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Ab initio molecular dynamics simulations of the two-step melting of NaSn

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Ab initio density-functional molecular dynamics simulations were performed in order to study the melting behavior of the NaSn alloy. This alloy exhibits a phase transition at 756 K to a high-temperature solid showing rotational disorder, which has been described as an assembly of rapidly rotating Sn_4 tetrahedral clusters surrounded by mobile Na cations. Various simulation temperatures and volumes were considered in order to distinguish the features of both solid β-NaSn and plastic α-NaSn phases. The results show that the ability of Na cations to diffuse is strongly linked to the deformation of Sn_4 tetrahedra. In addition, the α-NaSn phase seems to be characterized by a sizable degree of structural disorder, with frequent breaking of the Sn_4 tetrahedral units. The influence of the volume of the simulation cell on the dynamical behavior of the alloy was found to be very important, with increasing disorder as the volume was reduced. Finally, strong correlations between structural and electronic properties were found, with increased disorder leading to more metallic behavior.

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I. INTRODUCTION

The NaSn equiatomic alloy shows interesting behavior on passing from the solid to the liquid phase. It has been observed[1] that the solid phase (β-NaSn) undergoes a phase transition at 757 K to a new high-temperature phase (α-NaSn). Further heating results in a second phase transition at 854 K from the high-temperature phase to the liquid. The structural features of the β-NaSn phase are unusual: the crystalline solid has a body-centered-tetragonal (bct) structure, based on tetrahedral Sn_4 units (see Fig. 1). Simple models for explaining this clustering effect go back to the 1930s. Zintl[2] proposed that because of the electronegativity difference between the alkali and the group-IV elements, one electron per Na atom is transferred to Sn, which then having five electrons is isoelectronic with P or As, that are well known to form tetrahedral P_4 (or As_4) molecules in the gas phase. *Ab initio* studies of the similar NaPb alloy involving tetrahedral Pb_4 units have shown that these alloys can be considered to a great extent as natural "cluster-assembled solids."[3]

Here our focus is on the high-temperature α phase between 757 and 854 K. Neutron-diffraction measurements by Saboungi and co-workers[4,5] indicate that this intermediate phase maintains translational order within the crystal structure to a high degree, together with some orientational disorder. These authors proposed a microscopic model in which Na atoms diffuse through the bct arrangement of rotating Sn_4 tetrahedra, the rotational motion of the Sn_4 being strongly coupled to the motion of a passing Na so that the whole mechanism thus resembles a "mill wheel."

In this paper we report the results of *ab initio* molecular dynamics simulations of the NaSn compound in the temperature range of the "plastic" α phase. Simulations of this system at temperatures above the melting point have been performed by Seifert and co-workers,[6,7] in an attempt to shed light on the possible survival of the Sn_4 tetrahedra in the liquid. Their results suggest that these units do not survive as stable tetrahedra, and the structure of the liquid phase can be best visualized as an irregular network of Sn atoms with some transient Sn_4 units breaking and reconstructing. The same *ab initio* method has been used by Miyata *et al.*[8] in a short simulation of the behavior of the alloy at 790 K (the simulation lasted for only 2.5 ps, following 1 ps for equilibration). They discuss the relationship between diffusion of Na cations and the deformations of Sn_4 tetrahedra, as well as the effects on the electronic structure and bonding. We have carried out a more detailed study than Miyata *et al.*, extending the simulation times, and for different conditions of tem-

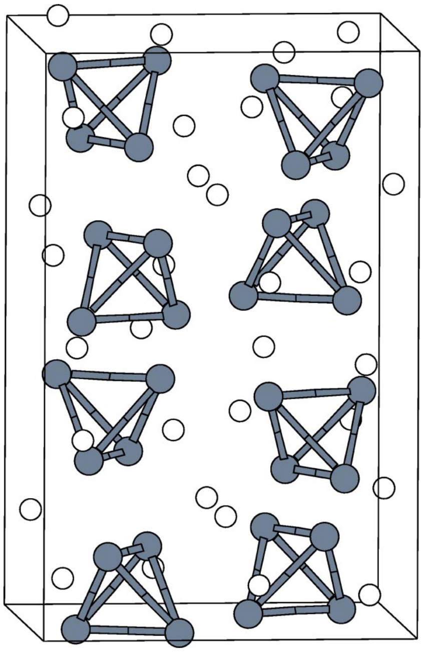

FIG. 1. (Color online) Crystalline structure of the β-NaSn solid.

perature and volume. We feel that this further study was warranted in order to characterize in a convincing way the structural and electronic properties of the high-temperature phase, as well as to determine the precise dynamical differences between the solid β-NaSn and the α-NaSn phase. Furthermore, because of the small temperature range where the α phase occurs, it is crucial to simulate the system at several temperatures, to ensure that it is the α-NaSn phase that is being modeled; approximations in the theory often lead to discrepancies in transition temperatures. Finally, we note that the phase transition from β- to α-NaSn leads to a 6.5% expansion of the alloys, suggesting that the volume is an important factor in the dynamics of the α phase which should be investigated in the simulations.

