PHYSICAL REVIEW B, VOLUME 64, 144417

Magnetic structure of the $HoNiO_3$ perovskite

M. T. Fernández-Díaz
Institut Laue Langevin, BP 156x, F-38042 Grenoble Cedex 9, France

J. A. Alonso, M. J. Martínez-Lope, and M. T. Casais
Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, E-28049, Madrid, Spain

J. L. García-Muñoz
Institut de Ciència de Materials de Barcelona, C.S.I.C., Campus UAB, E-08193, Bellaterra, Barcelona, Spain

(Received 12 April 2001; published 19 September 2001)

Neutron diffraction data collected on polycrystalline $HoNiO_3$ have been used to investigate the magnetic behavior of the Ni and Ho sublattices in the monoclinic insulating phase of this oxide. Different propagation vectors, $\mathbf{k}=(\frac{1}{2},0,\frac{1}{2})$ and $\mathbf{k}=0$, are found for the Ni and Ho sublattices, respectively. Possible collinear and noncollinear magnetic ordering of the Ni moments are discussed, supporting the idea that even in the insulating phase, carriers keep a certain degree of delocalization as a consequence of the strong p-d hybridization.

DOI: 10.1103/PhysRevB.64.144417 PACS number(s): 71.30.+h, 71.45.Lr, 71.38.−k, 75.25.+z

I. INTRODUCTION

The electronic properties of $3d$ transition-metal oxides with high valence are far from clear in spite of their richness. The RNiO$_3$ (R=rare earth) family is one of these systems, where two phase transitions take place; a metal-insulator transition (MI) at T_{MI} (Ref. 1) and antiferromagnetic ordering at $T_N \leqslant T_{\mathrm{MI}}$. Most of the published work on this system deals with the origin of the MI transition and the nature of the insulating state. The first studies carried out in the compounds with the lightest elements of the series (R=Pr, Nd, Sm, and Eu),[2–7] showed slight changes in the structure at T_{MI}, the most relevant being a subtle expansion of the cell volume when charges localize. Nevertheless, the huge effect on the transition temperature observed in these nickelates by the isotopic substitution of ^{16}O for ^{18}O, settled the importance of the electron-phonon coupling in the mechanism responsible for the metal-insulator transition.[8]

Recently, synchrotron and neutron diffraction data through the metal-insulator transition in $YNiO_3$ proved the existence of a striking structural transition concomitant with the charge localization.[9] This transformation consists of a change of symmetry from orthorhombic (space group $Pbnm$) in the metallic phase to monoclinic (space group $P2_1/n$) in the insulating phase. As a consequence, the single Ni site in the orthorhombic phase splits into two independent positions in the monoclinic symmetry. The two NiO_6 octahedra show very significant differences in their respective average Ni-O bond length, giving rise to a pattern of contracted and expanded NiO_6 octahedra alternating along the three directions of the crystal. The different mean Ni-O distances on each kind of octahedron are the result of the appearance of a partial charge disproportionation $2\ \mathrm{Ni}^{3+} \rightarrow \mathrm{Ni}^{3+\delta} + \mathrm{Ni}^{3-\delta}$, concomitant with the metal-insulator transition found for the heaviest rare earths, from Ho to Lu compounds. A complete description of the structure as well as the structural changes associated with the metal-insulator transition in these monoclinic oxides have been thoroughly discussed in Refs. 10 and 11.

The second transition to the antiferromagnetic state is also of great interest as it gives rise to an uncommon magnetic ordering. In the insulating state, the magnetic structure is characterized by the propagation vector $\mathbf{k}=(\frac{1}{2},0,\frac{1}{2})$, which is highly unusual. Nominally, there is one electron in the doubly degenerate e_g orbital, therefore one expects a Jahn-Teller distortion in the insulating RNiO$_3$ compounds and, associated with it, the stabilization of a particular orbital ordering. Thus far, however, no evidence for Jahn-Teller distorted octahedra or orbital ordering has been found.

This paper deals with the magnetic structure and the magnetic behavior of the Ni and Ho sublattices in $HoNiO_3$, studied using neutron-diffraction techniques. Different propagation vectors are found for Ho and Ni. Possible collinear and noncollinear ordering of Ni moments is presented in connection with the striking propagation vector of this magnetic sublattice.

