PHYSICAL REVIEW B VOLUME 49, NUMBER 1 1 JANUARY 1994-I

# Local geometries and stabilities of $Cu^+$ centers in alkali halides

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(Received 13 August 1993)

The local geometry, energy stabilization, and pseudolocal $t_{1u}$ vibration mode of the $Cu^+$ impurity in the alkali halide crystals have been investigated with the *ab initio* perturbed ion cluster-in-the-lattice methodology. The electronic structure of different clusters, containing up to 179 ions, has been computed for nine Cu:$AX$ systems ($A$=Li, Na, K; $X$=F, Cl, Br). The calculations clearly show that the nearest-neighbor relaxations induced by impurity substitution are essentially determined by the substituted cation, the anion playing a rather minor role. In contrast with predictions deducible from empirical ionic radii, we find negligible or very small relaxations for Cu:Li$X$ systems, and inward relaxations of about $-0.1$ Å for Cu:Na$X$ systems [in very good agreement with recent extended x-ray absorption fine-structure (EXAFS) measurements on Cu:NaCl]. For the Cu:K$X$ family we found inward relaxations as large as $-0.3$ Å. The stabilization energy associated to the substitution reaction turns out to range from $-0.2$ to $-1.8$ eV, with a remarkable dependence upon the substituted cation. The $t_{1u}$ frequencies, computed without including the intershell coupling, decrease with increasing cationic size, showing a trend that agrees with the experimental data reported by McClure for Cu:LiCl, Cu:NaF, and Cu:NaCl. Our methodology, in its present form, does not reproduce the off-center equilibrium position of the $Cu^+$ ion observed in Cu:NaBr, Cu:KCl, and Cu:KBr.

## I. INTRODUCTION

The atomic displacements around an impurity in a crystal are, in general, little known. This is a serious limitation in the study of impurity centers because the equilibrium geometry of the atoms or ions surrounding the impurity plays a fundamental role in many observable properties of the center. For instance, a large number of spectroscopic studies on $Cu^+$-doped alkali halides, and Cu:NaF in particular,[1] would greatly benefit from the exact determination of a $Cu^+$ environment. Unfortunately, the small concentration of impurity in the samples precludes, in most cases, the experimental determination of the impurity center geometry using extended x-ray absorption fine-structure (EXAFS) techniques. Alternatively, the distance from the impurity to its nearest neighbors could, in principle, be inferred from the observed spectral properties, as Moreno *et al.* did for $Mn^{2+}$-doped fluorides.[2] However, there is a lack of experimental information needed to calibrate the distance-dependence laws of the $3d$-$4s$ transitions in the $Cu^+$-doped alkali halides. Under those circumstances, an accurate theoretical calculation seems to be the only available approach, at the present time, to determine the equilibrium geometry of these impurity centers.

To be reliable, a theoretical model must describe accurately the delicate balance between the few-body interactions of the impurity ion with its immediate neighborhood and the many-body embedding effects induced by the rest of the crystal. The problem is, thus, a severe test for any quantum-mechanical embedding methodology as well as a most interesting challenge for theoreticians.

In this paper we report the results of a theoretical investigation on the electronic structure, equilibrium geometry, and stability of nine Cu:$AX$ impurity systems ($A$=Li, Na, K; $X$=F, Cl, Br). The main objectives of this study are (a) to determine the ionic displacements around the $Cu^+$ ion in these nine crystals; (b) to compute the stabilization energies involved in the impurity substitution reaction; (c) to estimate the trend, along this nine-term series, of the pseudolocal $t_{1u}$ vibration mode of the $Cu^+$ ion.

To complete this research we have used the *ab initio* perturbed ion (aiPI) model.[3] This is a cluster-in-the-lattice approach that deals accurately with the cluster-lattice interaction and allows for cluster-size study in a way that is theoretically rigorous and computationally very efficient.

Quantum-mechanical calculations of impurity centers are usually performed by using very small clusters, most times limited to the impurity and the first shell of neighbors. It is implicitly assumed that by embedding this cluster within an appropriate frozen representation of the rest of the crystal, the equilibrium properties (the geometry in particular) of the cluster will closely resemble those of the real impurity center. We have recently presented aiPI cluster-in-the-lattice calculations on the nearest-neighbor geometry of Cu:NaF and Cu:NaCl, in which the dependence of the predicted geometry on the cluster size was explicitly considered.[3] It was observed there that the artificial interface introduced between the cluster (whose electronic structure is relaxed along with its geometry) and the lattice (for which the electronic structure is held frozen) gives rise to a poor prediction of the geometry of the cluster surface. In particular, the calculation on the $CuF_6^{5-}$ cluster predicted an equilibrium

0163-1829/94/49(1)/69(7)/$06.00

value for $R$(Cu-F) 0.05 Å smaller than that obtained in calculations done on clusters of 13, 25, and 33 ions.

