Molecular dynamics simulation of CuI using a three-body potential

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Abstract. A three-body potential coupled with a molecular dynamics method have been used to simulate structural properties of CuI in the zincblende and tetragonal phases. It is found that the diffusion constant is well reproduced for the α-phase of CuI using this model rather than a two-body potential. This study predicts also the presence of cation disorder at elevated temperature within the tetragonal phase of CuI.

1. Introduction

The copper(I) and silver(I) halides have been widely studied because they form a group of compounds which show high ionic conductivity at elevated temperature [29]. These compounds possess the diamond zincblende structure and form the end of the class of tetrahedrally coordinated semiconductors. They are not purely ionic and it is believed that the polarizability of the ions, and the small size of the cation, encourages fast-ion conduction [2].

Of the I–VII compounds, CuI is a unique material in that both its ordered low-temperature γ-phase and disordered high-temperature fast-ion conducting α-phase have identical anion face centred cubic (fcc) structures. In the γ-phase, Cu^+ ions sit on an fcc sub-lattice shifted by (1/4, 1/4, 1/4) from the I^- sub-lattice, forming the zincblende structure. In the β-phase, which exists in the narrow temperature range between 642 and 680 K, CuI has a hexagonal structure, similar to wurtzite. At 680 K, it transforms back to an fcc I^- sub-lattice with Cu^+ randomly distributed over the (1/4, 1/4, 1/4) sites (the α-phase) [3–7]. In all three crystalline phases, Cu^+ are tetrahedrally coordinated by I^-.

The application of pressure to the I–VII compounds often results in a transformation from the zincblende to the rocksalt structure with the corresponding increase in cation–anion coordination from tetrahedral to octahedral. However, in CuCl, CuBr, CuI and AgI this is achieved via intermediate structures, which appear to possess lower symmetry. In the specific case of CuI, it transforms from the zincblende (CuI-III) to a rhombohedral structure (CuI-IV) at 1.63 GPa [6] and then to a tetragonal phase (CuI-V) at 4.70 GPa [8] following the notation of Merril [9]. In recent works, structural properties of CuI have been investigated at pressures up to 40.0 GPa using the angle-dispersive x-ray diffraction technique [10]. No evidence for an octahedrally coordinated cubic rocksalt phase is observed. A previously unreported pressure-induced phase transition is observed at 17.1 GPa from CuI-V to VII phase. The latter is found

to be orthorhombic with a heavily distorted rocksalt arrangement in which the cation is in roughly fivefold coordination to the anion sublattice. This finding is contrary to previous x-ray diffraction studies on CuI [11]. Previous diffraction studies to pressures of 10.0 GPa [8] suggested that the structural trends in I–VII compounds were markedly different from the more covalent II–VI systems. This observation does not hold at high pressures, since the crystal structure of CuI-VII appears similar to the recently observed high-pressure structures of CdTe-VI and ZnTe-III [12].

Using two-body interatomic potentials, previous studies are investigated using molecular dynamics simulation (MD) in order to describe the microscopic mechanisms of ionic conduction of CuI [13]. This model reproduces exactly the γ–α transition, but the diffusion constants were much higher in both phases than the experimental values. As a consequence, the diffusion constant is extremely sensitive to the exact potential chosen.

In this paper, we report the results of computer experiments that simulate the structural properties of CuI (III and V) using a three-body potential model (Tersoff model) coupled with a molecular dynamics method. We are also interested to simulate the α-phase of CuI using the Tersoff potential.

The main point of the present work is to reproduce exactly the diffusion constant of CuI using a three-body potential and then to test the transferability of this model to predict physical properties of the high-pressure phases of CuI which are observed in the experimental studies of Hull and Keen [8]. We are also interested in predicting the development of any structural disorder in the tetragonal phase of CuI with increasing temperature. Using neutron powder diffraction [14, 15], it appears that CuCl, CuBr and AgI exhibit superionic behaviour with Cu^+ randomly distributed over the tetrahedral voids formed by a body-centred anion sublattice. This fact is confirmed using a molecular dynamics method based on a Tersoff potential [16, 17].

