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First-principles investigation of the electronic structure and magnetism of eskolaite*

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The electronic structure and magnetism of eskolaite are studied by using first-principles calculations where the on-site Coulomb interaction and the exchange interaction are taken into account and the LSDA+U method is used. The calculated energies of magnetic configurations are very well fitted by the Heisenberg Hamiltonian with interactions in five neighbour shells; interaction with two nearest neighbours is found to be dominant. The Néel temperature is calculated in the spin-3/2 pair-cluster approximation. It is found that the measurements are in good agreement with the calculations of lattice parameters, density of states, band gap, local magnetic moment, and the Néel temperature for the values of U and J that are close to those obtained within the constrained occupation method. The band gap is of the Mott–Hubbard type.

Keywords: transition-metal oxide, electronic structure, magnetism, first-principles calculations
PACC: 7500, 7280G, 7125

WITHDRAWN

1. Introduction

Corundum-type Cr_2O_3 is one of the antiferromagnetic transition-metal oxides which present a significant challenge to electronic band theory due to the relevant character of the partially filled, spin-polarized 3d shell. It also has numerous applications in electronic devices, fuel cell electrodes, gas sensors, heterogeneous catalysis, and thermal barrier coatings. Surface properties of Cr_2O_3 are of particular interest. The nominally polar, but compensated (0001) surface exhibits structural phase transitions which are poorly understood.[1,2] It is therefore very desirable to ascertain whether electronic correlations can be reliably included in first-principles calculations in a way that structural, electronic, and magnetic properties can be predicted accurately.

On the theoretical side, as expected for a transition-metal oxide,[3−6] conventional density functional theory (DFT) studies of bulk Cr_2O_3[7−9] have shown that the strong correlation effect cannot be reasonably treated within the local spin density approximation (LSDA) or within the generalized-gradient approximation (GGA), thus not reproducing the electronic and magnetic properties of bulk Cr_2O_3. Rohrbach *et al* [10] performed a GGA+U calculation for Cr_2O_3 by using the simplified (spherically averaged) $U-J$ correction[11] and obtained more reasonable results for the band structure. However, this approach is inaccurate for structural and magnetic properties. First, both GGA and the LSDA+U corrections reduce the LSDA overbinding problem in Cr_2O_3 and increase the equilibrium volume which becomes close to the experimental value. However, the GGA+U results in a double correction, and the volume is too large, about 7% bigger. Also, compared with the

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experimental value of about 308 K,[12] the magnetic energies quoted by Rohrbach *et al* [10] within this method lead to a Néel temperature which is too small, a factor of 5 less. Here we analyse the properties of Cr_2O_3 in more detail with a particular emphasis on its magnetism. We find that the LSDA+U method can provide very good agreement with experiment for structural, spectral, and magnetic properties with the same values of U and J which are close to those found from the constrained occupation method within DFT.

2. Theoretical method

The first-principles calculations are carried out by using the projected augmented wave (PAW) method[13,14] implemented within the Vienna *ab initio* simulation package (VASP).[15,16] We treat the $Cr(3d^5 4s^1)$ and $O(2s^2 2p^4)$ electrons as valence states, while the remaining electrons are kept frozen as core states. Exchange correlation is employed with an LDA functional by Perdew and Zunger.[17] The spin interpolation of Vosko *et al* [18] is used. Calculations are performed in a rhombohedral cell. The Monkhorst–Pack scheme[19] with $4\times4\times4$ k-points is used for integration in the irreducible Brillouin zone, which is carried out by using the linear tetrahedron method with Blöchl corrections. Densities of states (DOSs) are calculated with $8\times8\times8$ k-points. Note that for the calculation of total energies of twelve magnetic ordering configurations, the hexagonal cell and $4\times4\times1$ k-points are used. The energy cutoff for the plane waves is 520 eV. These parameters assure a total energy convergence of 2 meV/atom.

