PHYSICAL REVIEW B **78**, 054425 (2008)

Band versus localized electron magnetism in $CaCrO_3$

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(Received 12 June 2008; published 19 August 2008)

The results of the calculation of the electronic and magnetic properties of the perovskite $CaCrO_3$ in the local spin-density approximation (LSDA) and local spin-density with the account of on-site Coulomb correlations (LSDA+U) approximations are presented. Both approaches provide correct magnetic ground state [C-type antiferromagnet (AFM-C)], but electronic structure is rather different: metallic in LSDA and insulating in LSDA+U. The character of magnetic interactions and the mechanism of stabilization of the AFM-C structure are also qualitatively different: if in LSDA it is a Stoner-like band magnetism with a rather strong next-nearest-neighbor ("diagonal") exchange, in LSDA+U it is due to a superexchange interaction of localized electrons with an orbital ordering thereof. As one can conclude from both theoretical and experimental results, apparently $CaCrO_3$ is in a crossover regime between localized and itinerant electrons.

DOI: 10.1103/PhysRevB.78.054425 PACS number(s): 75.30.Et, 71.30.+h, 75.50.Ee

I. INTRODUCTION

As is well known, d electrons in transition-metal compounds may show both the features of localized and itinerant electrons. The state of these electrons becomes especially tricky in systems with small or negative charge transfer (CT) gap.[1–3] Depending on the crystal and magnetic structure, such systems may be both metals and insulators. Their metallic state may often be connected with the phenomenon of self-doping.[4] This, in particular, seems to be the case in CrO_2, formally containing Cr in a rather high-oxidation state Cr^{4+}. In this respect other materials containing Cr^{4+} ions are of definite interest. Their study and comparison to CrO_2 may reveal general tendencies and the systematics of the appearance of localized or itinerant states in systems with small or negative CT gap in different situations.

There exists a group of Cr^{4+}-based perovskites: $CaCrO_3$, $SrCrO_3$, and $PbCrO_3$. The preparation of these materials usually requires high-pressure synthesis, and there may be problems with oxygen stoichiometry (because of high-oxidation states of Cr) and phase coexistence.[5] Probably because of that there are not many experimental results reported for these compounds, and those existing in the literature are often rather controversial. Thus there exist conflicting claims even whether they are metallic or insulating.

One would expect that $CaCrO_3$ should show less metallic character than $SrCrO_3$, since the ionic radius of Ca is smaller and hence the crystal lattice distortions are larger in $CaCrO_3$ than in $SrCrO_3$. This is clearly seen from the absolute values of the Seebeck coefficient.[6] However, the general question of whether these compounds are metals or insulators is still under debate. On the basis of the resistivity measurements different points of view were put forth. From the study of the resistivity of a small single crystal Chamberland[7] found that $CaCrO_3$ is a metal. In contrast Williams *et al.*[8] obtained slow decrease in the resistivity with increasing temperature, but considered $SrCrO_3$ to be a metal, while Zhou and co-authors[6] believe that both $CaCrO_3$ and $SrCrO_3$ at ambient pressure are insulators. Recent reflectivity measurements show the presence of the Drude-like peak in $CaCrO_3$, which strongly suggests the metallic character of the electronic spectra.[9]

The key to the problem is a possible importance of strong Coulomb correlations. This unsettled question is met already in the study of electronic and magnetic properties of CrO_2 by two different approaches: local spin-density approximation (LSDA) (Ref. 10) and local spin-density approximation with on-site Hubbard U (LSDA+U).[4] Both approaches have experimental support. Optical data seem to be more similar to the LSDA results if the energy scale would be compressed by $\sim 10-15\%$.[10] On the contrary x-ray absorption and resonant photoemission spectroscopy support the importance of Coulomb correlations in CrO_2.[11]

For CrO_2 it is at least known that it is a [ferromagnetic (FM)] metal. To clarify the question of the electronic state of perovskite chromates, we undertook a detailed theoretical study of one of them, for which there exist good structural and magnetic data on a rather well-characterized sample:[9] $CaCrO_3$. To this end, in the present paper we carried out the *ab initio* band-structure calculations, using both LSDA and LSDA+U approaches.