2. Calculations

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been the most successful in that it reproduces many of the properties of semiconductors. The form of the energy E, between two neighbouring atoms i and j, is taken to be [18]

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \tag{1}$$

with

$$
\begin{aligned}
&V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \\
&f_R(r) = A \exp(-\lambda_1 r) \\
&f_A(r) = -B \exp(-\lambda_2 r) \\
&f_C(r) = \begin{cases} 1 & r < R - D \\ \dfrac{1}{2} - \dfrac{1}{2} \sin\left[\dfrac{\pi}{2} \dfrac{(r - R)}{D}\right] & R - D < r < R + D \\ 0 & r > R + D. \end{cases}
\end{aligned}
\tag{2}
$$

b_{ij} is the many-body order parameter describing how the bond-formation energy is affected by local atomic arrangement due to the presence of other neighbouring atoms (the k atoms). It is a many-body function of the positions of atoms i, j and k. It has the form

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n} \tag{3}$$

with

$$\zeta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3]$$

$$g(\theta) = 1 + \frac{c^2}{d_2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n}$$

$$\eta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3].$$

ζ is called the effective coordination number and $g(\theta)$ is a function of the angle between r_{ij} and r_{ik} that has been fitted to stabilize the tetrahedral structure. We note that λ_3 and α are put equal to zero [18].

Our potential parameters are summarized in table 1. They are fitted to the cohesive properties of CuI [19, 20].

Table 1. The adjusted Tersoff parameters for CuI-III.

	CuI
A (eV)	688.00
B (eV)	61.50
λ_1 (Å^{-1})	2.3832
λ_2 (Å^{-1})	1.1916
n	21.45
h	-0.3333
β	0.3333
c	69219.5
d	0.15
R (Å)	3.17
D (Å)	0.15

We carry out our MD simulations within the canonical NVT ensemble. We simulate 216 atoms in a simple cubic simulation cell with periodic boundary conditions. To integrate the Newtonian equations of motion, we use the fifth-order predictor–corrector algorithm with a time step of 4.22×10^{-15} s. After 20 000 iterations (≈ 84 ps), different average properties are calculated.

3. Numerical results

A Tersoff potential coupled with MD simulation was performed to determine the theoretical lattice constant, bulk modulus B and its derivative B' for the zincblende structure of CuI. These constants are obtained by fitting the results of total energy versus volume to the Murnaghan equation of state [22] (figure 1). The elastic constants are calculated using the method developed in detail in [21]. Our results are listed in table 2. They agree well with experiments [30] and with other theoretical calculations [31–33]. We notice that the lattice parameter of the zincblende structure of CuI is in excellent agreement with the experimental value of 6.054 Å [8] (with an accuracy of 0.13%). The accuracy is about 4% for the bulk modulus and between 4 and 8% for C_{ij}. The overall agreement confirms the validity of our adjusted potential parameters.

Under pressure, CuI-III transits to a tetragonal phase via a rhombohedral structure. On the basis of the above results, it should be interesting to test the transferability of our adjusted

Table 2. Equilibrium properties of CuI in the zincblende (CuI-III) and tetragonal phases (CuI-V)

	CuI-III				CuI-V	
	TP[a]	Exp.	Other calculations		TP[a]	Exp.
a (Å)	6.062	6.054[b]	6.042[c]	6.051[d]	4.3797	4.0229[b]
c (Å)					5.65	5.65[b]
c/a					1.29	1.39[b]
E (eV/atom)	−2.66	−2.66[e]			−2.41	
B (GPa)	3.52	3.66[b] 3.10[f]			5.92	5.70[f] 5.02[b]
B′	3.22	4[b]			12.05	4[b]
C_{11} (GPa)	41.3	45.1[g]	52.82[h]			
C_{12} (GPa)	32.1	30.7[g]	34.47[h]			

[a] Present work. [b] [8]. [c] [31]. [d] [32]. [e] [19]. [f] [10]. [g][30]. [h][33].

