Stability of the chain structure in liquid K$_x$Te$_{1-x}$ ($x = 0.0$, 0.2, and 0.5): 
*Ab initio* molecular-dynamics simulations

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The stability of local chain structures formed by Te atoms in liquid K$_x$Te$_{1-x}$ mixtures ($x = 0.0$, 0.2, and 0.5) is studied by *ab initio* molecular-dynamics simulations. It is confirmed by investigating the atomic and electronic structures that at $x = 0.2$, the chain structure of Te is stabilized by the presence of K atoms compared with the pure liquid Te, and that, at the equiatomic concentration, most of the Te atoms form the Te$^{2-}$ dimers, as expected by the Zintl rule. From the time evolution of local atomic configurations, it is found that the Zintl Te$^{2-}$ dimers interact with each other, and the bond breaking and the rearrangement of dimers occur rather frequently.

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I. INTRODUCTION

Liquid Te exhibits metallic properties with an electrical conductivity of about 2000 $(\Omega \text{ cm})^{-1}$ near the melting point, while its solid phase is a typical semiconductor. It has been experimentally known$^{1-3}$ that the electrical conductivity decreases monotonically with the addition of alkali elements; at 50% of alkali concentration, it is only about 1 $(\Omega \text{ cm})^{-1}$. Both experimental$^{4-6}$ and theoretical$^{7}$ studies have suggested that this metal-semiconductor transition in the liquid alkali tellurides is closely related to the change in the chain structure of Te atoms by adding alkali elements.

The neutron-diffraction experiments$^{4,6}$ for liquid K$_x$Te$_{1-x}$ and Rb$_x$Te$_{1-x}$ mixtures showed the persistence of covalently bonded Te atoms in the liquids. For lower alkali concentrations $x \leq 0.2$, the measured structures are similar to that of the pure liquid Te. However, the separation of the first peak of the pair distribution function from the rest of neighbors becomes clear when alkali elements are added, and the Te-Te coordination number decreases with increasing alkali concentration. In the case of the equiatomic mixture K$_{0.5}$Te$_{0.5}$, the measured structure shows a virtually complete pairing of Te atoms that are identified with Zintl ions Te$^{2-}$.

Recently,$^7$ *ab initio* molecular-dynamics (MD) simulations were carried out for liquid Rb$_x$Te$_{1-x}$ mixtures ($x = 0.0$, 0.2, and 0.5). It was shown that the interchain interactions are suppressed by Rb$^+$ ions, and therefore the Te chains are relatively stabilized in comparison with the pure liquid Te. For $x = 0.5$, more than half of Te atoms form Te$^{2-}$ dimers, which are mixed with short Te chains and Rb$^+$ ions. These results are consistent with the experimental observations. It was also shown by calculating the partial density of states that almost complete charge transfer from Rb to Te occurs in the mixtures. The spatial distribution of the transferred charge in the Te chains was investigated. The structure of liquid K$_x$Te$_{1-x}$ mixtures was also investigated by *ab initio* MD simulations.$^8$ It was reported that Te dimers are formed in the equiatomic K$_{0.5}$Te$_{0.5}$ mixture.

It is, therefore, undoubted that the Te chains are stabilized by adding alkali elements so as to reduce the number of threefold-bonded defects$^4$ that are believed to be contained in pure liquid Te and are responsible for the metallic conductivity, and that there exist the Zintl ions Te$^{2-}$ at the equiatomic concentration. These facts explain the decrease in the electrical conductivity with increasing alkali elements. However, there have been no quantitative discussions about the stability of the Te chain in liquid alkali tellurides. Especially, it is interesting to investigate the stability of the Zintl ions Te$^{2-}$ in the liquids. In the structure of crystalline alkali-Te compounds at the equiatomic concentration,$^{2,9}$ all Te atoms exist as Te$^{2-}$ dimers, being consistent with the Zintl rule,$^{10,11}$ which suggests the presence of Te$^{2-}$ dimers if a complete charge transfer from the alkali atom to Te occurs. Since the results of the *ab initio* MD simulations$^7$ showed that the charge transfer is almost complete in the liquid alkali tellurides, there is an indication that the Te$^{2-}$ anions are also stable in the liquids. However, in the snapshots of the atomic configuration obtained by the MD simulations, there exist short chains that consist of more than two Te atoms and isolated Te atoms, as well as the Te$^{2-}$ dimers. It is, therefore, worthwhile investigating the stability of the Zintl anions.