In view of these results, we have used here large clusters containing up to 179 ions, namely, $\mathrm{Cu}X_{92}A_{86}^{5-}$. These clusters are embedded in a fixed lattice described by the pure-crystal aiPI wave functions. Several crystal models have been considered, as described below, in order to examine the consistency of the method and the significance of the cluster-size effects. The good results obtained previously in Cu:NaF and Cu:NaCl (Refs. 3 and 4) give confidence to our predictions and to the physical consequences extracted from them.

The paper is divided in three sections. In the next one we give very briefly the more important characteristics of the theoretical model, mainly to introduce the notation and details of the simulation. Section III contains the results. It is divided in four subsections dedicated to examine the consistency of the method, the equilibrium geometry of the impurity center, the stability of the nine systems, and the motion of the $\mathrm{Cu}^+$ ion in these crystals, respectively. The main conclusions of our work complete the paper.

## II. THE METHOD AND THE CLUSTER MODEL

The aiPI method[3–5] begins by assuming the electronic wave function of the doped crystal to be an antisymmetric product of group functions, each of them representing an ion in the crystal. Two disjoint sets of ions are considered: the cluster ($\mathcal{C}$), formed of the ions relevant to the problem under study, and the lattice ($\mathcal{L}$), containing the ions of the rest of the crystal. All ions receive a quantum-mechanical treatment in the calculation. The difference between $\mathcal{C}$ ions and $\mathcal{L}$ ions is that the group wave functions of the former are self-consistently solved, while pure-crystal wave functions, obtained in the appropriate aiPI calculations,[4] are maintained frozen to describe the ions in $\mathcal{L}$.

A further development has given significant physical insight on the behavior of the impurity neighborhood: the $\mathcal{C}$ set is partitioned into the $\mathcal{C}_1$ subset, made of all ions that are geometrically as well as electronically relaxed, and the $\mathcal{C}_2$ subset, collecting the ions that suffer only electronic relaxation. In this way, the $\mathcal{C}_2$ territory attenuates the sudden boundary effects on the cluster wave functions and supplies an interface to accommodate the cluster electronic density to the fixed lattice density.

To obtain the group wave function of an ion in $\mathcal{C}$, we minimize the effective energy of such ion, which is made of the energy components internal to the ion (net energy) and all the interaction terms with the remaining ions in the crystal.[5,6] Every ion contributes to the interaction energy with a Coulombic potential, a nonlocal exchange term, and a projection operator that procures the orthogonality between the group wave functions and corrects the total energy for any residual nonorthogonality.[5–7] The aiPI equations are solved iteratively for every different ion in the cluster up to a required convergence. At the end, the aiPI wave functions are self-consistent within $\mathcal{C}$ and consistent with the frozen description of $\mathcal{L}$.

The calculations discussed here have been done on clusters containing up to 179 ions. The 179-ion cluster is formed of a $\mathrm{Cu}^+$ ion at the origin of coordinates plus its 12 first shells of neighbors, as described in Table I of Ref. 4. The experimental host geometry [cubic, space group $Fm3m$, $A^+$ at (0,0,0) and $X^-$ at the ($\frac{1}{2}$,0,0) positions] is used for the cluster and the lattice, except for the position of the shells that are allowed to relax. We will denote as $Cn$-$m$ a calculation in which the cluster is formed of a central ion and its $n$ first shells of neighbors, the first $m$ of them (defining the $\mathcal{C}_1$ set) being allowed to relax its positions along independent breathing modes.