parameters to study the structural properties of CuI in the tetragonal phase. This phase was found to be stable up to at least 182 GPa [10]. The I^- are placed in 2(b) sites at $(0, 1/2, Z_I)$ and $(1/2, 0, \bar{Z}_I)$ with Z_I allowed by symmetry to vary away from its close packed ideal value of $1/4$. The Cu^+ are located in 2(a) sites at $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ [8]. Our calculations are investigated in the pressure range of $(4.0–18.0$ GPa$)$. The equation of state is illustrated in figure 2 (E versus V). The isothermal bulk modulus, its derivative and the equilibrium lattice constant are determined by fitting the Murnaghan equation of state to our data. The obtained results for the lattice parameter and the bulk modulus (see table 2) agree well with the experimental values of Hull and Keen [8] and Hoffman *et al* [10] (with an accuracy of 7% for the lattice and 4% for the bulk modulus).

Under increasing temperature, CuI transforms to β-phase between 658 and 680 K and then to the α-phase between 680 and the melting point 873 K. In the γ- and α-phases, anions form an fcc structure. Recently, Trullàs *et al* [23] have performed the MD simulation of α-CuI with the use of the interionic potential used by Vashishta and Rahman [24]. They investigated the effect of the effective charge on its crystal structure and on the superionic characteristic. However, they did not obtain good agreement between the calculated and experimental diffusion coefficient [25, 26].

A fairly good agreement between calculated and experimental values of the cation diffusion was obtained by Zheng-Johansson *et al* [13, 27]. They also used the same form of the interatomic potential as used by Vashishta and Rahman, but values of parameters appearing in the potential were different from those of Vashishta and Rahman. Other improvements are made by Ihata and Okazaki [28] by assuming the effective charge of the Cu^+ ions to be $0.70\,e$ instead of $0.60\,e$, which is used by Vashishta and Rahman. So the use of two-body potentials is clearly a severe limitation on the level of agreement with experiment that can be achieved, and consequently it is necessary to use a three-body potential to improve these results.

Using Tersoff potentials, MD simulations were carried out at two temperatures $T = 710$ K and 830 K which are within the range covered by the α-case of CuI. We plot in figure 3 the pair distribution function $g(r)$ of α-CuI. At both temperatures, the results are qualitatively similar and the distribution is a liquid-like structure where the first peak position is at 2.5 Å. This effect is supported by the results obtained for the mean squared displacements (MSDs) (figure 4). On the other hand, the obtained diffusion constant is proportional to 10^{-5} cm^2 s^{-1}. This constant is evaluated from the inclination of the linear relation between MSD and time

$(t_1 - t_2)$ by the relation.

$$D = \frac{\langle [r(t_2) - r(t_1)]^2 \rangle}{6(t_2 - t_1)} \tag{4}$$

where $r(t)$ means the position vector of a cation at time t. Values of D evaluated by equation (4) increase linearly with temperature as shown in figure 5. We notice from this figure that our results are in good agreement with the available experimental works [25, 26] and seem to be much more accurate than those of Zheng-Johansson *et al* [13] using the Vashishta–Rahman model.

