Stability of Copper Atoms Embedded in Sodium-Chloride Crystals

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Because it has been pointed out by Nagasaka *et al.* that the optical absorption spectrum of copper atoms embedded in alkali-chloride crystals may depend on the position of the copper atoms, we calculate the relation between the optimal position and the total energy of copper atom embedded in NaCl crystal by means of the first-principles pseudopotential plane-wave-expansion method. These results shows that most stable position of embedded Cu⁺ ion in these alkali halide system are not the substitutional on-center site but off-center site along $\langle 111 \rangle$ axis.

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In order to study optical properties of transition metal ions, alkali halide crystals doped with transition metal atoms and compounds play an important role. Because alkali halide crystals have a wide energy gap, these crystals are transparent around optically visible ranges. So one may directly investigate optical properties of impurity ions embedded in these crystals.

Nagasaka *et al.* has proposed that a model for the impurity Cu⁺ ions in alkali halide crystals in which a charge-transfer excitation between the impurity ion and the neighboring halogen ions is assumed to play an essential role in the off-center instability.^{1,2)} They have also measured optical absorption spectrum of alkali (Na and K) halide crystals doped with some impurity copper atoms.³⁾ This experiment showed that the absorption peak intensity at the lowest photon energy (~ 4.8 eV) decreases when the NaCl sample is cooled down, and hardly changes when the KCl sample is cooled down. This fact suggests that in the NaCl crystal, the optical absorption peak is assigned to $3d^{10} \rightarrow 3d^9 4s$ transition of the Cu⁺ ion near the normal lattice site (referred to as the on-center site) and that this transition is a parity-forbidden at the on-center site but is partially allowed by the lattice vibration. So they concluded that Cu⁺ ion is stable at the on-center site in NaCl. In contrast, in the KCl crystal Cu⁺ ion is located at a slightly displaced position (referred as off-center site), away from the on-center sites.

In this paper, we investigate the relation between the optimal position and the total energy of the embedded copper atom in NaCl crystal to study whether these systems have really the different optimal positions or not.

We carry out the structural optimization for these systems in the following way. We assume the $2 \times 2 \times 2$ face-centered-cubic unit cell of the NaCl crystal structure, and replace one Na⁺ ion with one copper ion. The copper ion is placed either at the on-center or off-center sites along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ axis. We optimized all atomic positions inside the unit cell by means of the standard *ab initio* ultrasoft-pseudopotential approach (VASP)^{4,5)} with the 17 Ry cutoff energy for the plane waves (PW's) simulated

annealing the conjugate-gradient algorithm. From this calculation, we have found the following facts:

- i When the embedded copper atom is put at the on-center site, it does not move. That is, the on-center site is at least locally stable.
- ii If the copper atom is put on some particular axis like $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, then the copper atom roams and moves toward the most stable position along the same axis.
- iii The copper atom tends to move toward to positions on $\langle 111 \rangle$ axis when it is put at an off-center site that is not on a particular axis. And then it moves as the same as (ii).
- iv The axis having the most stable position is $\langle 111 \rangle$ and the next stable axis is $\langle 110 \rangle$, $\langle 100 \rangle$, and so on. The on-center site is not the most stable position.

Because the energy optimize calculation is performed with fixed crystal symmetry, the copper atom at on-center site cannot move off from the particularly axis. Moreover, these calculations do not take into account the thermodynamic effect, so that this optimization is limited to the absolute zero temperature only. But in the NaCl:Cu systems, difference in the total energy between the on-center site and the most

Fig. 1 Schematic illustration of the unit cell. It is a $2 \times 2 \times 2$ face-centered-cubic lattice of the sodium-chloride crystal structure with the center atom replaced by copper atom. The white spheres represent sodium atoms, and black and silver spheres represent chlorine and copper atoms, respectively.

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Fig. 2 These figures represent optimal positions and total energies in eV after the ionic relaxation in the NaCl:Cu system. The arrow shows the direction of the movement of copper atom that was put on various positions. The vertical axis represents the total energy and the horizontal axis represents the distance away from the on-center site. The on-center site is (0.5, 0.5, 0.5). The displacements of copper atom along (a) the $\langle 100 \rangle$ axis, (b) $\langle 110 \rangle$ axis and (c) $\langle 111 \rangle$ axis are represented in separate figures.

stable site along $\langle 111 \rangle$ is no less than 0.3 eV. So we need not take into account the thermal vibration around the room temperature.

It is worth mentioned that ionic sizes are almost same for Na^+ and Cu^+ ions. But the ionic size of Cu^+ ion is smaller than that of K^+ ion (the Pauling ionic radii of Li^+ , Na^+ , K^+ and Cu(I)^+ are 0.60, 0.95, 1.33 and 0.96, respectively). Therefore we can imagine that copper ion embedded in NaCl crystal is more tight compared with that in KCl crystal and is more flexible compared with that in LiCl crystal. Therefore one may say that NaCl:Cu system is in the middle of these LiCl:Cu and KCl:Cu system. It is left for the future study to compute their optical absorption spectra and compare with experiments.

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Note added in proof: We have performed similar calculation also for LiCl:Cu and found that the result is qualitatively similar to the present case of NaCl:Cu. The optical position of Cu ion along the $\langle 111 \rangle$ axis in the LiCl:Cu case is, however, (0.56, 0.56, 0.56) instead of the present (0.57, 0.57, 0.57).