Large Slater-type orbital (STO) basis sets have been used on every ion.[8] The wave functions describing the ions in the lattice are taken from previous aiPI calculations on the pure host crystals. The unrelaxed Coulomb-Hartree-Fock model[9] has been used to estimate the correlation energies without modifying the self-consistent aiPI wave functions.[10] All the calculations performed on the clusters and on the $AX$ as infinite crystals have been done using the PI7 program,[10,11] the optimizations and numerical calculation of derivatives being conducted by specific driver programs.[4]

## III. RESULTS AND DISCUSSION

The calculations have been performed in two steps. In the first one, we have relaxed the geometry of the $m$ first shells of neighbors around $\mathrm{Cu}^+$ by allowing independent breathing motions of each shell. These $m$ shells constitute the $\mathcal{C}_1$ set in our simulation. The same treatment was applied to the equivalent cluster model of the pure hosts, in order to check for the consistency of the calculations and to estimate any systematic error. Then, we have verified whether the impurity ion is stable at the on-center position, and thus the impurity neighborhood maintains the nominal octahedral symmetry. We have also obtained the $t_{1u}$ vibrations associated with the independent motion of the $\mathrm{Cu}^+$ ion.

### A. Consistency of the aiPI method

As advanced in Ref. 3, the consistency of an embedding scheme can be examined with two criteria. First, there is the so-called self-embedding consistency, according to which the cluster-in-the-lattice calculations on the pure crystal should reproduce the quantum description attained in the calculation for the infinite crystal. We have shown for NaF and NaCl in Ref. 3 that whereas the simplest $AX_6$ cluster model fails to meet this requirement, models involving clusters like $A_7X_6$, $A_{19}X_6$, and $A_{19}X_{14}$ satisfy this consistency. We find now that the 33-ion cluster and 179-ion cluster calculations presented here give full self-embedding consistent descriptions of the nine alkali halides. This means that the pure-crystal calculations give negligible ionic relaxations (geometric self-embedding consistency) as well as negligible stabilization energies (energetic self-embedding consistency). Thus, we confirm with these nine cases the significant

TABLE I. Optimal NN distances, $R_{\rm th}(A\text{-}X)$ (Å), for the pure crystals, according to the aiPI calculations on 33-ion and 179-ion clusters. $Cn\text{-}m$ indicates that the cluster is made up of the central ion and the $n$ nearest shells, the $m$ first of them being allowed to geometrically relax.

| $AX$ | C4-1 | C4-2 | C12-4 | Experiment |
|---|---|---|---|---|
| LiF | 1.991 | 2.076 | 2.021 | 2.014 |
| LiCl | 2.533 | 2.580 | 2.555 | 2.570 |
| LiBr | 2.724 | 2.772 | 2.753 | 2.751 |
| NaF | 2.286 | 2.386 | 2.325 | 2.317 |
| NaCl | 2.782 | 2.867 | 2.811 | 2.820 |
| NaBr | 2.963 | 3.048 | 2.992 | 2.989 |
| KF | 2.593 | 2.664 | 2.654 | 2.674 |
| KCl | 3.071 | 3.158 | 3.135 | 3.147 |
| KBr | 3.242 | 3.324 | 3.303 | 3.298 |

role of the $\mathcal{C}_1+\mathcal{C}_2$ partition of the cluster in fulfilling this first criterion of model consistency.

The second test refers to the agreement with observed data. The performance of the aiPI method in this test can be appreciated by looking at the numbers in Table I, where we summarize the nearest-neighbor (NN) distances, $R_{\rm th}(A\text{-}X)$, obtained for the nine pure alkali halides by using the 33-ion (C4-1 and C4-2 calculations) and 179-ion (C12-4 calculations) cluster models. The agreement between our best, C12-4, theoretical results and the experimental geometries is excellent, indicating that the local equilibrium geometries of the clusters are consistent with the lattice parameters.

From Table I it is also interesting to note how the C4-1 calculations predict a slight inwards relaxation of the nearest neighbors. When two shells are allowed to relax, as in the C4-2 case, the first shell uniformly moves outward, with respect to the C4-1 picture, by amounts ranging from 0.05 to 0.1 Å. The 179-ion cluster calculation, involving relaxation of four shells, tends to recover the C4-1 geometries, giving great consistency with the observed data. It is satisfactory to see that the more complex model produces the better agreement with the experimental values.

### B. Local geometry of the Cu:$AX$ systems

Table II contains our results for the local relaxation of the first shell around $\mathrm{Cu}^+$. The relaxation is computed as the difference between the equilibrium distance found for Cu:$AX$, $R_{\rm th}(\mathrm{Cu}\text{-}X)$, and that found for $A$:$AX$, $R_{\rm th}(A\text{-}X)$. In this way our prediction is corrected for the (small) systematic error, $R_{\rm th}(A\text{-}X) - R_{\rm exp}(A\text{-}X)$, found in the reference $A$:$AX$ calculations. The relaxations experienced by the second, third, and fourth shells around $\mathrm{Cu}^+$ are small and do not appreciably differ from those found on the $A^+$-centered clusters. Thus the best we can say is that no significant relaxation of those shells is predicted.

