Formal Valence, 3*d*-Electron Occupation, and Charge-Order Transitions

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(Received 10 April 2012; revised manuscript received 3 September 2012; published 20 November 2012)

While the formal valence and charge state concepts have been tremendously important in materials physics and chemistry, their very loose connection to actual charge leads to uncertainties in modeling behavior and interpreting data. We point out, taking several transition metal oxides (La_2VCuO_6, $YNiO_3$, $CaFeO_3$, $AgNiO_2$, V_4O_7) as examples, that while dividing the crystal charge into atomic contributions is an ill-posed activity, the 3*d* occupation of a cation (and more particularly, differences) is readily available in first principles calculations. We discuss these examples, which include distinct charge states and charge-order (or disproportionation) systems, where different "charge states" of cations have identical 3*d* orbital occupation. Implications for theoretical modeling of such charge states and charge-ordering mechanisms are discussed.

DOI: 10.1103/PhysRevLett.109.216401 PACS numbers: 71.30.+h, 71.20.−b, 71.28.+d

Spin ordering, and often orbital ordering, is normally unambiguous, as these properties are subject to direct observation by magnetic and spectroscopic measurements, respectively. Charge ordering (CO) and the actual charge of an ion is rarely measured directly, and the formal charge of an ion in the solid state can be a point of confusion and contention. Valence, oxidation number, and formal charge are concepts borrowed from chemistry, where it is emphasized they do not represent actual charge [1,2] and have even been labeled hypothetical [1]. As the interplay between spin, charge, orbital, and lattice degrees of freedom becomes more closely watched [3] and acknowledged to be a complex phenomenon, disproportionation and CO have become entrenched as the explanation of several high profile metal-insulator transitions (MIT). The possibility that CO in the charge transfer regime is associated with the oxygen sublattice, with negligible participation of the metal, has been raised [4] and considered as an alternative [5].

Charge density is a physical observable of condensed matter, and the desire to assign charge to atoms has evident pedagogical value, so theoretical approaches have been devised to share it amongst constituent nuclei. Mulliken charge population, which socializes shared charge (divides it evenly between overlapping orbitals) is notoriously sensitive to the local orbital basis set that is required to specify it. Born effective charges are dynamical properties and are often quite different from any conceivable formal charge or actual charge. Integrations over various volumes have been used a great deal, but dividing the static crystal charge density into atomic contributions is, undeniably, an ill-defined activity.

A possibility that has not been utilized is that, taking 3*d* oxides as an example, there is a directly relevant metric that is well defined: the *d* occupation n_d. This quantity is in fact what the physical picture of formal charge or oxidation state brings to mind. 3*d* cations, in their various environments and charge states, have maxima in their spherically averaged radial density $\bar{\rho}(r)$ in the range 0.6–0.9 a_o. At this short distance from the nucleus, the only other contribution to the density is the core contribution, which can be subtracted out and is unchanged during chemical processes or CO. Most relevant to the understanding of CO-driven transitions and disproportionation is the (actual or relative) difference in 3*d* occupations Δn_d, which is given directly, without any integration, by the difference in the radial 3*d* densities at their peaks, where there are no competing orbital occupations to confuse charge counting. This specifically defined 3*d* occupation difference provides a basis for building a faithful picture of CO and of characterizing formal valence differences more realistically. We consider our computational results [6,7] for a selection of systems, then discuss some of the implications.

La_2VCuO_6 (LVCO) is a double perovskite compound providing a vivid and illustrative example. Our earlier study [8] revealed two competing configurations for the ground state. Using conventional identifications, one is the V^{4+} d^1, Cu^{2+} d^9 magnetic configuration (with bands shown in Fig. 1) identified as such because (i) there is one band of strong V *d* character occupied and one band of strong Cu *d* character unoccupied, and (ii) the moments on both V and Cu, $0.7\mu_B$, are representative of many cases of spin-half moments reduced by hybridization with O 2*p* orbitals. The other configuration is the nonmagnetic $d^0 - d^{10}$ band insulator: all Cu *d* bands are occupied, all V *d* bands are unoccupied—a conventional ionic band insulator in all respects. The identification of formal valence (or oxidation state) is crystal clear.

