Different Look at the Spin State of Co^{3+} Ions in a CoO_5 Pyramidal Coordination

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Using soft-x-ray absorption spectroscopy at the Co $L_{2,3}$ and O K edges, we demonstrate that the Co^{3+} ions with the CoO_5 pyramidal coordination in the layered Sr_2CoO_3Cl compound are unambiguously in the high spin state. Our result questions the reliability of the spin state assignments made so far for the recently synthesized layered cobalt perovskites and calls for a reexamination of the modeling for the complex and fascinating properties of these new materials.

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The class of cobalt-oxide based materials has attracted considerable interest in the last decade because of expectations that spectacular properties may be found similar to those in the manganites and cuprates. Indeed, giant magnetoresistance effects have been observed in the $La_{1-x}A_xCoO_3$ ($A = $ Ca, Sr, Ba) perovskites [1] and RBaCo$_2$O$_{5+x}$ ($R = $ Eu, Gd) layered perovskites [2,3]. Very recently, superconductivity has also been found in the $Na_xCoO_2 \cdot yH_2O$ material [4]. In fact, numerous one-, two-, and three-dimensional cobalt-oxide materials have been synthesized or rediscovered in the last five years, with properties that include metal-insulator and ferro-ferri-antiferro-magnetic transitions with various forms of charge, orbital, and spin ordering [5–23].

A key aspect of cobalt oxides that distinguishes them clearly from the manganese and copper materials is the spin state degree of freedom of the $Co^{3+/III}$ ions: it can be low spin (LS, $S = 0$), high spin (HS, $S = 2$), and even intermediate spin (IS, $S = 1$) [24]. This aspect comes on top of the orbital, spin (up/down), and charge degrees of freedom that already make the manganite and cuprate systems so exciting. It is, however, also precisely this aspect that causes considerable debate in the literature. For the classic $LaCoO_3$ compound, for instance, various early studies attributed the low temperature spin state change to be of LS-HS nature [25], while studies in the last decade put a lot of effort to propose a LS-IS scenario instead [26,27]. More topical, confusion has arisen about the Co spin state in the newly synthesized layered cobalt perovskites [2,3,8–23]. In fact, all possible spin states have been claimed for each of the different Co sites present. There is even no consensus in the predictions from band structure calculations [28–30].

In this Letter we are questioning the reliability of the spin states as deduced from magnetic, neutron, and x-ray diffraction measurements for the newly synthesized layered cobalt perovskites [2,3,8–21]. We carried out a test experiment using a relatively simple model compound, namely Sr_2CoO_3Cl, in which there are no spin state transitions present and in which there is only one kind of Co^{3+} ion coordination [22,23]. Important is that this coordination is identical to the pyramidal CoO_5 present in the heavily debated layered perovskites [2,3,8–21]. Using a *spectroscopic* tool, that is soft x-ray absorption spectroscopy (XAS), we demonstrate that pyramidal Co^{3+} ions are not in the often claimed IS state but are unambiguously in a HS state. This outcome suggests that the spin states and their temperature dependence in layered cobalt perovskites may be rather different in nature from those proposed in the recent literature.

Bulk polycrystalline samples of Sr_2CoO_3Cl were prepared by a solid state reaction route [22]. The magnetic susceptibility is measured to be very similar to the one reported by Loureiro *et al.* [22] and Knee *et al.* [23]. We find that up to 600 K the susceptibility does not follow a Curie-Weiss behavior, making a simple determination of the spin state impossible. Spectroscopic measurements were carried out using soft x rays in the vicinity of the Co $L_{2,3}$ ($h\nu \approx 780$–800 eV) and O K ($h\nu \approx 528$–535 eV) absorption edges. The experiments were performed at the Dragon beam line at the NSRRC in Taiwan, with a photon energy resolution of about 0.30 and 0.15 eV, respectively. Clean sample surfaces were obtained by scraping *in situ* with a diamond file, in an ultrahigh vacuum chamber with a pressure in the low 10^{-9} mbar range. The Co $L_{2,3}$ XAS spectra were recorded in the total electron yield (TEY) mode by measuring the sample drain current. The O K XAS spectra were collected by both the TEY and the bulk sensitive fluorescence yield (FY) modes simultaneously. The close similarity of the spectra taken with these two modes is used to verify that the TEY mode spectra are representative for the bulk material. A single crystal of $EuCoO_3$ is included as an unambiguous reference for a LS Co^{III} system [31].