Our C12-4 results show qualitatively different NN relaxations depending on the cation being substituted. Negligible or very small inwards relaxations are obtained for Cu:Li$X$, inwards relaxations close to $-0.1$ Å are obtained for Cu:Na$X$, and values around $-0.3$ Å are encountered for Cu:K$X$. The effect of the anion is small, increasing slightly the inwards relaxations as the size of the anion decreases. Similar results are obtained in the C4-1 and C4-2 calculations.

Emura *et al.*[12] did EXAFS measurements of the local geometry of Cu:NaCl, and found an inwards relaxation of $-0.10 \pm 0.02$ Å. We want to stress that our prediction for Cu:NaCl, $-0.10$ Å, agrees with this value, that constitutes the only direct experimental evidence of the local geometry of a $\mathrm{Cu}_A$ center. Given the uniform behavior of the aiPI method shown above within these nine crystals, the isolated experiment by Emura *et al.*[12] suggests that our method may give experimentally consistent descriptions of the lattice relaxations induced by the $\mathrm{Cu}^+$ impurity in alkali halides.

A detailed comparison of the aiPI results with other cluster-in-the-lattice theoretical calculations has already been presented in Ref. 3 for Cu:NaF and Cu:NaCl. The local geometry of the impurity was found to be far more sensitive to the embedding scheme than to the quantum technique used to solve the cluster. Winter *et al.*,[13] using an embedding method based on finite sets of point charges plus effective core potentials representing the cationic shells, predict a negligible relaxation of the $\mathrm{Cu}^+$

TABLE II. Geometries for the Cu:$AX$ and $A$:$AX$ clusters. The relaxations are computed as the differences $\Delta R = R_{\rm th}(\mathrm{Cu}\text{-}X) - R_{\rm th}(A\text{-}X)$ (see text). Distances are given in Å.

| | C4-1 | C4-2 | C12-4 | C12-4 | C12-4 | Ref. 19 | Ref. 20 | Ionic radii |
|---|---|---|---|---|---|---|---|---|
| $AX$ | $\Delta R$ | $\Delta R$ | $R_{\rm th}(\mathrm{Cu}\text{-}X)$ | $R_{\rm th}(A\text{-}X)$ | $\Delta R$ | $\Delta R$ | $\Delta R$ | difference |
| LiF | 0.005 | −0.026 | 2.021 | 2.021 | 0.000 | 0.177 | 0.14 | 0.18 |
| LiCl | −0.015 | −0.033 | 2.522 | 2.555 | −0.033 | 0.174 | 0.10 | 0.18 |
| LiBr | −0.004 | −0.015 | 2.734 | 2.753 | −0.020 | | | 0.18 |
| NaF | −0.089 | −0.082 | 2.201 | 2.325 | −0.124 | 0.040 | 0.00 | −0.01 |
| NaCl | −0.084 | −0.090 | 2.706 | 2.811 | −0.105 | 0.011 | −0.03 | −0.01 |
| NaBr | −0.070 | −0.072 | 2.906 | 2.992 | −0.086 | | | −0.01 |
| KF | −0.267 | −0.273 | 2.276 | 2.654 | −0.378 | −0.132 | −0.19 | −0.37 |
| KCl | −0.286 | −0.261 | 2.769 | 3.135 | −0.365 | −0.120 | −0.20 | −0.37 |
| KBr | −0.250 | −0.212 | 3.004 | 3.303 | −0.299 | | | −0.37 |

neighborhood. The same tendency is found by Meng *et al.*[14] using the ICECAP technique developed by Vail and co-workers,[15] in which a quantum cluster is embedded into a classical shell-model lattice. In contrast, Barandiarán and Seijo,[16] who proposed the use of free-ion *ab initio* model potentials to account for the quantum and classical lattice effects, found a $-0.1$ Å inwards relaxation in the case of Cu:NaCl, in close agreement with the Emura *et al.*[12] experiment and the aiPI results. The $X$-$\alpha$ calculations of Till *et al.*,[17,18] on the other hand, appear to be extremely sensitive to the arbitrary parameters that define the muffin-tin environment used to modelize the lattice, up to the point that the predicted Cu-F distance in Cu:NaF varies between 2.12 and 2.44 Å and the $a_{1g}$ breathing mode frequency varies between 428 and 1750 $\text{cm}^{-1}$.