According to Ref. 9, below $T_N=90$ K $CaCrO_3$ is C-type antiferromagnet (AFM-C), i.e., it consists of ferromagnetic chains in a c direction stacked antiferromagnetically. This in itself is a rather unexpected result requiring explanation. Usually such magnetic structures can appear in perovskites, which are almost cubic systems, due to a particular orbital ordering.[12,13] However if the electrons in $CaCrO_3$ would be itinerant, the usual picture of orbital ordering would not be appropriate. The stabilization of such an anisotropic magnetic state in a metallic system in an almost cubic compound would present a very unusual and puzzling situation. To understand which picture of the electronic state is appropriate for $CaCrO_3$ and to try to explain the C-type magnetic ordering in it were the goals of our calculations.

We found that both methods, LSDA and LSDA+U, reproduce the correct magnetic ground state, while the electronic states (and the character of exchange interactions) are rather different: a metal in LSDA and an insulator in LSDA+U. Correspondingly, the nature of the C type of magnetic structure seems to be different in these pictures too: it is the strong next-nearest-neighbor “diagonal” exchange in the first case, and a particular orbital ordering in the second.

II. CALCULATION DETAILS

In the present paper we used the structural (for $T=3.5$ K) and magnetic data recently obtained by Komarek *et al.*[9] In this structure, besides the usual $GdFeO_3$-type distortion, there appears below T_N an extra distortion of CrO_6 octahedra (flattening along the c direction), but no superstructure or deviations from the *Pbnm* symmetry were detected. Magnetic structure was found to be of the C type (ferromagnetic chains along the c direction stacked antiferromagnetically).

The calculations within the LSDA and LSDA+U were performed in the framework of the linear muffin-tin orbitals method (LMTO).[14] The Cr($4s$,$4p$,$3d$), O($2s$,$2p$,$3d$), and Ca($4s$,$4p$,$3d$) orbitals were included to the basis set in our calculations. In our LMTO calculations we use the von Barth–Hedin exchange-correlation potential.[15] The values of the on-site Coulomb interaction (U) and Hund’s rule coupling (J_H) parameters used in LSDA+U calculations were taken to be $U=3$ eV and $J_H=0.87$ eV. These values of U and J_H were previously calculated within the constraint LDA scheme using the same computation method (LMTO).[4]

The Brillouin-zone (BZ) integration in the course of self-consistency iterations was performed over a mesh of 144 **k** points in the irreducible part of the BZ. The exchange constants were computed for the Heisenberg Hamiltonian, which is written in the following form:

$$H=\sum_{ij} J_{ij}\vec{S}_i\vec{S}_j, \tag{1}$$

where the summation runs twice over every pair i and j.

III. LDA, CRYSTAL-FIELD SPLITTING

First of all, in order to grasp the energy scale of the system we calculate the crystal-field splitting (CFS). Local density approximation (LDA) is the most suitable approach for that since it includes all the required contributions such as Madelung potential, kinetic energy part, and covalency effects, and neglects additional terms such as the correlation effects.

The Wannier function projection procedure was applied to extract the CFS.[16] In octahedral coordination the $3d$ electrons of Cr^{4+} occupy some of the t_{2g} levels, which may be split by local distortions. The e_g levels lie much higher, but the high-oxidation state of Cr implies substantial mixing between O-$2p$ states and Cr-$3d$, especially e_g ones, which hybridize more strongly. Therefore, in order to account for the influence of the oxygen on the CFS more accurately, we used both t_{2g} and e_g subshells for the construction of the small 5×5 on-site Hamiltonian in the Wannier function’s basis set.