II. MODEL

The molecular dynamics simulations were carried out using the FHI96MD code,[9] which employs an *ab initio* approach based on a plane-wave basis set,[10] Hamman's norm-conserving pseudopotentials[11] with the Kleinman-Bylander decomposition[12] for treating the electron-ion interactions, and density-functional theory (DFT) within the local-density approximation (LDA) (Ref. 13) for exchange-correlation effects. The cutoff energy for the plane-waves expansion was set to 8 Ryd. The tetragonal unit cell of the β-NaSn solid[14,15] was chosen as the simulation cell, with 32 Sn atoms (8 Sn_4 units) and 32 Na atoms per unit cell. Since we wish to compare the behavior of the system in both β-NaSn and α-NaSn phases, and the plane-wave approach requires the system to be periodic, the simulation cell should be a multiple of the solid unit cell. We have chosen the smaller $1\times1\times1$ supercell, since the next largest alternative, a $2\times2\times1$ cell (256 atoms) would have an excessive computational cost at an *ab initio* molecular dynamics level. The size of the unit cell is large enough for only 1 k point to be used. For the constant temperature molecular dynamics simulations a Nosé-Hoover thermostat[16,17] was employed, and the Verlet algorithm[18] (with a 5-fs time step) was used to integrate the equations of motion along a trajectory. The simulation temperature T_{sim} is taken to be the time average of the "instantaneous" temperature, defined in terms of the ionic kinetic energies:

$$T_{\mathrm{inst}}=\frac{\sum_i \frac{1}{2} m_i v_i^2}{k_B}. \tag{1}$$

The initial ionic velocities are chosen randomly following a Gaussian distribution, with average value T_{sim}.

III. LOW-TEMPERATURE SOLID PHASE

First, we describe results of simulations showing expected behavior of the low-temperature solid phase. Initially, the temperature of the thermostat was set at 550 K for 4.5 ps. It was then raised to 600 K for 4.5 ps, and finally to 650 K for a further 5 ps. One efficient discriminator of solid- or liquid-like behavior of the alloy is the mean-square deviation of the atomic positions from their initial values:

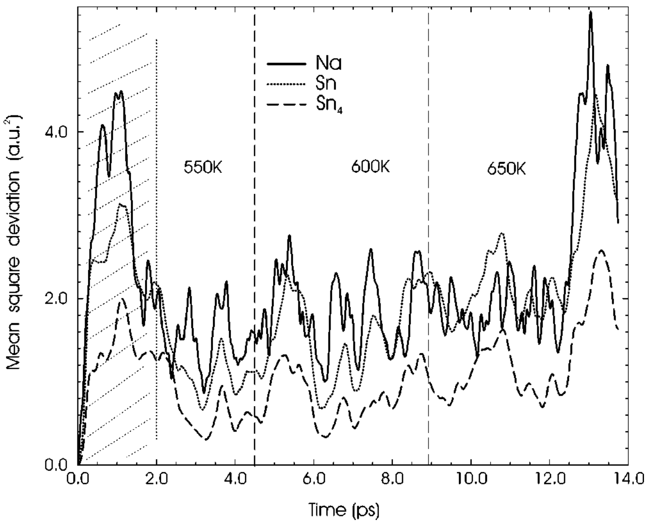

FIG. 2. Mean-square deviations $\langle R^2\rangle$ for three simulations of the β-NaSn solid at 550, 600, and 650 K. The shaded region represents the thermal equilibration of the system.

$$\langle \mathrm{R}^2(t)\rangle=\frac{1}{N_{at}}\sum_{i=1}^{N_{at}}|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2, \tag{2}$$

where the sum is over all the Na or Sn atoms, or the centers of mass of the Sn_4 tetrahedra. When one of these quantities increases, rather than oscillating, with time, diffusion of the species (Na, Sn, or Sn_4 tetrahedra) is indicated.

Figure 2 shows $\langle R^2\rangle$ for the three simulations described above. All the curves oscillate. The absence of any steady increase with time indicates solidlike behavior. Since the average value of the deviations amounts to 1.3–1.4 a.u., and the first-neighbor distances in the crystal range from 5.5 to 6.0 a.u., these deviations can be clearly assigned to vibrations of the atoms about their equilibrium positions. A visual examination of the structural evolution of the system confirmed this point. Two sharp increases of $\langle R^2\rangle$ followed by sharp decreases are displayed. The first is a spurious effect during the initial, ≈ 2 ps, thermal equilibration of the system. The second was due to a transient deformation of one Sn_4 tetrahedra that was accompanied by a sizable but also transient deviation of the neighboring Na atoms from their equilibrium positions. Evidently, Sn_4 deformations and displacement of the Na atoms are highly correlated processes. After 1 ps, the system recovered its original structure, suggesting that at 650 K the simulated alloy is still in the β-NaSn phase. However, the excursion described above suggests that this temperature is close to the $\beta\rightarrow\alpha$ phase transition.