To study the stability of polyanions predicted by the Zintl rule,$^{10,11}$ several *ab initio* MD simulations have been carried out for liquid mixtures, such as KSi,$^{12}$ NaSn,$^{13}$ LiPb,$^{14}$ NaPb,$^{15}$ KPb,$^{16}$ CsPb,$^{17}$ and KSB.$^{18}$ In the liquid mixtures of group IV elements with alkali metals, the Zintl anions are supposed to have tetrahedral complexes. In the liquid K-Sb (group V element) mixture, chainlike polyanions are considered to be present. However, no theoretical study for investigating the stability of Zintl anions in the liquid alkali group VI element mixtures has been reported so far.

In this paper, we present the results of our *ab initio* MD simulations for investigating the dynamic properties of the Te chain structure in liquid alkali tellurides, especially the stability of the Zintl ions Te$^{2-}$. In the liquid alkali-Te mix-
tutes, only for K-Te mixtures the neutron-diffraction measurements were carried out for higher alkali concentrations (up to 50%). Therefore, we have chosen to calculate the properties of liquid $K_xTe_{1-x}$ mixtures so as to compare the calculated structures with the experimental results.

In Sec. II, the method of \textit{ab initio} MD simulations used here is briefly described. The results of our simulation and discussions are given in Sec. III. Finally we summarize our work in Sec. IV.

II. METHOD OF CALCULATION

Our calculations were performed within the framework of the density-functional theory, in which the generalized gradient approximation\textsuperscript{19} was used for the exchange-correlation energy. The electronic wave functions were expanded in the plane-wave (PW) basis set. The energy functional was minimized using an iterative scheme based on the preconditioned conjugate-gradient method.\textsuperscript{20–22} For the interaction between the valence electrons and ions, we used the ultrasoft pseudopotentials\textsuperscript{23,24} obtained from the electronic structure calculations for $K(3p^2d^4s^1)$ and $Te(5s^2p^4d^5)$ atoms.

The cubic supercell contains 80 atoms and the periodic boundary conditions were imposed. The simulations were carried out at three K concentrations; $K_xTe_{1-x}$ with $x = 0.0, 0.2$, and $0.5$. The temperatures and densities are $(750 \text{ K}, 0.0272 \text{ Å}^{-3})$, $(710 \text{ K}, 0.0244 \text{ Å}^{-3})$, and $(710 \text{ K}, 0.0196 \text{ Å}^{-3})$ for $x = 0.0, 0.2$, and $0.5$, respectively. Using the Nosé-Hoover thermostat technique,\textsuperscript{25,26} the equations of motion were solved via the velocity Verlet algorithm with a time step $\Delta t = 2.4 \times 10^{-15} \text{ s}$. The $\Gamma$ point was used for the Brillouin-zone sampling, and the PW cutoff energies for the wave functions and the charge density are $10$ and $65$ Ry, respectively, which are chosen so as to give a good convergence of the total energy. The quantities of interest are obtained by averaging over about $5$ ps after the initial equilibration taking about $2$ ps.