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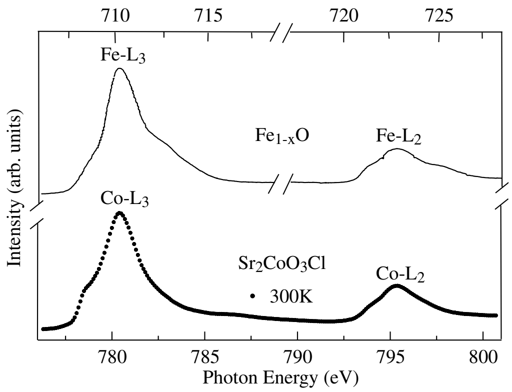

FIG. 1. Co $L_{2,3}$ XAS spectrum of Sr_2CoO_3Cl measured at 300 K (●) and Fe-$L_{2,3}$ XAS spectrum of $Fe_{1-x}O$ ($x \leq 0.05$) reproduced from Ref. [32] (solid line).

Figure 1 shows the Co $L_{2,3}$ XAS spectrum of Sr_2CoO_3Cl taken at room temperature. It is dominated by the Co $2p$ core-hole spin-orbit coupling that splits the spectrum roughly in two parts, namely, the L_3 ($h\nu \approx$ 780 eV) and L_2 ($h\nu \approx$ 796 eV) white lines regions. The line shape of the spectrum depends strongly on the multiplet structure given by the Co $3d$-$3d$ and $2p$-$3d$ Coulomb and exchange interactions, as well as by the local crystal fields and the hybridization with the O $2p$ ligands. Unique to soft x-ray absorption is that the dipole selection rules are very effective in determining which of the $2p^5 3d^{n+1}$ final states can be reached and with what intensity, starting from a particular $2p^6 3d^n$ initial state ($n = 6$ for Co^{3+}) [33,34]. This makes the technique extremely sensitive to the symmetry of the initial state, i.e., the valence [35], orbital [36,37], and spin [38–41] states of the ion.

Utilizing this sensitivity, we compare the Co $L_{2,3}$ XAS spectrum of Sr_2CoO_3Cl to that of another $3d^6$ compound, namely $Fe_{1-x}O$ ($x \leq 0.05$), reproduced from the thesis of Park [32]. This spectrum was taken at room temperature. Except for the different photon energy scale and the smaller $2p$ core-hole spin-orbit splitting, the $Fe_{1-x}O$ spectrum as shown in Fig. 1 is essentially identical with that of Sr_2CoO_3Cl. From this we can immediately conclude that the Co^{3+} ions in Sr_2CoO_3Cl are in the HS state, since the Fe^{2+} ions are also unambiguously HS.

To find further support for our conclusion, we also compare the Co $L_{2,3}$ XAS spectrum of Sr_2CoO_3Cl with that of $EuCoO_3$, which is known to be a LS system [31]. From Fig. 2 one now can clearly see large discrepancies between the spectra of the two compounds. Not only are the line shapes different, but also the ratios of the integrated intensities of the L_3 and L_2 regions: in comparison with Sr_2CoO_3Cl, the LS $EuCoO_3$ has relatively less intensity at the L_3 and more at the L_2, characteristic for a spin state difference [38–41]. Figure 2 thus demonstrates that Sr_2CoO_3Cl is definitely not a LS system.

It would have made our case even easier to prove if we could have excluded experimentally the IS scenario for Sr_2CoO_3Cl by comparing the spectrum to that of a known Co^{3+} IS reference system. However, there is to date no consensus for such an oxide reference system. Nevertheless, the spin state can also be deduced from theoretical simulations of the experimental spectra. To this end, we use the successful configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O $2p$ ligands [33,34,42]. We have carried out the calculations for a Co^{3+} ion in the CoO_5 pyramidal cluster as present in Sr_2CoO_3Cl and for the ion in the CoO_6 octahedral cluster found in $EuCoO_3$. We use parameter values typical for a Co^{3+} system [27]. The Co $3d$ to O $2p$ transfer integrals are adapted for the various Co-O bond lengths according to Harrison's prescription [43,44]. This together with the crystal field parameters determines whether the Co^{3+} ion is in the HS or LS state [24]. The results are shown in Fig. 2, and one can clearly see that the calculated spectrum of the HS pyramidal CoO_5 cluster reproduces very well the experimental Sr_2CoO_3Cl spectrum and that the calculated LS octahedral CoO_6 spectrum matches nicely the experimental $EuCoO_3$ spectrum. This demonstrates that our spectroscopic assignments are firmly founded.

