Cu^{2+} impurities in fluorite-type crystals: Mechanisms favoring an off-center motion

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Magnetic resonance data on Cu^{2+}-doped lattices with fluorite structure reveal that the equilibrium geometry for $SrCl_2:Cu^{2+}$ involves an important off-center displacement of Cu^{2+} along $\langle 001\rangle$ type directions ($Z_0 \approx 1.3$ Å) while in $CaF_2:Cu^{2+}$ the impurity remains on-center though with a orthorhombic distortion of the ligand shell. In the case of $SrF_2:Cu^{2+}$ an off-center motion is also observed though the estimated displacement ($Z_0 \approx 0.8$ Å) is substantially smaller than that for $SrCl_2:Cu^{2+}$. A microscopic explanation of these challenging facts has been attempted through calculations in the density functional theory framework on clusters involving up to 51 atoms. Total energy calculations using the hybrid nonlocal B3LYP functional on clusters of only 21 atoms are shown to reproduce reasonably main experimental features leading to $Z_0 = 0$, 0.3, and 1.1 Å for Cu^{2+}-doped CaF_2, SrF_2, and $SrCl_2$, respectively. The well depth $\delta = 0.12$ eV obtained for $SrF_2:Cu^{2+}$ is substantially smaller than that for $SrCl_2:Cu^{2+}$ ($\delta = 0.29$ eV) and is consistent with the incoherent hopping observed in the former case upon temperature raising leading to an isotropic EPR spectrum. The origin of these surprising facts is shown to come mainly from a competition between the electrostatic barrier due to the rest of lattice ions upon the impurity ion and the electronic energy gain from bonding when the coordination number of the d^9 impurity changes from 8 to 4. This simple argument explains that keeping the same d^9 ion, an increase of the host lattice parameter and a decrement of ligand electronegativity favor the occurrence of an off-center motion. Following these ideas calculations on $SrL_2:Mn^{2+}$ ($L = F$, Cl) give $Z_0 = 0$ in agreement with available EPR data. At variance with what happens for Jahn–Teller distortions off-center displacements are shown to be related from the beginning to modifications of involved wavefunctions as described by the pseudo Jahn–Teller theory.

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INTRODUCTION

The study of the local geometry around an impurity in solids and surfaces is a field that has greatly benefited from the important development of *ab initio* calculations in the last decade.[1–8] A very interesting problem in the realm of impurities concerns the symmetry lowering that can appear when a transition metal cation is introduced as impurity in a high symmetry host lattice. In many cases, the impurity substitutes a host lattice cation and remains *on-center*, though first neighbors (ligands) can experience a nonsymmetric relaxation leading to a lowering of local symmetry. This situation is found for instance for d^9 ions (Ni^+, Cu^{2+}, and Ag^{2+}) doped alkali and silver halides, cubic fluoroperovskites, and also some cubic oxides.[9–11] A local tetragonal symmetry is also found for d^7 ions doped silver halides and alkali halides like NaCl which have recently received a great deal of attention.[12–14] Despite this fact, experimental data reveal that *another kind* of phenomenon can be observed placing d^9 impurities in lattices which are cubic as well. So, in $SrCl_2:Cu^{2+}$ or $SrCl_2:Ag^{2+}$ electron paramagnetic resonance (EPR) experiments[15–17] clearly reveal the existence of a big off-center motion along $\langle 001\rangle$ type directions undergone by the d^9 impurity as depicted in Fig. 1. According to EPR data the equilibrium position of Cu^{2+} in $SrCl_2$ for the off-center motion along $\langle 001\rangle$ can be described[15] by (0, 0, Z_0) where $Z_0 \approx 1.3$ Å and (0, 0, 0) depicts the on-center position. This huge displacement means that the coordination number of Cu^{2+} changes in practice from eight to four, thus inducing drastic changes into the associated physical-chemical properties. As salient feature EPR spectra of $SrCl_2:Cu^{2+}$ and $SrCl_2:Ag^{2+}$ exhibit[14–17,9] between 4.2 K and room temperature an angular pattern which is *always* characteristic of a *static* C_{4v} symmetry. When $SrCl_2$ is replaced by SrF_2, which also displays the fluorite structure, EPR and electron nuclear double resonance (ENDOR) data[18–23] on $SrF_2:Cu^{2+}$ confirm the existence of an off-center displacement with $Z_0 \approx 0.8$ Å, substantially smaller than that for $SrCl_2:Cu^{2+}$. Moreover, when the temperature is raised the EPR spectrum of $SrF_2:Cu^{2+}$ changes at about

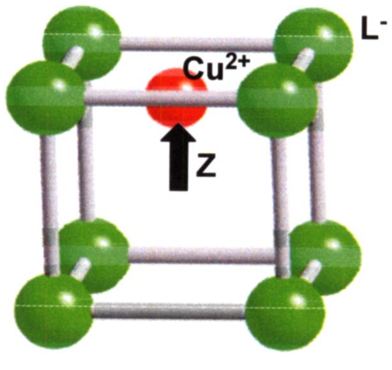

FIG. 1. Picture of the off-center motion of Cu^{2+} in a ML_2 ($M = Ca^{2+}, Sr^{2+}$; $L = F^-, Cl^-$) type lattice, where *a* means the lattice parameter.