II. EXPERIMENTAL

$HoNiO_3$ compound was prepared as polycrystalline powder by high-pressure solid state reactions, as described in Ref. 9. The sample was confirmed to be single phase by diffraction measurements. On heating, the monoclinic-to-orthorhombic transition occurs at $T_{\mathrm{MI}}=583$ K.[13] Neutron diffraction data were collected in the temperature range 1.5–300 K on the D1B diffractometer of the Institute Laue-Langevin in Grenoble. A wavelength of 2.52 Å was used, and the data were analyzed following the Rietveld method, using the program FULLPROF.[12]

III. RESULTS

Below $T_N=145$ K, the NPD patterns of $HoNiO_3$ show the presence of small magnetic reflections that are indexed with a $2a\times b\times 2c$ cell, and they correspond to the same propagation vector $\mathbf{k}=(\frac{1}{2},0,\frac{1}{2})$ found for all the members of the series previously studied.[7,13] An exhaustive analysis of

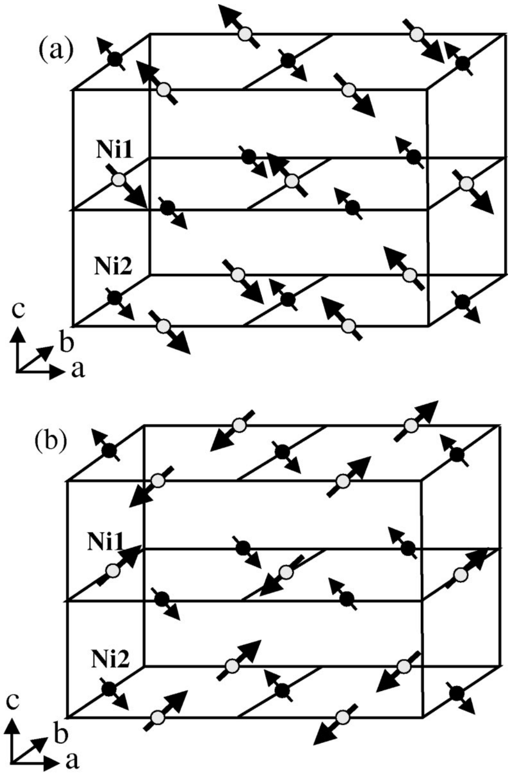

FIG. 1. Schematic representations of the Ni^{3+} antiferromagnetic structures: (a) collinear arrangement; (b) noncollinear arrangement.

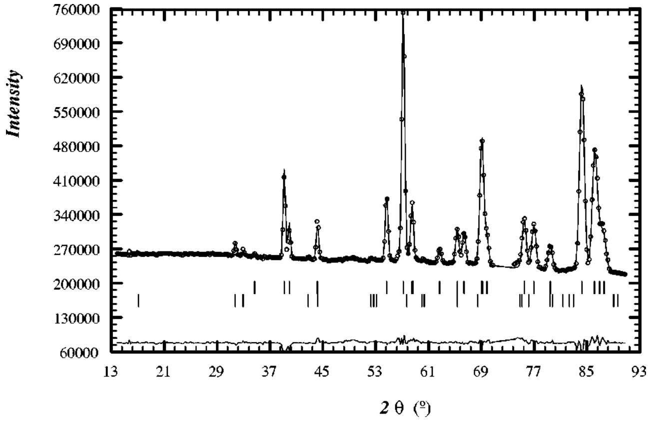

FIG. 2. Observed (circles), calculated (full line), and difference (bottom) NPD Rietveld profiles for $HoNiO_3$ at $T = 10$ K.

the possible magnetic structures based on group theory was given in the Appendix of Ref. 7 for the orthorhombic nickelates. For the monoclinic compounds, the only variation comes from the fact that Ni ions are split in two independent sites in the $P2_1/n$, s.g.: the reference atoms Ni1 and Ni2 occupy the positions $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$, respectively. Accordingly, the magnetic structure can be considered to be composed of two independent sublattices: one with $m1$ in $(\frac{1}{2},0,0)$ and $m2$ in $(0,\frac{1}{2},\frac{1}{2})$; the other with $m3$ in $(0,\frac{1}{2},0)$ and $m4$ in $(\frac{1}{2},0,\frac{1}{2})$. Below $T_N = 145$ K, the best fit of the magnetic intensities is obtained when considering the basis function $m_{1x}+m_{2x}$, $m_{1y}-m_{2y}$, $m_{1z}+m_{2z}$ for the first sublattice and: $m_{3x}+m_{4x}$, $m_{3y}-m_{4y}$, $m_{3z}+m_{4z}$ for the second sublattice.

