Effect of covalency and interactions on the trigonal splitting in Na$_2$CoO$_2$

A. A. Aligia

Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina

We calculate the effective trigonal crystal field $\Delta$ which splits the $t_{2g}$ levels of effective models for Na$_2$CoO$_2$ as the local symmetry around a Co ion is reduced from $O_h$ to $D_{3d}$. To this end we solve numerically a Co$_6$ cluster containing a Co ion with all 3$d$ states and their interactions included, and its six nearest-neighbor O atoms, with the geometry of the system, in which the Co$_6$ octahedron is compressed along a $C_3$ axis. We obtain $\Delta \approx 130$ meV, with the sign that agrees with previous quantum chemistry calculations, but disagrees with first-principles results in the local density approximation (LDA). We find that $\Delta$ is very sensitive to a Coulomb parameter which controls the Hund coupling and charge distribution among the $d$ orbitals. The origin of the discrepancy with LDA results is discussed.

PACS numbers: 71.27.+a, 74.25.Jb, 74.70.-b

dateMay 11, 2014

I. INTRODUCTION

The doped layered hexagonal cobaltates Na$_x$CoO$_2$ have attracted great interest in the last years due to the high thermopower and at the same time low thermal conductivity and resistivity for $0.5 < x < 0.9$.\textsuperscript{2} and the discovery of superconductivity in hydrated Na$_x$CoO$_2$.\textsuperscript{3} Further attention was motivated by the fact that first-principles calculations in the local density approximation (LDA)\textsuperscript{4} predicted a Fermi surface with six prominent hole pockets along the $\Gamma - K$ direction, which are absent in measured angle-resolved photoemission (ARPES) spectra.\textsuperscript{5} To explain the discrepancy, several calculations including correlation effects were made.\textsuperscript{4-6} These studies used an effective model $H_{\text{eff}}$ for the $t_{2g}$ 3$d$ states of Co, split by the trigonal crystal field $\Delta$ into an $a_{1g}$ singlet and an $e'_g$ doublet.\textsuperscript{6} Except for some simplifications used in the different works, $H_{\text{eff}}$ has the form

$$H_{\text{eff}} = \sum_{i,\sigma} \Delta (\sum_{\beta \in c'_g} \tilde{d}_{\beta,i\sigma}^\dagger \tilde{d}_{\beta,i\sigma}^\dagger - \tilde{d}_{\sigma,i\gamma}^\dagger \tilde{d}_{\sigma,i\gamma}^\dagger)$$
$$+ \sum_{i,\gamma} \tilde{t}_{\gamma}^{\beta} (\tilde{d}_{\gamma+\delta,i\beta}^\dagger \tilde{d}_{\gamma,i\sigma}^\dagger + \text{H.c.}) + U_{\text{eff}} \sum_{i} \tilde{n}_{i\beta\uparrow} \tilde{n}_{i\beta\uparrow}$$
$$+ \frac{1}{2} \sum_{i,\gamma\neq\beta,\sigma} (U_{\text{eff}} \tilde{n}_{i\gamma\sigma} \tilde{n}_{i\beta\beta'} + J_{\text{eff}} \tilde{d}_{i\gamma\beta\sigma}^\dagger \tilde{d}_{i\gamma\beta'\sigma'}^\dagger \tilde{d}_{i\beta\sigma'} \tilde{d}_{i\beta\beta'}),$$

(1)

where $\tilde{d}_{\beta,i\sigma}^\dagger$ creates a hole on an effective $t_{2g}$ orbital at site $i$ with spin $\sigma$. The first term is the effective trigonal splitting mentioned above, the second term describes the hopping between orbitals at a distance $\delta$ and the remaining terms are effective interactions discussed for example in Ref. \textsuperscript{17}

In most works, $\Delta$ and $\tilde{t}_{\gamma}^{\beta}$ were derived from fits to the LDA bands and the interaction parameters were estimated. These fits give either $\Delta = -10$ meV or $\Delta = -130$ meV.\textsuperscript{18} With these parameters and realistic values of the Coulomb repulsion $U_{\text{eff}}$, correlations are not able to reconcile theory with experiment, as shown by different dynamical-mean-field-theory (DMFT) studies.\textsuperscript{12,13,15} The pockets still remain in the calculations.