The eigenvalue spectrum around the Fermi level is shown as a function of time in Fig. 3, with the top of the valence band, i.e., the highest occupied molecular orbital (HOMO), and the bottom of the conduction band, i.e., the lowest unoccupied molecular orbital (LUMO), highlighted with thick continuous and dashed lines, respectively. In the low-temperature solid phase, the semiconductor character is maintained, with the value of the band gap lowered from 0.7 eV, calculated at 0 K, to an average of about 0.4 eV at 550–

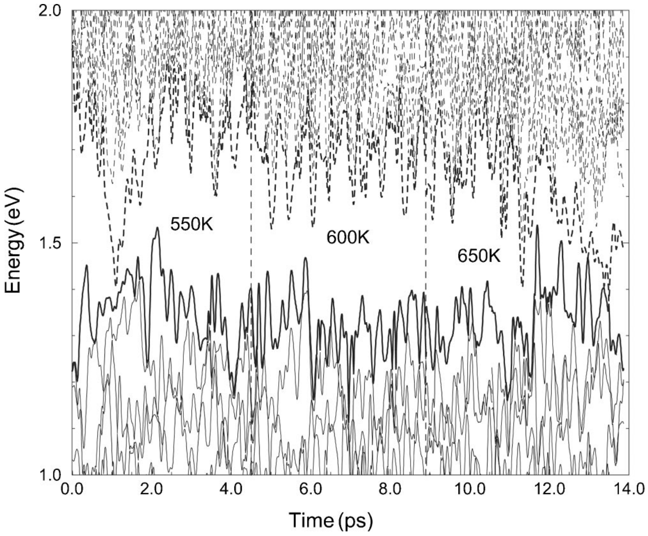

FIG. 3. Eigenvalue spectrum around the Fermi level for the β-NaSn solid between 550 and 650 K. The HOMO and LUMO are highlighted with continuous and dashed thick lines, respectively.

600 K. Noteworthy is the reduction of the band gap that occurs at 650 K between 12 and 14 ps which coincides with the distortion of one Sn_4 tetrahedron discussed above. The semiconductor character of the solid is related to the formation of Sn_4^{4-} units with tetrahedral symmetry;[3] deformation of these units results in a reduction of the HOMO-LUMO gap.

In order to analyze in more detail the dynamical behavior of the tetrahedral Sn_4 units, we have studied the evolution of two further structural parameters. One measure of the shape of a Sn_4 unit is the root-mean-square deviation of the Sn-Sn bond length from its mean value:

$$\Delta(\mathrm{Sn}_4^k,t)=\sqrt{\frac{\sum_{i,j}(d^{ij}_{\text{Sn-Sn}}-d^{(k)}_{av})^2}{6}}, \tag{3}$$

where k identifies the tetrahedron among the eight in the simulation volume. For a perfect tetrahedron, the bond lengths are equal and $\Delta(\mathrm{Sn}_4^k)=0$. Distortion of the tetrahedron increases this quantity, for example, for a rhombus $\Delta(\mathrm{Sn}_4^k)\approx 2$. Figure 4 shows the time evolution of these distortion parameters for each of the eight Sn_4 units and for the three simulations between 550 and 650 K. The deformations are relatively small indicating stable tetrahedra. Occasionally, one undergoes a significant distortion, but recovers its original shape after 0.5–1 ps. Near the end of the simulation a major deformation occurs which has already been discussed in connection with the eigenvalue spectrum, but after 2 ps the tetrahedron had recovered its shape. Although some distortions associated with the higher temperature phases begin to appear, the system is solid at 650 K simulation temperature. Finally, the inset in Fig. 4 shows the average values of the Sn-Sn distances for four of the Sn_4 units as functions of time. Oscillations with a well defined period of 0.2 ps can be observed in all cases due to a vibrational ‘‘breathing’’ mode of the tetrahedra.

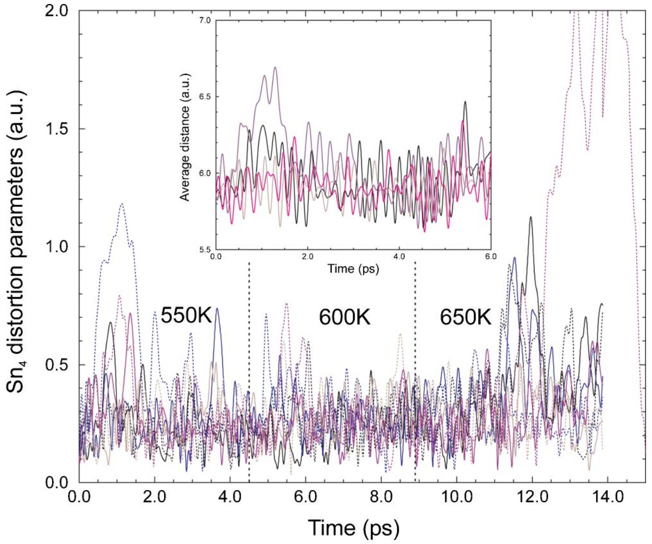

FIG. 4. (Color online) Distortion parameters $\Delta(\mathrm{Sn}_4^k,t)$ for the simulations of the β-NaSn phase, for each of the Sn_4 tetrahedra. Inset: average Sn-Sn distance within the Sn_4 units.