220 K from anisotropic to isotropic, a fact associated with incoherent hopping among the six equivalent minima corresponding to a T_{1u} distortion.[21,22] Regarding $CaF_2:Cu^{2+}$, the corresponding EPR data[23,19] unambiguously demonstrate, however, that copper ion remains on-center though the associated ligand shell undergoes an orthorhombic D_{2h} distortion. This description of experimental facts related to the same cation (Cu^{2+}) placed in isomorphous lattices already stresses that the occurrence of an off-center motion is a subtle effect indeed.

Despite that the off-center phenomenon has been detected in many systems,[24–27] including those with technological applications (such as oxygen or nitrogen impurities in silicon crystals[25]), its microscopic origin is often not well understood. Explanations of big displacements founded on model Hamiltonians involving series expansion of the interaction between active electrons and the distortion mode are in principle doubtful. In fact, when the distortions at equilibrium become *comparable* to interatomic distances, the phenomenon can hardly be ascribed to *only one* term in the series expansion. This situation is thus opposite to that normally found for Jahn–Teller (JT) distortions where the impurity ion remains on-center and ligand displacements are one order of magnitude smaller than interatomic distances.[28–31] In a first attempt Lacroix[32] tried to explain the big off-center displacement observed in $SrCl_2:M^{2+}$ ($M=$Cu, Ag) considering *only* the quadratic JT coupling between the electronic $^2T_{2g}$ ground state and the T_{1u} distortion mode. Nevertheless, using this idea it was found[32] that the displacement would occur along $\langle 111\rangle$ directions, which is thus against experimental findings.[15,17]

Very recently the strong off-center $\langle 001\rangle$ motion undergone by Ni^+ in CaF_2 ($Z_0\approx 1.1$ Å)[33] has been reasonably understood through density functional theory (DFT) calculations and the involved analysis on clusters of only 21 atoms.[34] In fact, the equilibrium Z_0 value varied by less than 10% on passing from a 21-atom cluster to a cluster involving up to 107 atoms.[34] Bearing in mind this fact, the present work is aimed to explain the quite different off-center motion observed for the *same* Cu^{2+} impurity placed in the *three isomorphous* lattices CaF_2, SrF_2, and $SrCl_2$. Since the origin of such differences is expected to be subtle and the covalency of Cu^{2+} and Ag^{2+} complexes is often overestimated[35,36] using local density approximation[37] (LDA) and generalized gradient approximation[37] (GGA) functionals, particular attention has been addressed to results reached through the hybrid nonlocal Becke–3–Lee–Yang–Parr (B3LYP) functional.[38,39] This functional usually leads to better agreement with experimental findings.[40–43] As the CPU time required for the energy calculation at a given configuration using the B3LYP functional is about 15 times bigger than using LDA, clusters involving a maximum of 51 ions have only been considered in the present work.

Although the off-center motion is also driven by the coupling between the electronic ground state and local vibrations, emphasis is also put through this work in clarifying the qualitative differences with small ligand distortions observed for d^9 or d^7 ions in octahedral symmetry coming from the JT effect.

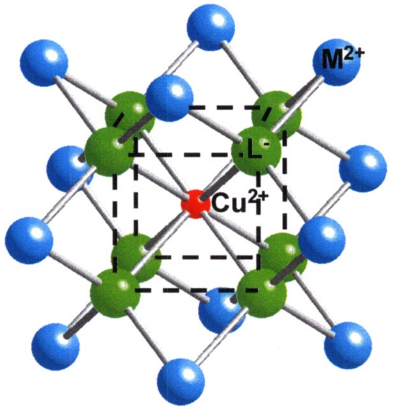

FIG. 2. Cluster of 21 ions $CuL_8M_{12}^{16+}$, used to simulate the Cu^{2+}-doped ML_2 ($M=Ca^{2+},Sr^{2+};L=F^-,Cl^-$) lattices.

COMPUTATIONAL DETAILS

DFT calculations for $ML_2:Cu^{2+}$ ($M=$Ca, Sr; $L=$F, Cl) centers have been carried out on clusters centered at the Cu^{2+} impurity. All employed clusters exhibit cubic symmetry. Previous results obtained for $CaF_2:Ni^+$ showed[34] that the off-center motion is well reproduced by a cluster containing *only* 21 atoms. Moreover, calculations carried out for clusters involving up to 107 atoms did not improve significantly[34] the results derived on the 21-atom cluster for $CaF_2:Ni^+$. So, most of the calculations in this work have been performed on 21-atom clusters (Fig. 2), but relevant results have been verified using 51-ion clusters.

Calculations have been performed for clusters *in vacuo* because the electrostatic potential due to the rest of the lattice on the cluster region is found to be very flat in the employed clusters. Finite clusters are often used for calculating the properties of impurities in insulators. For this approach to be valid it is required that active electrons are localized in a region whose size is smaller than that of the employed cluster. In present cases this condition is fulfilled as antibonding electrons coming from $3d$ orbitals of free Cu^{2+} are found to be essentially localized in the complex formed by Cu^{2+} and ligands. This strong localization is, however, not always found for insulating host lattices. In particular, when the highest occupied electronic level of the impurity is close to the bottom of the conduction band, it favors the existence of electronic density outside the complex region. This situation is encountered, for example, in the cationic Ag^0 center in KCl.[6]

First calculations were carried out using the Vosko–Wilk–Nusair functional[44] for the local LDA, and also the GGA in its Becke–Lee–Yang–Parr (BLYP) form.[45,39] The employed basis consists of three Slater type orbitals (STOs) plus a polarization function per atomic orbital as implemented in the Amsterdam density functional (ADF) program.[46] It made use of the larger frozen core available in the data base as these orbitals play only a minor role in the studied properties. Nevertheless, due to the shallow wells involved in the calculations and the difficulties[35,36] faced on treating Cu^{2+} or Ag^{2+} complexes through LDA or GGA, the three-parameter hybrid semiempirical B3LYP functional[38,39] implemented in GAUSSIAN 98[47] has also been used. These