The recent ICECAP calculations by Zuo *et al.*[19] and the empirical arguments of Bucher based on a simple rescaling of ionic radii,[20] both tend to predict large outwards relaxations (0.1–0.2 Å) for Cu:Li$X$, negligible relaxations in Cu:Na$X$, and large inwards relaxations ($-0.1$ to $-0.2$ Å) in Cu:K$X$. Contrarily, Harrison and Lin[21] suggest a small inwards relaxation for the $\text{Cu}_{\text{Li}}$ center in Cu:LiCl and this was indeed found in the local-density-approximation calculation published by Jackson *et al.*[22]

Of particular interest is to remark that the ligand relaxation upon impurity substitution, shown in Table II, largely contrasts with the picture that could be deduced for the $\text{Cu}_{\text{Li}}$ and $\text{Cu}_{\text{Na}}$ centers by considering the octahedral ionic radii usually adopted: $r(\text{Cu}^+) = 0.96$ Å, $r(\text{Li}^+) = 0.78$ Å, $r(\text{Na}^+) = 0.97$ Å, and $r(\text{K}^+) = 1.33$ Å. The discrepancy between the aiPI prediction and the reasoning based upon the ionic radii is noteworthy because the wide use of this type of argument and the conspicuous disagreement of its prognostic with the data reported by Emura *et al.*[12]

The ligand relaxations obtained in this work can be further analyzed by comparing the metal-ligand distances of the pure alkali halides with the corresponding distances of the hypothetical octahedrically coordinated copper halides. To estimate these hypothetical distances, we argue as follows.

Copper halides crystallize at room temperature and pressure in the sphallerite (B3) phase, having tetrahedral environments around both anions and cations. Relationships between the octahedral and tetrahedral NN distances have been proposed long ago. For instance, Pauling[23] proposed

$$\frac{R_6}{R_4} \simeq \left(\frac{6}{4}\right)^{1/8} = 1.052, \tag{1}$$

where $R_i$ is the NN distance for the coordination number $i$. Rock-salt (B1) and sphallerite phases have been found at room conditions for MnS and the NN distance ratio was found to be 1.074,[21] not too far from Pauling's prediction. In addition, we have performed aiPI calculations on the B1 and B3 phases of Cu$X$ crystals, and we found the $R_6/R_4$ ratio of theoretical distances to be 1.028 on CuF, 1.038 on CuCl, and 1.036 on CuBr.

Using these theoretical $R_6/R_4$ ratios and the experimental Cu-$X$ distances found in the B3 phase we derive the following NN distances for the hypothetical octahedrally coordinated Cu$X$ crystals: $R(\text{Cu-F}) = 1.890$ Å, $R(\text{Cu-Cl}) = 2.435$ Å, and $R(\text{Cu-Br}) = 2.554$ Å. We can expect that the $\text{Cu}^+$ impurity would exhibit a Cu-$X$ distance somewhat in between the two limiting Cu$X$ and $AX$ pure crystals with the same B1 phase. This assumption would imply inwards relaxations for all the three $\text{Cu}_{\text{Li}}$, $\text{Cu}_{\text{Na}}$, and $\text{Cu}_{\text{K}}$ types of centers, being larger in the order Li<Na<K. In the extreme scale, where the Cu-$X$ distance adopts the value of the Cu$X$ pure crystal, this would represent inwards relaxations of $-0.12$ to $-0.20$ Å for the $\text{Cu}_{\text{Li}}$ centers, $-0.39$ to $-0.44$ Å for the $\text{Cu}_{\text{Na}}$ centers, and $-0.71$ to $-0.78$ Å for the $\text{Cu}_{\text{K}}$ centers. Our theoretical predictions are far smaller than these extreme values, showing a tendency of the $\text{Cu}^+$ impurity to adapt to the geometry of the host rather than deforming the host to adopt its "natural" octahedral distance. Again, we stress that these extreme relaxations disagree with the experimental data by Emura *et al.*[12] Thus, this adaptative trend of the $\text{Cu}^+$ impurity seems to be consistent with the single observation available.