We have also studied rotation of the Sn_4 units in the β-NaSn phase through the index:

$$\mathrm{Rot}(\mathrm{Sn}_4^k,t)=\frac{1}{4}\sum_{i=1}^{4}\mathrm{Angle}\{\mathbf{r}_i^k(t)-\mathbf{r}_{cm}^k(t),\mathbf{r}_i^k(0)-\mathbf{r}_{cm}^k(0)\}, \tag{4}$$

where $\mathbf{r}_i^k(t)-\mathbf{r}_{cm}^k(t)$ and $\mathbf{r}_i^k(0)-\mathbf{r}_{cm}^k(0)$ are the position vectors of the i Sn atom within the k tetrahedron with respect to the center of mass at times t and $t=0$, respectively. The average of these angles for all Sn atoms in a tetrahedron provides a good measure of the Sn_4 orientation with respect to its original orientation. A rotation returning the tetrahedron to the original configuration, but with exchanged Sn positions, gives a value of 109°. In Fig. 5 the time evolution of these rotational indices for the Sn_4 units are shown. Some

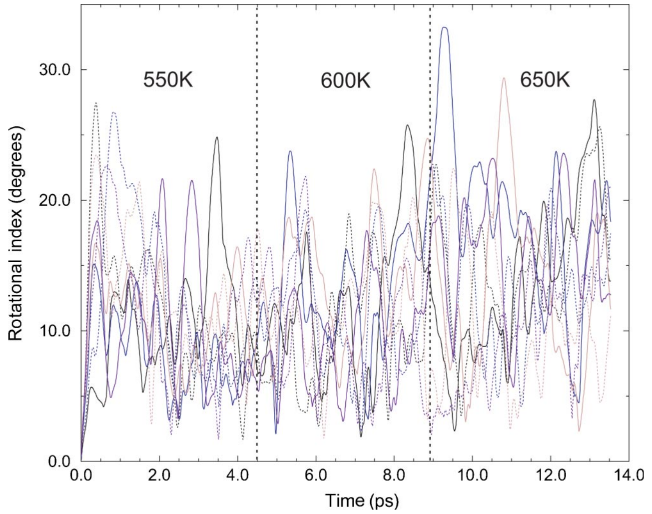

FIG. 5. (Color online) Rotational index $\mathrm{Rot}(\mathrm{Sn}_4^k,t)$ (in degrees) for each Sn_4 tetrahedra between 550 and 650 K.

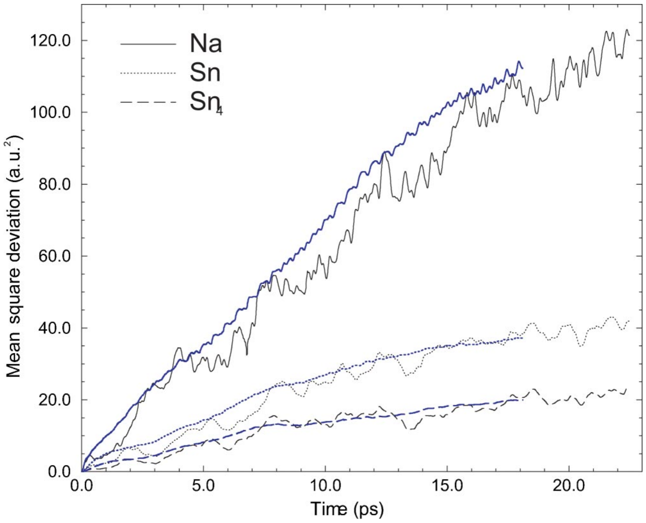

FIG. 6. (Color online) Mean-square deviations at 700 K using the volume of the α-NaSn alloy. The irregular curves represent $\langle R^2 \rangle$ calculated for one time origin ($t=0$); the smoother ones were obtained by averaging $\langle R^2 \rangle$ over ten time origins along the trajectory.

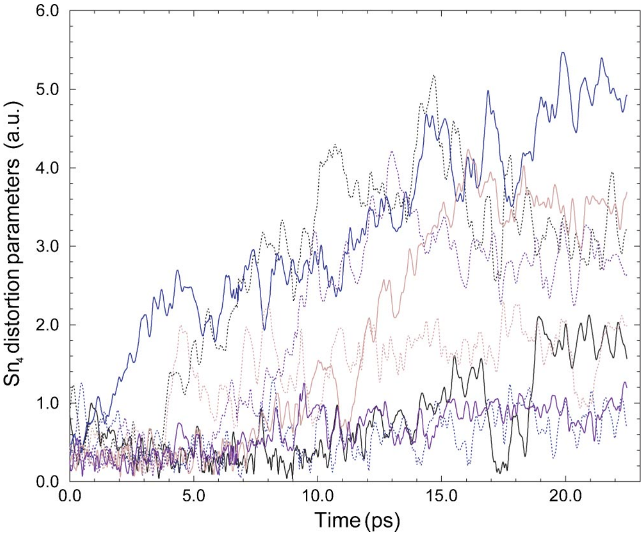

FIG. 7. (Color online) Distortion parameters $\Delta(\mathrm{Sn}_4^k,t)$ at 700 K and α-NaSn volume for each of the Sn$_4$ tetrahedra.

small rotations are seen but these never exceed 30–35°. Summarizing, the movements of the Sn$_4$ tetrahedra in the β-NaSn phase are relatively small oscillations superposed on which are breathing mode vibrations. No diffusion of the Na atoms is observed.