In order to correct the strong electronic correlation among the localized transition-metal $3d$ electrons, the LSDA+U method is employed in its full spherically symmetric form.[20] This extension is important for Cr_2O_3 where the correct representation of crystal field and exchange splittings within the partially filled $3d$ shell is critical. Reasonable values of U and J can usually be obtained within DFT by using the constrained occupation method.[21] These values are better suited for use in LSDA+U calculations compared with the Hartree–Fock values, because they include the screening of the $3d$ shell by the remaining electrons. We obtain $U = 3.3$ eV and $J = 0.58$ eV by using the full-potential linear augmented plane-wave (FLAPW) method implemented in the FLEUR package.[22] It is worthwhile mentioning that the constrained occupation method is somewhat ambiguous because the U parameter depends on the charge state of the ion.[23] On the contrary, the J parameter is usually very well defined. Therefore in the following calculations we fix J at its calculated value of 0.58 eV and vary U.

3. Results and discussion

3.1. Atomic and electronic structures

The electronic structure is calculated in the ground antiferromagnetic state with relaxed structural parameters (commonly denoted as $+-+-$ in accordance with the ordering of Cr spins along the z axis of the rhombohedral cell). The dependences of the equilibrium volume, magnetic moment and band gap on the U parameter are shown in Fig.1. We see that at $U = 4.0$ eV the volume is very close to the corresponding experimental values.[24] Other structural parameters are also in agreement with experimental values.[24] The calculated angle between the rhombohedral unit vectors is 55.11° comparable to the measured angle of 55.13°. The shortest spacing between Cr atoms along the [111] axis is 2.646 Å (1 Å=0.1 nm) comparable to the measured 2.650 Å.

The magnetic moment at $U = 4.0$ eV is 2.86 μ_B which is smaller than the GGA+U value of 3.01 μ_B.[10] Experimentally, the most recent neutron polarimetry measurement gives the sublattice magnetization of 2.48 μ_B,[25] which is notably low compared with an older estimate of 2.76 μ_B.[12] The magnetic moment is reduced from an "ideal" value of 3 μ_B due to two effects: (i) hybridization with oxygen, which is included in our calculation, and (ii) the quantum "zero-point spin deviation," which is absent in DFT. The zero-point deviation in Cr_2O_3 was estimated at 8% in Ref.[26], which amounts to 0.24 μ_B. Bearing this estimate in mind, our calculated magnetic moment at $U = 4.0$ eV is completely reasonable. We also note that the local magnetic moment depends very weakly on the magnetic configuration of Cr_2O_3. In the ferromagnetic state the local moment within the muffin-tin sphere is 2.94 μ_B, while the magnetization is exactly equal to 3 μ_B per Cr site as expected. The orbital moment in the calculation with spin-orbit coupling is small (about 0.04 μ_B) and antiparallel to the spin moment, which is in agreement with experimental g-factor of 1.97[27] and also consistent with the general rule for atomic shells that are less than half filled.

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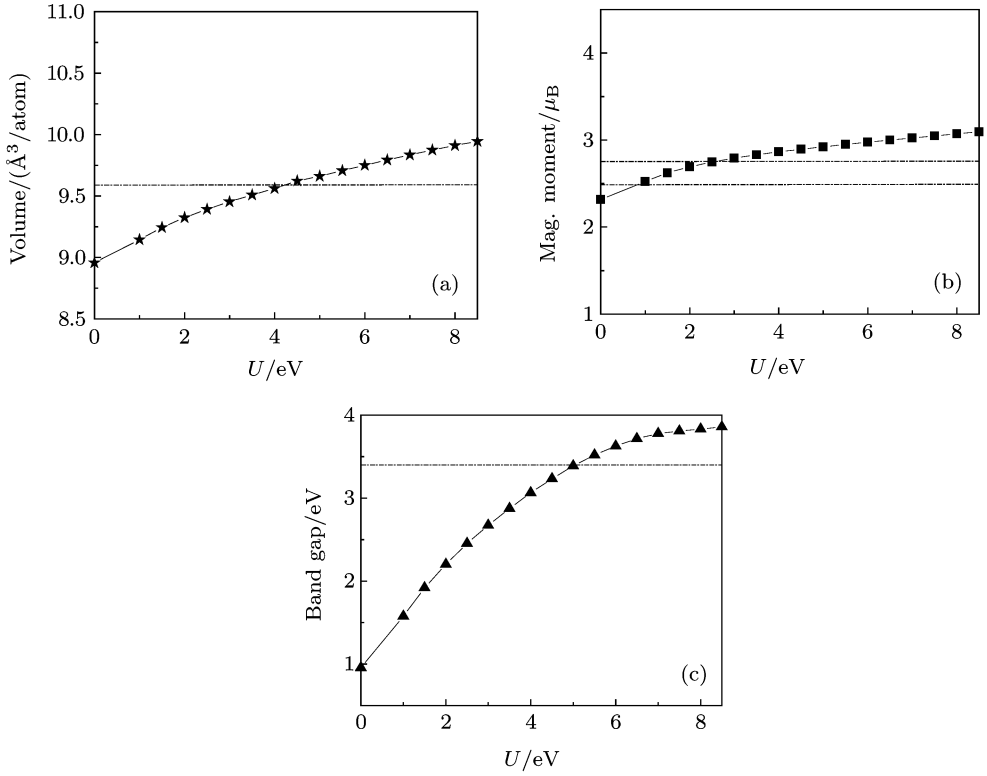