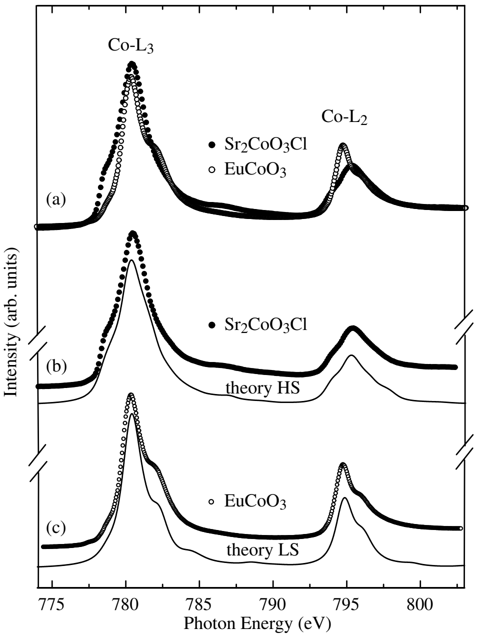

FIG. 2. (a) Co $L_{2,3}$ XAS spectra of Sr_2CoO_3Cl (●) and $EuCoO_3$ (○). (b) Comparison between the Sr_2CoO_3Cl spectrum (●) and a theoretical simulation for a high-spin (HS) CoO_5 pyramidal cluster (solid line). (c) Comparison between the $EuCoO_3$ spectrum (○) and a theoretical simulation for a low-spin (LS) CoO_6 octahedral cluster (solid line).

More spectroscopic evidence for the HS nature of the Co^{3+} in the pyramidal CoO_5 coordination can be found from the O K XAS spectrum as shown in Fig. 3. The structures from 528 to 533 eV are due to transitions from the O $1s$ core level to the O $2p$ orbitals that are mixed into the unoccupied Co $3d$ t_{2g} and e_g states. The broad structures above 533 eV are due to Sr $4d$, Co $4s$, and Cl $3p$

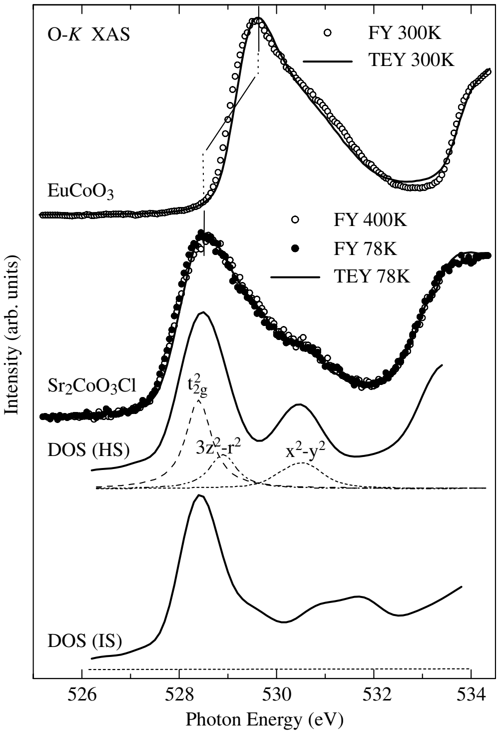

FIG. 3. O K XAS spectra of Sr_2CoO_3Cl and $EuCoO_3$. The solid lines below the experimental curves depict the LDA + U calculated unoccupied O $2p$ partial DOS for Sr_2CoO_3Cl in the real crystal structure with the HS state (upper) and in the artificial structure with the IS state (lower). The dashed, dash-dotted, and dotted lines are the t_{2g}^2, $3z^2$-r^2, and x^2-y^2 projections, respectively.