III. RESULTS

A. Atomic structure

In various kinds of partial structure factors to characterize the structure of a binary mixture, we employ the Ashcroft-Langreth formulas,\textsuperscript{27} which are defined as

$$S_{\alpha\beta}(k) = (N_\alpha N_\beta)^{-1/2} \left[ \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \exp\{-ik \cdot (r_{ai} - r_{\beta j})\} \right]$$

$$- (N_\alpha N_\beta)^{1/2} \delta_{\alpha\beta},$$

where $N_\alpha$ is the total number of $\alpha$-type atoms, and $r_{ai}$ is the position of $i$th $\alpha$-type atom. The $S_{\alpha\beta}(k)$ for $x = 0.2$ and $0.5$ are shown in Figs. 1(a) and 1(b), respectively. The $S_{TeTe}(k)$ has a peak at $k = 1.1 \text{ Å}^{-1}$, which becomes higher with increasing K concentration. In the $S_{KK}(k)$, the corresponding peak is recognized for $x = 0.2 \text{ Å}^{-1}$. For $x = 0.5$, this peak becomes broad, and a dip appears at about $k = 2.5 \text{ Å}^{-1}$. The $S_{KT}(k)$ has a negative dip at about $k = 1.1 \text{ Å}^{-1}$, a first peak at about $k = 2.1 \text{ Å}^{-1}$, and a oscillating profile at larger $k > 3 \text{ Å}^{-1}$. This behavior of the $S_{KT}(k)$ becomes marked with increasing K concentration.

Before we investigate the dynamic properties of a Te chain structure in the liquid mixtures, it is important to confirm, by comparing calculated atomic structure with the experimental data, that our simulations are correctly carried out. We show in Fig. 2 the structure factors $S(k)$ for three K concentrations, $x = 0.0, 0.2$, and $0.5$. The calculated $S(k)$ shown by the solid line is obtained from the partial structure factors with the neutron-scattering lengths ($b_{Te} = 5.43$ fm and $b_K = 3.7$ fm). The dashed and dotted lines show the results of neutron-diffraction measurements.\textsuperscript{16,28} We can see that the overall profile of the measured $S(k)$’s of the pure liquid Te and the liquid $K_{0.2}Te_{0.8}$ are reproduced fairly well by our simulation and that the calculated $S(k)$ of the liquid $K_{0.5}Te_{0.5}$ is in good agreement with the experiments.

The first peak of the total $S(k)$ is originated from the corresponding peaks of the $S_{TeTe}(k)$ and $S_{KT}(k)$. Up to $x = 0.2$, the oscillating profile for $k > 3 \text{ Å}^{-1}$ is almost determined by the $S_{TeTe}(k)$, while at $x = 0.5$, it is dominated by the $S_{KT}(k)$. It should be noted that the first sharp diffraction peak (FSDP) appears at $x = 0.5$, being in agreement with the experiment. In the case of the liquid Rb$_x$Te$_{1-x}$ mixture,\textsuperscript{7} the FSDP was not observed even at $x = 0.5$, despite the fact that the $S_{ab}(k)$’s are similar to those of the liquid K$_x$Te$_{1-x}$. This difference is simply caused by the fact that the neutron-scattering length of an Rb atom is larger than that of a K atom.

Figure 3 shows the partial pair distribution functions $g_{ab}(r)$. The solid, dashed, and dotted lines show the $g_{TeTe}(r)$, $g_{KT}(r)$, and $g_{KK}(r)$, respectively. From Fig. 3(a), we can see that there is no well-defined first coordination shell in the $g_{TeTe}(r)$ for the pure liquid Te. From Figs. 3(b) and 3(c), we see that the peaks of the $g_{TeTe}(r)$ and $g_{KT}(r)$ become higher with increasing K concentration. The first
minimum of the $g_{\text{TeTe}}(r)$ becomes deeper when the K concentration is increased. These facts indicate that the chain structure of Te is stabilized by the presence of K atoms. As for the $g_{\text{KK}}(r)$, it has broad distribution for both concentrations $x=0.2$ and $0.5$, though a broad peak around 4.5 Å is recognized at $x=0.5$.

### B. Electronic density of states

Figure 4 shows the concentration dependence of the electronic density of states (DOS) in the liquid K-Te mixtures, which is obtained from a time average of the distribution of the single-electron eigenvalues. The bold solid lines show the total DOS. The thin solid and thin dotted lines show the partial DOS for Te and K atoms, respectively. The partial DOS for $\alpha$-type atom was obtained by projecting the wave functions on the spherical harmonics within a sphere of radius $S=1.1$ Å centered at each $\alpha$-type atom. The origin of the energy is taken to be the Fermi level ($E_F=0$). The solid, dashed, and dotted lines show the $g_{\text{TeTe}}(r)$, $g_{\text{KTe}}(r)$, and $g_{\text{KK}}(r)$, respectively.