IV. HIGH-TEMPERATURE PHASE

As mentioned in the Introduction, it has been observed that on the $\beta \rightarrow \alpha$ phase transition the system expands by 6.5%. In view of this several simulations between 650 and 750 K were performed, using two different volumes for the unit cell: the volume characteristic of the β-NaSn solid phase at a temperature just below T_{critical}, and second, the volume of the α-NaSn phase just above T_{critical}.

A. Simulations at the volume of the α phase

Simulations using the experimental volume of the α-NaSn phase were performed at 650, 675, 700, and 750 K, with qualitatively very similar results. We will study in detail the behavior of the system at 700 K. At this temperature the simulation time was extended to 23 ps. Both quantitative and qualitative differences from the behavior observed for the β-NaSn phase appear. Figure 6 shows the values of the mean-square deviations $\langle R^2(t) \rangle$ for Na and Sn atoms, and for the centers of mass of Sn$_4$ units. The irregular lines correspond to the evaluation of $\langle R^2(t) \rangle$ using a single time origin ($t=0$) along the trajectory, while the smoother lines were obtained by averaging over ten time origins spaced 0.25 ps apart. The latter show a smoother time evolution, but the general trends are already present for just one time origin. In contrast with their behavior up to 650 K the Na atoms are diffusing very easily. However, any diffusion of the Sn atoms is difficult to discern. The average deviation for these atoms grows very slowly, and due to the limited time of the simulation it is unclear if the curves will saturate at some value or grow indefinitely at a small rate proportional to the diffusion coefficient. Another interesting feature is the small but significant movement of the Sn$_4$ centers of mass, indicating that, in addition to distortions and rotations, these units possess some freedom for small translational movements.

The distortion parameters $\Delta(\mathrm{Sn}_4^k,t)$ indicating the dynamical behavior of the Sn$_4$ units are shown in Fig. 7. After 15 ps, four Sn$_4$ are still well defined tetrahedral or rhombohedral units with values of Δ less than 2. The other four are very distorted, in some cases losing one of the Sn atoms that attaches to a neighboring Sn$_4$, and in others breaking into two dimers. In all the dynamical simulations using the volume of the α-NaSn phase we have found that complete rotations with values of the rotational index larger than 100° are extremely rare. The simulations started from a configuration very close to the perfect crystal, but the system evolved into a rather disordered state with sizable distortions of the Sn$_4$ units and some occasional exchange of Sn atoms between them, but no significant degree of rotation. A detailed study of the configurations shows that the diffusion of Na atoms is not accompanied by rotation of Sn$_4$ units. Slight deformations of the Sn$_4$ tetrahedra are enough for the creation of empty spaces allowing for jumps of Na atoms to new positions. The evolution of the system during the first picoseconds confirms this point; during this initial period the tetrahedra have neither suffered strong distortions nor rotations, but diffusion of Na atoms is already evident.

The results show a qualitative difference between the behavior of the system at 650 and 700 K. Below 650 K, the system behaves as a solid, while starting at 675 the Na atoms begin to diffuse readily. Therefore the simulation indicates a T_{critical} for the $\beta \rightarrow \alpha$ phase transition between 650 and 675 K. From now on we will denote as α-NaSn simulations all the runs between 675 and 750 K. Not surprisingly, there is a shift of around 100 K between the experimental and the simulation T_{critical}'s arising from some significant approximations in the model, mainly the local-density approximation

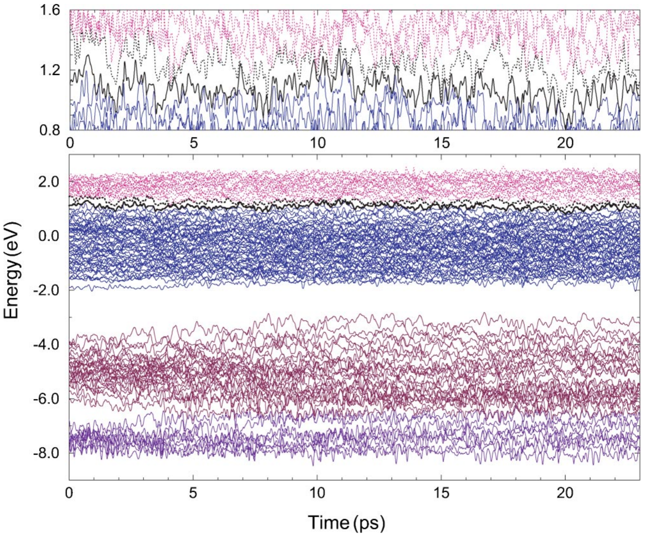

FIG. 8. (Color online) Complete eigenvalue spectrum as a function of time for the system at 700 K with α-NaSn volume. In the upper panel the region around E_{Fermi} is enlarged. Thick continuous and dotted lines highlight the HOMO and LUMO levels, respectively.

and the limited size of the unit cell. However, we do not believe that this discrepancy will affect our main conclusions.