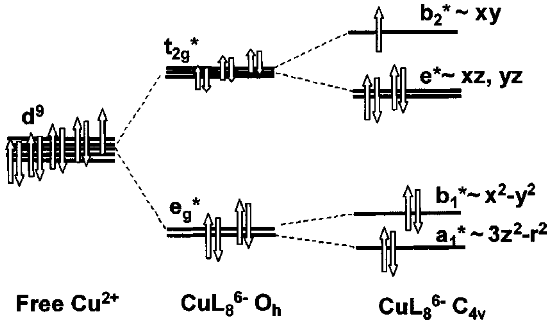

FIG. 3. Qualitative description of the splitting of antibonding d-levels of Cu^{2+} in ML_2 (M=Ca,Sr;L=F,Cl) lattices. From left to right the following situations are depicted: (1) free Cu^{2+} ion, (2) on-center Cu^{2+}: cubal CuL_8^{6-} complex in the *artificial* $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ reference configuration, and (3) off-center Cu^{2+}: CuL_8^{6-} complex in C_{4v} symmetry in the $(xy)^1(xz)^2(yz)^2$ configuration.

calculations use the double zeta LANL2DZ basis, which employ Gaussian type orbitals (GTOs) and pseudopotentials to simulate the core electrons. In all performed calculations it has been verified that the number of electrons occupying the mainly $3d$ antibonding orbitals is equal to nine.

Following a previous work[34] energy calculations have been carried out for both $(xy)^1(xz)^2(yz)^2$ and also $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ electronic configurations (Fig. 3). The artificial $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration gives rise to an electronic density displaying cubic symmetry from which the equilibrium metal-ligand distance keeping O_h symmetry can be evaluated.[34,14,31] Moreover, the comparison of results derived for both electronic configurations can provide us with some insight into the influence of bonding on the off-center motion. So, when the impurity is placed at different $(0,0,Z)$ positions and $Z \approx a/4$ there is only one electron in the antibonding $b_2^*(xy)$ orbital (Fig. 3) while there are two in the b_2 orbital with dominant bonding character. The difference between both occupations, B_o, changes from $B_o=1$ for the $(xy)^1(xz)^2(yz)^2$ configuration to $B_o=\frac{1}{3}$ for the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ electronic configuration.

In the calculations performed in C_{4v} symmetry (Fig. 1), apart from Z the size of squares corresponding to eight ligands in upper and lower planes as well as their distance to the origin are also taken as variables. Moreover, some calculations have also been performed without imposing *a priori* any symmetry to the complex formed by impurity and eight ligands, thus considering the whole 27 coordinates as variables. In the search of a possible off-center local minimum along ⟨001⟩ type directions the initial position of the impurity is chosen along the OZ axis of lattice while those of ligands are fixed at random. This makes it easy to get convergence to one of the equivalent local minima.

RESULTS

TABLE I. For the three ML_2: Cu^{2+} (M=Ca, Sr; L=F, Cl) systems studied in this work, it is shown the $Cu^{2+}-L^-$ distances, R_M, obtained in the DFT calculations (LDA functional) at the reference $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ octahedral configuration. It can be observed the ligand relaxations due to the Cu^{2+} impurity with respect to the $M^{2+}-L^-$ distance, R_H, in the pure ML_2 lattices.

	R_H (Å)	R_M (Å)
CaF_2: Cu^{2+}	2.366	2.290
SrF_2: Cu^{2+}	2.511	2.327
$SrCl_2$: Cu^{2+}	3.021	2.815

Values of the equilibrium impurity-ligand distance, R_M, calculated using the GGA functional for Cu^{2+}-doped CaF_2, SrF_2, and $SrCl_2$ in the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ electronic configuration keeping O_h symmetry are gathered in Table I. When compared to those for the perfect host lattice, denoted by R_H (Table I), such values show the existence of an inwards relaxation quite similar to that encountered in the case of Mn^{2+} impurity.[48,49] For instance, from the analysis of the experimental superhyperfine constant it was determined $R_M=2.26$ and 2.30 Å for Mn^{2+}-doped CaF_2 and SrF_2, respectively.[48] Despite that a change of 0.14 Å on R_H induces differences on R_M of only ~0.04 Å, significant changes on the luminescence efficiency are detected[50] on passing from $CaF_2:Mn^{2+}$ to $SrF_2:Mn^{2+}$.

