

## Embedded-cluster study of $\text{Cu}^+$ -induced lattice relaxation in alkali halides

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We use an embedded-cluster approach to study the lattice relaxation induced by a substitutional  $\text{Cu}^+$  impurity in alkali halides. The crystalline lattice is modeled as a quantum-mechanical molecular cluster embedded in a classical lattice. The cluster is treated by using the unrestricted Hartree-Fock approximation and the embedding lattice is described by the shell model. The relaxations are obtained by comparing the equilibrium configurations of the pure and  $\text{Cu}^+$ -doped clusters. We found that, when the  $\text{Cu}^+$  ion is introduced into the alkali halides, the lattice relaxes in accordance with the free-ion size difference between the  $\text{Cu}^+$  ion and the host cation. The correlation correction does not make a significant contribution to the lattice relaxation.

### I. INTRODUCTION

The lattice distortion around an isolated defect in ionic crystals is a subject of scientific and industrial interest. An accurate prediction of the behavior of such a distortion can be obtained by computer simulations while it is usually difficult to determine by experiments. For obvious reasons, one cannot stimulate an infinitely large crystal on a computer; thus, finite-cluster methods are always used for simulations. If bulk properties, such as lattice relaxation around a defect, are to be obtained by using such methods, the size of the finite cluster must be sufficiently large and/or proper boundary conditions must be placed on the cluster so that the lattice field in the region of interest is reasonably close to that of the bulk material. For ionic crystals, if free-space conditions are used, a very large cluster of ions may be required to achieve acceptable accuracy because of the long-range Coulomb potentials. Such large clusters are likely to be computationally unaffordable. A technique to overcome this difficulty is to use quantum mechanics to treat the defect and the region near the defect and to embed this defect region in a lattice. Because the embedding lattice is weakly perturbed by the defect region, it can be described by a much simpler model. In this study, we apply an embedded-cluster method, which is based on the unrestricted Hartree-Fock approximation and the shell model, to calculate the lattice relaxation due to a substitutional  $\text{Cu}^+$  ion in the eight alkali halides LiF, LiCl, NaF, NaCl, KF, KCl, RbF, and RbCl. In order to see the contribution of the electronic correlation of the electronic correlation to the lattice relaxation, we include the second-order many-body-perturbation-theory (MBPT) correction in the calculation of the lattice relaxation of LiF: $\text{Cu}^+$  and LiCl: $\text{Cu}^+$ .

### II. METHOD

The methodology we use is called ICECAP (Ionic Crystal with Electronic Cluster, Automatic Program). This embedded-cluster approach is developed specifically for studying defects in ionic crystals and has been described in detail in a number of publications.<sup>1,2</sup> Briefly, the crystalline lattice is modeled as two regions. The first region is a molecular cluster (also referred to as the electronic cluster), which contains the defect and is often called the defect cluster. This cluster is treated quantum mechanically under the unrestricted Hartree-Fock (UHF) approximation. The second region is an embedding lattice in which the ions are described by the shell mode of Dick and Overhauser.<sup>3</sup> Each shell-model ion has a charged core and a charged shell, coupled harmonically through a force constant. It is dipole polarizable. The interactions among these shell-model ions include the long-range Coulomb interactions and the short-range interactions described by a Buckingham-type potential,

$$V(r) = Be^{-r/\rho} - Cr^{-6}.$$

The self-consistency between the Hartree-Fock cluster and the embedding lattice is achieved by matching the multipole moments of the two regions. Charge neutrality is also maintained in the entire modeling lattice.

The basis sets used for the UHF calculation are Gaussian-type functions. The following sets are taken from Huzinaga:<sup>4</sup>  $\text{Li}^+(4)$ ,  $\text{Na}^+(4, 3/4)$ ,  $\text{K}^+(4, 3, 3/4, 3)$ ,  $\text{Rb}^+(4, 3, 3, 3/4, 3, 3/4)$ ,  $\text{F}^-(4, 3/4)$ , and  $\text{Cl}^-(4, 3, 3/4, 3)$ . The  $\text{Cu}^+(5, 3, 3/5, 3/5)$  set is developed by Meng and Kunz.<sup>5</sup> The parameters of the Buckingham-type potentials and the shell parameters are taken from the work of Catlow, Diller, and Norgett.<sup>6</sup>

TABLE I. Perfect lattice spacings (Å).

Material	Experimental <sup>a</sup>	Calculated
LiF	1.996	2.056
LiCl	2.539	2.641
NaF	2.295	2.329
NaCl	2.789	2.817
KF	2.648	2.701
KCl	3.116	3.085
RbF	2.789	2.845
RbCl	3.259	3.292

<sup>a</sup>Extrapolated to 0 K, taken from P. B. Ghate [Phys. Rev. **139**, A 1666 (1965)].

### III. RESULTS AND DISCUSSION

The equilibrium configuration of the  $\text{Cu}^+$ -doped alkali halides are determined by using seven-ion clusters. Each cluster has a cation (the host cation or the  $\text{Cu}^+$  ion) at the center and six anions as first neighbors. We first calculated the equilibrium configuration of the perfect lattice. Table I lists the calculated first-neighbor spacings of the pure alkali halides, showing close agreement with the corresponding experimental values. Then, with the  $\text{Cu}^+$  ion substituting for the cation at the center of the cluster, we calculated the equilibrium configuration of the defect cluster. Since the defect is not charged, distortions in the lattice can only arise from the size difference between the host cation and the substitutional  $\text{Cu}^+$  ion. Thus, we compare in Table II the difference between the calculated first-neighbor spacings and the difference between the free-ion sizes of the  $\text{Cu}^+$  ion and the host cation. The first column is the calculated perfect lattice first-neighbor spacing. The second column is the first-neighbor spacing when the host cation is substituted by the  $\text{Cu}^+$  ion. The third column gives the change in the first-neighbor spacing. The fourth column shows the difference between the free-ion size of the  $\text{Cu}^+$  ion and that of the host cation. The changes in the first-neighbor spacings are consistent

with the ion size differences. Note that negative change means inward relaxation of the first neighbors. Table II also shows the energy gains resulting from the relaxation of the lattice.