The close connection between the electronic structure of the alloy and the structural properties is evident in Fig. 8, where the energies of the different electronic levels as a function of time are plotted for the simulation at 700 K, with the region around the Fermi level enlarged in the upper panel. In the first 4 ps of the simulation two bands associated with the Sn 5s electrons can be seen in the lower part of the spectrum. After some time they merge into one broader band. This feature is related to the distortion of the Sn_4 units. Their tetrahedral symmetry is responsible for the splitting of the 5s levels into two subbands of relative weights 1 and 3. As the simulation proceeds and the tetrahedra become distorted, the symmetry is lost and the subbands mix. Also, around the Fermi level occasional merging occurs between the HOMO (thick continuous line) and the LUMO (thick dashed line). This merging is caused mainly by the deformation of the Sn_4 tetrahedra, although detailed analyses of the electronic levels and the atomic trajectories show that close proximity and linking between two neighboring tetrahedra also contribute to closing the HOMO-LUMO gap.

Useful information on the electronic structure is also provided by the density of states (DOS) averaged along a trajectory, which is plotted in Fig. 9 for several simulations performed at different temperatures and with a volume close to that of the α-NaSn phase. For comparison, we show on the same graph the DOS at 600 K and the β-phase volume. We observe that for the solid phase the two 5s subbands are well separated, consistent with the highly symmetrical structure of the Sn_4 units. Also for the solid, the HOMO-LUMO gap remains open along the simulation leading to a nearly vanishing DOS at the Fermi level. In contrast, the simulations for the α phase show very different behavior. The two 5s subbands form one broader band (with some structural remnants of the two subbands), and the 5p valence band overlaps slightly with the conduction band, with a marked minimum of the DOS at the Fermi level.

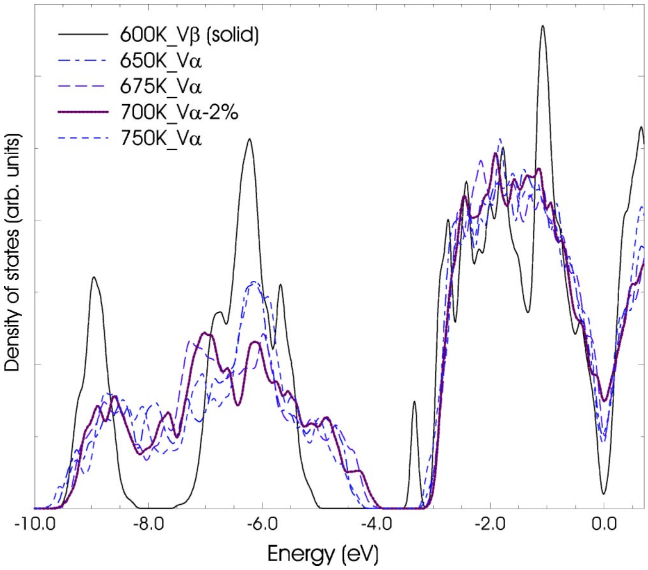

FIG. 9. (Color online) Densities of states of the NaSn alloy at several temperatures and volumes, averaged along a trajectory. Energies are relative to the Fermi level.

The simulation at 700 K was performed at a volume slightly smaller (2%) than that observed for the α phase; for the others, the observed volume of the α phase was taken, which is 6.5% larger than the β-phase volume at T_{critical}. The smaller volume was taken to compensate somewhat for the intrinsic underestimation of interatomic distances characteristic of the LDA (about 2% for NaSn), and in addition, to investigate the effect of small volume changes on the properties of the alloy. A comparison of the DOS curves in Fig. 9, especially the value of the DOS at the Fermi level, shows that the results do not depend strongly on the temperature, but change markedly with a small volume change. At constant volume, the values at the Fermi level change little over a 100-K range, but are raised 50% by a slight volume change. This effect results from a stronger overlap of 5p molecular orbitals associated with neighboring tetrahedra as the volume is reduced. The increased overlap broadens the conduction and valence bands, increasing the band overlap and raising the DOS at the Fermi level. This effect appears along with the band crossings due to the thermal disorder which were discussed earlier. Finally, we note that no sizable differences were found between the structural indicators at temperatures between 650 and 750 K and those for the simulation at 700 K. This is probably due to the short simulation times for the former.