For the observed magnetic intensities, the determination of the magnetic structure is not unique. In fact, we obtain satisfactory magnetic fits with two different arrangements of the magnetic moments at the Ni sites. The first one corresponds to a collinear magnetic structure and it is sketched in Fig. 1(a). It is an intermediate situation between model 1 and model 2 described in Ref. 7. In this model we assume that the magnetic moments of Ni1 and Ni2 sublattices are parallel and adopt the identical modes $(m_{1x}+m_{2x},0,m_{1z}+m_{2z})$ for Ni1 and $(m_{3x}+m_{4x},0,m_{3z}+m_{4z})$ for Ni2. The second possibility consists on a non-collinear magnetic structure of the type represented in Fig. 1(b). It can be described as $(m_{1x}+m_{2x},0,m_{1z}+m_{2z})$ for Ni1 sites and $(m_{3x}+m_{4x},0,-m_{3z}-m_{4z})$ for Ni2 sites (or, equivalently $(m_{1x}+m_{2x},0,m_{1z}+m_{2z})$ and $(-m_{3x}-m_{4x},0,m_{3z}+m_{4z})$]. In both models all magnetic moments lie in the $a-c$ plane. From purely symmetry considerations, both structures are allowed since, as previously mentioned, the monoclinic symmetry splits the Ni position in two independent Ni sites. Consequently, the relative orientation of the magnetic moments belonging to the two independent sublattices is no longer predetermined by symmetry transformations.

An appealing result is the fact that the refinements improve considerably when we let the value of the magnetic moment at the two Ni sites refine independently. In both models refinements converge to two different values for the magnetic moment of Ni1 $(m1 = m2 \approx 1.4\mu_B)$, and Ni2 $(m3 = m4 \approx 0.6\mu_B)$. It is worth recalling that the existence of two magnetically different Ni ions supports the charge disproportionation phenomenon inferred from the structural data.[11] The refinement of the NPD pattern at 10 K gives for the collinear magnetic structure

$$\mathbf{m}(\mathrm{Ni1}) = [1.1(2),0,1.0(2)]$$

$$\mathbf{m}(Ni2) = [0.4(1),0,0.34(7)]$$

and for the noncollinear magnetic structure

$$\mathbf{m}(\mathrm{Ni1}) = [0.9(1),0,1.1(1)]$$

$$\mathbf{m}(\mathrm{Ni2}) = [0.35(9),0,-0.4(1)].$$

The refinement of the experimental NPD pattern at 10 K is displayed in Fig. 2.

Cooling down to 3 K, no changes in the position of the magnetic reflections or in their relative intensity have been observed, confirming the stability of the described magnetic ordering in all the temperature range. Nevertheless, below 3 K the sudden appearance of new peaks indicates the onset of the Ho magnetic moment ordering. The magnetic reflections appearing below $T_R = 3$ K correspond to a magnetic periodicity different to the Ni one. In fact, they can be indexed with the lattice parameters of the crystallographic cell $(a \times b \times c)$. Hence, at 1.5 K the diffraction pattern contains mag-

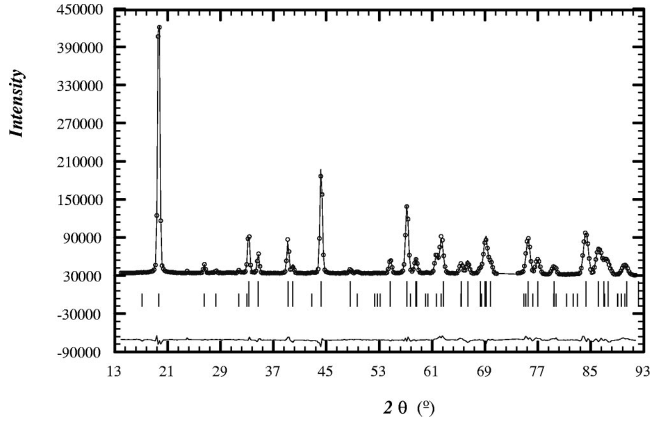

FIG. 3. Observed (circles), calculated (full line), and difference (bottom) NPD Rietveld profiles for $HoNiO_3$ at $T = 1.5$ K.

netic reflections defined by two different wave vectors $\mathbf{k}_1 = (\frac{1}{2},0,\frac{1}{2})$, associated to the magnetic ordering of Ni sublattices, and $\mathbf{k}_2 = (0,0,0)$ related to the periodicity of Ho ordered moments.