Using instead an $H_{\text{eff}}$ derived from a multiband Co-O model $H_{\text{mb}}$ through a low-energy reduction procedure and the value $\Delta = 315$ meV obtained from quantum-chemistry configuration-interaction calculations these pockets are absent and the electronic dispersion near the Fermi energy agrees with experiment.\textsuperscript{15} In this procedure, no LDA results were used. The parameters of $H_{\text{mb}}$ were taken from previous fits of polarized x-ray absorption spectra\textsuperscript{19} and the parameters of $H_{\text{eff}}$ other than $\Delta$ were obtained fitting the energy levels of an undistorted Co$_6$ cluster ($O_h$ symmetry) and calculating the effective hopping between different CoO$_6$ clusters\textsuperscript{20}, following similar ideas that were successful in the superconducting cuprates.\textsuperscript{20-22} In these systems, low-energy reduction procedures that eliminate the O degrees of freedom, simplifying the problem to an effective one-band one,\textsuperscript{20,21,23,24} have been very successful, in spite of the fact that doped holes enter mainly at O atoms.\textsuperscript{20-22} Optical properties related with O atoms were calculated using these one-band models, which do not contain O states.\textsuperscript{20,21}

Summarizing previous results, if $\Delta$ is taken as a parameter, a positive $\Delta$ has the effect of shrinking the pockets, and for large enough $\Delta$, the pockets disappear from the Fermi surface, reconciling theory with ARPES experiments.\textsuperscript{12,13,15} A positive value has been obtained by quantum-chemistry methods\textsuperscript{18}, and a negative one is obtained fitting the LDA dispersion with $H_{\text{eff}}$.\textsuperscript{9,10} Thus, the origin of the discrepancy between different methods and the actual value of $\Delta$ remains a subject of interest.

It is known that in general, the LDA underestimates gaps and has difficulties in predicting one-particle excitations energies. Thus one might suspect that the parameters of $H_{\text{eff}}$, including $\Delta$ calculated with LDA are
not accurate enough when covalency and interactions are important. This is the case of NiO, for which agreement with experiment in LDA+DMFT calculations is only achieved once the O bands are explicitly included in the model or when the O atoms have been integrated out using low-energy reduction procedures, which take into account correlations from the beginning.

In covalent materials, the crystal-field splitting of transition-metal ions is dominated by the hopping of electrons between these ions and their nearest ligands. In particular for Na$_2$CoO$_2$, an estimate based on point charges gives $\Delta = -25$ meV. This shows that the effect of interatomic repulsions is small and of the opposite sign as that required to explain the ARPES spectra. The effects of covalency of Co and its nearest-neighbor O atoms and all Co-Co interactions are included in a CoO$_6$ cluster in the realistic ($D_{3d}$) symmetry. In this work, we solve numerically this cluster and calculate the effective splitting $\Delta$, neglecting interatomic repulsions. We also analyze the effects of different parameters on $\Delta$. The main result is that $\Delta \simeq 130$ meV and very sensitive to a parameter which controls the Hund rules. It is also sensitive to the cubic crystal-field splitting $10Dq$. A possible reason of the discrepancy with the LDA results is discussed.

In Section II, we describe the model, parameters, and briefly the formalism. Section III contains the results. Section IV is a summary and discussion.

II. THE MODEL AND ITS PARAMETERS

The multiband model from which $H_{\text{eff}}$ is derived, describes the 3$d$ electrons of Co and the 2$p$ electrons of the O atoms, located in the positions determined by the structure of Na$_2$CoO$_2$ at 12 K. In this work we restrict the calculation to a cluster of one Co atom and its six nearest-neighbor O atoms. The relevant filling for the calculation of $\Delta$ corresponds to formal valences Co$^{4+}$ and O$^{2-}$, or 41 electrons to occupy the 3$d$ shell of Co and the 2$p$ shells of the six O atoms. This corresponds to 5 holes in the CoO$_6$ cluster. Thus, it turns out to be simpler to work with hole operators (which annihilate holes) assuming spherical symmetry [the symmetry is reduced to $O_h$ by the cubic crystal field $10Dq$ and to $D_{3d}$ by the last (hopping) term of Eq. (2)]. The expression of $H_I$ is lengthy. It is included in the Appendix [Eq. (A1)] together with a brief description of its derivation for the interested reader. A more detailed discussion is in Ref. 17. The form of $H_I$ is rather simple and well known when either only $e_g$ orbitals or only $t_{2g}$ orbitals [as in Eq. (1)] are important, although the correct expressions were not always used. Some of the effects of these simplifications were discussed in Ref. 17.