The above results can be compared with the local geometries found by Moreno *et al.*[2,24] on $\text{Mn}^{2+}$-doped fluoride crystals. They used the distance dependence of the isotropic superhyperfine constants or that of some spectral $d$-$d$ lines to obtain the $\text{Mn}^{2+}$-$\text{F}^-$ distances in the doped crystals. In their analysis of $AM\text{F}_3$ fluoroperovskites, they noticed that the introduction of substitutional $\text{Mn}^{2+}$ gives rise to an inwards (outwards) relaxation when the pure crystal $A$-F distance is greater (lower) than the Mn-F distance in the pure $\text{Mn}^{2+}$ compounds with the same structure. The comparison of the $\text{Mn}^{2+}{:}AM\text{F}_3$ and $\text{Cu}^+{:}AX$ systems shows an interesting difference in the character of these two impurities. Whereas the Mn-F distances appear to be very concentrated around some value that can be viewed as the "natural distance," the Cu-$X$ distances are far more dispersed around the average values. This can be ascribed to the more deformable character of the monovalent ion or, alternatively, to the more covalent nature of the Mn-F bond.

### C. Formation energy of the $\text{Cu}_A$ centers

The formation of the $\text{Cu}_A$ centers should be discussed in terms of the free-energy difference for the exchange reaction

$$A^+ : AX_{(s)} + \text{Cu}^+_{(g)} \rightleftharpoons \text{Cu}^+ : AX_{(s)} + A^+_{(g)}. \tag{2}$$

At very low pressure and temperature, the reaction will be governed by the internal energy change, $E_{\text{form}}(\text{Cu}_A)$, that can be obtained from our quantum-mechanical calculations.

Results concerning $E_{\text{form}}(\text{Cu}_A)$ are found in Table III. We show the results of calculations in which the cluster is reduced to a single ion (C0-0), as well as for the 179-ion cluster using the pure crystal geometry (C12-0), and for the 179-ion cluster using the optimal geometry found for the first four shells (C12-4). The comparison between

TABLE III. Formation energies, $E_{\mathrm{form}}(\mathrm{Cu}_A)$ (eV), of the $\mathrm{Cu}_A$ centers.

| $AX$ | C0-0 | C12-0 | C12-4 |
|---|---|---|---|
| LiF | 1.103 | 0.208 | −0.252 |
| LiCl | −0.349 | −0.414 | −0.688 |
| LiBr | −0.221 | −0.260 | −0.392 |
| NaF | 0.387 | −0.765 | −1.022 |
| NaCl | −0.162 | −0.666 | −0.867 |
| NaBr | −0.073 | −0.570 | −0.684 |
| KF | −0.239 | −1.044 | −1.771 |
| KCl | −0.234 | −1.018 | −1.646 |
| KBr | −0.192 | −0.905 | −1.377 |

these calculations shows, separately, the importance of ensuring consistency between the electronic structure of the cluster and that of the rest of the lattice, and the importance of the geometrical relaxation of the impurity neighborhood.

Some important conclusions can be deduced from Table III. First, we observe that according to the rigid C0-0 model, that accounts for the impurity substitution into a geometrically and electronically frozen lattice, seven out of these nine species are stable centers. The two unstable systems are Cu:LiF [$E_{\mathrm{form}}(\mathrm{Cu_{Li}}) = 1.1$ eV] and Cu:NaF [$E_{\mathrm{form}}(\mathrm{Cu_{Na}}) = 0.4$ eV]. Second, the cluster electronic relaxations, extended to a cluster of 179 fixed ions in the C12-0 model, accommodates the cluster wave function to the lattice background and produces large stabilization effects, from 0.50 to 1.15 eV, with the exceptions of Cu:LiCl and Cu:LiBr. These effects make the Cu:NaF system stable. Third, comparison between the C0-0 and C12-0 schemes reveals that although the cluster-lattice interaction is properly described in both models, the size of the cluster and the corresponding intracluster electronic reorganization are important factors in the calculation of the stability of these centers. Fourth, the four-shell geometric relaxation encompassed in the C12-4 model induces a further stabilization, from 0.11 to 0.73 eV, that makes the Cu:LiF center also stable.