When Cu^{2+} is allowed to move along a ⟨001⟩ direction and the electronic configuration is $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$, the energy minimum is found to be $Z_0=0$ for the three host lattices as shown in Fig. 4(a). It is worth noting, however, that the energy raising obtained for the same Z value increases along the series $SrCl_2:Cu^{2+} \rightarrow SrF_2:Cu^{2+} \rightarrow CaF_2:Cu^{2+}$. This increase resembles that displayed by the interaction energy of the impurity ion (with a total charge q_M) with the electrostatic potential, V_R, coming from the rest of ions as depicted in Fig. 4(b). The total charge on the cation, q_M, is smaller than the nominal charge (equal to $+2e$ for Cu^{2+}, with e=proton charge) due to covalency with ligands. In fact, as halide ligands have a closed shell structure, covalency leads to a net flow of electronic charge from ligands to the impurity. In the present case charges calculated by means of a Mulliken population analysis are found to be $q_M=+1.0e$ and $q_M=+0.7e$ for $SrF_2:Cu^{2+}$ and $SrCl_2:Cu^{2+}$, respectively, when symmetry around Cu^{2+} is cubal. It is worth noting that this charge is found to vary *only*

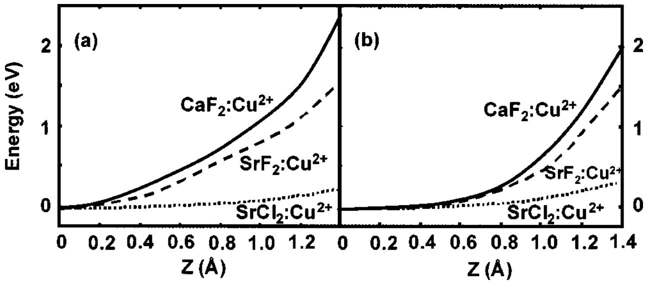

FIG. 4. (a) Profiles of energy for the different systems for $(xy)^{5/3}(yz)^{5/3}(zx)^{5/3}$ occupations as calculated in DFT-GGA. The curvature of the different curves represents the opposition that the lattice presents to the off-center movement of the impurity. (b) Simple model representing the barrier through the potential generated by punctual charges located at lattice sites.

by about 10% on passing from the origin to $Z_0 = 1$ Å.

When the variation of total energy against Z is calculated for the $(xy)^1(xz)^2(yz)^2$ configuration qualitative variations with respect to results of Fig. 4(a) are found. In fact, using the GGA functional, off-center minima are now calculated at $Z_0 = 0.15$, 1.0, and 0.4 Å for Cu^{2+}-doped CaF_2, SrF_2, and $SrCl_2$, respectively. Although this result together with that depicted in Fig. 3 support that the off-center motion can happen more easily in $SrCl_2:Cu^{2+}$ or $SrF_2:Cu^{2+}$ than in $CaF_2:Cu^{2+}$ some experimental findings[15,18–23] are, however, not so well reproduced. For instance, Cu^{2+} in CaF_2 remains on-center according to experimental EPR data[20,23] while the observed off-center distortion in $SrCl_2:Cu^{2+}$ is bigger than that for $SrF_2:Cu^{2+}$. We have verified that this situation is not improved using the procedure suggested by Solomon *et al.*[35] and Deeth[36] for ameliorating LDA or GGA results on Cu^{2+} complexes.

Results reached by means of calculations on a 21-atom cluster with the B3LYP hybrid functional for the $(xy)^1(xz)^2(yz)^2$ configuration keeping a C_{4v} symmetry are displayed in Fig. 5. It can be noted first that such a figure better reproduces the main trends observed experimentally.[15,18–23] So, $Z_0 = 0$ for $CaF_2:Cu^{2+}$ while the off-center distortion ($Z_0 = 1.10$ Å) and the associated well depth ($\delta = 0.29$ eV) calculated for $SrCl_2:Cu^{2+}$ are found to be bigger than those for $SrF_2:Cu^{2+}$ where it is calculated $Z_0 = 0.30$ Å and $\delta = 0.12$ eV. Although this result supports that, according to experiments,[15,22,23] an incoherent hopping among the six quasi-equivalent minima can be observed more easily on $SrF_2:Cu^{2+}$ than on $SrCl_2:Cu^{2+}$, the computed Z_0 values are somewhat smaller than the corresponding figures $Z_0 \approx 0.80$ Å and $Z_0 \approx 1.30$ Å derived from the analysis of the experimental superhyperfine tensor. It is worth stressing, however, that in the case of $SrF_2:Cu^{2+}$ the calculated Z_0 value is found to be extremely sensitive to very small variations of the lattice parameter a. So, if a is increased by only 0.35%, the calculated Z_0 value increases by about 25%.

Calculations have also been performed on a 21-atom cluster for $SrF_2:Cu^{2+}$ without imposing any symmetry to the CuF_8^{6-} complex, thus taking the 27 coordinates of this complex as variables. The minimum found for $a = 5.80$ Å corresponds to an off-center displacement with $Z_0 = 0.30$ Å.

For being sure that main facts embodied in Fig. 5 are not significantly dependent on the cluster size calculations for the $(xy)^1(xz)^2(yz)^2$ configuration keeping C_{4v} symmetry for a 51-atom cluster have also been performed using the B3LYP functional. For $SrF_2:Cu^{2+}$ the obtained value is again $Z_0 = 0.30$ Å while for $SrCl_2:Cu^{2+}$ the value $Z_0 = 0.90$ Å is a bit smaller than $Z_0 = 1.10$ Å derived through a 21-atom cluster. It is worth noting that for $SrCl_2:Cu^{2+}$ the big off-center motion undergone by the impurity is found to be accompanied by a 3% reduction of the size corresponding to the square described by the four ligands of the upper plane in Fig. 1. This result obtained in the present calculations is thus consistent with expectations founded on Pauling rules[51] relating the cation-anion separation to the coordination number.

