# Big off-center displacements of ions in insulators:   The Jahn-Teller ion Ni$^+$ in CaF$_2$

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The big off-center displacement along $\langle 001 \rangle$ directions observed for Ni$^+$ in CaF$_2$ is explored through density functional theory (DFT) calculations on a NiF$_8$Ca$_{12}^{17+}$ cluster, placing the Ni$^+$ ion at different $(0,0,z)$ points. For supporting the results additional calculations on clusters with a total of 51, 99, and 107 atoms have also been carried out. In a first step calculations have been performed for the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration where the three $xy, xz$, and $yz$ antibonding crystal-field levels (degenerated in cubal geometry) are forced to have the same electronic occupancy. While the energy minimum for this configuration of NiF$_8$Ca$_{12}^{17+}$ appears at $z = 0$, it is found, however, at $z_0 = 1.07$ Å when the unpaired electron is fully located on the $b_2$ orbital transforming like $xy$. The $z_0$ values obtained for clusters with 51 ($z_0 = 1.13$ Å), 99 ($z_0 = 1.17$ Å) and 107 ($z_0 = 1.17$ Å) atoms outline the small dependence of the phenomenon on cluster size. This big off-center motion, which concurs with electron paramagnetic resonance data, is shown to arise mainly from a delicate balance between an electrostatic barrier, avoiding the impurity displacement and the energy gained through bonding on passing from eightfold to fourfold coordination. Following this analysis an increase of the lattice parameter and a diminution of ligand electronegativity both favor the off-center motion of $d^9$ ions in lattices with fluorite structure. First DFT calculations by means of a 21-atom cluster lead in fact to an off-center motion for Ag$^{2+}$ and Cu$^{2+}$ in SrCl$_2$, while both ions would be on center in CaF$_2$, these results being in agreement with experimental findings. At variance with the normal situation for on-center $3d$ impurities the energy minimum for the crystal-field excited state corresponding to the $xy \rightarrow x^2 - y^2$ transition is found at $z = 0$, thus involving a huge displacement with respect to the ground state. To our knowledge this DFT study is the first one on off-center $d^9$ ions in CaF$_2$-type lattices. The present results stress that the phenomenon though subtle can be understood with a modest computational effort.

Attractive phenomena can appear in a cubic insulating lattice when the host cation is replaced by a Jahn-Teller impurity[1–3] $M$. In lattices like NaCl or MgO displaying octahedral coordination Jahn-Teller impurities like Cu$^{2+}$, Ag$^{2+}$, Ni$^+$, or Rh$^{2+}$ are found to remain *on center*. Nevertheless, the angular pattern of the low-temperature electron paramagnetic resonance (EPR) spectra reflects in some systems a local tetragonal symmetry and in others a cubic one, while an isotropic spectrum can be reached by raising the temperature.[1–3] These different behaviors have been accounted for through a parametrized model Hamiltonian involving a *linear* coupling between the orbitally degenerate $E_g$ ($\sim x^2 - y^2, 3z^2 - r^2$) state and the $E_g$ mode of the $MX_6$ unit ($X$ = anion) and taking into account the key role played by random strains[3] unavoidably present in any real crystal. The vibrational $E_g$ mode involving ligands is characterized[1–3] by the $Q_\theta$ (transforming like $3z^2 - r^2$) and $Q_\varepsilon$ ($\sim x^2 - y^2$) normal coordinates. The *linear* approximation is only meaningful provided the adiabatic minimum characterized by $Q_\theta = Q_\theta^0$ and $Q_\varepsilon = 0$ verifies $Q_\theta^0 \ll R_{ML}$, where $R_{ML}$ denotes the average metal-ligand distance. This condition is usually fulfilled by $d^9$ and $d^7$ ions in octahedral coordination.[1–4]

