

Electronic structure and magnetism in the frustrated antiferromagnet LiCrO_2 : First-principles calculations

I. I. Mazin

Code 6391, Naval Research Laboratory, Washington, DC 20375, USA

(Received 22 January 2007; published 6 March 2007)

LiCrO_2 is a two-dimensional triangular antiferromagnet, isostructural with the common battery material LiCoO_2 and a well-known Jahn-Teller antiferromagnet NaNiO_2 . As opposed to the latter, LiCrO_2 exhibits antiferromagnetic exchange in the Cr planes, which has been ascribed to direct Cr-Cr d - d overlap. Using local density approximation (LDA) and LDA+ U first-principles calculations, I confirm this conjecture and show that (a) direct d - d overlap is indeed enhanced compared to isostructural Ni and Co compounds, (b) the p - d charge-transfer gap is also enhanced, thus suppressing the ferromagnetic superexchange, (c) the calculated magnetic Hamiltonian maps well onto the nearest-neighbor Heisenberg exchange model, and (d) the interplanar interaction is antiferromagnetic.

DOI: 10.1103/PhysRevB.75.094407

PACS number(s): 75.30.Et, 71.70.Gm, 71.10.-w

The series of compounds with a common formula AMO_2 , where A is an alkali or noble metal, usually Li or Na, and M is a $3d$ metal, formed by triangular MO_2 layers stacked hexagonally (e.g., LiCoO_2) or rhombohedrally (e.g., LiNiO_2) with full or partial intercalation by A , has been attracting considerable recent interest, largely driven by the immense importance of the LiCoO_2 compound in the electrochemical industry and by the unconventional superconductivity discovered in hydrated $\text{Na}_{1/3}\text{CoO}_2$. The nickelates LiNiO_2 , NaNiO_2 , AgNiO_2 , and Ag_2NiO_2 have also been subjects of numerous studies, mostly because of their magnetic properties coupled with interesting structural transformations. However, the chromates, such as LiCrO_2 , NaCrO_2 , and KCrO_2 , despite their potential use for rechargeable batteries¹ and as catalysts² have been studied experimentally only sporadically,³⁻⁸ and no first-principles calculations, to the best of my knowledge, have been reported so far.

In this paper I report all-electron full-potential electronic structure calculations for LiCrO_2 . In agreement with the experimental findings, the magnetic interaction in plane is found to be strongly antiferromagnetic. Interplane magnetic interaction is very weak and also antiferromagnetic. The total energy calculations for three different collinear magnetic configurations map perfectly well onto the standard nearest-neighbor Heisenberg model. As conjectured in the first experimental papers³ the main reason for switching the in-plane magnetic interactions from ferromagnetic in LiNiO_2 to antiferromagnetic in LiCrO_2 is mainly the enhanced direct overlap between the metal d orbitals in chromates, while, additionally, the increased charge-transfer p - d gap reduces the ferromagnetic superexchange in chromates as well.⁹ Finally I will discuss the role of Coulomb correlations as revealed by local density approximation (LDA)+ U calculations.

LiCrO_2 crystallizes in the rhombohedral $R\bar{3}m$ structure⁴ with the lattice parameters $a=2.898$ Å, $c=14.423$ Å, and with the O height $z_{\text{O}}=0.261$. Its magnetic structure is close to the ideal 120° structure characteristic of the nearest-neighbor Heisenberg model on a triangular plane. The computational results reported below were obtained using the standard full-potential linearized augmented plane wave code WIEN2K.¹⁰

Exchange and correlation were taken into account in a gradient approximation of Perdew *et al.*¹¹ Convergence with respect to both the cutoff parameter RK_{max} and the number of inequivalent k points (up to 400+) was checked.

I start first with the hypothetical ferromagnetic structure. Cr d states are split by the crystal field into three t_{2g} and two e_g states, separated by roughly 3 eV in the spin-majority and 2 eV in the spin-minority channel (Fig. 1). The difference is because the crystal field due to O-Cr hybridization is stronger in the spin-majority channel where the energy separation between the oxygen p states and the Cr d states is smaller. Cr^{3+} has exactly three electrons, and due to the strong exchange splitting it turns out to be well insulating already in the LDA; thus it can be treated as a band insulator (I will