related bands. For comparison, Fig. 3 also includes the spectrum of the LS $EuCoO_3$, and clear differences can be seen in the line shapes and energy positions of the Co $3d$–O $2p$ derived states. This again is indicative that Sr_2CoO_3Cl is not a LS system. To interpret the spectra, we also have carried out full-potential band structure calculations [28] for Sr_2CoO_3Cl in the local density approximation with correction for electron correlation effects (LDA + U) [45]. We find the ground state of the system to be an antiferromagnetic insulator with a band gap of 1.3 eV and a magnetic moment of $3.2\mu_B$. Although less than $4\mu_B$, this indicates that the Co is in the HS state since in an antiferromagnet the moment is reduced due to covalency. The calculated unoccupied O $2p$ partial density of states (DOS) is depicted in Fig. 3, and good agreement with the experimental spectrum can be observed.

It is now interesting to look for more detail in the character of the states relevant for the O K XAS spectra. For the LS $EuCoO_3$ with the $3d$ t_{2g}^6 configuration, the lowest energy structure in the spectrum at about 529.5 eV is due to transitions into the unoccupied Co $3d$ e_g states. The fact that Sr_2CoO_3Cl has a lower energy structure thus indicates that transitions to the lower lying t_{2g} are allowed, i.e., that the t_{2g} states are not fully occupied. In other words, Sr_2CoO_3Cl is in the HS $t_{2g}^4e_g^2$ or IS $t_{2g}^5e_g^1$ state. At first sight, one might then expect a much larger spectral weight for the higher lying e_g level, since the hybridization with the O $2p$ is larger for the e_g than for the t_{2g}. However, our LDA + U calculations in which we find the HS ground state, indicate that, because of the missing apical oxygen in the CoO_5 coordination, the unoccupied $3z^2$-r^2 level is pulled down by 1.6 eV from the x^2-y^2 and comes close to the unoccupied t_{2g}^2. Moreover, because of the large displacement (0.33 Å) of the Co ion out of the O_4 basal plane of the pyramid [22], the hybridization of the x^2-y^2 with the O $2p$ ligands is strongly reduced. Therefore, the dominant lower energy structure at 528.3 eV consists of the unoccupied minority t_{2g}^2 (dashed line in Fig. 3) and minority $3z^2$-r^2 (dash-dotted line) levels, and the shoulder at 530.4 eV of the minority x^2-y^2 (dotted line).

From the LDA + U calculations, we have found that the IS state [29] is unstable with respect to the HS ground state for the real crystal structure of Sr_2CoO_3Cl. We have also found, nevertheless, that the IS state *can* be stabilized by *artificially* moving the Co ion into the O_4 basal plane of the CoO_5 pyramid. For the latter, however, the calculated unoccupied O $2p$ partial DOS does not reproduce the experimental O K XAS spectrum that well, as one can see from the discrepancies in the 531–532 eV range in Fig. 3. What happens is that the x^2-y^2 level is pushed up by the increased hybridization with the O $2p$ ligands, since the Co ion is within the O_4 basal plane in this artificial crystal structure. Moreover, the uprising majority x^2-y^2 becomes unoccupied, resulting in the IS state. Apparently, the actual large base corrugation of the CoO_5 pyramid helps to stabilize the HS state [28], a trend that should not be overlooked if one is to understand the real spin state of CoO_5 pyramids. We find from our LDA + U calculations that the HS is more stable than the IS for out-of-basal-plane Co displacements larger than a critical value of about 0.15 Å.