As discussed above, pressure induces several phase transitions leading to the intriguing questions of whether the high-pressure phases, especially the tetragonal phase, also becomes superionic at elevated temperatures. In recent works, it appears that AgI [15] presents a fast-ionic behaviour in the rocksalt structure. CuCl and CuBr are found to be isostructual with AgI [16]. The most interesting feature here is the mean squared displacement (MSD) of Cu^+ in the tetragonal phase. We plot in figure 6 the MSD of cations as function of time at $p = 18.0$ GPa at different temperatures (710 and 873 K). The obtained values of D are proportional to 10^{-5} cm^2 s^{-1} and increase linearly with temperature as shown in figure 7. From these results, we predict that CuI-V adopts a superionic phase with cation disorder with increasing temperature. This diffusion constant decreases with increasing pressure (figure 8). This is due to the reduction of the gaps in the anion sublattice through which the cation migrates. This hypothesis is also supported by generally higher values of ionic conductivity observed in b.c.c. based superionics [29]. The behaviour of the pair correlation function of CuI-V at $p = 18.0$ GPa and $T = 873$ K is shown in figure 9. The distribution is quite liquid-like. So,
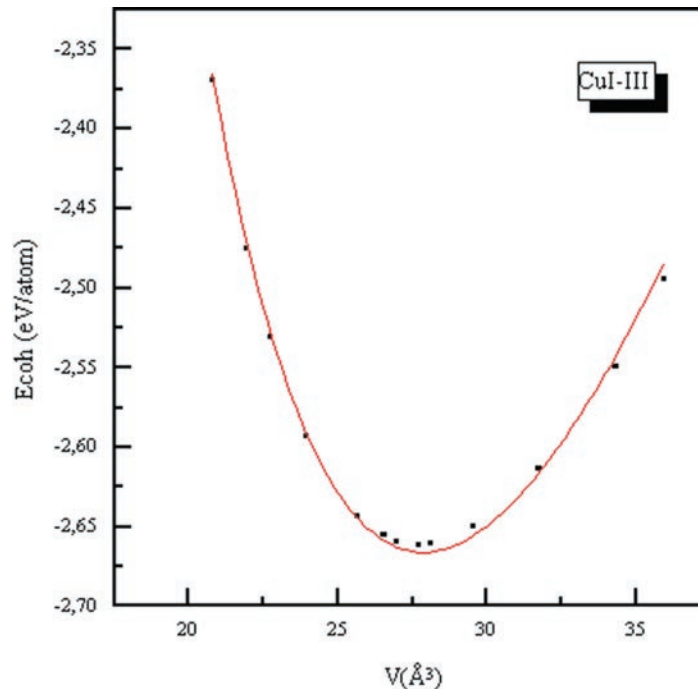

Figure 1. Cohesive energy of CuI-III as a function of volume. Circles represent our simulation results while the line represents the fitted curve using the Murnaghan equation of state.
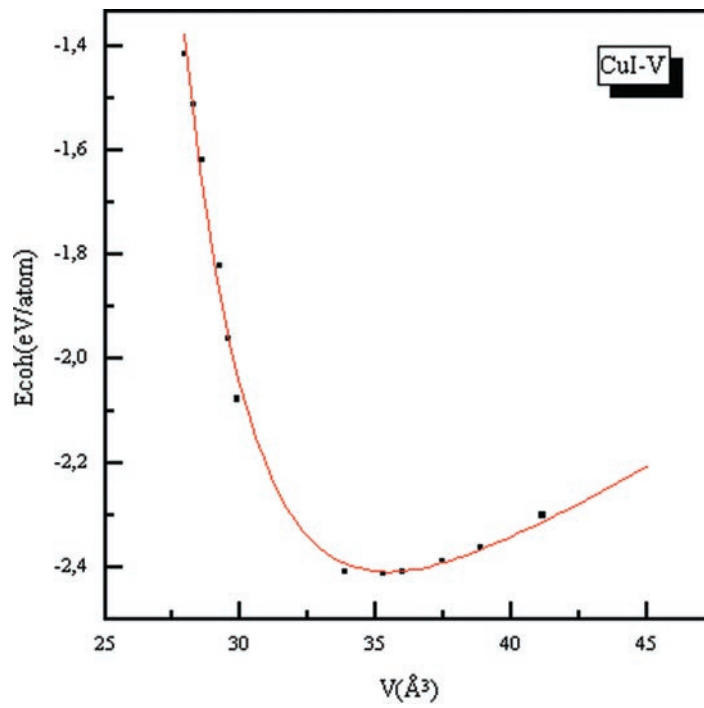
Figure 2. Cohesive energy as a function of volume for CuI-V. Circles represent our simulation results while the line represents the fitted curve using the Murnaghan equation of state.
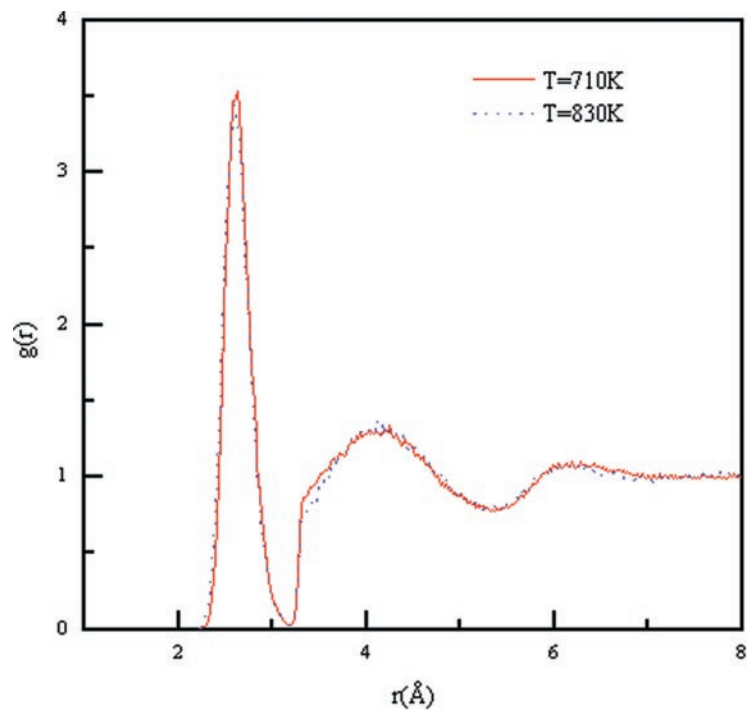