In the case of some crystals with fluorite structure doped with $d^9$ ions a quite different phenomenon has been *sometimes* observed by means of EPR and electron nuclear double resonance (ENDOR).[5–11] As shown in Fig. 1, experimental data are consistent with the existence of a huge off-center displacement of the impurity ion along $\langle 100 \rangle$ directions, leading to the creation of a local dipole moment and to a change of eightfold to fourfold coordination. This kind of attractive phenomenon has been observed, for instance,[2,7–9]
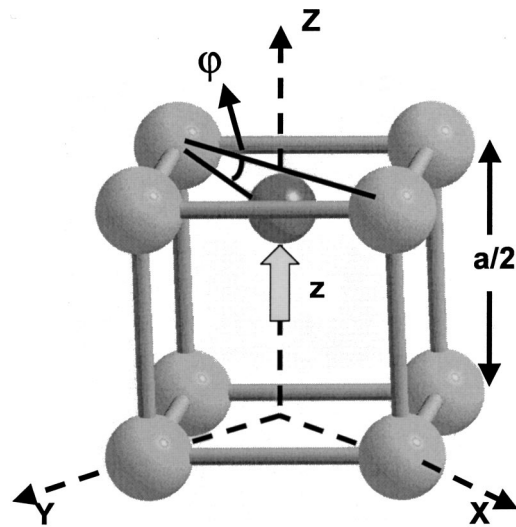


FIG. 1. Picture of the off-center motion in a CaF$_2$-type lattice where $a$ means the lattice parameter. The local axes $X$, $Y$, and $Z$ are also indicated. The dark sphere represents the $d^9$ ion. If the $d^9$ impurity is on center and no relaxation of eight ligands occurs, $R_{ML} = \sqrt{3}a/4$.

for $Cu^{2+}$, $Ag^{2+}$, and $Ni^+$ in $SrCl_2$, but only[5,6] for $Ni^+$ in $CaF_2$. The angle $\varphi$ depicted in Fig. 1 is found to be around $10°$ for these systems. If the equilibrium position of the $d^9$ ion is at $(0,0,z_0)$, then $z_0 \approx 1$ Å for $CaF_2$:$Ni^+$, which is about 80% of the $a/4$ quantity (where $a = 5.45$ Å is the $CaF_2$ lattice parameter), and thus the local symmetry is $C_{4v}$. For $Cu^{2+}$ and $Ag^{2+}$ in $SrCl_2$, $z_0$ would be around 1.4 Å.

This big off-center displacement involves a coupling with a $T_{1u}$ mode that then *cannot* give rise to any linear coupling with the electronic ground state $T_{2g}$ ($\sim xy,xz,yz$). In a first attempt Lacroix[12] tried to ascribe the big off-center displacement considering *only* the quadratic Jahn-Teller coupling though $z_0$ is *comparable* to interatomic distances. When the parameters of that model were estimated[12] it was found that the displacement would occur along $\langle 111 \rangle$ directions. The present phenomenon was also related to a pseudo Jahn-Teller effect.[2] By means of this idea it is however not easy to *predict* that the off-center motion occurs[5,6] for $CaF_2$:$Ni^+$, while for $Ag^{2+}$- or $Cu^{2+}$-doped $CaF_2$ the $d^9$ ion is found to be on center.[13,14,10] Moreover, this experimental evidence stresses that the occurrence of the off-center displacement can hardly be related to the size of the $d^9$ cation.[2]

Theoretical calculations on this kind of systems could be of help for clarifying the origin of the off-center motion. Particularly important is to determine whether such a big displacement is spontaneous or might be driven by another defect. Results on the model system $CaF_2$:$Ni^+$ carried out in the framework of density functional theory (DFT) are reported in this work. Recent DFT calculations on the Jahn–Teller system $NaCl$:$Rh^{2+}$ have provided a reasonable explanation of its geometrical and electronic properties.[4] Moreover, as DFT allows one to deal with fractional electronic occupancy,[15] it is simple to analyze the influence of orbital degeneracy on the ground-state energy.[4] Total energy calculations are employed in the present work as they represent an advantage on model Hamiltonians based in series expansion.[1,3] This is particularly true for systems like the present ones where the distortion parameter at equilibrium, $z_0$, can be *comparable* to interatomic distances of the host lattice and thus phenomena can hardly be associated only with a given term of the series.