The magnetic arrangement of the Ho sublattice has also been determined with the help of group theory. The unique solution that fits the measured diffraction pattern corresponds to an antiferromagnetic arrangement of Ho moments in accordance with the basis function $G_xA_yG_z$ of the $\Gamma(+-)$ irreducible representation of $P2_1/n$ space group. Labeling the four equivalent Ho atoms as 1: $(x,y,1/4)$; 2: $(1-x,1-y,3/4)$; 3: $(x+1/2,1/2-y,3/4)$; 4: $(1/2-x,y+1/2,1/4)$, the magnetic structure corresponds to the next sequence of signs: G_x(+-+-);A_y(+--+); and G_z(+-+-). The agreement of the model with the experimental intensities at 1.5 K can be observed in Fig. 3. The value of the ordered magnetic moment at the lowest temperature is 7.56 μ_B per Ho^{+3} cation, which indicates that all the layers are magnetically ordered. We obtain the following value for the components of the Ho^{+3} mangetic moments:

$$\mathbf{m}(\mathrm{Ho}) = [-3.14(8), 6.71(4), 1.5(1)].$$

The moments are mostly oriented along the *b* axis, that is, almost perpendicular to the direction of Ni moments. A representation of the magnetic structure at 1.5 K is depicted in Fig. 4.

IV. DISCUSSION AND CONCLUSIONS

The Ni sublattice of $HoNiO_3$ has the same propagation vector $\mathbf{k}_1 = (\frac{1}{2},0,\frac{1}{2})$ as the previous studied compounds of the series, a feature inherent to this family of oxides, independently of their degree of structural distortion. We call to mind that the superexchange interaction between $S = \frac{1}{2}\mathrm{Ni}^{III}(t_{2g}^6 e_g^1)$ spins is expected to be antiferromagnetic resulting in the *G*-type magnetic structure, in which every Ni ion is antiferromagnetically coupled to its six nearest neighbors as proposed by Demazeau for $YNiO_3$ and $LuNiO_3$.[14] However, the magnetic structure corresponding to a propagation vector $(\frac{1}{2},0,\frac{1}{2})$ cannot be stabilized for nearest-neighbors exchange integrals of the same sign and absolute values greater than those for any other neighbors, which is usually the case for the 180° TM-O-TM exchange topology in perovskite oxides. Therefore the only way to stabilize a collinear magnetic structure with $(\frac{1}{2},0,\frac{1}{2})$ propagation vector is to accept that nearest-neighbors exchange integrals can have different signs. This is what happens when considering a collinear magnetic structure of the type represented in Fig. 1(a) where each Ni cation is antiferromagnetically coupled to three of its nearest-neighbors and ferromagnetically to the three others. This is in contradiction with a uniform distribution of e_g electron. That is actually what the structural results of the insulating phase indicates; the stabilization of an uncompleted charge disproportionation. Moreover, taking into account that one of the two Ni types tends to a diamagnetic state, the Ni1-Ni1 interactions between second nearest neighbors could became significant compared with those between the nearest-neighbor Ni1-Ni2 atoms. But in spite of these considerations the origin of the anisotropic magnetic coupling of each Ni ion with its six nearest-neighbors remains unclear as in fact, we observe that each Ni ion has three ferromagnetic and three antiferromagnetic couplings to its neighbors which from the structural point of view, are equivalent two by two. Recent Hartree-Fock calculations[15] pointed out that the collinear magnetic ordering with $\mathbf{k} = (\frac{1}{2},0,\frac{1}{2})$ can be realized assuming a charge ordering of holes at the oxygen sites. In such a state the excess holes located at some oxygen sites cause ferromagnetic coupling between Ni spins. But in this model, all the Ni sites have the same number of *d* electrons, which is not the case for $HoNiO_3$. As discussed in Ref. 13, if we consider that the isotropic exchange between neighbors is the most important term responsible for the magnetic ordering, the stabilization