The radial charge densities of V and of Cu for both configurations reveal an unsettling feature: the actual 3*d* occupations n_d of each of these V and Cu ions are identical for both configurations, in spite of the unit difference in

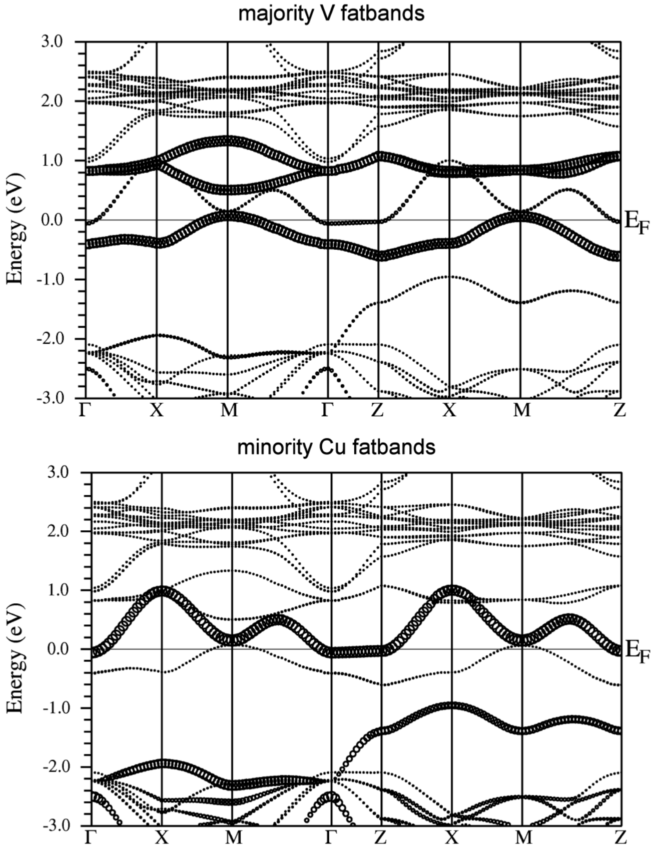

FIG. 1. Bands near the Fermi energy (band gap) in the $d^1 - d^9$ magnetic, nearly Mott insulating, configuration of La_2VCuO_6. Top: the V d_{xy}-up band is JT- and correlation-split off from the other two t_{2g} bands and fully occupied. Bottom: the Cu fat bands for the same system, showing one unoccupied Cu minority $d_{x^2-y^2}$ band that is JT- and correlation-split from the d_{z^2} band. The other d bands fall outside this energy range.

their formal charges. (Identical in this Letter means to better than 0.5% $\sim 0.01e^-$, in terms of the differences of charge density at their peaks.) Thus ions with no real difference in $3d$ occupation can behave as if they comprise charge states differing by unity. Changes in spin-orbital occupations $n_{m\sigma}$, which quantify spin, orbital, and charge differences between the two states, can be quantified by the LDA + U spin-orbital occupations. For the V d^1 d_{xy} (Jahn-Teller split) orbital, the majority-minority difference is $n_{xy\uparrow} - n_{xy\downarrow} = 0.77 - 0.07 = 0.70$, which accounts for all of the moment. The difference of $n_{xy\uparrow}(d^1) - n_{xy\downarrow}(d^0) = 0.77 - 0.11 = 0.66$ between d_{xy} and the other two t_{2g} occupations characterizes the Jahn-Teller distortion. The increase in charge of the d_{xy} orbitals (both spins), 0.55, compared to the d^0 state (with only 0.30), is absorbed more or less uniformly from all other (nominally unoccupied) spin orbitals. Similarly for Cu, the d^9 hole results from a difference of charge in the minority $d_{x^2-y^2}$ orbital of 0.6, with the remaining hole charge being distributed nearly uniformly over the other nine (nominally but not actually fully occupied) spin orbitals. In both cases the moment arises entirely from the single magnetic orbital as the simple picture would suggest, while all other orbitals are unpolarized. This happens, conspicuously, with no change in n_d for either V or Cu. Charge is redistributed to one orbital from the others, and strongly spin-imbalanced within that orbital. Even with insulators with "obvious" charge states, $3d$ orbital occupations can range over the values [0,1].