The diagonalization of this Hamiltonian shows that the values of the splitting are 26 meV between the lowest and middle t_{2g} levels, and 14 meV between the middle and the third one. This agrees with the local distortions of the CrO_6 octahedron: as a result of small compression along the c direction (local z axis) the xy orbital splits off, while the other two t_{2g} orbitals may be considered as almost degenerate. The e_g levels lie much higher, at ~2.7 eV above the lowest xy orbital.

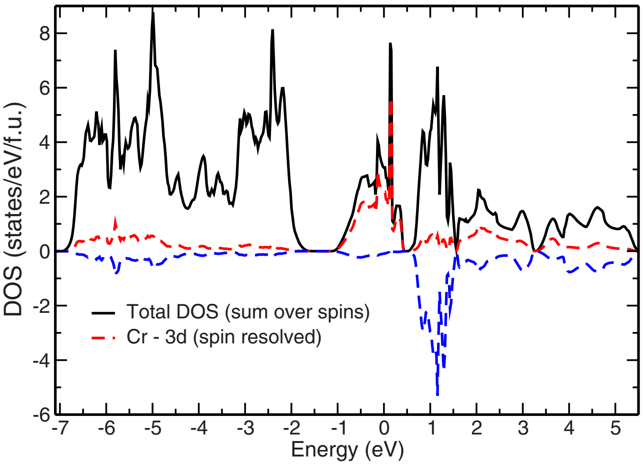

FIG. 1. (Color online) Total and Cr-$3d$ DOSs obtained in LSDA calculations for the AFM-C type of magnetic ordering. Cr-$3d$ DOSs are presented for two spins: up (down) panel corresponds to spin majority (minority). Total DOS is shown summed over spins. The Fermi energy is at zero.

IV. LSDA CALCULATIONS

In the LSDA $CaCrO_3$ was found to be a metal. The DOS obtained in the LSDA is presented in Fig. 1. An interesting feature of the electronic structure of $CaCrO_3$ is that it is a half metal in this approximation. The splitting between different spin subbands exceeds 1 eV.

We calculated FM, A-type antiferromagnetic (AFM-A), G-type antiferromagnetic (AFM-G), and AFM-C types of magnetic ordering. AFM-C type has the lowest total energy. This fully agrees with the experimental findings.[9] The spin magnetic moment on Cr in the AFM-C configuration was found to be 1.52 μ_B. The AFM-C structure is stabilized in LSDA because of the strong magnetic coupling along diagonals in the ac and bc planes. All of the exchange constants are AFM. In LSDA, $J_{ab}=80$ K (in the ab plane), $J_c=60$ K (along the c axis), and $J_d=33$ K,[17] where J_d is the next-nearest-neighbor interaction along diagonals in the ab, ac, and bc planes.[18] The AFM-C structure has lower total energy than the fully antiferromagnetic solution (AFM-G) because of the strong diagonal exchange J_d (four J_d competes with one J_c). This AFM-C state has ferromagnetic chains running along the c axis since antiferromagnetic nearest-neighbor exchange in this direction is smaller than along the a and b axes.

Large diagonal exchange in perovskites is rather unusual since it needs to operate via two atoms of oxygen. However, this is not a unique situation; a similar phenomenon was found in the brownmillerite $A_2MnGaO_{5+\delta}$, where A is Sr or