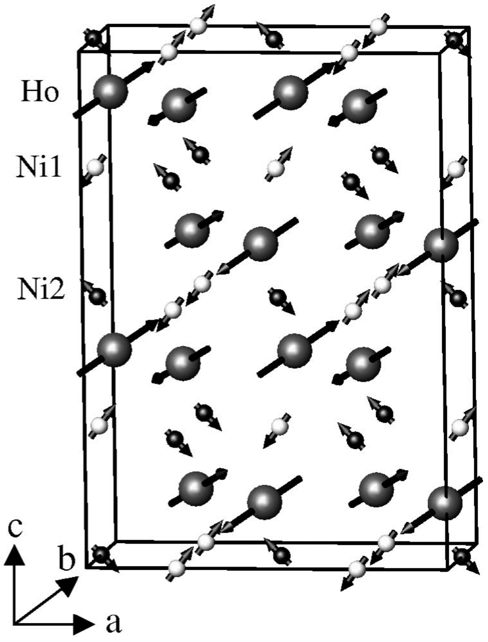

FIG. 4. Representation of the relative orientation of Ho and Ni magnetic moments at 1.5 K. White and black spheres correspond to the two Ni sites, grey spheres represent Ho atoms.

of the magnetic structure with propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ is only possible if J1 (nearest neighbor interaction) is null. Even if that condition is contrary to what is expected for superexchange theory, it could apply if a complete charge disproportionation of the type 2 $Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$ is assumed. In that case the Ni lattice would be composed of two interpenetrating sublattices, one of magnetic high-spin Ni^{2+} $(S=1)$ ions and a second of nonmagnetic Ni^{4+} ions. In Ref. 15 the same kind of charge-ordered state has been considered to explain the type of magnetic ordering. This assumption would give an antiferromagnetic ordering of Ni^{2+} sites, which is also consistent with the neutron diffraction data. However, the structural data and in particular the Ni-O distances give a charge disproportionation which is only $\delta = 0.3$, and as a consequence we must discard this justification for the magnetic structure.

We are led therefore to consider a noncollinear magnetic structure that, as stated before, is compatible with symmetry considerations and reproduces the observed neutron diffraction patterns. For such an ordering, the magnetic couplings are neither ferromagnetic nor antiferromagnetic but the angle between magnetic moments takes intermediate values. Even if the collinear magnetic structure is the simplest model that explains the data, we lean towards the noncollinear model because it has the advantage of giving a magnetic structure in which all the magnetic couplings between Ni cations are of the same type. The stabilization of a noncollinear magnetic structure can be justified by considering different characteristics of this material. First, the superexchange angle Ni-O-Ni has a value of about 147° which is far from the 180° for which the Goodenough-Kanamori rules forecast a strong antiferromagnetic coupling. The charge disproportionation in the insulating phase can be interpreted as a redistribution of charge. That means that the conduction electrons of the metallic state are now localized, in the sense of a strong reduction of their mobility, but their wave functions are expanded over more that one Ni site even in the insulating phase, minimizing the Coulomb repulsion energy of two electrons at the same atomic orbital by a spatial extension of the orbital. Such an "extended localization" denotes a high covalent character of the bonds where the carriers can be shared by several atoms in a kind of Ni-O-Ni molecular orbital. That situation can set up the appearance of ferromagnetic interactions between neighboring Ni spins as a consequence of an intramolecular orbital exchange obeying Hund's rule. As pointed out by Goodenough,[16] as the result of the strong hybridization of e_g and ligand p bands, p-d transfer interactions could give rise to the existence of holes in the oxygen p orbitals and therefore the existence of ferromagnetic covalent interactions. It seems reasonable then to consider that the magnetic structure is the result of different magnetic interactions, some of antiferromagnetic and some of ferromagnetic character, giving rise to competition in the resulting magnetic structure.

To elucidate which of these models correspond to the real magnetic structure of $R\mathrm{NiO}_3$, experiments on single crystals must be done. But whatever the result might be, both types of ordering raise important questions about the character of the magnetic interactions in transition metal oxides with a large electronic correlation effect.

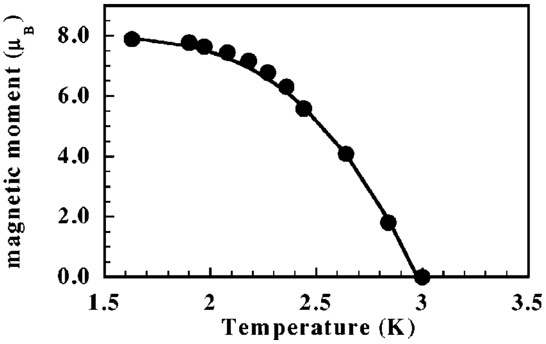

FIG. 5. Temperature dependence of the ordered Ho^{+3} moment.

