibrational features are completely smeared out in the experimental results. What one can see is that, as temperature increases, the stretching band substantially broadens towards lower energies both in the experiment and in our calculations. As discussed by Chiba *et al.*,⁶ this is due to the presence of longer (weaker) bonds in the metallic phase, which is consistent with the shift in the position of the TeTe peaks commented on when discussing Fig. 2. In any case, one should note that these apparent vibrational densities of states obtained either from the Fourier transform of the velocity autocorrelation functions or from the longitudinal current correlation refer to a liquid, i.e., the collective excitations, whose density of states is depicted in Figs. 8 and 9, are not only vibrational but include also atomic diffusion.

In summary, we have presented the results of series of neutron and X-ray diffraction experiments and *ab initio* molecular dynamics calculations aimed at providing a deeper insight and better description of the dynamics and microscopic structure of molten $\text{Se}_{50}\text{Te}_{50}$. Experiment and *ab initio* MD agree reasonably well and confirm the view that the semiconductor/metal transition brought about by temperature is correlated with a subsequent increase in the coordination numbers, a lower tendency to heterocoordination, and the presence of longer (weaker) bonds in the metallic phase, which becomes apparent by the widening of the stretching band.

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