Thus, our best calculation predicts all the $\mathrm{Cu}_A$ centers to be stable. The values of $E_{\mathrm{form}}(\mathrm{Cu}_A)$ are mainly determined by the cation being substituted: Cu:K$X$ are stable by 1.4–1.8 eV, Cu:Na$X$ by 0.7–1.0 eV, and Cu:Li$X$ by 0.2–0.7 eV. The effect of the anions is, in most cases, small: for a given cation $E_{\mathrm{form}}(\mathrm{Cu}_A)$ slightly decreases as the anionic size increases. Our best $E_{\mathrm{form}}(\mathrm{Cu_{Na}})$ for Cu:NaF is in close agreement with simulations done using state-of-the-art empirical potentials.[25] It should be mentioned here that even if we predict $E_{\mathrm{form}}(\mathrm{Cu}_A)$ to be negative and the centers to be stable, doping the alkali fluorides with $Cu^+$ is experimentally difficult due, apparently, to the disproportion of two $Cu^+$ ions into $Cu^0$ and $Cu^{2+}$, the $Cu^0$ tending to migrate and to form metallic microaggregates.[26]

### D. Off-center displacements and the $t_{1u}$ frequencies

As discussed in Ref. 1, several spectroscopic studies of $Cu^+$ in alkali halides give information about the position of $Cu^+$ in the lattice as well as on the potential function that describes its motions. In some alkali halides, $Cu^+$ lies off the ion site in an appreciable extent. Qualitative information about this fact has been reviewed and extended by Payne.[27] This author noted that the off-center displacement of $Cu^+$ smoothly increases with the nearest-neighbor distance of the alkali halide crystal. As a consequence, three of the systems analyzed here have an off-center ground state: $Cu^+$ in NaBr has a shallow off-center position and $Cu^+$ in KCl and KBr have deep off-center positions. For Cu:NaBr, Emura and Ishiguro[28] have obtained the corresponding off-center parameters by analyzing the pressure effects on the absorption bands. The off-center stabilization energy is estimated to be 25±3 meV, and the off-center displacement 0.55 Å in the [110] or [111] directions. The small amount of this stabilization energy makes the prediction of the off-center geometry an extremely difficult task for any *ab initio* calculation.

This interesting observation can be investigated in some detail with the aiPI method. Here we present results of calculations appropriate to interpret the possible off-center displacements of the $Cu^+$ ion as well as to inform about the basic trends of the associated $t_{1u}$ vibration modes of the Cu:$AX$ systems. To study these matters we used again the 179-ion cluster model. Fixing the cluster ions at the positions optimized in the way described above, we move the $Cu^+$ ion along the [100] direction and compute the effective energy of the cluster for every new position of the impurity. In the same way, we obtain the [110] and [111] energy curves. We want to point out that these movements of the $Cu^+$ ion out of the center of the cluster largely reduce the symmetry and significantly add to the computational cost of each geometry.

The most relevant result of these calculations is that the $Cu^+$ remains on-center in the nine systems analyzed here, that is, the (0,0,0) site is the point of minimum energy along the [100], [110], and [111] axes. The three curves are rather flat and highly similar near the minimum, progressively separating each other for displacements of 0.3 Å or larger. The movement of the $Cu^+$ ion is easiest along the [111] axis and most difficult along the [100] axis. In consequence, our model does not explain the off-center position observed for $Cu^+$ in the three above-mentioned compounds. This failure might probably be related to the absence of nonspherical deformations of the ionic wave functions in the present aiPI calculations.

Nagasaka[29] has proposed that the stability of the off-center position of $Cu^+$ ion in some alkali halides is due to the mixing between the closed-shell electronic ground state and an $X^- \to Cu^+$ charge-transfer excitation state. This interpretation suggests that the polarization of the anions surrounding the $Cu^+$ ion plays a key role in the stabilization of the off-center position, thus posing a particular difficulty for the present aiPI calculations to reproduce the phenomenon.

By fitting the [100] energy curves to a polynomial we have obtained an estimation of the uncoupled $t_{1u}$ vibrational frequency associated to the $Cu^+$ [100] displacement.[4] These values should be considered as a

TABLE IV. $t_{1u}$ frequencies (cm$^{-1}$) for the [100] motion of Cu$^+$ in the Cu$_A$ centers.