The large peak at about $-14$ eV originates from the K $3p$ states. The Te $5s$ states are located between $-13$ and $-9$ eV, and the Te $5p$ states are located above $-5$ eV. At $x=0.5$, there are several sharp peaks in the partial DOS for Te; two peaks in the $5s$ states and three peaks in the $5p$ states below $E_F$ correspond to the energy levels of the Te$_2$ dimer, which clearly indicates that the liquid mixture consists mainly of the Zintl anions at the equimolar concentration. The partial DOS for K atoms has very small values.

![FIG. 2. The structure factors $S(k)$ of the liquid K$_x$Te$_{1-x}$ for three K concentrations $x=$(a) 0.0, (b) 0.2, and (c) 0.5. The calculated $S(k)$ shown by the solid line is obtained from the partial structure factors with the neutron-scattering lengths. The dashed and dotted lines show the results of neutron-diffraction measurements carried out by Kawakita et al. (Ref. 6) (dashed line for pure liquid Te and liquid K$_{0.2}$Te$_{0.8}$), Takeda et al. (Ref. 28) (dotted line for pure liquid Te), and Fortner et al. (Ref. 4) (dashed line for liquid K$_{0.5}$Te$_{0.5}$).](image)

![FIG. 3. The pair distribution functions $g_{\alpha\beta}(r)$ of the liquid K$_x$Te$_{1-x}$ for three K concentrations $x=$(a) 0.0, (b) 0.2, and (c) 0.5. The solid, dashed, and dotted lines show the $g_{\text{TeTe}}(r)$, $g_{\text{KTe}}(r)$, and $g_{\text{KK}}(r)$, respectively.](image)

![FIG. 4. The electronic density of states (DOS) of the liquid K$_x$Te$_{1-x}$ for three K concentrations $x=$(a) 0.0, (b) 0.2, and (c) 0.5. The bold solid lines show the total DOS. The thin solid and thin dotted lines show the partial DOS for Te and K atoms, respectively. The origin of the energy is taken to be the Fermi level ($E_F=0$).](image)
by analyzing the distance $d_{ij}$ between $i$th and $j$th Te atoms as a function of time $t$, and (3) the Te coordination number $n_i(t)$ of an $i$th Te atom. Not only by seeing the atomic arrangements but also by analyzing the $d_{ij}(t)$ and $n_i(t)$, will we be able to obtain highly detailed information about the time change of local atomic configurations.

Figure 6 shows the snapshots of the atomic configurations obtained by ab initio MD simulations. In the pure liquid Te [Fig. 6(a)] as many of the threefold coordinated Te atoms exist as do the twofold coordinated ones, and the chain structure cannot be clearly seen. In the liquid $K_{0.2}Te_{0.8}$ [Fig. 6(b)], the number of the twofold coordinated Te atoms increases, and the chain structure can be recognized. We see from Fig. 6(b) that the Te chains are separated by the K atoms. At the equiatomic concentration [Fig. 6(c)], almost all Te atoms form $Te_2$ dimers. It should be noted that there exists short Te chains, which consist of more than two Te atoms, and isolated Te atoms.

Figure 7 displays some examples of the time evolution of the distance $d_{ij}(t)$, where the $d_{ij}(t)$ between a focused (i)th Te atom selected arbitrarily and all other (j)th Te atoms are shown for three K concentrations. From the $d_{ij}(t)$s in the pure liquid Te, we see that the distances between two Te atoms change largely with time, and that each Te atom is almost always surrounded by more than one Te atom. We can recognize the stretching motion between pairs of Te atoms [oscillation of $d_{ij}(t)$ around 3 Å with small amplitudes].
 increases suddenly, and instead the other distance $d_{ij}$ decreases, although the structure does not change largely in the sense that Te atoms change the value of $n_i(t)$ less frequently. (Taking the average, Te atoms change the value of $n_i(t)$ about 50 times for 4.5 ps in the liquid Te, while about 40 times in the liquid $K_{0.5}Te_{0.5}$.) These features clearly show that the chain structure is stabilized by the presence of K atoms.