All interactions are given in terms of three free parameters $F_0 \gg F_2 \gg F_4$. For example the Coulomb repulsion between two holes or electrons at the same 3$d$ orbital is $U = F_0 + 4F_2 + 36F_4$, and the Hund rules exchange interaction between two $e_g$ ($t_{2g}$) electrons is $J_e = 4F_2 + 15F_4$ ($J_t = 3F_2 + 20F_4$). Thus $F_2$ is the main parameter responsible for the spin and orbital polarizations related with the first and second Hund rules respectively.

Note that in Eq. (2) there is no trigonal splitting. This means that we take the bare value of the splitting $\Delta_0 = 0$ (neglecting the effect of interatomic repulsions). The dressed value $\Delta$ that enters the effective Hamiltonian Eq. (2) is calculated as

$$\Delta = E(e_g') - E(a_{1g}),$$

where $E(\Gamma)$ is the energy of the lowest lying state that transforms under symmetry operations according to the irreducible representation $\Gamma$ of the point group $D_{3d}$.

As in previous calculations for the regular CoO$_6$ octahedron (with symmetry $O_h$) the diagonalization is simplified by the fact that several linear combinations of O 2$p$ orbitals do not hybridize with the Co 3$d$ ones, forming non-bonding orbitals. However in the present case, the reduced $D_{3d}$ symmetry increases the bonding 2$p$ combinations to seven, and a different basis should be used, but still the size of the relevant Hilbert space is small enough to permit the diagonalization numerically by the Lanczos method.
As a basis for the present study, we take parameters determined previously from a fit of polarized x-ray absorption spectra of Na$_x$CoO$_2$ to the results of a CoO$_6$ cluster with 4 and 5 and holes including the core hole. In the present case, we have neglected the O-O hopping for simplicity (this allows a reduction of the relevant Hilbert space). Thus, the parameters of $H_{mb}$ in eV are

$$
F_0 = 3.5, \quad F_2 = 0.2, \quad F_4 = 0.006,
$$
$$
\epsilon_{t_2g} = 13, \quad \epsilon_{e_g} = 1.2, \quad \epsilon_{e_s} = 0,
$$
$$
(pd\pi) = -\frac{\sqrt{3}}{4}(pd\sigma) = 1.
$$

(4)

The choice of the origin of on-site energies $\epsilon_{e_s} = 0$ is arbitrary. The resulting values of $U = 4.516$ eV and charge transfer energies are similar to those derived from other x-ray absorption experiments. We note that while above $\epsilon_{t_2g} - \epsilon_{e_g} = 10Dq = 1.2$ eV, the effect of hybridization increases the splitting between $t_{2g}$ and $e_g$ orbitals to more than 3 eV.

### III. RESULTS

The splitting $\Delta$ is determined from Eq. (3). We have also calculated the occupation of the $a_{1g}$ 3$d$ orbital in each state to verify that the expected physics is obtained.

For the parameters determined previously [Eq. (4)], we obtain $\Delta = 124$ meV. The sign agrees with quantum-chemistry configuration-interaction calculations which obtained $\Delta \approx 300$ meV, although our magnitude is smaller. The difference might be at least partially due to some uncertainty in our parameters determined from a fitting procedure. Motivated by this possibility, we have studied the effect of different parameters on the results. Of course, since we have neglected interatomic interactions, $\Delta$ vanishes if the hopping parameters $pd\sigma$ and $pd\pi$ are zero, and one would expect than an increase in these parameters, has the largest impact on $\Delta$. However, we find that an increase of 50% in the hopping increases $\Delta$ by only 25%. In addition, changes of the oxygen energy $\epsilon_{t_2g}$ (the charge transfer energy) or $F_0$ (which determines the intra-orbital Coulomb repulsion $U$) by 1 eV have an effect of only a few percent on $\Delta$.

Instead, and rather surprisingly, as shown in Fig. 1 $\Delta$ is very sensitive to $F_2$, the most important parameter in the expressions for the exchange between $d$ electrons $J_v$ with $\nu = e, t, a$ or $b$ in Eq. (3) and the inter-orbital repulsions ($U - 2J_v$) among other interactions. Thus, it is the main responsible for the spin and orbital polarizations resulting in the first and second Hund rules. In particular, the repulsion between different $e_g$ ($t_{2g}$) orbitals is reduced with respect to the intra-orbital repulsion $U$ by $2J_v$ (2$J_s$) (see the Appendix).