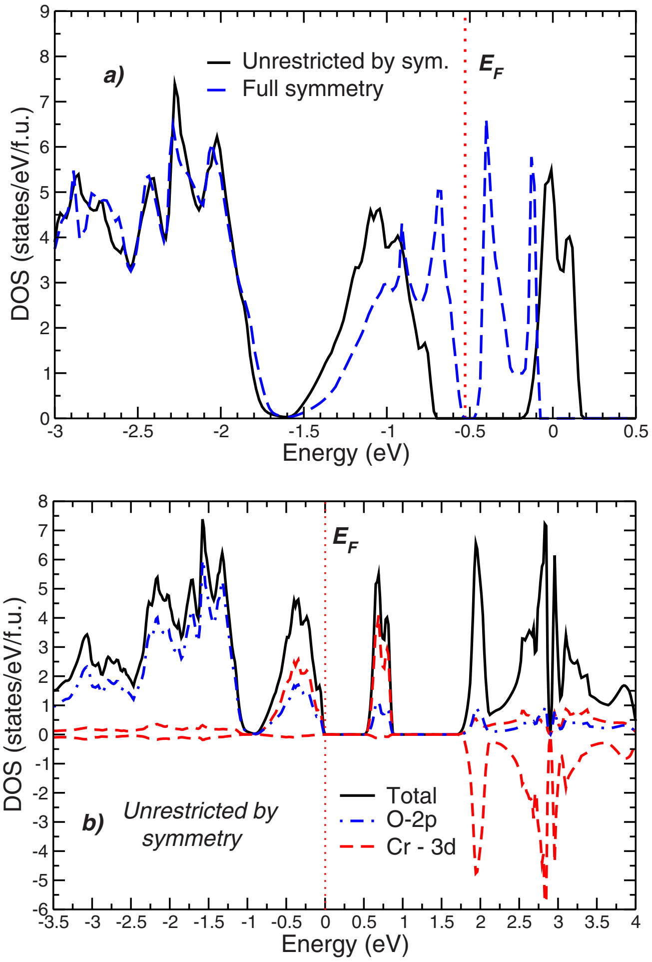

FIG. 2. (Color online) Results of LSDA+U calculations for AFM-C type of magnetic ordering. (a) Comparison between total DOSs obtained with the use of full set of symmetry operations of *Pbnm* group (blue dashed line) and with the symmetry constrains lifted, i.e., the symmetry-unrestricted solution (black solid line). Note that the plot is presented in the absolute scale; the position of the Fermi energy is indicated by dotted line. (b) Total (solid line) and partial (dashed and dash-dotted lines) DOSs for the symmetry-unrestricted solution. Cr-3d DOS are presented for two spins: up (down) panel corresponds to spin majority (minority). Total and O-2p partial DOSs are shown summed over spins. The Fermi energy is at zero.

Ca,[19] although there the origin of strong diagonal interaction was mostly structural. In CaCrO$_3$ diagonal exchange becomes important because of the high-oxidation state of Cr^{4+} and strong mixing between Cr-3d and O-2p states.

V. CORRELATION EFFECTS IN THE FRAMEWORK OF LSDA+U

Next we consider an influence of the on-site Coulomb correlations on the electronic and magnetic properties of CaCrO$_3$. We used the LSDA+U approach[20,21] to take into account such correlations in a static mean-field way.

The resulting DOSs for the experimentally observed C-type antiferromagnetic structure are presented in Fig. 2. One can see that the orbitally unrestricted LSDA+U potential shifts occupied and unoccupied Cr-3d states away from the Fermi level. However, going deeper, occupied Cr-3d states fall on the top of the O-2p bands and begin to hybridize strongly with them. As a result the Hubbard U correction acts now not on the pure well-localized d states, but as one can see from Fig. 2(b), on a mixed combination of O-2p and Cr-3d states, which goes down in energy less than half of U.

Thus, the general effect of the on-site Coulomb correlations consists of the strong mixing of occupied Cr-3d and O-2p states and of the formation of a gap or pseudogap. In addition, the system turns out to be quite sensitive to the symmetry. If one keeps the positions of atoms as they are, but allows charge density to have lower symmetry, then CaCrO$_3$ was found to be an insulator with the band gap $\sim$0.5 eV. It happens because it is allowed for the charge density in LSDA+U to have lower symmetry than the symmetry of the crystal lattice. This result is quite stable for different muffin-tin (MT) radii of atoms or basis sets used in the calculations. The band gap remains with decreasing U down to U=1.8 eV. In addition, the total energy of the symmetry-unrestricted solution is lower by 93 meV per formula unit than that of the fully symmetric one. The symmetry-unrestricted AFM-C solution was found to have the lowest total energy among all the other solutions with different sets of symmetry operations and magnetic structures. This is due to a substantial shift of the top of the valence band downwards, as can be seen in Fig. 2(a), where DOSs are plotted in absolute scale. The reasons for this lowering will be discussed later on.