Figure 3. Pair correlation function for α-CuI at $T = 710$ K (solid line) and $T = 830$ K (dotted line).
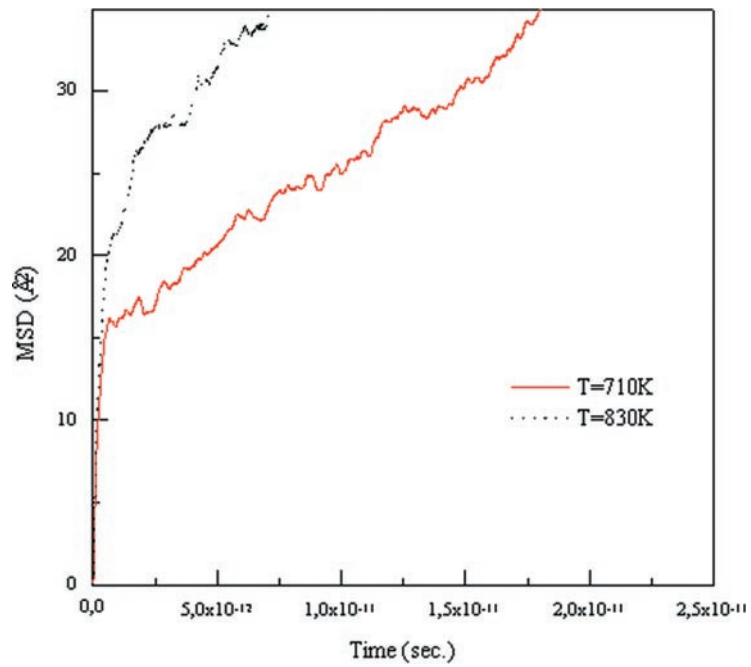
Figure 4. Mean squared displacement of α-CuI at $T = 710$ K (solid line) and $T = 830$ K (dotted line).
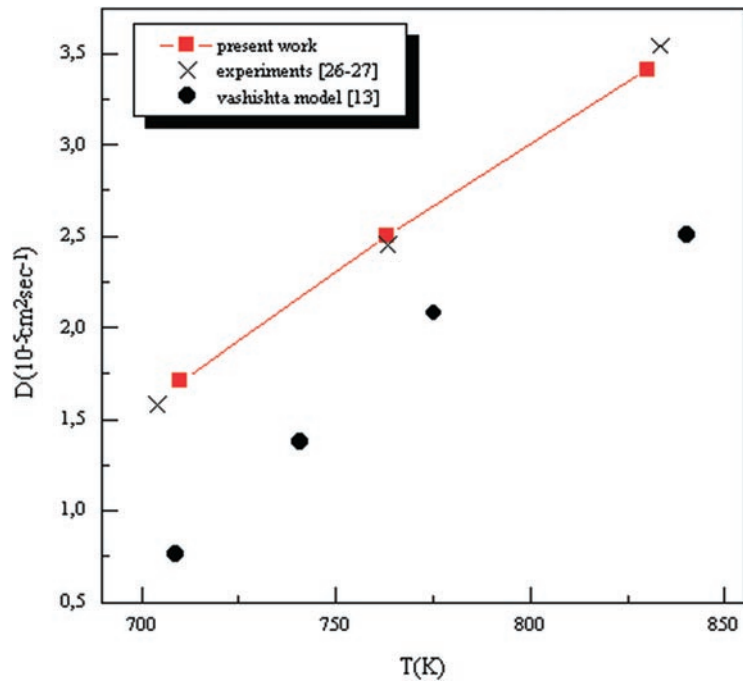