Fig.1. Atomic volume (a), magnetic moment (b), and band gap (c) of bulk Cr_2O_3 versus the Coulomb U parameter for the antiferromagnetic + − + − state, where the value of J is fixed at 0.58 eV and horizontal lines represent experimental values.

The band gap of 3.07 eV at $U = 4.0$ eV is somewhat smaller than the experimental value of 3.4 eV[28] but greater than that (2.6 eV) found in Ref.[10] by using GGA+U with $U - J = 4$ eV. Underestimation of the addition energy is a common feature of the LSDA+U method. Further, the DOSs shown in Fig.2 are in excellent agreement with x-ray photoemission data.[29,30] Namely, the sharp and narrow (Cr-3d) peaks at low binding energies separated by a (pseudo) gap from the rest of the valence band are very well reproduced. Figure 2 also shows the partial DOS decomposition into O and Cr contributions from t_{2g} and e_g states. The t_{2g} and e_g subbands are well defined because the ligand field of the Cr site is approximately octahedral. It can be seen from Fig.2 that the peaks at low binding energies correspond to the filled Cr t_{2g} spin subband with some admixture of oxygen p orbitals. At least some of this admixture is fictitious,

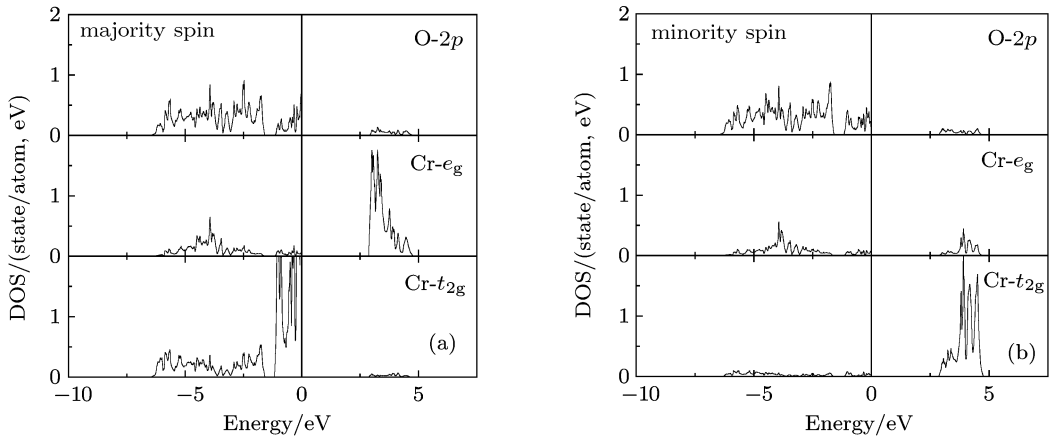


Fig.2. Orbital projected DOSs for the antiferromagnetic + − + − ground state of bulk Cr_2O_3, calculated within the LDA+U for $U = 4.0$ eV, $J = 0.58$ eV, where panels (a) and (b) show majority-spin and minority-spin O-2p with Cr-e_g and Cr-t_{2g} projections, respectively.

because the Cr d orbitals extend into oxygen projection spheres. The same ambiguity is also involved in the definition of the Cr magnetic moment. Since nonmagnetic Cr_2O_3 is metallic with the Fermi level lying inside the t_{2g} subband which is separated by a gap from the oxygen p band, the insulating gap forms by the Mott–Hubbard mechanism.