The unattended feature of the Ho compound is the fact that the rare-earth sublattice orders with a different propagation vector than the Ni one. This finding indicates that in this compound, the rare-earth and the transition-metal sublattices are magnetically decoupled at least below 3 K and that the Ho-Ho interactions are stronger than the possible Ni-Ho interactions. That behavior is different to what has been observed for all the rest of the studied nickelates, where the presence of the same propagation vector suggests that the ordering of the A sublattice is mainly due to the polarization of R^{+3} moments in the presence of a local field induced by the Ni, rather than from the R-R interaction. This conclusion is confirmed by the dependence on temperature of the ordered Ho^{+3} moment plotted in Fig. 5. As observed, the magnetic moment does not show the linear-like dependence expected in the case of polarization under the resulting local field of Ni moments. Although it is quite usual in perovskites of rare earths and transition metals that both sublattices are magnetically coupled, there are other cases where the R-R interactions induce a different kind of ordering, including $TbCrO_3$ (Ref. 17) and $DyCrO_3$ (Ref. 18). A complete study of the rare-earth ordering along the whole series is underway in order to elucidate the relative interaction of both magnetic sublattices.

To summarize, the study of the magnetic structure presented in this paper shows that the unusual magnetic ordering appearing in RNiO3 perovskites cannot be explained in terms of antiferromagnetic superexchange interactions from a localized ionic picture. On the contrary, it can be understood when considering strong covalent bonds of Ni-O-Ni entities where interactions are ferromagnetic. Finally, in the case of HoNiO3, we find that the rare-earth and the transition-metal sublattices are magnetically decoupled.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support by the MEC (PB97-1175 and PB97-1181), Generalitat de Catalunya (GRQ95-8029). The provision of beam time at ILL is acknowledged.

[1] P. Lacorre, J.B. Torrance, J. Pannetier, A.I. Nazzal, P.W. Wang, and T.C. Huang, J. Solid State Chem. **91**, 225 (1991).

[2] J.B. Torrance, P. Lacorre, A.I. Nazzal, E.J. Ansaldo, and Ch. Niedermayer, Phys. Rev. B **45**, 8209 (1992).

[3] J.L. Garca-Muñoz, J. Rodríguez-Carvajal, P. Lacorre, and J. B. Torrance, Phys. Rev. B **46**, 4414 (1992).

[4] M. Medarde, A. Fontaine, J.L. García-Muñoz, J. Rodríguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi, and P. Lacorre, Phys. Rev. B **46**, 14975 (1992).

[5] J. L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Europhys. Lett. **20**, 241 (1992).

[6] J.A. Alonso, M.J. Martínez-Lope, and I. Rasines, J. Solid State Chem. **120**, 170 (1995).

[7] J.L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Phys. Rev. B **50**, 978 (1994).

[8] M. Medarde, P. Lacorre, K. Conder, F. Fauth, and A. Furrer, Phys. Rev. Lett. **80**, 2397 (1998).

[9] J.A. Alonso, J.L. García-Muñoz, M.T. Fernández-Díaz, M.A.G. Aranda, M.J. Martíinez-Lope, and M.T. Casais, Phys. Rev. Lett. **82**, 3871 (1999).

[10] J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, J.L. García-Muñoz, and M. T. Fernández-Díaz, Phys. Rev. B **61**, 1756 (2000).

[11] J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, and J.L. García-Muñoz, Phys. Rev. B (to be published).

[12] J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).

[13] J. Rodríguez-Carvajal, S. Rosenkranz, M. Medarde, P. Lacorre, M. T. Fernández-Díaz, F. Fauth, and V. Trounov, Phys. Rev. B **57**, 456 (1998).

[14] G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **3**, 582 (1971).

[15] T. Mizokawa, D.I. Khomskii, and G.A. Sawatzky, Phys. Rev. B **61**, 11 263 (2000).

[16] J.B. Goodenough, J. Solid State Chem. **127**, 126 (1996).

[17] E.F. Bertaut, J. Mareschal, and G.F. de Vries, J. Phys. Chem. Solids **28**, 2143 (1967).

[18] E.F. Bertaut and J. Mareschal, J. Phys. (France) **29**, 67 (1968).