With the correlation (MBPT) corrections included, the lattice relaxation in  $\text{LiF}:\text{Cu}^+$  and  $\text{LiCl}:\text{Cu}^+$  are not found to be significantly different from those obtained without the MBPT corrections. With the MBPT corrections, the perfect lattice spacings are 2.038 and 2.641 Å for LiF and LiCl, respectively. Upon introduction of the  $\text{Cu}^+$  ion, the first-neighbor spacings become 2.215 Å (increased by 0.177 Å) and 2.802 Å (increased by 0.161 Å) for  $\text{LiF}:\text{Cu}^+$  and  $\text{LiCl}:\text{Cu}^+$ , respectively.

Recently, Jackson, Pederson, and Klein<sup>7</sup> reported results of their calculation of the lattice relaxation of  $\text{LiCl}:\text{Cu}^+$ , using the local-density approximation (LDA). With a 27-ion cluster (in free space), they found virtually no lattice relaxation in the lattice, contrary to our result and that of Meng and Kunz.<sup>5</sup> In order to make a comparison, we did an ICECAP calculation on  $\text{LiCl}:\text{Cu}^+$  with the same 27-ion cluster used by Jackson, Pederson, and Klein. It turned out that the lattice relaxed outward considerably, consistent with the result with the seven-ion cluster. A comparison between our result and that of Jackson, Pederson, and Klein is given in Table III. A significant difference exists between our result and the result of Jackson, Pederson, and Klein. Although we used different approximation procedures, we believe that neither the UHF approximation nor the LDA is the source of the discrepancy. The following may be a more reasonable explanation for the disagreement.

When doing finite-cluster calculations of ionic crystals, one must include a large number of ions to obtain a reasonably accurate Coulomb field in the region of interest. Besides, if the finite set of ions has a net charge, a spurious tunneling effect may arise even if a large number of ions are included, as pointed out by Kunz and Vail.<sup>8</sup> Jackson, Pederson, and Klein did their calculations with a cation-centered 27-ion cluster (with a net charge of  $-1$ ) in free space, thereby taking into account up to the third neighbors only. The Coulomb field in such a small cluster is expected to be significantly different from that in the bulk material. Besides, since the cluster is in free

TABLE II. First-neighbor spacings obtained with seven-ion clusters (distance in Å, energy in eV).

Material	Perfect lattice	$\text{Cu}^+$ doped cluster	Change	Ion size difference <sup>a</sup>	Energy gain <sup>b</sup>
LiF	2.056	2.233	0.177(8.6%)	0.18	1.127
LiCl	2.641	2.815	0.174(6.6%)	0.18	0.212
NaF	2.329	2.369	0.040(1.7%)	0.01	0.044
NaCl	2.817	2.828	0.011(0.4%)	0.01	0.010
KF	2.701	2.569	-0.132(-4.9%)	-0.40	0.159
KCl	3.085	2.965	-0.120(-3.9%)	-0.40	0.162
RbF	2.845	2.629	-0.216(-7.6%)	-0.52	0.281
RbCl	3.292	3.091	-0.201(-6.1%)	-0.52	0.188

<sup>a</sup>Calculated from the data of V. M. Goldschmidt (1926) and L. Pauling (1960).

<sup>b</sup>Energy difference between unrelaxed and relaxed configuration.

TABLE III. Calculated lattice relaxation in  $\text{LiCl}:\text{Cu}^+$  with a 27-ion cluster.

	This study (embedded cluster)	Jackson, Pederson, and Klein (free space)
First-neighbor relaxation	7%	0.2%
Second-neighbor relaxation	6%	fixed
Third-neighbor relaxation	4%	fixed
Energy gain <sup>a</sup>	1.116 eV	<0.01 eV

<sup>a</sup>Energy difference between unrelaxed and relaxed configuration.

space, its interaction with the environment is completely neglected. Such interaction is often too important to be neglected in defect-structure calculations. Furthermore, Jackson, Pederson, and Klein did not allow all the ions in the cluster to move freely. In our ICECAP calculation, the quantum-mechanical 27-ion cluster is embedded in a shell-model lattice and the entire region (the cluster and the embedding lattice) is kept charge neutral. The Coulomb field seen by the cluster is very close to that in the bulk material and the interactions among the ions (in the cluster and in the embedding lattice) are adequately described. There is no constraint on the ions so that they are all free to move. Therefore, the ICECAP methodology is expected to give a reliable prediction of the  $\text{Cu}^+$ -induced lattice relaxation in the alkali halides.

#### IV. CONCLUSIONS

In summary, the results of this study predict significant lattice relaxations in alkali halides when  $\text{Cu}^+$  is intro-

duced as an isolated substitutional impurity. The lattice will relax outward if the  $\text{Cu}^+$  ion is larger than the host cation or inward if the  $\text{Cu}^+$  ion is smaller than the host cation. When calculating defect properties of ionic crystals using finite-cluster methods, one must therefore employ an accurate description of the long-range Coulomb field in the region of interest.

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