| *AX* | C12-0 | C12-4 |
|---|---|---|
| LiF | 247.0 | 227.4 |
| LiCl | 151.5 | 154.5 |
| LiBr | 146.5 | 145.4 |
| NaF | 132.3 | 154.8 |
| NaCl | 93.1 | 111.2 |
| NaBr | 92.7 | 106.0 |
| KF | 51.5 | 112.0 |
| KCl | 38.5 | 91.1 |
| KBr | 42.3 | 81.2 |

crude estimation of the correct $t_{1u}$ vibration frequencies, as we have recently shown that strong couplings between symmetry modes appear that largely modify the uncoupled frequencies.[4] Values obtained at the C12-0 and C12-4 levels are given in Table IV. Comparison between both sets shows the effect of the relaxation of the four inner shells. This effect is negligible in Cu:Li$X$, with the exception of Cu:LiF where we obtain a decreasing of 20 cm$^{-1}$ in this frequency. In Cu:Na$X$ frequencies increase by 13–22 cm$^{-1}$ and in Cu:K$X$ by 39–61 cm$^{-1}$, the relaxation being a very important effect in the potassium compounds. With the exception of Cu:LiF, the changes correlate with the relaxations obtained for the NN distances.

The best (C12-4) $t_{1u}$ frequency values decrease in passing from Cu:Li$X$ to Cu:K$X$. The smallest values, 91.1 and 81.2 cm$^{-1}$, are obtained for Cu:KCl and Cu:KBr, respectively. This result shows that the central position is less stable in these two crystals than in those systems where the on-center position of the Cu$^+$ ion is experimentally known.

Our values for Cu:LiCl (154.5 cm$^{-1}$), Cu:NaF (154.8 cm$^{-1}$), and Cu:NaCl (111.2 cm$^{-1}$) correlate with the experimental data quoted by McClure, namely: 100, 93, and 23 cm$^{-1}$ (Ref. 1). We recall from Ref. 4 that the coupling of this Cu$^+$ motion to the vibrations of the first four shells of neighbors reduces, in Cu:NaF, the lowest $t_{1u}$ frequency from 155 to 108 cm$^{-1}$, leading to a much better agreement with the experiments. The eigenvalue analysis shows[4] that this strongly coupled mode is dominated by the motion of the Cu$^+$ impurity, with a significant contribution from the first shell of neighbors. This result and the trend shown by the values in Table IV suggest that the extended analysis undertaken in Ref. 4 may give uniformly good description of the local vibrations in these impurity centers.

## IV. CONCLUSIONS

We have presented in this work *ab initio* perturbed ion calculations on up to 179-ion cluster-in-the-lattice models of Cu$^+$ in nine alkali halides. The linear dependence in computer time that this method shows with the cluster size made feasible these otherwise prohibitive calculations.

Our results show qualitatively different NN relaxations depending on the cation being substituted. For Cu:Li$X$, negligible or very small inwards relaxations are obtained, whereas large inwards relaxations around −0.1 Å are obtained for Cu:Na$X$, and very large relaxations around −0.3 Å are encountered for Cu:K$X$. The effect of the anion is small, increasing slightly the inwards relaxations as the size of the anion decreases. Our best calculation predicts that the first shell around Cu$^+$ relax inwards −0.10 Å in NaCl, in close agreement with the EXAFS measurements.

The above cationic trends can be understood by comparing the $A$-$X$ distance in the pure alkali halides with the Cu-$X$ distance in the hypothetical octahedral Cu$X$ crystals. Our relaxation values can be recovered by assuming that the Cu-$X$ distances in Cu:$AX$ compounds lie somewhat in between the first-neighbor distances in the two limiting pure crystals.

These ionic relaxations induced by impurity substitution differ from the values that can be deduced from the usually accepted ionic radii. We interpret this discrepancy in terms of an accommodation of the impurity ion to the crystal constrains, not contemplated in the argument of constant ionic radii.

Our model does not explain the off-center position of Cu$^+$ in Cu:NaBr, Cu:KCl, and Cu:KBr. This failure could be due to the absence of nonspherical deformation of the ionic wave functions in the aiPI method and the assumption of a closed-shell electronic ground state for the impurity center. However, the small value obtained for the $t_{1u}$ frequencies in deep off-center systems adequately correlate with the experimental relative on-center stability of the systems analyzed here. Our best $t_{1u}$ frequency values decrease in passing from Cu:Li$X$ to Cu:K$X$. Our model also predicts negative values for the formation energy of all Cu$_A$ centers.

## ACKNOWLEDGMENTS

All calculations have been done on the Convex C-120 (Centro de Cálculo Científico) and HP9000 (Centro de Cálculo) computer facilities at the Universidad de Oviedo. One of us (MAB) is indebted to the Spanish Ministerio de Educación y Ciencia for a postgraduate grant. Financial support was provided by the Spanish DGICyT of the Ministerio de Educación y Ciencia under Grant No. PB90/0795.

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