Figure 5. Copper-ion diffusion coefficient versus temperature of CuI in the α-phase. Squares are MD results using the Tersoff potential. Crosses are experimental tracer diffusion results. Circles are MD results using the Vashishta–Rahman potential.
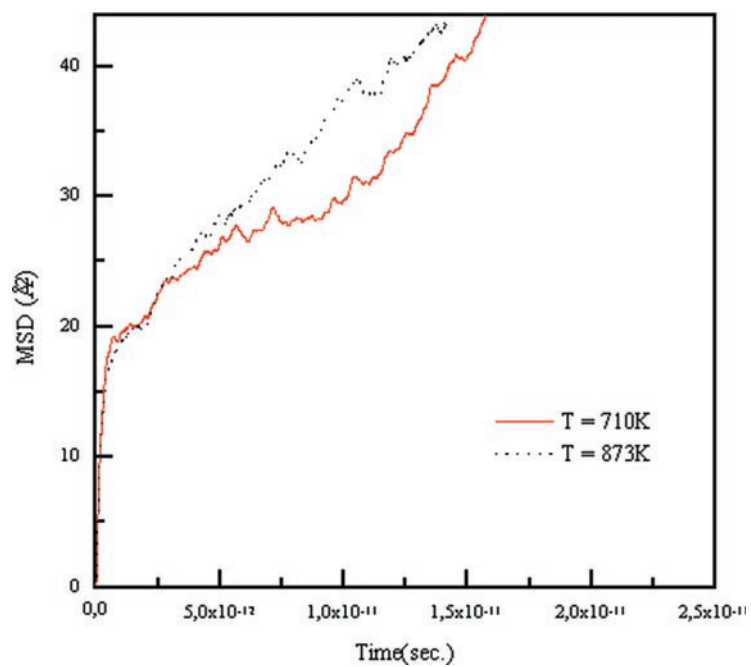
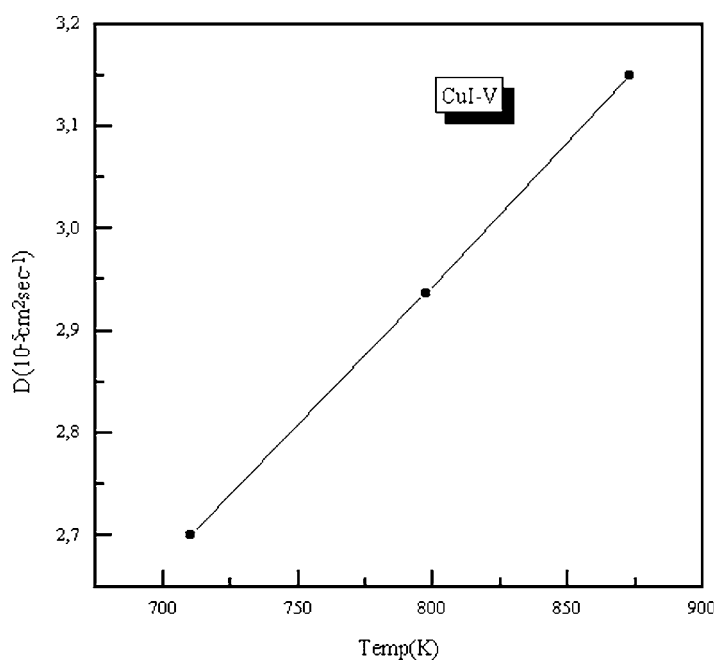**Figure 6.** Mean squared displacement of the tetragonal structure of CuI at $p = 18.0$ GPa.