B. Simulations at the volume of the β-phase

Two simulations were performed at 700 and 750 K using the volume corresponding to the low-temperature β-NaSn phase around T_{critical}. In Fig. 10 the mean-square deviations $\langle \mathrm{R}^2 \rangle$ for each of these simulations are shown. Noting that the

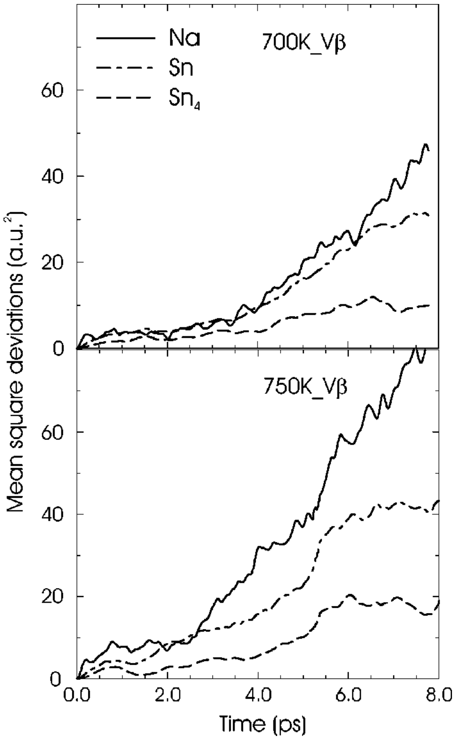

FIG. 10. Mean-square deviations for the alloy at 700 and 750 K, using the β-NaSn volume.

scale is the same in both panels, it is clear that the diffusivity of both Na and Sn atoms increases with temperature, as expected. Comparison of the simulations at 700 K of the alloy with the α-NaSn volume and that with the smaller β-NaSn volume reveals interesting behavior. The mean-square deviation of the Sn atoms is much larger in the simulation at the smaller volume. This higher diffusion is correlated with the larger disorder and distortions of the Sn_4 units, as can be seen in Fig. 11. At around 8 ps, with the simulations starting from configurations close to the perfect crystal, several of the distortion parameters $\Delta(Sn_4^k,t)$ shown in Fig. 11 for the β-NaSn volume exceed 2 a.u. In contrast, those for the α-NaSn volume (see Fig. 7) are generally less than 2 a.u. at this time. This behavior can be understood in terms of an increasing destabilization of the tetrahedral Sn_4 units in the smaller volume as they are pressed closer together, in a similar way to the Pb_4 tetrahedra in equiatomic alkali-Pb alloys.[3] The smaller volume results in more frequent deformation and breaking of the Sn_4 units. Nevertheless, comparison of the diffusivity of the Na atoms at the same temperatures but at the β and α volumes shown in Figs. 6 and 10 shows higher Na diffusion at the larger volume. This is because there is less free space at the β volume, making Na movements more difficult, despite the greater deformation of the Sn_4 units.

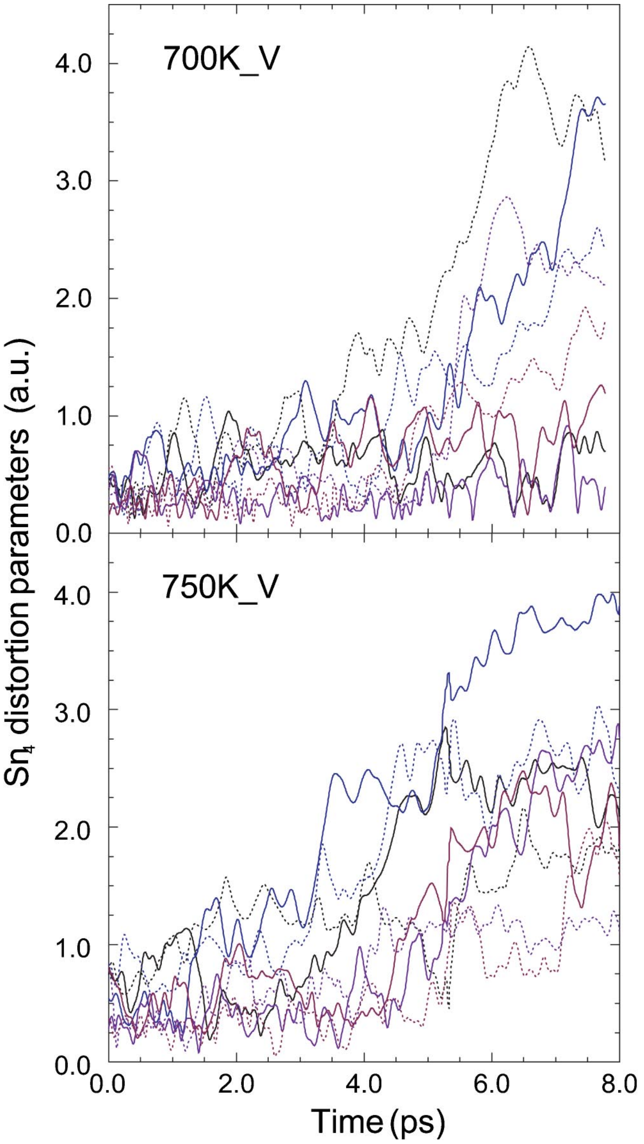

FIG. 11. (Color online) Distortion parameters for the Sn_4 units at 700 and 750 K, with the β-NaSn volume.