We look at additional cases before addressing some of the implications.

Rare earth ($\mathcal{R}$) nickelates $\mathcal{R}NiO_3$ display a first order structural and MIT of great current interest. The $Pbnm$ ($GdFeO_3$ structure) $\rightarrow$ $P2_1/n$ transformation results in a large $Ni1O_6$ and a small $Ni2O_6$ octahedron, with Ni-O distances of 2.015 ± 0.015 and 1.915 ± 0.025 Å, respectively, that are not otherwise strongly distorted; see the inset of Fig. 2. At a temperature that varies smoothly from 600 to 300 K with increasing $\mathcal{R}$ ionic radius, the resistivity of these nickelates changes sharply [9,10]. We focus on $YNiO_3$; with its small ionic radius, it is one of the more strongly distorted members, and the resulting narrowed bandwidths make it more prone to strong correlation and CO tendencies [5]. Structural changes at the MIT have been studied extensively [9,11–14], which together with x-ray absorption spectral splittings [15–17] have been

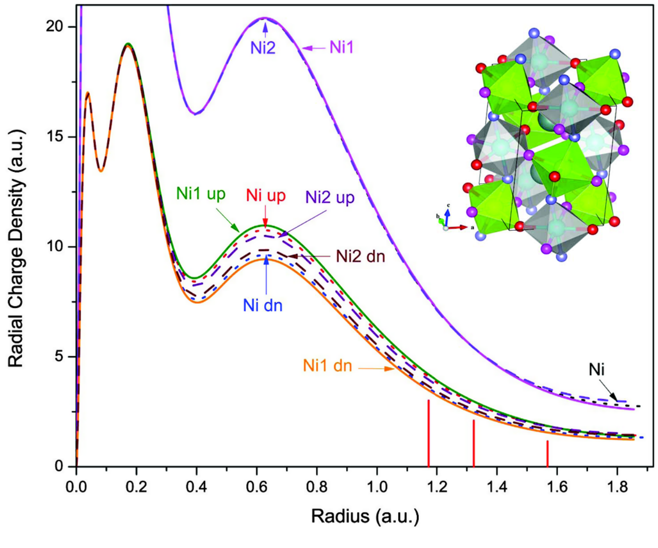

FIG. 2 (color online). Radial charge density (upper curve) of $YNiO_3$ for $Pbnm$ Ni and $P2_1/n$ Ni1 and Ni2, showing there is no difference at the peak, which reflects the $3d$ occupation of the ion; a small difference shows up near the sphere boundary. The spin decompositions give easily visible differences. The vertical lines at the bottom right indicate conventional Ni^{4+}, Ni^{3+}, and Ni^{2+} ionic radii, which have no relation to the (unvarying) $3d$ occupation. Inset: Structure of the broken symmetry $P2_1/n$ phase, showing the rotation in the a-b plane and tilting along the c axis of the NiO_6 octahedra (Ni is inside) and the (π, π, π) ordering of the Ni1 and Ni2 octahedra.

interpreted in terms of charge disproportionation (or CO) $2\mathrm{Ni}^{3+} \longrightarrow \mathrm{Ni}^{3+\delta} + \mathrm{Ni}^{3-\delta}$, with $\delta \approx 0.3$ for YNiO_3 [15].

This MIT in the nickelates has been recognized as paradigmatic by theorists. Mizokawa *et al.* modeled this system [18] with a multiband Hartree-Fock model in the charge-transfer regime and found evidence for CO on the oxygen sublattice for larger $\mathcal{R}$ cations, but concluded that YNiO_3 was representative of a CO transition on the Ni sites. Mazin *et al.* [5] surveyed the competition between Jahn-Teller distortion of the d^7 ion and CO and also concluded that YNiO_3 is a prime example of a CO $d^6 + d^8$ system. Lee *et al.* have investigated [19] a two band model for this system with a CO interaction in mean field, emphasizing CO effects. On the other hand, Yamamoto and Fujiwara [20] reported a very small ($\sim 0.03e^-$) density functional based charge difference.