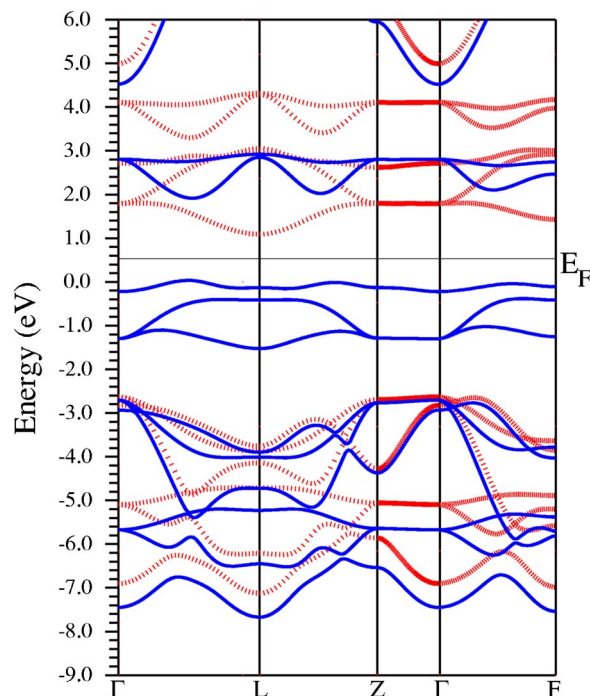


FIG. 1. (Color online) Band structure of LiCrO_2 in the hypothetical ferromagnetic state. Spin-majority bands are solid and blue, spin-minority ones dotted and red.

show later that the effect of the Mott-Hubbard correlations is relatively small), with the band gap between the occupied spin-up and unoccupied spin-down t_{2g} bands. The minimum spin-flip gap is slightly larger than 1 eV. The average spin-flip energy between the two bands is close to 2.9 eV. The oxygen states are well separated from the d states, as opposed to the isostructural oxides of the late $3d$ metals (Co,Ni), where the corresponding bands essentially overlap. The calculated magnetic moment is, obviously, $3\mu_B$, not too far from the experimentally measured noncollinear magnetic moment of $(2.68 \pm 0.13)\mu_B$.⁵ Structural optimization with experimentally constrained cell dimensions a and c leads to the O position $z_O=0.258$, corresponding to an approximately 4% larger distance between Cr and O planes compared to the experiment,⁴ and a Cr-O-Cr angle of 93° compared to the experimental 94.6° . I will discuss later the possible relation of this deviation to the magnetic properties.

LiCrO_2 , being a good insulator already in the LDA, should exhibit an antiferromagnetic superexchange interaction between the CrO_2 layers, proportional to $t_{\perp}^2/\Delta_{\text{sf}}$, where t_{\perp} is the effective interlayer hopping, a small number since it proceeds via a long path of Cr-O-O-Cr,¹² and Δ_{sf} is the energy cost for flipping a d electron spin [in the local spin-density approximation (LSDA), it is Stoner I , in the Hubbard model U]. To get an estimate (from above¹³) of this interaction I compare the total energy of the ferromagnetic state and the A -type antiferromagnetic state (ferromagnetism in plane, antiferromagnetic stacking). The energy difference appears to be 3 ± 1 meV per two formula units, a very small number indeed. This strongly suggests that LiCrO_2 is a very good model material for studying frustrated magnetism in two dimensions. NaCrO_2 may be even a better example of the same physics, as discussed in Ref. 8 from an experimental point of view.

Let me now discuss the magnetic interaction in plane. The above-described exchange splitting that renders LiCrO_2 a band insulator in LDA calculations, being essentially a local effect, should be operative in an antiferro- as well as in any ferrimagnetic arrangement. In other words, no new magnetic physics is introduced by Mott-Hubbard effects. Indeed, in the antiferro- and ferrimagnetic calculations, described in more detail below, I invariably found insulating ground states (a corollary of this finding is that the magnetically disordered state above T_N will also be insulating even in the LDA).

The isostructural compounds with higher transition metals (Co,Ni), when they order magnetically, assume the so-called A -type antiferromagnetism, that is, ferromagnetic planes, stacked antiferromagnetically. The mechanisms for the in-plane ferromagnetism are well understood: this is the classical 90° superexchange, plus, in metallic compounds like $\text{Na}_{0.7}\text{CoO}_2$, Stoner ferromagnetism. LiCrO_2 is not metallic; however, the O-Cr-O bond angle is fairly close to 90° and one expects the corresponding superexchange to be ferromagnetic.