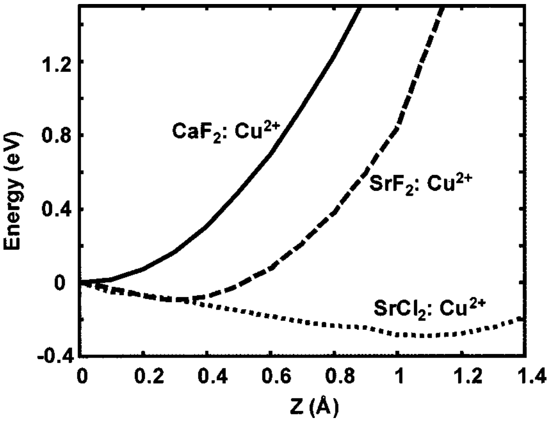

FIG. 5. Profile of energy for Z movement in the studied systems. They present a minimum at $Z_0 = 0$, 0.33, and 1.1 Å for CaF_2, SrF_2, and $SrCl_2$, respectively.

The comparison of results gathered in Figs. 4(a) and 5 for $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ and $(xy)^1(xz)^2(yz)^2$ configurations, respectively, strongly suggests that chemical bonding plays a key role for stabilizing the off-center displacement. When the B_0 quantity is reduced from 1 to $\frac{1}{3}$ the residual chemical bonding is not enough to overcome the electrostatic barrier created by the rest of ions on the impurity as a whole. As this electrostatic barrier scales with a^{-1} ($a =$ lattice parameter) this explains qualitatively why the off-center distortion increases along the series $CaF_2:Cu^{2+} \rightarrow SrF_2:Cu^{2+} \rightarrow SrCl_2:Cu^{2+}$. Moreover, if the lattice parameter is reduced by applying an external pressure this simple reasoning suggests a diminution of the off-center distortion. Very recently Ulanov *et al.*[22] performed EPR experiments on $SrF_2:Cu^{2+}$ under hydrostatic pressure finding that a pressure *of only* 6 Kbar is able to reduce Z_0 by about 15%.

Let us now have a look on the behavior of antibonding $b_2^*(xy)$ and $e^*(xz;yz)$ orbitals arising from t_{2g}^* in cubal symmetry (Fig. 3). The dependence of their orbital energy against Z is portrayed in Fig. 6 for $SrF_2:Cu^{2+}$. It can first be noticed that the separation between $b_2^*(xy)$ and $e^*(xz;yz)$

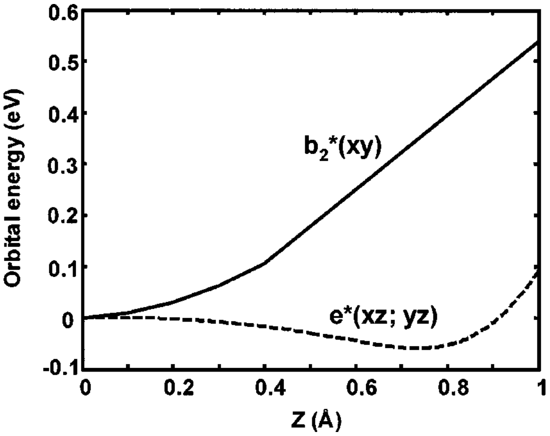

FIG. 6. Variation of the $\varepsilon(b_2^*)$ and $\varepsilon(e^*)$ one-electron energies on the Z coordinate for $SrF_2:Cu^{2+}$. Results correspond to the $(xy)^1(xz)^2(yz)^2$ configuration in the LDA.

orbitals *is not linear* in Z as it was already found[34] for $CaF_2:Ni^+$. This situation is thus quite different to that found for d^9 or d^7 ions in cubic lattices with sixfold coordination where the Jahn–Teller effect takes place.[28–31] Figure 6 clearly demonstrates the existence of stronger antibonding effects on $b_2^*(xy)$ than on $e^*(xz;yz)$ although the separation between both levels is higher than 0.25 eV only when $Z > 0.55$ Å. The existence of two electrons in the b_2 level with dominant bonding character is thus an important source for stabilizing the off-center distortion. This means that the electronic density lying in the middle region between the impurity and upper ligands plays an important role in the occurrence of an off-center displacement. In fact a truly *rigid* cation (in the sense that its electronic cloud is frozen) would not overcome the electrostatic barrier depicted in Fig. 4(b). These ideas are thus related to the general view on the pseudo Jahn–Teller (PJT) effect given by Bersuker[29] who demonstrates that when chemical bonding is not modified off-center motions cannot be produced.

OFF-CENTER MOTION VERSUS JAHN–TELLER DISTORTION

Ions with d^9, d^7, or d^4 configurations placed in cubic lattices with sixfold coordination exhibit JT distortions.[9,12] At variance with what is usually observed for off-center instabilities, the displacements of ions in JT distortions are smaller than interatomic distances.[28–31] For instance, the equatorial and axial metal-ligand distances in $NaCl:Rh^{2+}$ are shifted by about 0.08 and 0.16 Å, respectively, with regard to the octahedral situation.[14,31] This relevant point allows one to explain a great number of facts in the realm of JT distortions considering *only* the linear terms emerging from the expansion of the electron-vibration (or vibronic) potential.[28–31]