It is seen that in the three liquids, Te atoms have the onefold coordination for the longest time in the liquid $K_{0.5}Te_{0.5}$, although they have also the twofold coordination at irregular intervals. We conclude that the most stable structure is formed at the equiatomic concentration [in the sense that Te atoms change the value of $n_i(t)$ less than 20 times on average for 4.5 ps], although the structure does depend on the time.

As stated in the previous subsection, the partial DOS for Te atoms (Fig. 4) clearly indicates that the liquid mixture consists mainly of the $Te_2^{2-}$ dimers at the equiatomic concentration. This was confirmed by seeing the spatial configuration of atoms [Fig. 6(c)]. These results are quite consistent with the expectation of the Zintl rule.\textsuperscript{10,11} However, the time evolution of the $n_i(t)$ (Fig. 8) seems to be inconsistent with this expectation. If all Te atoms formed the $Te_2^{2-}$ dimers, the $n_i(t)$ would be one and would not change with time. To solve this puzzle, we have to see the time change of local atomic configurations directly as shown in Fig. 9, where the balls show the positions of Te atoms. Two Te atoms, whose distance apart is smaller than 3.25 Å, are connected by the bond.

Comparing the results for the pure liquid Te with those for the liquid $K_{0.2}Te_{0.8}$, we see that in the liquid $K_{0.2}Te_{0.8}$, Te atoms have the twofold coordination for a longer time and change the value of $n_i(t)$ less frequently. (Taking the average, Te atoms change the value of $n_i(t)$ about 45 times for 4.5 ps in the liquid Te, while about 40 times in the liquid $K_{0.2}Te_{0.8}$.) These features clearly show that the chain structure is stabilized by the presence of K atoms.
In conclusion, it is certain that the liquid K-Te mixture consists mainly of the Te$_2^{2-}$ dimers at the equiatomic concentration as expected by the Zintl rule. However, it is not correct to consider that the Te$_2^{2-}$ dimers exist stably in the same way as a neutral Te$_2$ dimer exists in a vacuum. In fact, since two extra electrons in a Te$_2^{2-}$ dimer occupy the antibonding π states, the covalent bond in the Te$_2^{2-}$ dimer must be weaker than that in the neutral Te$_2$ dimer. As shown in Fig. 9, in the liquid K$_{0.5}$Te$_{0.5}$ mixture, the Zintl Te$_2^{2-}$ dimers interact with each other, and the bond breaking and the rearrangement of dimers occur rather frequently.

IV. SUMMARY

The stability of local chain structures formed by Te atoms, as well as the atomic structure and the electronic density of states in liquid K$_x$Te$_{1-x}$ mixtures with $x = 0.0$, $0.2$, and $0.5$ have been investigated by *ab initio* molecular-dynamics (MD) simulations. It is shown that the calculated structure factors are in good agreement with the experimental results in a wide range of K concentration, and that the transition from the metallic to the semiconducting states with increasing alkali elements is well reproduced by our *ab initio* MD simulations. By investigating the distances between two Te atoms and the coordination number of each Te atom as a function of time, it is seen that with increasing K concentration, the stretching motion of Te atoms appears more clearly and continues for a longer time, and the bond switching in the chain structure occurs less frequently, which means the chain structure is more stabilized by the presence of K atoms. The partial electronic density of states and the spatial atomic configuration show that at the equiatomic concentration, most of the Te atoms form the Te$_2^{2-}$ anions, as expected by the Zintl rule. It is, however, found from the detailed analysis of the time evolution of local atomic structures that the Zintl Te$_2^{2-}$ anions interact with each other, and the bond breaking and the rearrangement of dimers occur rather frequently in the liquid K$_{0.5}$Te$_{0.5}$ mixture.

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