Figure 7. Copper-ion diffusion coefficient versus temperature at $p = 18.0$ GPa.
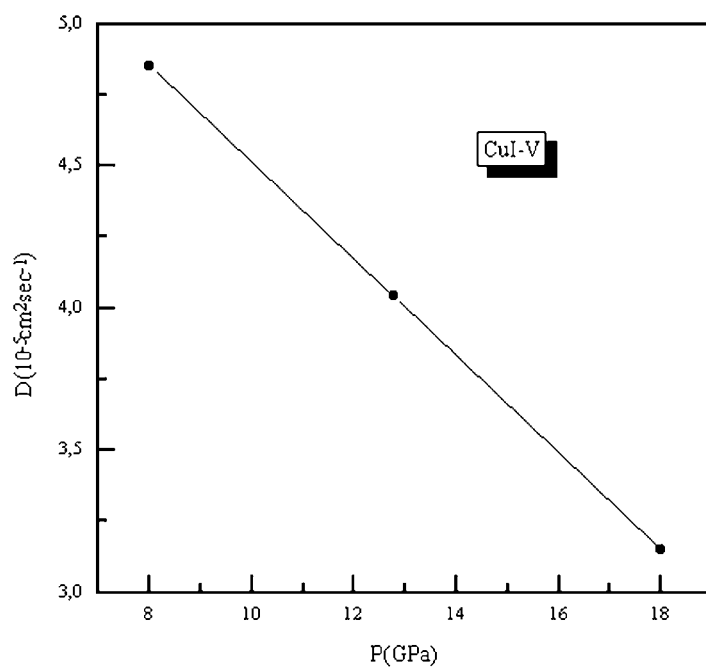
Figure 8. Copper-ion diffusion coefficient versus pressure at $T = 873$ K.
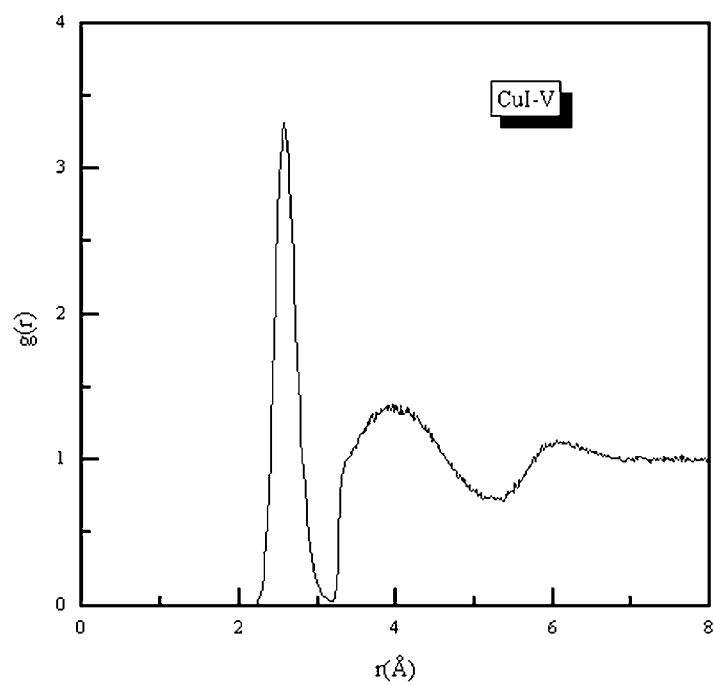

Figure 9. The pair correlation function for CuI-V at $p = 18.0$ GPa and $T = 873$ K.

the first peak position is at 2.5 Å and the corresponding coordination number is four. This has prompted us to say that CuI-V under the above conditions may transit to an fcc structure.

In summary, we conclude that an empirical three-body potential with the MD method reproduces well the structural properties of CuI in the zincblende and tetragonal structures. It is also found that the diffusion constant of the α-phase is in good agreement with experiment rather than the two-body potential. The presence of cation disorder at high pressure and in a temperature range of 710–873 K is also predicted for CuI-V.

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