For the assumed (for simplicity) ferromagnetic order the calculated Ni1 and Ni2 moments are 1.4 and $0.65\mu_B$, respectively, for YNiO_3 and several other members of this class, so these values are not sensitive to the magnitude of the distortion. They coincide with the values obtained from neutron diffraction [11], 1.4(1) and $0.7(1)\mu_B$, respectively, in the magnetically ordered phase. It is intriguing that the same moments were obtained in fully relaxed $\mathrm{LaNiO}_3/\mathrm{LaAlO}_3$ monolayer superlattices [21].

The $3d$ occupations, obtained as above directly from the maximum in the radial charge density plots in Fig. 2, are identical for Ni1, Ni2, and the single Ni site in the high temperature phase: there is no $3d$ charge transfer, or disproportionation, across the transition. The majority and minority radial densities and integrated charges of course differ (see Fig. 2) as they must to give the moment, but the total $3d$ occupation is inflexible. This constancy of the $3d$ occupation across the transition, and equality for Ni1 and Ni2, is inconsistent with microscopic disproportionation.

To illustrate the spin-orbital spectral density redistribution, the projected densities of states are shown in Fig. 3. All t_{2g} states are filled and irrelevant. The e_g spectral distribution is nonintuitive: weight from -5 eV spin-down is transferred to -1 eV spin-up. The majority e_g states just below the gap are strongly Ni1 in character, while the unoccupied bands just above the gap are primarily Ni2. Such behavior is expected for different charge states, similarly to the behavior in LVCO above; however, the total $3d$ occupation is identical.

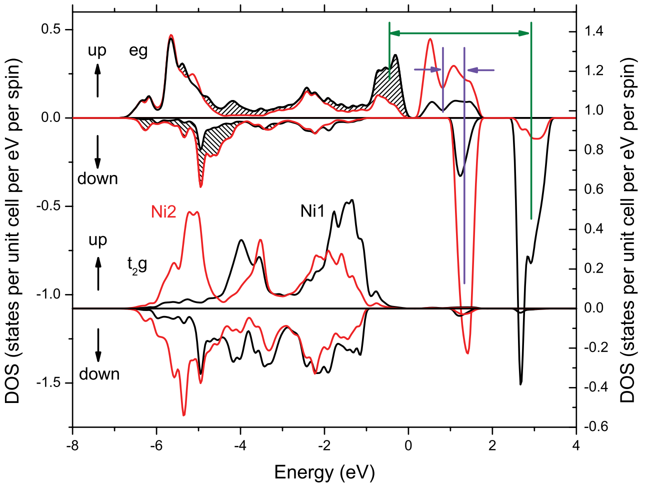

FIG. 3 (color online). Spin-decomposed Ni t_{2g} and e_g density of states for the Ni1 and Ni2 ions in the insulating $P2_1/n$ broken symmetry phase. The hashed regions illustrate the spectral origin of the enhanced moment of Ni1 relative to Ni2. The horizontal arrows illustrate the large difference in spin splittings, the result of the combination of Hund's coupling and Coulomb $U = 5.7$ eV.

The main differences between Ni1 and Ni2 show up in the unoccupied e_g states: the Ni1 spin splitting is 3.5 eV, a reflection of the on-site repulsion that opens the Mott gap in the majority e_g states, rather than Hund's exchange splitting. The origin of the Ni2 moment is murky, not identifiable with any occupied spectral density peak. Note that in a $\mathrm{Ni}^{2+} + \mathrm{Ni}^{4+}$ CO picture, Ni2 would be nonmagnetic. Not only is this calculated behavior not consistent with a CO picture, it involves redistribution not accounted for in any simple model. In spite of identical $3d$ occupations, the Ni1 and Ni2 core energies differ by up to 1.5 eV.

CaFeO_3, another perovskite that displays the same $Pbnm \longrightarrow P2_1/n$ structural change at T_{MI} as the nickelates, is also explained [22] in CO language that invokes the unusually high (penta)valent state Fe^{5+}. Analogously to YNiO_3, we obtain identical $3d$ occupations for Fe1 and Fe2 ions. Quantum chemical embedded cluster calculations [23] and LDA + U studies [24–26] had noted that the Fe charge in both "disproportionated" sites differed little, but neither quantified the occupation as we have for YNiO_3 and CaFeO_3. The pentavalent state of Fe has most often been identified from Mössbauer isomer shift data, but Sadoc *et al.* [23] concluded the difference in isomer shift is primarily a measure of the covalency (Fe-O distance) rather than any real charge on Fe.