$\Delta$ becomes negative for $F_2 < 21$ meV. Curiously, increasing $F_4$ has a small effect, but in the opposite sense as increasing $F_2$. This points to non-trivial effects of the correlations, particularly those involving both $e_g$ and $t_{2g}$ electrons. When both $F_2$ and $F_4$ vanish we obtain a small positive value $\Delta = 12$ meV. If one adds to this result the contribution -25 meV from the interatomic Coulomb repulsion estimated using point charges, one obtains a value close to -10 meV, obtained in one of the LDA calculations. This suggest that the LDA negative results for $\Delta$ might be due to the difficulties of LDA in treating correlations related with the Hund rules. In particular, it is known that orbital-related Coulomb interactions are underestimated in the spin LDA and empirical orbital polarization corrections are frequently used to cure this problem. This fact has been also analyzed in the framework of a self-consistent tight-binding theory.

The fact that correlations between both $e_g$ and $t_{2g}$

![Figure 1](image1.png)

**FIG. 1**: Trigonal splitting as a function of the cubic crystal field keeping the remaining parameters as given by Eq. (3).

![Figure 2](image2.png)

**FIG. 2**: Trigonal splitting as a function of the cubic crystal field keeping the remaining parameters as given by Eq. (3).
holes play a role is supported by the dependence of $\Delta$ on the cubic crystal field parameter $10Dq$, displayed in in Fig. 2. Note that this parameter in the present case represents only the contribution of interatomic repulsion to $10Dq$. The covalency part is included in our calculation and the splitting between hybridized $e_g$ and $t_{2g}$ is larger than 3 eV. Also in the fitting procedure, the best value of $10Dq$ depends on composition $x$, being 1.2 eV for $x = 0.4$ and 0.9 eV for $x = 0.6_{12}^{14}$. For the latter value $\Delta$ increases to 134 meV. As it is apparent in Fig. 2, $\Delta$ increases with decreasing $10Dq$. This shows that the $e_g$ states play an important role. In fact, the results for the regular octahedron show that although these states are absent in the trigonal crystal-field parameter $\Delta$, which splits the $x^2-y^2$ states in $O_h$ symmetry into $a_1^g$ and $e_g'$ in the reduced $D_{3d}$ symmetry. This parameter enters effective models of the form of Eq. (11) for the description of the electronic structure of Na$_{x}$CoO$_2$ and only positive values (in contrast to the negative ones obtained from LDA) seem consistent with ARPES data $^{12,13,15}$. We obtain $\Delta \approx 130$ meV.

While changes of the order of 1 eV in charge-transfer energy or $F_0$ (which controls the part of the Coulomb repulsion which does not depend of the symmetry of the orbitals) do not affect $\Delta$ very much, we find that $\Delta$ is very sensitive to the parameter $F_2$ which controls (among others) interaction constants related with the Hund rules (exchange interactions and decrease of inter-orbital repulsions with respect to intra-orbital ones). To a smaller extent, it is also sensitive to the cubic crystal field $10Dq$ reflecting the importance of interactions between $t_{2g}$ and $e_g$ states, and the effect on the latter on the effective parameters.

Since the LDA underestimates correlations that affect the orbital polarization of the $d$ states $^{18,50}$ this is likely to be the reason of the failure of LDA approaches and effective models based on LDA parameters, to reproduce the observed ARPES data. In fact, since the exchange and correlations in LDA are based on a homogeneous electron gas, it is expected that this approximation treats $F_0$ (the part of the repulsion which does not distinguish between different orbitals) in mean field, but does not contain the effects of $F_2$ and $F_4$, which depend on the particular orbitals. The exchange of the electron gas taken into account in the LDA helps to follow the first Hund rule (maximum spin), but the second one, related with orbital polarization, is not well described and seems crucial to establish effective energy differences between different orbitals inside an incomplete $d$ shell.

**Acknowledgments**

Useful comments of G. Pastor and C. Proetto are thankfully acknowledged. AAA is partially supported by CONICET, Argentina. This work was sponsored by PIP 112-200801-01821 of CONICET, and PICT 2010-1060 of the ANPCyT.