In order to clarify the important differences between JT and off-center instabilities, we will consider the vibronic coupling mechanism following the formalism of Bersuker.[29] He starts dividing the total Hamiltonian into three parts

$$H = H_r + H_Q + V(\mathbf{r},Q), \tag{1}$$

where H_r is the electronic part (including the kinetic energy of the electrons and the interelectron interaction), H_Q is the kinetic energy of the nuclei and $V(\mathbf{r},Q)$ is the vibronic potential (including the internuclei repulsion). Here $\mathbf{r}$ and Q denote the entire set of coordinates of the electrons and nuclei, respectively. This vibronic operator can be expanded in a series of small displacements of the nuclei around the point $Q_k = 0$ chosen as the origin:

$$V(\mathbf{r},Q) = V(\mathbf{r},0) + \sum_k (\partial V/\partial Q_k) Q_k + (1/2)\sum_{k,l} (\partial^2 V/\partial Q_k \partial Q_l) Q_k Q_l + \cdots . \tag{2}$$

Within the adiabatic approximation, the electronic Hamiltonian where nuclei are frozen at equilibrium positions and only electronic coordinates, $\mathbf{r}$, are variables is

$$H_e(\mathbf{r},0) = H_r + V(\mathbf{r},0). \tag{3}$$

Then the Hamiltonian, H_{ref}, characteristic of the reference system (before the vibronic effect) can simply be written as

$$H_{\mathrm{ref}}(\mathbf{r},Q) = H_e(\mathbf{r},Q) + (1/2)\sum_{\gamma,k} K_\gamma (Q_k^\gamma)^2 + \cdots , \tag{4}$$

where Q_k^γ is a symmetrized normal coordinate corresponding to the γ irreducible representation and K_γ is the corresponding force constant. This reference system can be approximated by an impurity ion with an electronic configuration where orbital degeneracy is suppressed.[14,31] If G denotes an operator of the symmetry group, then

$$H_e(G\mathbf{r},0) = H_e(\mathbf{r},0). \tag{5}$$

When the impurity in its right ground state (after the vibronic effect) is considered it is assumed that the corresponding adiabatic Hamiltonian, H_{vib}, can be described by

$$H_{\mathrm{vib}} = H_{\mathrm{ref}} + V(\mathbf{r},Q) \tag{6}$$

where in $V(\mathbf{r},Q)$ *both* $\mathbf{r}$ and the distortion coordinates Q are taken as variables. When the action of group operators on both $\mathbf{r}$ and Q variables is taken into account symmetry is preserved if

$$V(G\mathbf{r},GQ) = V(\mathbf{r},Q). \tag{7}$$

In the case of d^9 or d^7 ions in sixfold coordination coupled to the local E_g mode the coordinates of the JT distortion are the *even* Q_θ $(\sim 3z^2 - r^2)$ and Q_ε $(\sim x^2 - y^2)$ coordinates which thus involve only ligand displacements. If only linear terms in Q_θ and Q_ε are important, then $V(\mathbf{r},Q)$ can be approximated by

$$V(\mathbf{r},Q) = V(\mathbf{r},0) + \{V_\theta(\mathbf{r})Q_\theta + V_\varepsilon(\mathbf{r})Q_\varepsilon\}, \tag{8}$$

where the vibronic coupling constants $V_\theta(\mathbf{r})$ and $V_\varepsilon(\mathbf{r})$ depend only on electron coordinates and transform like Q_θ and Q_ε, respectively. If ligand displacements are small indeed and thus $V(\mathbf{r},Q)$ can be well approximated by (8), then the effects of vibronic coupling can reasonably be derived through the $\langle \phi_\alpha^0 | V_\gamma(\mathbf{r}) | \phi_\beta^0 \rangle$ matrix elements,[28–31] where $\gamma = \theta,\ \varepsilon$, and ϕ_α^0 $(\alpha,\beta = 3z^2 - r^2, x^2 - y^2)$ stand for the two orbitals of the electronic doublet *in octahedral symmetry* (reference system), ε_α being the corresponding energies. When this process is carried out the effects of (6) considering *only* the basis of the electronic doublet can be represented by the effective Hamiltonian[28–30]

$$H_{\mathrm{eff}} = V_{\mathrm{JT}}(U_\theta Q_\theta + U_\varepsilon Q_\varepsilon), \tag{9}$$

where $V_{\mathrm{JT}} = \langle \phi_{3z^2-r^2}^0 | V_\theta(\mathbf{r}) | \phi_{3z^2-r^2}^0 \rangle$ is the JT vibronic coupling constant, and

$$U_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{10}$$

Thus if the equilibrium geometry corresponds to an elongated or compressed octahedron (described, for instance, by

$Q_\varepsilon^0 = 0$ and $Q_\theta^0 = c$), then there is a splitting of the initial degeneracy following the center of the gravity theorem[52]

$$\Delta\varepsilon_{3z^2-r^2} + \Delta\varepsilon_{x^2-y^2} = 0, \tag{11}$$

where

$$\Delta\varepsilon_{3z^2-r^2} = -cV_{\mathrm{JT}}. \tag{12}$$

Therefore, Eq. (11) tells us that a JT distortion can be energetically favorable when the two orbitals of the electronic doublet are not equally populated in O_h symmetry. Moreover, the JT constant, V_{JT}, is determined by the *unperturbed* wavefunctions, ϕ_α^0, corresponding to octahedral symmetry. In other words, changes on chemical bonding induced by a Q_θ distortion are of secondary importance as regards the JT constant.