AgNiO_2, a triangular, magnetically frustrated lattice compound with nominal Ni^{3+} ions, undergoes a structural transition at 365 K although remaining metallic [27–30]. Three inequivalent Ni sites arise, with a high spin Ni1 ion in an enlarged octahedron and two low spin Ni2, Ni3 = Ni2, 3 ions in small octahedra. Based on the structural changes (which were quantified in terms of bond valence sums), the magnetic moments, and resonant x-ray scattering that confirms a calculated ~ 1 eV difference in core level energies between Ni1 and Ni2,3, this transition has been welcomed as the first realization of such a highly unusual $3e_g^1 \longrightarrow e_g^2 + 2e_g^{0.5}$ type of CO. Furthermore, using the charge difference per unit core level splitting of 0.66 e/eV led to an inferred charge disproportionation of $\sim 1.65e$, i.e., $\mathrm{Ni1}^{2+} + 2\mathrm{Ni2},3^{3.5+}$. We have reproduced several of the first principles results [27,30] that were used to support CO. The calculations give a large moment ($>1\mu_B$) on high-spin Ni1 and very weak moments ($\sim 0.1\mu_B$) on low-spin Ni2,3 ions. We find, as in the cases above, that n_d for the three sites are *identical*. Moreover, our calculated core level differences, 0.6–0.8 eV, are roughly consistent with reported values [30] (~ 1 eV).

V_4O_7 represents another oxide currently explained by a CO-driven MIT. It is structurally more involved, but first principles calculations of moments and geometries again have produced several results corroborating the experimental data [31,32] and were used to support CO into V^{3+} and V^{4+} charge states on specific sites. As in the instances above, we find no differences in n_d: the occupations are indistinguishable. The site energy differences, measured by differences in $1s$, $2s$, $2p$ core levels, differ by 0.9–1.2 eV for two sites, similar to the nickelates. The interplay of orbital order, structural distortions, and possible spin-singlet formation of half of the V ions provide a rich array of degrees of freedom, which can operate without need for disproportionation.

Implications.—We have established that, for several instances of CO transition systems as well as for the two self-evident charge states of LVCO, there is no difference in the $3d$ occupations for the different charge states that have been used to categorize their behavior. Such identification is possible because a choice of a region for integration is avoided; the peak charge region rather than tails of orbitals are used in the identification. This finding of constancy sharpens several reports of ''small charge differences'' between differing charge states (viz., Luo *et al.* [33] for doped manganites; Haldane and Anderson [34] in a multiorbital Anderson model, and Raebiger *et al.* [35] from DFT calculations for TM impurities in semiconductors; Yamamoto and Fujiwara [20] and also Park *et al.* [36] for nickelates).

We see two primary implications: (i) the conceptual basis underlying a substantial aspect of transition metal physics is misleading, and (ii) modeling of structural and electronic transitions has, at least in several conspicuous cases, incorporated the wrong mechanisms by invoking inactive degrees of freedom. Actual cases of CO very likely do exist, but the burden of proof has shifted.

For these CO systems, the constancy of n_d suggests that U_d is too large to allow change in occupation n_d in or near the ground state (in the cases we discuss, and similar ones). In insulators the charge is more physically pictured in terms of (fully occupied) Wannier functions (WFs) than in terms of ambiguous populations of atomic orbitals, making them appear to be inviting. However, WFs are far from unique and, like molecular orbitals, WFs contain charge that cannot objectively be assigned to one atom or another, so a WF viewpoint is not promising.

A broader implication is that modeling of coupled structural and electronic transitions in terms of charges [5,19] from atomic-like orbitals must be treated with caution: charge fluctuations in these systems are too high in energy to comprise a relevant degree of freedom. The important energy differences are characterized in terms of differences in hopping amplitudes, anion-cation distances, and (not recognized in most models) resulting changes in site energies, as well as very important Hund's rule energies. Models that try to parametrize (for example) Ni1-Ni2 differences by on-site charge will not be treating the relevant microscopic degrees of freedom. CO on the oxygen sublattice [4,5] may also be problematic.