**Appendix A: Interactions inside a $d$ shell**

The part of the Hamiltonian that contains the interaction among the 10 d spin-orbitals is $^{51}$

$$H_I = \frac{1}{2} \sum_{\lambda \mu \rho \nu} V_{\lambda \mu \rho \nu} d_\lambda^+ d_\mu d_\rho \varphi_\nu,$$

where $d_\lambda^+$ creates an electron or a hole at the spin-orbital $\lambda$ ($H_I$ is invariant under an electron-hole transformation) and (neglecting screening by other electrons)

$$V_{\lambda \mu \rho \nu} = \int d_1 dr_2 d_2 r_2 \varphi_\lambda(r_1) \varphi_\mu(r_2) \frac{e^2}{|r_1 - r_2|} \varphi_\nu(r_1) \varphi_\rho(r_2),$$

where $\varphi_\lambda(r_1)$ is the wave function of the spin-orbital $\lambda$. Assuming spherical symmetry, these integrals can be calculated using standard methods of atomic physics in terms of three independent parameters $F_j$, $j = 0, 2, 4$, which are related to decomposition of the Coulomb interaction $e^2/|r_1 - r_2|$ in spherical harmonics of degree $j$. To remove uncomfortable denominators, the three free parameters are defined as $F_0 = R^0$, $F_2 = R^2/49$ and $F_4 = R^4/4141$, where

$$R^k = e^2 \int_0^\infty \int_0^\infty \frac{r_2}{r_1} R_1^2(r_1) R_2^2(r_2) r_1^2 r_2^2 dr_1 dr_2.$$

$R(r)$ is the radial part of the wave function of the $d$ orbitals and $r_<$ ($r_>$) is the smaller (larger) between $r_1$ and $r_2$. The angular integrals are given in terms of tabulated coefficients $^{17,52}$. Screening reduces $F_0$ significantly, but not $F_2$ and $F_4$.

The final result can be written in the form below $^{15}$ to express it in a more compact form, we introduce different sums which run over a limited set of orbitals as follows. The sums over $\alpha$ run over the five $d$ orbitals, those over $\beta, \gamma$ run only over the $t_{2g}$ orbitals $xy$, $yz$, $zx$, and those over $\chi$ ($\zeta$) run over the pair of orbitals $x^2-y^2$, $xy$ ($zx$, $yz$).

The values of the different interactions energies below are given in terms of the $F_j$ as follows: $U = F_0 + 4F_2 + 36F_4$, $J_e = 4F_2 + 15F_4$, $J_J = 3F_2 + 20F_4$, $J_a = 35F_4$, $J_b = F_2 + 30F_4$, and $\lambda = \sqrt{3}(F_2 - 5F_4)$.
The interaction is

\[
H_I = U \sum_{\alpha} n_{\alpha,\uparrow} n_{\alpha,\downarrow} \\
+ (U - 2J_e) \sum_{\chi} \sum_{\sigma_1,\sigma_2} n_{\chi,\sigma_1} n_{\chi,\sigma_2 - r^2,\sigma_2} \\
+ \frac{U - 2J_t}{2} \sum_{\beta \neq \gamma} \sum_{\sigma_1,\sigma_2} n_{\beta,\sigma_1} n_{\gamma,\sigma_2} \\
+ (U - 2J_t) \sum_{\zeta} \sum_{\sigma_1,\sigma_2} n_{\zeta - y^2,\sigma_1} n_{\zeta_2,\sigma_2} \\
+ (U - 2J_h) \sum_{\zeta} \sum_{\sigma_1,\sigma_2} n_{\zeta - x^2 - y^2,\sigma_1} n_{\zeta - x^2 - y^2,\sigma_2} \\
+ J_e \sum_{\chi} \sum_{\sigma_1,\sigma_2} d_{\chi,\sigma_1}^\dagger d_{\chi,\sigma_2 - r^2,\sigma_2} d_{\chi,\sigma_2} d_{\chi,\sigma_2 - r^2,\sigma_1} \\
+ \frac{J_t}{2} \sum_{\beta \neq \gamma} d_{\beta,\sigma_1}^\dagger d_{\gamma,\sigma_2} d_{\beta,\sigma_2} d_{\beta,\sigma_1} \\
+ J_t \sum_{\zeta} d_{\zeta - x^2 - y^2,\sigma_1}^\dagger d_{\zeta - x^2 - y^2,\sigma_2} d_{\zeta_2,\sigma_2} d_{\zeta_2,\sigma_2} \\
+ J_h \sum_{\sigma_1,\sigma_2} d_{\sigma_1,\sigma_2}^\dagger d_{\sigma_1,\sigma_2} - y^2,\sigma_1} d_{\sigma_1,\sigma_2} d_{\sigma_1,\sigma_2} - y^2,\sigma_2} d_{\sigma_1,\sigma_2} \\
+ \lambda \sum_{\sigma_1,\sigma_2} [2(n_{yz,\sigma_1} - n_{xx,\sigma_1}) (d_{sz,\sigma_1,\sigma_2}^\dagger d_{sz,\sigma_1,\sigma_2}^\dagger) + \text{H.c.}] \\
- 2(d_{sz,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1} + \text{H.c.}) + 2(d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1} + \text{H.c.}) \\
+ \sqrt{3}(d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) (d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) \\
+ (d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) (d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) \\
+ (d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) (d_{sx,\sigma_1,\sigma_2}^\dagger d_{sx,\sigma_1}^\dagger + \text{H.c.}) \\
+ \lambda [(d_{zy,\sigma_1}^\dagger d_{zy,\sigma_1}^\dagger - d_{zy,\sigma_1}^\dagger d_{zy,\sigma_1}^\dagger) + \text{H.c.}] (A4)
\]