Having established that the pyramidal coordinated Co^{3+} ions in Sr_2CoO_3Cl are in the HS state, we now turn our attention to other layered cobalt materials that have the same structural units. Neutron diffraction experiments on $R$$BaCo_2O_{5.0}$ (R = rare earth) have revealed the existence of alternating Co^{3+} and Co^{2+} ions, both in pyramidal CoO_5 coordination. The magnetic structure is G-type antiferromagnetic with moments of $2.7\mu_B$ and $4.2\mu_B$ [10] or $2.7\mu_B$ and $3.7\mu_B$, respectively [12]. For the R = Nd compound, charge ordering was not observed, but an average moment of $3.5\mu_B$ was measured [13,14]. These studies suggested two possible scenarios for the Co^{3+} ions, namely, either HS with spin-only moments or IS with an orbital moment. Our findings based on Sr_2CoO_3Cl, on the other hand, strongly suggest the HS state of such pyramidal Co^{3+} ions. Here we keep in mind that the out-of-plane Co displacements of the pyramids in $R$$BaCo_2O_{5.0}$ are larger than 0.35 Å [10,12,13], i.e., much larger than the previously mentioned 0.15 Å critical value. The first scenario is thus favored, with the note that neutron diffraction techniques tend to observe smaller magnetic moments due to the Co-O covalency, which is responsible for the antiferromagnetic superexchange interactions present in these materials.

The experimental situation for the $R\mathrm{BaCo_2O_{5.5}}$ system is more complicated. Neutron and x-ray diffraction measurements indicate the presence of all Co^{3+} ions in alternating pyramidal $\mathrm{CoO_5}$ and octahedral $\mathrm{CoO_6}$ units [13–19,21]. The magnetic structure is most likely not a simple G type [19,20], and, depending on the model, values between $0.7\mu_B$ and $2.0\mu_B$ have been extracted for the pyramidal Co^{3+} [19,21]. The IS state is thus proposed, and, in fact, most other studies also assume this starting point [13–18,20]. Nevertheless, structural data indicate that the $\mathrm{CoO_5}$ pyramids in these compounds have very similar Co-O bond lengths and angles as in $\mathrm{Sr_2CoO_3Cl}$. The out-of-plane Co^{3+} displacements in the pyramids are larger than 0.3 Å [13,16–18], and, again, much larger than the 0.15 Å critical value. We therefore infer that in these compounds the pyramidal Co^{3+} must also be HS, which is supported by the observation that the effective magnetic moment as extracted from the high temperature Curie-Weiss behavior indicates a HS state for all Co^{3+} [2,3,15]. In fact, the average Co-O bond length for the $\mathrm{CoO_5}$ pyramids even increases at lower temperatures [17,18], thereby stabilizing the HS state even more. The fact that neutron diffraction detects lower moments may indicate a complex magnetic structure as a result of a delicately balanced spin state of the octahedral Co^{3+} ions affecting the various exchange interactions in the compounds in which the pyramidal Co^{3+} remains HS.

To summarize, we have found an overwhelming amount of evidence for the HS nature of the pyramidal coordinated Co^{3+} ions in $\mathrm{Sr_2CoO_3Cl}$: (1) the Co $L_{2,3}$ spectrum has essentially the identical line shape as the Fe $L_{2,3}$ in $\mathrm{Fe}_{1-x}\mathrm{O}$ ($x \leq 0.05$); (2) the Co $L_{2,3}$ spectrum can be reproduced in great detail by model calculations with the Co ion in the HS state; (3) the O K spectrum can be well explained by LDA + U calculations with the Co in the HS state, but not with the Co in the IS state; and (4) LDA + U calculations yield the HS ground state and no stable IS state for the real crystal structure. With other newly synthesized layered cobalt oxides having very similar pyramidal $\mathrm{CoO_5}$ units, we infer that those Co^{3+} ions must also be in the HS state, contradicting the assignments made so far. It is highly desirable to investigate the consequences for the modeling of the properties of these new materials.