The system $CaF_2$:$Ni^+$ has first been studied through a $NiF_8Ca_{12}^{17+}$ cluster (Fig. 2). This approximation is reasonable as the active $3d$ electrons are localized in the region formed by $Ni^+$ and ligands.[16] Moreover, the impurity-ligand distance for $Mn^{2+}$- and $Fe^{3+}$-doped cubic fluoroperovskites has been well reproduced[17,18] using a 21-atom cluster. We have also verified that the electrostatic potential $V_R$, due to lattice ions outside the cluster (obtained through the procedure of Ref. 19), is very flat indeed. So $eV_R$ is found to change by less than 0.01 eV in the $0<z<1.3$ Å domain. Calculations made using the Amsterdam density functional (ADF) code[20] have been carried out for two different electronic configurations in order to clarify the role played by orbital degeneracy. In a first step calculations have been performed for the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration where the three $xy,xz$, and $yz$ antibonding crystal-field levels are forced to have the same electronic occupancy. In this step the impurity-ligand
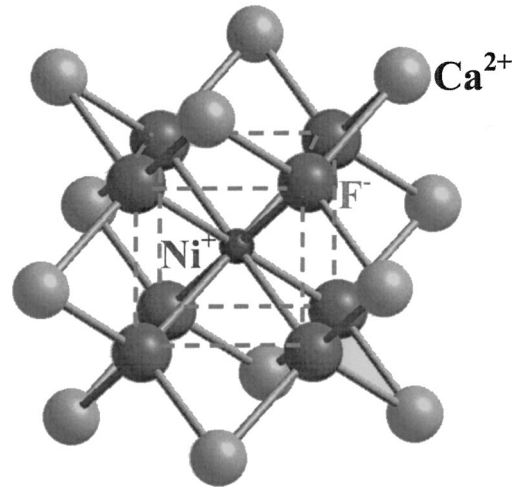


FIG. 2. Picture of the cluster used in the present calculations.

distance $R_{ML}$ is varied, keeping the cubic symmetry. In a second step the same electronic configuration is kept, but the $d^9$ ion is allowed to move along the $\langle 001 \rangle$ direction. Total energy is then calculated for different values of the $z$ coordinate. In a last step the unpaired electron is fully located in the antibonding $b_2$ ($\sim xy$) orbital [$(xy)^1(xz)^2(yz)^2$ configuration] and the total energy is calculated at different $(0,0,z)$ points. In this process relaxation of top and bottom ligands is *always* taken into account. Calculations have been carried out using different exchange-correlation functionals: the Vosko-Wilk-Nusair one for the local density approximation[15] (LDA), the Becke-Lee-Yang-Parr one for the generalized gradient approximation[15] (GGA), and also through the B3LYP hybrid functional.[21] In the calculations electrons up to the $3p$ shell of $Ni^+$ and $Ca^{2+}$ are kept frozen and so are the $1s$ electrons of $F^-$ ions.[18]

The energy minimum for the cubal $NiF_8Ca_{12}^{17+}$ cluster in the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration is found at $R_{ML} = 2.48$ Å in the LDA, implying a 5% outwards relaxation. In this process the 12 second neighbors are fixed at their positions in the $CaF_2$ lattice. The total charge on Ni, $q_M$, is found to be $q_M = 0.63e$, outlining a small covalency. The $R_{ML} = 2.48$ Å value is quite reasonable for a *monovalent* $3d$ ion in cubal coordination. A test calculation performed on the $CaF_8Ca_{12}^{17+}$ cluster leads to $R_{ML} = 2.35$ Å, practically coincident with the experimental value for the perfect $CaF_2$ lattice.

The variation of the total energy, $E(z)$, when $Ni^+$, in the same $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration, is moved along $\langle 001 \rangle$ is depicted in Fig. 3(a). According to this figure, obtained in the LDA, the energy minimum for this electronic configuration is $z_0 = 0$, implying that if orbital degeneracy is excluded, $Ni^+$ wants to be on center. It is interesting to compare the $E(z)$ curve with the potential energy $q_M V_M(z)$ experienced by the *impurity* with total charge $q_M$, coming from the electrostatic potential $V_M(z)$ due to the *rest of the ions* in the lattice at a $(0,0,z)$ point. Taking $q_M = 0.63e$, the comparison made in Fig. 3(a) points out that the increase of $E(z)$ is certainly related to the Coulomb barrier against the off-center motion of the $d^9$ ion.

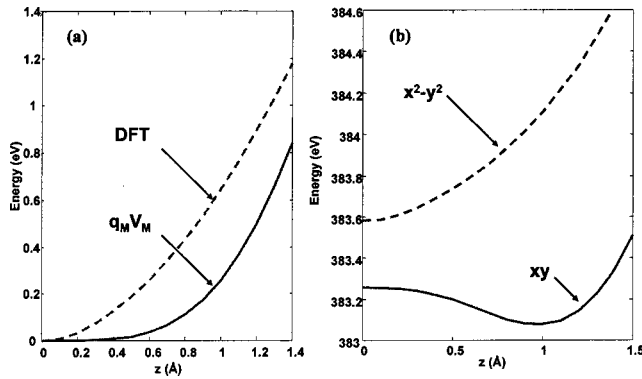Results reached when the unpaired electron is fully lo-