\(^*\) Electronic address: aligia@cab.cnea.gov.ar

1. I. Terasaki, I. Tsukada, and Y. Iguchi, Phys. Rev. B 65, 195106 (2002).
2. M. Mikami, M. Yoshimura, Y. Mori, T. Sasaki, R. Funahashi, and M. Shikano, Jpn. J. Appl. Phys., Part 1, 42, 7383 (2003).
3. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature, London 422, 53 (2003).
4. D. J. Singh, Phys. Rev. B 68, 020503(R) (2003).
5. P. Zhang, W. Luo, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 93, 236402 (2004).
6. K. W. Lee, J. Kunes, and W. E. Pickett, Phys. Rev. B 70, 045104 (2004).
7. H. B. Yang, Z.-H. Pan, A. K. P. Sekharan, T. Sato, S. Souma, T. Takahashi, R. Jin, B. C. Sales, D. Mandrus, A. V. Fedorov, Z. Wang, and H. Ding, Phys. Rev. Lett. 95, 146401 (2005).
8. D. Qian, L. Wray, D. Hsieh, L. Viciu, R. J. Cava, J. L. Luo, D. Wu, N. L. Wang, and M. Z. Hasan, Phys. Rev. Lett. 97, 186405 (2006).
9. S. Zhou, M. Gao, H. Ding, P. A. Lee, and Z. Wang, Phys. Rev. Lett. 94, 206401 (2005).
10. H. Ishida, M. D. Johannes, and A. Liebsch, Phys. Rev. Lett. 94, 196401 (2005).
11. A. Bourgeois, A. A. Aligia, T. Kroll, and M. D. Núñez-Regueiro, Phys. Rev. B 75, 174518 (2007).
12. C. A. Marianetti, K. Haule, and O. Parcollet, Phys. Rev. Lett. 99, 246404 (2007).
13. A. Liebsch and H. Ishida, Eur. Phys. J. B 61, 405 (2008).
14. G.-T. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 101, 066403 (2008).
15. A. Bourgeois, A. A. Aligia, and M. J. Rozenberg, Phys. Rev. Lett. 102, 066402 (2009).
16. We use the primes in \( a' \) and \( c' \) to differentiate the irreducible representations of the point group \( D_{3d} \) of the octahedron compressed along a \( z \) axis, to those of the point group \( O_h \) of the regular octahedron.
17. A. A. Aligia and T. Kroll, Phys. Rev. B 81, 195113 (2010).
18. S. Landron and M.B. Lepetit, Phys. Rev. B 74, 184507 (2006); Phys. Rev. B 77, 125106 (2008).
19. T. Kroll, A. A. Aligia, and G. A. Sawatzky, Phys. Rev. B 74, 115124 (2006).
20. M. E. Simon, A. A. Aligia, and E. R. Gagliano, Phys. Rev. B 56, 5637 (1997); references therein.
21. J.M. Eroles, C.D. Batista and A. A. Aligia, Phys. Rev. B 59, 14092 (1999).
22. C. D. Batista and A. A. Aligia, Phys. Rev. B 47, 8929 (1993).
23. J.I. Jefferson, H. Eskes and L.F. Feiner, Phys. Rev. B 45, 7959 (1992).
24. H.-B. Schüttler and A.J. Fedro, Phys. Rev. B 45, 7588 (1992).
25. M. E. Simon and A. A. Aligia, Phys. Rev. B 48, 7471 (1993).
26. V.I. Belinicher and A.L. Chernyshev, Phys. Rev. B 49,
9746 (1994).
27 V.I. Belinicher, A.L. Chernyshev and L.V. Popovich, Phys. Rev. B 50, 1366 (1994).
28 A. A. Aligia, M. E. Simon, and C. D. Batista, Phys. Rev. B 49, 13061 (1994).