Among the other symmetry operations the presence/absence of a mirror plane perpendicular to the c axis is of great importance. If one removes this mirror plane from the set of symmetry operations used in the calculations, then the charge density becomes asymmetric, and the system shows an orbital ordering presented in Fig. 3. The same effect was found for KCuF$_3$, where even without Jahn-Teller distortions, i.e., keeping atomic coordinates fixed in symmetric positions, an orbital ordering, which decreases the total energy of the system, appears.[21] Here we observe a similar situation.

The superexchange interaction[13] favors certain types of orbital order, which lower the symmetry of the system, and if one would allow the lattice to relax, then the ions are expected to follow this “orbitally given symmetry.” However, distortions due to such kinds of orbital ordering in the t_{2g} sector must be much smaller than those arising in e_g systems such as KCuF$_3$.

In the symmetry-unrestricted solution with orbital ordering, one of the Cr electrons localizes on the orbital, which mostly has xy character [see Fig. 3(a)], while the other on alternating both along the c axis and in the ab plane $xz+yz/xz-yz$ orbitals [Fig. 3(b)]. Such an orbital alternation is crucial for the magnetic and electronic properties of CaCrO$_3$. According to Goodenough-Kanamori-Anderson (GKA) rules[22] an antiferro-orbital (AFO) ordering in the c direction must result in a ferromagnetic coupling, which, however, should be small, since exchange constants are proportional to $J\sim t^2J_H/U(U-J_H)$. On the contrary, in the ab plane there is (1) ferro-orbital ordering of xy orbitals, which again accord-

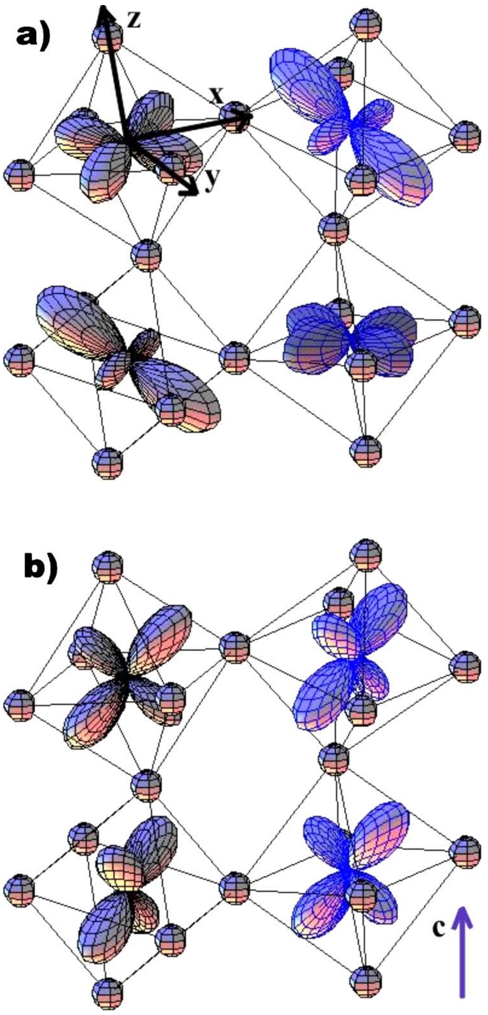

FIG. 3. (Color online) Orbital structure (two orbitals on which electrons are localized) obtained in symmetry-unrestricted solution in LSDA+U calculation for $CaCrO_3$ for AFM-C type of magnetic order. (a) One electron occupies the orbital with mostly xy character, while (b) another, alternating $xz+yz/xz-yz$ orbitals. Local coordination system is shown. Atoms of oxygen are shown as balls.

ing to GKA will result in AFM interactions with large exchange proportional t^2/U. In addition, (2) since the only possible hopping between $xz+yz$ and $xz-yz$ orbitals on neighboring Cr sites in the ab plane occur via the same O-p_z orbital, such an orbital ordering also leads to an AFM exchange in the plane. Corresponding exchange constant $J_{yz+xz/yz-xz}$ should be, however, smaller than $J_{xy/xy}$ because $yz \pm xz$ orbitals are directed at 45° to the Cr-O bonds.