FIG. 3. (a) Solid line: $E(z)$ curve for the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration for $Ni^+$ in $CaF_2$. Dashed line: dependence of the potential energy, $q_M V_M(z)$, on the $z$ coordinate. (b) $E(z)$ curves for the ground state (unpaired electron in the $xy$ orbital) of $Ni^+$ in $CaF_2$ and for a crystal-field state (where the unpaired electron is in the $x^2-y^2$ orbital). All the $E(z)$ curves have been calculated though the LDA.

cated in the $b_2$ ($\sim xy$) orbitals are displayed in Fig. 3(b). In comparison to results collected in Fig. 3(a) drastic changes can be noticed. The energy minimum for the $(xy)^1(xz)^2(yz)^2$ configuration is found to occur not at $z = 0$, but at $z_0 = 1.07$ Å, implying a value $\varphi = 10°$. The latter value is thus comparable to that inferred from EPR data. Moreover, Fig. 3(b) stresses the lack of barrier for reaching the off-center position from $z = 0$. Therefore this result supports that the off-center situation can be reached *spontaneously* once the $Ni^{2+}$ ion, introduced as impurity in $CaF_2$, traps an additional electron released by x-ray irradiation. No evidence of a defect in the neighborhood of the $Ni^+$ center in $CaF_2$ has been obtained from ENDOR experiments.[6] The calculated well depth in Fig. 3 is close to 0.2 eV, which is consistent with the observation at room temperature of EPR spectra, associated with the $Ni^+$ center.[5] At $z_0 = 1.07$ Å it is found $q_M = 0.43e$, while the distance between $Ni^+$ and the four closest $F^-$ ions, $R(Ni\text{-}F)$, is equal to 2.02 Å. This value, implying a 5% outwards relaxation, is not far from previous estimations.[16] In comparison to $R_{ML} = 2.47$ Å [corresponding to the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration] the value $R(Ni\text{-}F) = 2.02$ Å reflects qualitatively the transition from eightfold to fourfold coordination. The *main facts* displayed by Fig. 3 are not modified substantially when other functionals or bigger clusters are employed. So using a $NiF_8Ca_{12}^{17+}$ cluster, a value $z_0 = 0.97$ Å is obtained in the GGA, while a similar value is found through the B3LYP functional. LDA and GGA calculations on a bigger $NiF_8Ca_{12}F_{24}Ca_6^{5+}$ cluster *both* lead to $z_0 = 1.13$ Å, which is only 5% higher than that reached through the 21-atom cluster. When the number of cluster atoms rises from 51 to 99, $z_0$ is found to increase only by 3%, while clusters with 99 and 107 atoms both lead to $z_0 = 1.17$ Å.

Some hints for understanding the origin of results displayed in Fig. 3 can be obtained looking at the $z$ dependence of the one-electron energies $\varepsilon^b$ and $\varepsilon^e$ associated with the antibonding $b_2$ ($\sim xy$) and $e$ ($\sim xz, yz$) orbitals, respectively (Fig. 4). Though both $\varepsilon^e(z)$ and $\varepsilon^b(z)$ decrease when $z$ in-
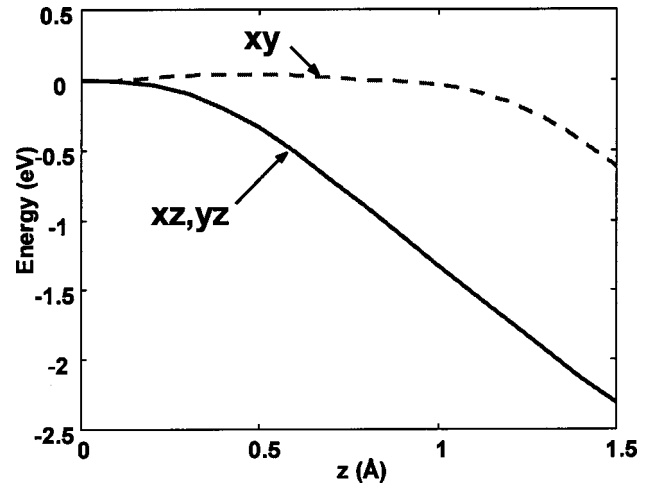