Charge states of ions serve to specify the occupations of spin orbitals. The essential degrees of freedom in determining this popular characterization, which professes to be quantitative, are the spin-orbital occupations, not as determined from the (real) density matrix but rather from the site symmetry, crystal symmetry, and the local moment. The LVCO example illustrates vividly how two different charge states, for both *highly charged* V and *moderately charged* Cu, can be represented by integer occupation of different numbers of orbitals while there is no change in n_d. The concept of charge state projects onto integrally occupied orbitals, while the distribution of real charge is strongly nonintegral and often nonintuitive. These projections are backed up by the number of occupied spin-polarized bands (an integer), by the (discrete) local symmetry (JT distortion), by the local moment (with its quantization smeared by hybridization), and by the atomic radii, but each one of these characterizations is extremely flexible with a given amount of $3d$ charge.

More specifically to CO systems, the ionic environment in the high symmetry phase requires closer scrutiny. In both the nickelates and in V_4O_7 there is evidence of distinct metal sites *above* the transition, in the (on average) symmetric phase, and the structural similarities of $CaFeO_3$ to $RNiO_3$ suggest similar behavior there. For nickelates, x-ray absorption spectra [16,17] reveal that local signatures of Ni1 and Ni2 sites persist continuously across the MIT, and both sites also remain when driven across the phase boundary by pressure [37]. As we have shown, the coordination alone (i.e., with identical n_d) accounts for on-site energy differences of $\sim$1 eV in spectra that have often been used to support disproportionation. The MITs in some of these materials may be primarily order-disorder type; the onset of long-range order in nickelates results in carrier localization and gap formation, ergo a MIT but one due to structural order rather than CO.

We propose therefore that charge order should be used as the name, hence the interpretation, of a phase transition only if an objective, relevant charge difference is the likely mechanism; otherwise, the underlying mechanisms should be identified. Formal developments may be useful; for example, Jiang *et al.* have provided a specification [38] of integer charges in an insulator that they propose as oxidation states (which are identical to charge states in metal oxides.) Based on integration over a configuration space path of the dynamic Born effective charge, their expression assigns (in principle) an integer charge to each atom in any insulator. Notably, their specification does not refer to $3d$ charge explicitly and furthermore depends explicitly on dynamical effects (electron response to ion motion). Also, many CO interpretations only hold water if the supposed charge difference $\pm\delta$ is much smaller than unity ($\delta \sim 0.3$ for the nickelates). More experience will be needed to learn how best to interpret their definition.

Work at UC Davis was supported by DOE Grant No. DE-FG02-04ER46111. V.P. acknowledges support from the Spanish Government through the Ramón y Cajal Program.

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[1] G. Parkin, J. Chem. Educ. **83**, 791 (2006).

[2] D. W. Smith, J. Chem. Educ. **82**, 1202 (2005).

[3] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).

[4] T. Mizokawa, A. Fujimori, H. Namatame, K. Akeyama, and N. Kosugi, Phys. Rev. B **49**, 7193 (1994).

[5] I. I. Mazin, D. I. Khomskii, R. Lengsdorf, J. A. Alonso, W. G. Marshall, R. M. Ibberson, A. Podlesnyak, M. J. Martínez-Lope, and M. M. Abd-Elmeguid, Phys. Rev. Lett. **98**, 176406 (2007).

[6] The density functional based linearized augmented plane wave code WIEN2K [7] has been used in our calculations, where we have applied correlation corrections (LDA + U) as is usually necessary to describe $3d$ oxides. Computational methods are as described in Ref. [8].

[7] K. Schwarz and P. Blaha, Comput. Mater. Sci. **28**, 259 (2003).

[8] V. Pardo and W. E. Pickett, Phys. Rev. B **84**, 115134 (2011).

[9] J. L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Physica (Amsterdam) **180B**, 306 (1992).

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

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

[12] 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).