It is interesting to note that in the other magnetic structures different orbital patterns are stabilized. Then the direct calculation of the exchange constants from the total energies of several magnetic structures will give us contributions of both spin and orbital exchanges, which can be used in a general spin-orbital Kugel-Khomskii-like Hamiltonian.[13] However, since our aim is to extract the spin-only part of the exchange for the Heisenberg Hamiltonian defined in Eq. (1), we utilized Lichtenstein's exchange interaction parameter (LEIP) calculation procedure.[23] According to the LEIP formalism, exchange constants J can be calculated as the second derivatives of the energy variation at small spin rotation. Such an infinitesimal rotation obviously will not change the orbital pattern.

The direct calculation of the exchange constants in the AFM-C type of magnetic ordering for the symmetry-unrestricted solution using LEIP formalism shows that the exchange in the c direction is indeed FM, $J_c=-21.7$ K, while in the ab plane it is AFM and two times larger, $J_{ab}=40.8$ K. The diagonal exchange in the ac/bc planes $J_d=12$ K. Since J_c is FM, then in LSDA+U (in strong contrast to LSDA) a diagonal exchange does not frustrate the system. All of the exchange couplings are working in the same direction.

The great advantage of the LEIP is the possibility to calculate not only total exchange constants, but also the partial exchanges between different orbitals. In order to extract the contribution to the exchange constants due to virtual hopping between occupied and unoccupied orbitals, we go over to the local coordinate system where the LSDA+U occupation matrix is diagonal. In agreement with a qualitative picture based on GKA analysis of the orbital ordering, the largest exchange interactions in the ab plane were found to be between xy/xy ($J^{ab}_{xy}=43$ K) and $yz+zx/yz-zx$ orbitals ($J^{ab}_{yz\pm zx/yz\mp zx}=26$ K).

In addition there are ferromagnetic contributions which come from hoppings between two occupied t_{2g} and empty t_{2g} and e_g orbitals via oxygen orbitals. These are here rather large due to a very strong p-d hybridization typical for systems with small or negative charge-transfer gap, and due to substantial $GdFeO_3$-type distortion, which makes Cr-O-Cr angles in the ab plane ~158°. In the c direction the largest exchange is indeed between occupied and empty orbitals on different sites $J^{c}_{yz\pm zx/yz\mp zx}=-21$ K.

The electronic ground state of the solution with the full set of the $Pbnm$ symmetry operations [blue dashed lines in Fig. 2(a)] is a small gap (0.05 eV) insulator. However, the variation of the parameters of calculations (O-2$s \rightarrow$O-3s states in the basis set, or small change of the U parameter) closes the gap. In contrast, the presence of the band gap in the symmetry–unrestricted solution [black solid lines in Fig. 2(a)] is robust. It seems to be related to a modulation of t_{dd} hopping along the c axis due to an antiferro-orbital pattern. Indeed the band gap is developed between Cr-3d bands of the *same* spin [see Fig. 2(b)], and cannot be attributed to magnetic splitting. The crystal field provided by the nearest atoms of oxygen is the same. The difference is in the occupied orbitals. The $yz+xz/yz-xz$ orbital ordering stabilized in the symmetry–unrestricted situation allows for the d-d hopping via oxygen 2p_x and 2p_y orbitals along the c direction in the AFM-C states: there are $(yz+xz)-(yz+xz)$ and $(yz-xz)-(yz-xz)$ hoppings from occupied to empty states with the same spin. In contrast, for the yz/yz orbital pattern (observed in the solution with full symmetry) such transitions $yz \leftrightarrow xz$ are forbidden. Thus, the presence of the hoppings between occupied and empty Cr-3d states along the c direction in the symmetry–unrestricted solution (in other words, the hybridization) leads to the opening of the band gap and to an additional (to the magnetic contribution described above) lowering of the total energy of this solution.