This situation is, however, fully modified when an off-center motion induced by an *odd* T_{1u} mode occurs. If the displacement of the metal impurity from the origin is described by the $\delta\mathbf{R}_M$ vector (*X*, *Y*, *Z* Cartesian components), then a *linear* vibronic operator, $V^{(1)}$, involving *X*, *Y*, and *Z* and the electronic coordinates, *x*, *y*, *z*, which is invariant in the cubic group, can have the form

$$V^{(1)}(\mathbf{r};X,Y,Z) = -f_A(x,y,z)\{Xx + Yy + Zz\}, \tag{13}$$

where $f_A(x,y,z)$ is a function that belongs to the A_{1g} representation in O_h. This linear operator can play a significant role for describing the *first steps* of the off-center motion and in particular when $Z \ll a/4$ if the impurity goes along $\langle 001\rangle$ directions. Let us now consider the three orbitals ϕ_μ^0 ($\mu = xy,xz,yz$) which are degenerated in cubal symmetry. By symmetry it is obvious that all $\langle\phi_\mu^0|z|\phi_\nu^0\rangle$ matrix elements ($\mu,\nu = xy,xz,yz$) are zero so there is *not any splitting* of three orbitals caused by (13) which is *linear* in *Z*. This simple argument stresses that *even* when $Z \ll a/4$ the electronic energy gain favoring the off-center motion comes necessarily from changes on wavefunctions induced by the interaction described by (13). This modification leads to an energy gain which depends on Z^2, as it can be observed in Fig. 5. Therefore, modifications in the chemical bonding appear to play a key role even for describing the first steps of the off-center instability. This point was not considered in a previous work.[34] The change of wavefunctions induced by $V^{(1)}$ when $Z \ll a/4$ makes that $\langle z\rangle \neq 0$. In other words, the electronic cloud of the CuL_8^{6-} complex ($L = \mathrm{F,Cl}$) is polarized by the action of the $-f_A(x,y,z)Zz$ interaction upon electrons which can be viewed as coming from an external electric field whose magnitude is proportional to *Z*. At the end of the off-center motion described by Fig. 1 it is known that bonding occurs essentially with ligands placed in the upper plane. It seems thus reasonable that *at the beginning* of the displacement when $Z \ll a/4$ there is an electronic energy gain by transferring electronic density from the lower $z < 0$ region to the upper $z > 0$ region thus making $\langle z\rangle > 0$. This requires that the $f_A(x,y,z)$ function defined in (13) be positive. Let us now consider an electron placed in the middle region between the impurity and ligands and a small displacement $\delta\mathbf{R}_M$ ($|\delta\mathbf{R}_M| \ll a/4$) of central cation so $|\mathbf{r}| \gg |\delta\mathbf{R}_M|$. The change of the electrostatic potential experienced by a valence electron due to the cation displacement can be approximated by

$$V^{(1)}(\mathbf{r};X,Y,Z) = -f_A(x,y,z)\,\delta\mathbf{R}_M\cdot\mathbf{r}, \tag{14}$$

where $f_A(x,y,z) \approx e^2(q_M + 1)/r^3$ and q_M denotes the total charge on the impurity. Therefore, though q_M is smaller than the nominal charge, $f_A(x,y,z)$ is expected to be positive for cations and even neutral impurities.

For an off-center motion along $\langle 001\rangle$ the interaction term $-f_A(x,y,z)Zz$ leads to an admixture of the $b_2^*(xy)$ orbital with those with a dominant ligand character belonging to b_2. In fact the *z* coordinate transforms like A_1 in C_{4v} symmetry. Globally the effect of $-f_A(x,y,z)Zz$, polarizing the electronic cloud of the $\mathrm{Cu}L_8^{6-}$ complex, can be viewed as the admixture of the ground state with charge transfer states characterized by $b_2 \rightarrow b_2^*(xy)$ excitations thus reflecting a PJT vibronic coupling.[29,53] This way the polarization of the electronic cloud which happens at the beginning of the off-center motion can be regarded as a precursor of strong rebonding effects taking place at the equilibrium $(0,0,Z_0)$ position. From the present analysis such a polarization is characteristic of the $\mathrm{Cu}L_8^{6-}$ complex as a whole rather than of the copper ion.

FINAL REMARKS

Ab initio calculations on clusters of only 21 atoms have been shown to reproduce reasonably a delicate phenomenon involving an energy gain around 0.1 eV. Moreover, they are of great help for gaining a better insight into the origin of the off-center motion.

Present results strongly support that the off-center displacement in $\mathrm{Sr}L_2{:}\mathrm{Cu}^{2+}$ ($L = \mathrm{F}$, Cl) is an spontaneous phenomenon at $T = 0$ K not driven by any neighbor defect. A similar situation was already found[34] for $\mathrm{CaF_2{:}Ni^+}$. The absence of another defect close to the d^9 impurity concurs with available EPR data[15,18,19,21,22] on $\mathrm{Sr}L_2{:}\mathrm{Cu}^{2+}$ ($L = \mathrm{F}$, Cl) as well as with the more accurate ENDOR data performed[20] on $\mathrm{SrF_2{:}Cu^{2+}}$ and also[33] on $\mathrm{CaF_2{:}Ni^+}$.