The structural behavior under these conditions is reflected in the electronic structure. Figure 12 shows the time evolution of the HOMO-LUMO gap for the simulations at 700 and 750 K with the β-NaSn volume. Clearly, the closings of the gap are more frequent than for the simulation at 700 K using the α-NaSn volume. This is a consequence of the larger Sn_4-Sn_4 interactions and the resulting distortions as discussed above. In addition, the frequency of gap closings increases with temperature, consistent with the greater disorder. These two effects are also evident in the averaged densities of states shown in Fig. 13. The more frequent crossings of valence and conduction energy levels at 750 K lead to a higher DOS at the Fermi energy. Also, in both cases the values at the Fermi level exceed those for simulations at volumes around the α-NaSn volume. Finally, the larger distortions of the Sn_4 tetrahedra at the smaller volume lead to larger mixing between the two 5*s* subbands.

V. CONCLUSIONS

The molecular dynamics simulations show important qualitative changes in the thermal behavior of the NaSn alloy at around 650–700 K indicative of a phase transition. The behavior of the high-temperature phase is characterized by

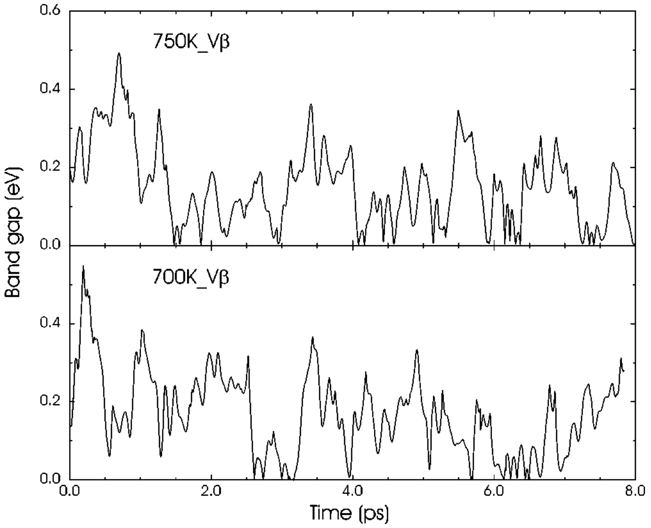

FIG. 12. Evolution of the HOMO-LUMO gap as a function of time at 700 and 750 K, with the β-NaSn volume.

significant diffusion of the Na atoms through the alloy strongly coupled to deformations of the Sn_4 tetrahedra. The picture obtained from the simulations differs somewhat from the ‘‘mill-wheel’’ model proposed by Saboungi *et al.*[4] Distortions of the Sn_4 tetrahedra creating space rather than rotations seem much more important in allowing Na movement.

The rather large distortions of the Sn_4 units seen above 700 K are also important. Although their identity is generally preserved, processes involving the breaking of the units into two dimers or the occasional exchange of Sn atoms between them should be noted. Comparing our results with those of Seifert and co-workers,[6,7] we suggest that the major qualitative difference between the α-NaSn phase and the liquid could be a much larger propensity of the Sn_4 tetrahedra in the α-NaSn phase to recover their shapes after distortions and to remain stable for longer times. However, larger cells and much longer simulation times would be required to clarify this issue.

Finally, we have found a critical influence of the volume of the unit cell on the dynamical behavior of the alloy. Compression leads to stronger interaction between the Sn_4 tetrahedra, reducing their stability. This results in a more disordered system with a larger number of broken tetrahedra. We note that the volume change occurring in the transition from the β to the α phase could be vital for the stabilization of the latter.

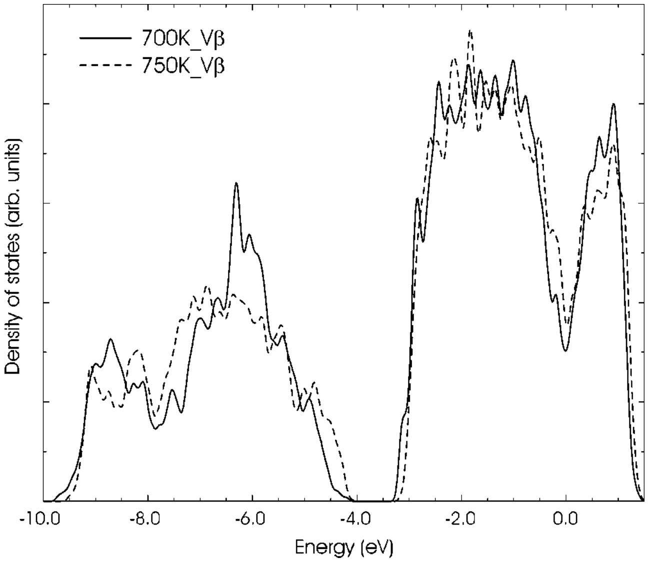

FIG. 13. Averaged densities of states for the simulations using the β-NaSn volume. Energies are relative to the Fermi level.

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