Therefore, we can say that the atomic and the electronic structures of bulk Cr_2O_3 are well reproduced by using the spherically symmetric LSDA+U method with $U = 4.0$ eV and $J = 0.58$ eV. This value of U is somewhat larger than that (3.3 eV) given by the constrained occupation method, but the latter is found by using FLAPW calculations with a different muffin-tin radius.

3.2. Magnetism

We now focus on the magnetic energetics which provides another stringent test of the validity of the LSDA+U method for Cr_2O_3. We calculate the energies of a number of magnetic configurations and fit them to the Heisenberg Hamiltonian

$$H = -\sum_n J_n \sum_{i>j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \qquad (1)$$

where J_n are exchange parameters and n is the index of the nearest-neighbouring shell. In these calculations, we restrict our considerations to the fifth nearest-neighbouring interactions, i.e. n ranges numbered from 1 to 5. To do this, we perform the total energy calculations on twelve different magnetic ordering configurations, which include the ferromagnetic ordering, three typical antiferromagnetic ordering (+ − + −, + + − − and + − − +) along [0001] and other eight arbitrary ordering, and here for convenience they are respectively labeled as $i = 1, \ldots, 12$. According to the model Hamiltonian, the energy of the hexagonal unit cell for the magnetic ordering configuration i can be written as

$$E_i = E_0 + N_{1i}J_1 + N_{2i}J_2 + N_{3i}J_3 + N_{4i}J_4 + N_{5i}J_5, \qquad (2)$$

where E_0 is the reference energy. For each magnetic ordering configuration i, its concrete spin states mapped on the twelve numbered Cr atoms in the hexagonal unit cell as shown in Fig.3, along with the values of N_{ji} $(j = 1, \ldots, 5)$, are summarized in Table 1.

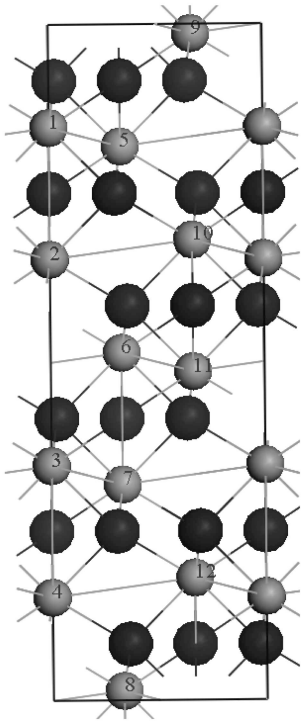


Fig.3. Hexagonal unit cell of bulk Cr_2O_3. The cell contains six Cr_2O_3 units, where gray and black balls represent Cr and O atoms, respectively.

Note that positive exchange parameters correspond to antiferromagnetic interactions while negative values correspond to ferromagnetic interactions. Based on these equations and the results obtained from the first-principles total energy calculations, those J parameters can be deduced by using the least-square method. The five exchange parameters obtained by using the different values of U are listed in Table 2. It is clearly seen that the first, second and fifth nearest-neighbouring interactions are antiferromagnetic, whereas the third and fourth ones are ferromagnetic. All exchange parameters except the third one reinforce the ground state. Also, we see that the first and second exchange parameters are significantly larger than those for more distant neighbours; this behaviour is natural for an insulator. In Cr_2O_3 the parameter J_1 corresponds to the short bond along the z axis, and J_2 to the nearest neighbouring bond within the buckled Cr layer. Each Cr atom has one J_1 neighbour and three J_2 neighbours. As the value of U is increased, all antiferromagnetic exchange parameters systematically decrease, while the ferromagnetic parameters systematically increase.