In agreement with a first view[34] there is always an electrostatic barrier against the motion of a *rigid* impurity *ion*. As this barrier scales with a^{-1} and depends on the ion charge this fact qualitatively explains why $Z_0 = 0$ for $\mathrm{CaF_2{:}Cu^{2+}}$ while Z_0 increases on passing to $\mathrm{SrF_2{:}Cu^{2+}}$ and specially to $\mathrm{SrCl_2{:}Cu^{2+}}$. From this reasoning it can reasonably be expected an off-center motion for $\mathrm{BaF_2{:}Cu^{2+}}$. EPR results on both[54,55] $\mathrm{BaF_2{:}Cu^{2+}}$ and $\mathrm{BaF_2{:}Ag^{2+}}$ clearly demonstrate the existence of off-center displacements along $\langle 001\rangle$ type directions. Moreover, this simple argument favors the observation[33] of an off-center motion in $\mathrm{CaF_2{:}Ni^+}$ due to the lower nominal charge of $\mathrm{Ni^+}$ in comparison with that of $\mathrm{Cu^{2+}}$. This fact also stresses that in fluorite-type lattices a small ionic radius does not mean at all an advantage on other bigger *d* ions for experiencing an off-center motion.[34]

According to present conclusions the substitution of $\mathrm{Cu^{2+}}$ in $\mathrm{Sr}L_2$ ($L = \mathrm{F,Cl}$) by another 3*d* cation with the *same nominal charge* but inducing a diminution of covalency does not favor an off-center displacement. In fact, a more ionic complex means an increase of q_M and a bigger separation between antibonding and bonding levels. A fingerprint of covalency induced by a given ion is the optical electronegativity,[56] χ, which in turn is related to the onset of charge-transfer excitations of a given complex.[56–58] Among the divalent $3d$ ions Cu^{2+} exhibits the highest value of the optical electronegativity[56] ($\chi=2.4$) while that for Mn^{2+} has been derived to be[59] substantially smaller ($\chi=1.4$). This strong diminution of χ reflects that the charge transfer onset is found[57,58,60] at ~3.2 eV for $CuCl_6^{4-}$ while[57,58] it is found at ~7 eV for $MnCl_6^{4-}$. For checking the present ideas calculations on $SrL_2{:}Mn^{2+}$ ($L=F,Cl$) using a 21-atom cluster and the B3LYP functional have also been undertaken. From them it is obtained $Z_0=0$ for both systems being thus in perfect agreement with available EPR data.[16]

The use of the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ reference configuration with fractional electronic occupancy[34,14,31] is shown to provide us with some insight into the key role played by bonding into the off-center stabilization. From the present analysis the existence of orbital degeneracy in the ground state is shown not to play a key role as far as off-center displacements are concerned. This result is thus against what is found for JT distortions and means that an off-center displacement can equally be produced in the case of d ions with an orbital singlet as ground state. It is worth noting that the existence of an off-center displacement has recently been reported[61,62] for $SrCl_2{:}Fe^{+}$. The ground state of this *monovalent* ion in cubal symmetry is $^4A_2$. Theoretical work on this system is now in progress.

The deformation of the electronic cloud in first steps has been pointed out to be the precursor of strong rebonding effects taking place at the equilibrium $(0,0,Z_0)$ position for the studied systems. This polarization arising from the vibronic coupling mixes at the beginning the ground state with an excited charge transfer state of equal symmetry an admixture which is the footprint of a linear PJT effect.[29,53] Thus the strong rebonding effects which occur at the equilibrium $(0,0,Z_0)$ position are in fact connected with a linear PJT effect in the first steps of the process.

It is worthwhile to remark that the present PJT effect is qualitatively different from a *quasi* JT situation encountered for d^9 ions placed in tetragonal lattices with sixfold coordination.[63] In this case the impurity remains on-center[63] and ligand distortions are much smaller than interatomic distances.[64] The only difference with a typical JT situation comes from the absence of strict orbital degeneracy in the ground state broken by the electrostatic potential of the rest of the lattice upon the d^9 complex. As it has recently been shown[64] this potential plays a relevant role on the equilibrium geometry displayed by the complex. It is worth noting, however, that the quasi JT effect can equally be well fitted within the general PJT formalism.[28,29] There is some confusion in the literature as to meaning of the PJT effect. So, Pantelides *et al.* argued[65] that the PJT effect occurs when quasi degenerate antibonding levels are partially occupied, this effect being qualitatively different from rebonding. This standpoint thus restricts the PJT effect to the so-called quasi JT effect previously discussed. From the present analysis, which concurs with the view by Bersuker[29] and DeLeo *et al.*,[66] a PJT effect leading to an off-center motion with rebonding requires the existence in first steps of a coupling between the ground state and an excited one via the vibronic interaction described by $V(\mathbf{r},Q)-V(\mathbf{r},0)$. Thus, an off-center displacement can also occur for systems involving atoms like Ag^0 or Cu^0 whose $5s$ or $4s$ level is not degenerate.[67,68] Even off-center motions could also happen for systems involving a *closed shell* ion like Cu^{+}. In this case the vibronic admixture with excited states coming from $3d^94s$ and $3d^94p$ configurations could be a driving force for the off-center instability. It is worth noting that the onset of $3d^{10}\rightarrow 3d^94s$ and $3d^{10}\rightarrow 3d^94p$ excitations appear[27] only at about 4 and 7 eV for NaF:Cu^{+}. In agreement with the present view results[26,27] on $KL{:}Cu^{+}$ ($L=Cl,Br$) and the anionic Ag^0 center[69,68] in KCl support the existence of off-center motions in these systems. Moreover, from optical absorption spectra on NaBr:Cu^{+} it has been concluded[70] that hydrostatic pressures up to only 6 Kbar favor a transition from the initial off-center situation to an on-center one.

First experimental EPR data under pressure[22] on $SrF_2{:}Cu^{2+}$ and the analysis carried out in the present work both support that the equilibrium Z_0 coordinate in $SrF_2{:}Cu^{2+}$ is extremely sensitive to the application of hydrostatic pressures. This interesting issue deserves a further study as well. Work in this direction is now underway.

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