FIG. 4. Dependence of $\varepsilon^b$ and $\varepsilon^e$ one-electron energies on the $z$ coordinate. Results correspond to the $(xy)^1(xz)^2(yz)^2$ ground state configuration in the LDA.

creases, this decrement is more pronounced for the $e$ than for the $b_2$ orbital. As the influence of the $V_M(z)$ potential on both electrons lying mainly on $Ni^+$ is similar, such a difference reflects higher antibonding effects on $b_2$ ($\sim xy$) than on $e$ ($\sim xz, yz$) orbitals. In particular, bonding at $z = a/4$ for $b_2$ ($\sim xy$) has a full $\sigma$ character. Calling $\Delta\varepsilon^i(z) = \varepsilon^i(z) - \varepsilon^i(0)$ ($i = e, b_2$), then $\Delta\varepsilon^i(z)$ can be approximated by

$$\Delta\varepsilon^i(z) \approx -e(\alpha^i)^2 V_M(z) + \eta_a^i(z), \qquad (1)$$

where $\eta_a^i(z)$ reflects the increase or decrement of antibonding effects and $(\alpha^i)^2$ means the electron fraction residing on the metal. For small distortions ($z \ll a/4$) the center of the gravity theorem[22] can be applied and the variation of the total energy, $\Delta E$, can be approximated by

$$\Delta E(z) \approx q_M V_M(z) - \eta_a^b(z). \qquad (2)$$

This expression reflects that the $(xy)^1(xz)^2(yz)^2$ configuration is not a closed shell. According to Eq. (2), it is now possible to understand qualitatively that, for $z \ll a/4$, $\Delta E(z)$ is negative, as shown in Fig. 3(b), provided $\eta_a^b(z) > 0$. Antibonding effects do reflect the overlap between a metal wave function like $|xy\rangle$ and the corresponding ligand wave function. As shown in Fig. 5, the $|p_\sigma(1)\rangle$ orbital is found to form an angle $\Phi = 50°$ with the $\langle 110 \rangle$ direction when $z = 0$, while $\Phi = 0°$ when $z = a/4$. Therefore the $\langle xy|p_\sigma(1)\rangle$ overlap increases substantially when $z$ does, and thus $\eta_a^b(z)$ can be positive, although bonds with four bottom $F^-$ ions (Fig. 1) are progressively broken. The increase of $\langle xy|p_\sigma(1)\rangle$ is also helped by the associated diminution of distance between $Ni^+$ and four top ligands depicted in Fig. 1. A simple extended Hückel calculation supports this view.

According to the present analysis, the off-center displacement observed for some $d^9$ ions in lattices with fluorite structure can be understood as a delicate balance between a Coulombian barrier avoiding the motion and the energy gained through bonding on passing from eightfold to fourfold coordination. It is worth noting (Fig. 3) that the increase under-
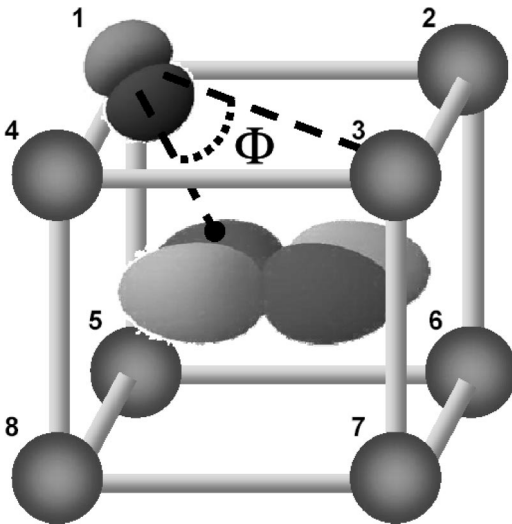
FIG. 5. Pictorial description of the $xy$ and the $|p_\sigma(1)\rangle$ orbitals in cubic coordination.

gone by $q_M V_M(z)$ on passing from $z=0$ to $z=1$ Å is equal *only* to 0.2 eV, while in the smaller $1$ Å$<z<1.3$ Å range it amounts to 0.5 eV. This important increase of the electrostatic barrier in the $1$ Å$<z<1.3$ Å range is against the location of the $d^9$ ion at $z=a/4$, and thus it allows one to understand why $z_0 < a/4$ and a $D_{4h}$ square-planar situation is not reached. Following this view, systems like CaF$_2$:$A^{2+}$ ($A$ = Cu,Ag) involving a *divalent* impurity are, in principle, less favorable than the present case where a monovalent Ni$^+$ ion is involved. In fact, in these cases covalency is moderate, while the Coulomb barrier is expected to be higher for a nominally divalent cation than for a monovalent one. First calculations carried out on CaF$_2$:$A^{2+}$ ($A$ = Cu,Ag) systems using a 21-atom cluster give the energy minimum for the $(xy)^1(xz)^2(yz)^2$ configuration at $z_0=0$. EPR studies of these systems[10,13,14] reveal that Ag$^{2+}$- and Cu$^{2+}$-doped CaF$_2$ remain on center indeed, although the ligand sphere is distorted from a cubal arrangement.