29 L. F. Feiner, J. H. Jefferson, and R. Raimondi, Phys. Rev. B 53, 8751 (1996); references therein.
30 N. Niicker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, Phys. Rev. B 37, 5158 (1988).
31 P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P.J.W. Weijs, F.M.F. de Groot, G.A. Sawatzky, H. Verweij, L.F. Feiner and H. Petersen, Phys. Rev. B 38, 6483 (1988).
32 E. Pellegrin, N. Niicker, J. Fink, S. L. Molodtsoy, A. Gutierrez, E. Navas, O. Streb, Z. Hu, M. Domke, G. Kaindl, S. Uchida, Y. Nakamura, J. Molk, M. Klauda, G. Saemann-Ischenko, A. Krol, J. L. Peng, Z. Y. Li, and R. L. Greene, Phys. Rev. B 47, 3354 (1993).
33 J. Kunes, V. I. Anisimov, S. L. Skornyakov, A. V. Lukoyanov, and D. Vollhardt, Phys. Rev. Lett. 99, 156404 (2007).
34 J. Bala, A. M. Oleś, and J. Zaanen, Phys. Rev. Lett. 72, 2600 (1994).
35 S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition Metal Ions in Crystals*, Academic Press, New York and London, 1970, chapter X.
36 W. Koshibae and S. Maekawa, Phys. Rev. Lett. 91, 257003 (2003).
37 J. D. Jorgensen, M. Avdeev, D. G. Hinks, J. C. Burley, and S. Short, Phys. Rev. B 68, 214517 (2003).
38 J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954); R.R. Sharma, Phys. Rev. B 19, 2813 (1979).
39 C. D. Batista, A. A. Aligia, and J. Eroles, Europhys. Lett. 43, 71 (1998).
40 R. Frésard and G. Kotliar, Phys. Rev. B 56, 12909 (1997). The correct value of the exchange interaction between $t_{2g}$ electrons is $J_t = 3F_2 + 20F_4$.
41 A. A. Aligia and M. A. Gusmão, Phys. Rev. B 70, 054403 (2004).
42 C. D. Batista, A. A. Aligia and J. Eroles, Phys. Rev. Lett. 81, 4027 (1998).
43 E. Kaneshita, T. Morinari, and T. Tohyama, Phys. Rev. Lett. 103, 247202 (2009).
44 A. M. Oleś, Phys. Rev. B 28, 327 (1983).
45 S. Gardonio, M. Karolak, T. O. Wehling, L. Petaccia, S. Lazzit, A. Goldoni, A. I. Lichtenstein, and C. Carbone, Phys. Rev. Lett. 110, 186404 (2013).
46 E. Gagliano, E. Dagotto, A. Moreo and F. C. Alcaraz, Phys. Rev. B 34, 1677 (1986).
47 W.B. Wu, D. J. Huang, J. Okamoto, A. Tanaka, H.J. Lin, F.C. Chou, A. Fujimori, and C.T. Chen, Phys. Rev. Lett. 94, 146402 (2005).
48 H. Eschrig, M. Sargolzaei, K. Koepenik, and M. Richter, Europhys. Lett. 72, 611 (2005); references therein.
49 O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B 41, R7311 (1990).
50 G. Nicolas, J. Dorantes-Dávila, and G. M. Pastor, Phys. Rev. B 74, 014415 (2006).
51 J.W. Negele and H. Orland, *Quantum Many-Particle Systems*, (Addison-Wesley, New York, 1988).
52 E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, (Cambridge University Press, Cambridge and New York, 1935).