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Table 1. Concrete spin states of twelve Cr atoms for magnetic configuration i ($i = 1, \ldots, 12$) within the hexagonal unit cell of bulk Cr_2O_3. The numerical labels of Cr atoms correspond to those in Fig. 3. Coefficients N_{ji} ($j = 1, \ldots, 5$) in expression (2) are also listed.

i	1 5 9 2 6 10 3 7 11 4 8 12	N_{1i}	N_{2i}	N_{3i}	N_{4i}	N_{5i}
1	+ + + + + + + + + + + +	12	36	36	36	12
2	+ − − − + + + − − − + +	–12	–36	–36	72	–12
3	− − + + − + + + − − + −	–12	36	–36	–72	12
4	− + − − − + + − + + + −	12	–36	36	–72	–12
5	+ − + + − + + − + + − +	12	–12	–12	–24	12
6	− − + − + − + − − + + +	4	12	–12	24	–12
7	+ + + + − + + − − + + −	4	12	12	0	4
8	+ + + + − + + + − + − −	–4	12	–12	0	4
9	+ + + + − − + + − + − +	4	12	–12	0	–4
10	+ − + − + − + − + − + −	–12	12	12	–24	–12
11	− + + − − + + − − + + −	4	–12	12	–24	–4
12	+ + + − + + − − + − − −	–4	12	12	0	4

Table 2. Exchange parameters J_n fitted by using the total energies of twelve magnetic configurations calculated for different values of U with J fixed at 0.58 eV. The last column represents the mean-square misfit in the fitting of the total energy. J_n and Δ are given in meV.

U	J_1	J_2	J_3	J_4	J_5	Δ
2.5	30.944	21.858	–0.596	–1.828	4.917	0.909
3.0	23.918	17.317	–1.256	–2.356	3.724	0.623
3.5	18.636	13.807	–1.739	–2.721	2.843	0.431
4.0	14.586	11.095	–2.107	–2.955	2.163	0.297
4.5	11.129	9.042	–2.413	–3.106	1.641	0.199

We now calculate the Néel temperature T_N. We have seen above that the local moments on Cr atoms are well localized, and the energies of spin configurations are well represented by the Heisenberg spin Hamiltonian. We therefore adopt the quantum Heisenberg model for localized spins of magnitude 3/2 with the exchange parameters listed in Table 1. Since each spin is strongly coupled only with four neighbours (one with J_1 and three with J_2), the mean-field approximation cannot be reliably used. However, the antiferromagnetic interaction is not frustrated. The important spin correlations should be generated by the dominant exchange interaction with four nearest neighbours. The networks of bonds corresponding to J_1 and J_2 are connected very weakly; the shortest closed path on this network is 6 bonds long. Therefore, it is sufficient to capture the pairwise spin correlations. In this situation, the pair cluster approximation appears to be an obvious choice. This approach is a special case of the cluster variation method when the set of clusters includes only pairs of sites. Here we follow the formulation of Ref.[31] which can be directly applied to our case.

The calculated T_N is shown in Fig.4 as a function

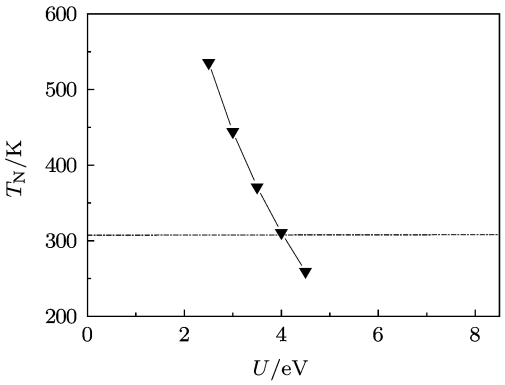


Fig.4. Néel temperature T_N of bulk Cr_2O_3 versus Coulomb U for antiferromagnetic + − + − state, where the value of J is fixed at 0.58 eV and the horizontal line represents experimental values.

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of U. We see that the best agreement with experiment[12] for T_N is obtained at the same value of $U \approx 4$ eV as that for the atomic and the electronic structures explored above. This overall agreement is a strong indication that the essential details of the electronic structure of Cr_2O_3 are captured very well by the LSDA+U approximation. Physically, this success of LSDA+U is explained by the presence of fully filled and empty subbands which are strongly split by crystal and exchange fields; LSDA+U usually reproduces such closed atomic-like subshells very well.

4. Conclusion

We find that the spherically symmetric LSDA+U method provides a very good description of structural, spectral, and magnetic properties of chromia with $J = 0.58$ eV found by using the constrained occupation method and $U \approx 4$ eV, which is also close to the calculated value. We find that the magnetic energies are well represented by a Heisenberg model with strong exchange interaction with nearest neighbours both in the plane and along the z axis and much weaker interaction with more distant neighbours.

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