The present reasoning also suggests that an increase of the host lattice constant $a$ and a decrement of ligand electronegativity (which in turn favors an increase of covalency) both help the existence of off-center displacements for divalent cations. First calculations by means of a 21-atom cluster have also been carried out for Cu$^{2+}$- and Ag$^{2+}$-doped SrCl$_2$ where $a=6.97$ Å. The off-center situation is found to be clearly more stable than the on-center one for the $(xy)^1(xz)^2(yz)^2$ configuration, a fact which concurs also with available experimental data.[2,7,8]

Interesting phenomena can also appear for excited states of systems where a big off-center displacement is taking place in its ground state. For instance, the $E(z)$ curve associated with the excited state corresponding to the crystal-field transition $xy \rightarrow x^2-y^2$ [Fig. 3(b)] shows the minimum at $z=0$. This situation markedly differs from that found for substitutional impurities where equilibrium metal-ligand distances for two different crystal-field states are usually coincident[19] within 5%. A situation like that in Fig. 3(b) would favor a broadening of absorption bands. Up to now no crystal-field excitations for CaF$_2$:Ni$^+$ or SrCl$_2$:$A^{2+}$ ($A$ = Cu,Ag) have been reported.

The present results appear as encouraging for gaining a better insight about off-center motions of ions in insulating materials using a moderate computational effort. Further work along this direction is now under way.

[1] I. Bersuker and V. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989).

[2] H. Bill, in *The Dynamical Jahn-Teller Effect in Localized Systems*, edited by Yu. E. Perlin and M. Wagner (Elsevier, Amsterdam, 1984).

[3] F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), p. 1.

[4] M. T. Barriuso, P. García-Fernández, J. A. Aramburu, and M. Moreno, Solid State Commun. **120**, 1 (2001).

[5] J. Casas Gonzalez, H. W. den Hartog, and R. Alcala, Phys. Rev. B **21**, 3826 (1980).

[6] P. Studzinski, J. Casas Gonzalez, and J. M. Spaeth, J. Phys. C **17**, 5411 (1984).

[7] H. Bill, Phys. Lett. **44A**, 101 (1973).

[8] M. Moreno, An. Fis. (1968-1980) **70**, 261 (1974).

[9] R. Alcala, R. Cases, and P. J. Alonso, Phys. Status Solidi B **135**, K63 (1986).

[10] V. Lefevre, A. Monnier, M. Schnieper, D. Lovy, and H. Bill, Z. Phys. Chem. (Munich) **200**, 265 (1997).

[11] S. K. Hoffmann and V. A. Ulanov, J. Phys.: Condens. Matter **12**, 1855 (2000).

[12] R. Lacroix, Helv. Phys. Acta **47**, 689 (1974).

[13] M. V. Eremin, V. A. Ulanov, and M. M. Zaripov, Appl. Magn. Reson. **14**, 435 (1998).

[14] M. M. Zaripov and V. A. Ulanov, Sov. Phys. Solid State **30**, 896 (1988).

[15] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989), p. 141.

[16] J. A. Aramburu, M. Moreno, and M. T. Barriuso, J. Phys.: Condens. Matter **4**, 9089 (1992).

[17] M. T. Barriuso, M. Moreno, and J. A. Aramburu, Phys. Rev. B **65**, 064441 (2002).

[18] J. A. Aramburu, J. I. Paredes, M. T. Barriuso, and M. Moreno, Phys. Rev. B **61**, 6525 (2000).

[19] J. A. Aramburu, M. Moreno, K. Doclo, C. Daul, and M. T. Barriuso, J. Chem. Phys. **110**, 1497 (1999).

[20] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).

[21] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[22] C. J. Ballhausen, *Ligand Field Theory* (McGraw-Hill, New York, 1962), p. 73.