[13] J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, M. A. G. Aranda, and M. T. Fernández-Díaz, J. Am. Chem. Soc. **121**, 4754 (1999).

[14] I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B **60**, R8426 (1999).

[15] U. Staub, G. I. Meijer, F. Fauth, R. Allenspach, J. G. Bednorz, J. Karpinski, S. M. Kazakov, L. Paolasini, and F. d'Acapito, Phys. Rev. Lett. **88**, 126402 (2002).

[16] C. Piamonteze, H. C. N. Tolentino, A. Y. Ramos, N. E. Massa, J. A. Alonso, M. J. Martínez-Lope, and M. T. Casais, Phys. Rev. B **71**, 012104 (2005).

[17] M. Medarde, C. Dallera, M. Grioni, B. Delley, F. Vernay, J. Mesot, M. Sikora, J. A. Alonso, and M. J. Martínez-Lope, Phys. Rev. B **80**, 245105 (2009).

[18] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **61**, 11263 (2000).

[19] S.-B. Lee, R. Chen, and L. Balents, Phys. Rev. B **84**, 165119 (2011).

[20] S. Yamamoto and T. Fujiwara, J. Phys. Soc. Jpn. **71**, 1226 (2002).

[21] A. Blanca-Romero and R. Pentcheva, Phys. Rev. B **84**, 195450 (2011).

[22] M. Takano, S. Nasu, T. Abe, K. Yamamoto, S. Endo, Y. Takeda, and J. B. Goodenough, Phys. Rev. Lett. **67**, 3267 (1991).

[23] A. Sadoc, C. de Graaf, and R. Broer, Phys. Rev. B **75**, 165116 (2007).

[24] J. B. Yang, M. S. Kim, Q. Cai, X. D. Zhou, H. U. Anderson, W. J. James, and W. B. Yelon, J. Appl. Phys. **97**, 10A312 (2005).

[25] T. Saha-Dasgupta, Z. S. Popović, and S. Satpathy, Phys. Rev. B **72**, 045143 (2005).

[26] J. Matsuno, T. Mizokawa, A. Fujimori, Y. Takeda, S. Kawasaki, and M. Takano, Phys. Rev. B **66**, 193103 (2002).

[27] E. Wawrzyńska, R. Coldea, E. M. Wheeler, I. I. Mazin, M. D. Johannes, T. Sörgel, M. Jansen, R. M. Ibberson, and P. G. Radaelli, Phys. Rev. Lett. **99**, 157204 (2007).

[28] E. Wawrzyńska, R. Coldea, E. M. Wheeler, T. Sörgel, M. Jansen, R. M. Ibberson, P. G. Radaelli, and M. M. Koza, Phys. Rev. B **77**, 094439 (2008).

[29] J.-H. Chung, J.-H. Lim, Y. J. Shin, J.-S. Kang, D. Jaiswal-Nagar, and K. H. Kim, Phys. Rev. B **78**, 214417 (2008).

[30] G. L. Pascut, R. Coldea, P. G. Radaelli, A. Bombardi, G. Beutier, I. I. Mazin, M. D. Johannes, and M. Jansen, Phys. Rev. Lett. **106**, 157206 (2011).

[31] A. S. Botana, V. Pardo, D. Baldomir, A. V. Ushakov, and D. I. Khomskii, Phys. Rev. B **84**, 115138 (2011).

[32] J.-L. Hodeau and M. Marezio, J. Solid State Chem. **23**, 253 (1978).

[33] W. Luo, A. Franceschetti, M. Varela, J. Tao, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. **99**, 036402 (2007).

[34] F. D. M. Haldane and P. W. Anderson, Phys. Rev. B **13**, 2553 (1976).

[35] H. Raebiger, S. Lany, and A. Zunger, Nature (London) **453**, 763 (2008).

[36] H. Park, A. J. Millis, and C. A. Marianetti, Phys. Rev. Lett. **109**, 156402 (2012).

[37] A. Y. Ramos *et al.*, Phys. Rev. B **85**, 045102 (2012).

[38] L. Jiang, S. V. Levchenko, and A. M. Rappe, Phys. Rev. Lett. **108**, 166403 (2012).