VI. SUMMARY

In the present paper we show that two theoretical methods, LSDA and LSDA+U, may both explain experimentally observed AFM-C type of the magnetic structure. These two approaches may be considered as two limiting cases. As a rule LSDA is more suitable for materials with Stoner-like magnetism. In contrast, LSDA+U is widely used for the description of systems with localized electrons. We found that the stabilization of the AFM-C magnetic structure in $CaCrO_3$ is caused by the band magnetism and strong diagonal exchange J_d in LSDA, and by the antiferro-ordering of orbitals in LSDA+U.

There were similar debates about which method, LSDA or LSDA+U, is better for the description of the electronic and magnetic properties of another Cr^{4+} based oxide, CrO_2,[4,10] and how important are the on-site Coulomb correlations in it. This issue is still unclear. Comparing our situation with the case of CrO_2, one would think that the LSDA+U method should be more appropriate for $CaCrO_3$. This is because the width of the t_{2g} band is smaller in $CaCrO_3$ ($W\sim 2$ eV) than in CrO_2 ($W\sim 2.4$ eV), since there is a direct overlap between Cr-3d orbitals in the rutile structure of the latter, but only hopping via atoms of oxygen in the perovskite lattice of $CaCrO_3$.

Nevertheless, the effective Coulomb repulsion U_{eff}, to be compared to the value of the bandwidth, is also reduced due to a large Hund's rule coupling and threefold degeneracy of the t_{2g} band: $U_{\text{eff}}=\sqrt{N_{\text{deg}}}U-N_{\text{deg}}J_H$.[24] Thus, one may consider $CaCrO_3$ as a compound with intermediate correlation strength, lying at the edge of a metal-insulator transition. In this regime the account of dynamical Coulomb correlations results not only in the development of upper and lower Hubbard bands, like in LSDA+U, but also in the formation of a narrow quasiparticle band at the Fermi level.[25] These heavy quasiparticles may provide unusual frequency dependence observed in optical measurements.[9]

At this stage, based on the mean-field calculations performed within the density functional theory, we cannot make a unique choice between these two limiting pictures: whether electrons in $CaCrO_3$ should be considered as localized with orbital ordering, or as itinerant, bandlike. Apparently this is connected with an intermediate character of d electrons. The crossover between localized and itinerant behavior makes this system especially interesting both from experimental and theoretical points of view. The investigations using x-ray and optical spectroscopy may shed light on the features of the electronic structure of this material. In addition it is interesting to check the degree of orbital polarization resulting in the antiferro-orbital ordering in LSDA+U by more sophisticated methods, which account for the dynamical nature of electron correlations.

ACKNOWLEDGMENTS

We are grateful to A. Komarek, M. Braden, and M. Grüninger for fruitful discussions and V. Mazurenko for the help in interpretation of the results of the magnetic calculations. This work is supported by the Dynasty Foundation and International Center for Fundamental Physics in Moscow, Russian Foundation for Basic Research through Contracts No. RFFI 07-02-91567 and No. 07-02-00041, INTAS through Contract No. 05-109-4727, the Civil Research and Development Foundation together with Russian Ministry of Science and Education through Grant No. Y4-P-05-15, Russian President Grant for Young Scientists MK-1184.2007.2, Grant of Ural Division of RAS for Young Scientists, and SFB 608.

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[17] It was found that the magnetic moments on Cr ions in FM solution are ~0.2 μ_B larger than almost equal moments in all AFM calculations. We applied the fix-spin-moment procedure in LSDA calculations to reduce the magnetic moments down to the value obtained for AFM-*C* type solution.

[18] In order to estimate diagonal exchange in the *ab* plane we additionally calculated AFM-*A* with FM planes stacked perpendicular to *a* direction.

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