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[1] G. Briceno *et al.*, Science **270**, 273 (1995).
[2] C. Martin *et al.*, Appl. Phys. Lett. **71**, 1421 (1997).
[3] A. Maignan *et al.*, J. Solid State Chem. **142**, 247 (1999).
[4] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
[5] H. Fjellvag *et al.*, J. Solid State Chem. **124**, 190 (1996).
[6] S. Aasland *et al.*, Solid State Commun. **101**, 187 (1997).
[7] H. Kageyama *et al.*, J. Phys. Soc. Jpn. **66**, 1607 (1997).
[8] K. Yamaura *et al.*, J. Solid State Chem. **146**, 277 (1999); Phys. Rev. B **60**, 9623 (1999); **63**, 064401 (2001).
[9] S. M. Loureiro *et al.*, Phys. Rev. B **63**, 094109 (2001).
[10] T. Vogt *et al.*, Phys. Rev. Lett. **84**, 2969 (2000).
[11] E. Suard *et al.*, Phys. Rev. B **61**, R11 871 (2000).
[12] F. Fauth *et al.*, Eur. Phys. J. B **21**, 163 (2001).
[13] J. C. Burley *et al.*, J. Solid State Chem. **170**, 339 (2003).
[14] J. F. Mitchell *et al.*, J. Appl. Phys. **93**, 7364 (2003).
[15] Y. Moritomo *et al.*, Phys. Rev. B **61**, R13 325 (2000).
[16] M. Respaud *et al.*, Phys. Rev. B **64**, 214401 (2001).
[17] H. Kusuya *et al.*, J. Phys. Soc. Jpn. **70**, 3577 (2001).
[18] C. Frontera *et al.*, Phys. Rev. B **65**, 180405(R) (2002).
[19] F. Fauth *et al.*, Phys. Rev. B **66**, 184421 (2002).
[20] A. A. Taskin *et al.*, Phys. Rev. Lett. **90**, 227201 (2003).
[21] M. Soda *et al.*, J. Phys. Soc. Jpn. **72**, 1729 (2003).
[22] S. M. Loureiro *et al.*, Chem. Mater. **12**, 3181 (2000).
[23] C. S. Knee *et al.*, Phys. Rev. B **68**, 174407 (2003).
[24] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).
[25] J. B. Goodenough and P. M. Raccah, J. Appl. Phys. Suppl. **36**, 1031 (1965); P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).
[26] M. Korotin *et al.*, Phys. Rev. B **54**, 5309 (1996).
[27] T. Saitoh *et al.*, Phys. Rev. B **55**, 4257 (1997).
[28] H. Wu, Phys. Rev. B **62**, R11 953 (2000); **64**, 092413 (2001); Eur. Phys. J. B **30**, 501 (2002); J. Phys. Condens. Matter **15**, 503 (2003).
[29] S. K. Kwon *et al.*, Phys. Rev. B **62**, R14 637 (2000).
[30] J. Wang *et al.*, Phys. Rev. B **64**, 064418 (2001).
[31] J. Baier, master's thesis, University of Cologne, 2003.
[32] J.-H. Park, Ph.D. thesis, University of Michigan, 1994.
[33] See review by F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. **67**, 529 (1994).
[34] See review in the Theo Thole Memorial Issue, J. Electron Spectrosc. Relat. Phenom. **86**, 1 (1997).
[35] C. T. Chen and F. Sette, Phys. Scr. **T31**, 119 (1990).
[36] C. T. Chen *et al.*, Phys. Rev. Lett. **68**, 2543 (1992).
[37] J.-H. Park *et al.*, Phys. Rev. B **61**, 11506 (2000).
[38] G. van der Laan *et al.*, Phys. Rev. B **37**, 6587 (1988).
[39] B. T. Thole and G. van der Laan, Phys. Rev. B **38**, 3158 (1988).
[40] C. Cartier dit Moulin *et al.*, J. Phys. Chem. **96**, 6196 (1992).
[41] H. F. Pen *et al.*, Phys. Rev. B **55**, 15 500 (1997).
[42] A. Tanaka and T. Jo, J. Phys. Soc. Jpn. **63**, 2788 (1994).
[43] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).
[44] Parameters for HS $\mathrm{CoO_5}$: $\Delta = 2.5$, $U_{dd} = 5.5$, $U_{cd} = 7.0$, $V_{b1} = 2.4$, $V_{a1} = 2.0$, $V_{b2} = 1.21$, $V_e = 1.23$, $10Dq = 0.9$, $Ds = 0.06$, $Dt = 0.05$, $T_{pp} = 0.3$ (eV). Parameters for LS $\mathrm{CoO_6}$: $\Delta = 2.5$, $U_{dd} = 5.5$, $U_{cd} = 7.0$, $V_{e_g} = 2.6$, $V_{t_{2g}} = 1.38$, $10Dq = 1.0$, $T_{pp} = 0.5$ (eV).
[45] V. I. Anisimov *et al.*, Phys. Rev. B **44**, 943 (1991).