A popular explanation³ is that this superexchange is indeed ferromagnetic but is surpassed by direct-overlap exchange between Cr d orbitals. It was also pointed out⁹ that the O p band in the higher metal (Co,Ni) is located higher with respect to the metal d band, which enhances the p - d hybridization and the superexchange, compared to that in

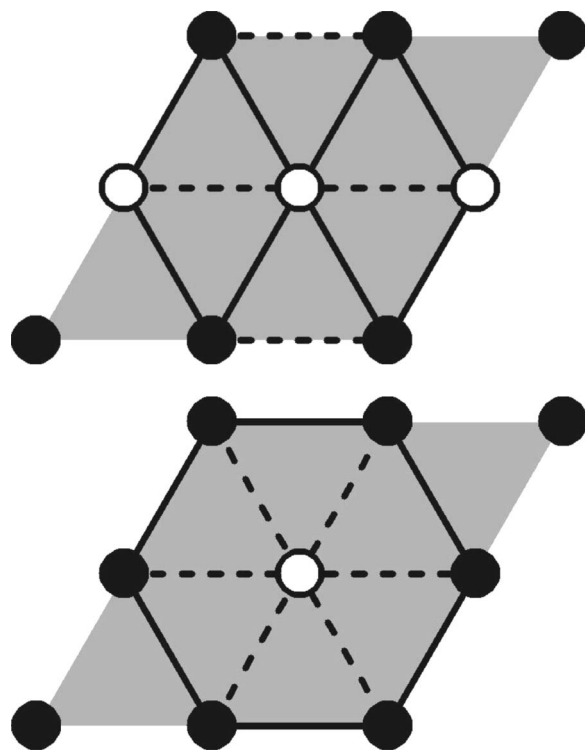


FIG. 2. Two different magnetic pattern (antiferromagnetic top, ferrimagnetic bottom) used in calculating the exchange constants. Filled (open) circles indicate up (down) moments within the supercell, solid (dashed) lines ferro- (antiferro)magnetic bonds.

LiCrO_2 . While logical *per se*, however, neither of these propositions has been subjected to a quantitative test. Besides, although among the physicists dealing with transition metal oxides it is generally known that direct d - d exchange is antiferromagnetic, this is not a trivial or obvious statement. Suffice it to remind the reader that essentially all textbooks in solid state physics describe direct exchange in terms of the original Heisenberg theory, which in fact leads to the *ferromagnetic* (FM) interactions. It is instructive to reconsider the issue of the net sign of the direct-exchange interaction from the local spin-density functional point of view, which is the foundation of all quantitative investigations in this direction, and I refer the reader to the Appendix where such an analysis is presented.

To address the nature of the magnetic interactions in LiCrO_2 , let us compare it with the isostructural LiNiO_2 . LSDA calculations predict in the latter a ferromagnetic exchange in plane, of the order of 5 meV.¹⁵ To compare with LiCrO_2 , I have performed LDA calculations in a $2 \times 2 \times 1$ supercell, assuming three different magnetic patterns inside the plane: ferromagnetic, antiferromagnetic (alternating ferromagnetic chains running along 100; see Fig. 2), and ferrimagnetic, retaining the hexagonal symmetry by flipping one spin out of four (Fig. 2). The results can be perfectly well mapped onto the nearest-neighbor Ising model, yielding *antiferromagnetic* (AFM) exchange ≥ 20 meV (22 or 23 meV, depending on which two lines in Table I are used). This is, of course, in excellent agreement with the experiment, but how does it answer the theoretical conjectures described above?

To this end, it is instructive to switch to a less accurate,

TABLE I. LSDA energies with respect to the energy of the FM state (in meV), magnetic moments inside the Cr MT spheres (in μ_B), and excitation gaps (in eV) for several magnetic states in a quadruple 2×2 LiCrO₂ supercell.

Ordering	Number of Cr \uparrow /Cr \downarrow	Number of FM/AFM bonds	\bar{M} (Cr)	M_{tot}	E	Gap
Ferromagnetic	4/0	12	2.6	12	0	1.1
Antiferromagnetic	2/2	4/8	2.5	0	-360	1.4
Ferrimagnetic	3/1	6/6	2.5	6	-265	1.25

but more flexible method, linear muffin-tin orbitals (LMTO), which provides a capability of eliminating particular radial functions from the basis, and thus assessing effects of particular orbital overlaps on the bands. I have calculated the band structure of LiCrO₂ and LiNiO₂, removing all oxygen orbitals from the basis, so that the resulting d -band width is essentially coming from direct d - d overlaps. The resulting bandwidths appear to be for LiCrO₂ and LiNiO₂, respectively, 1.4 and 0.5 eV, indicating that the direct d - d overlap integrals for Cr are three times larger than for Ni, in accord with earlier conjectures.³ Comparing these numbers with the bandwidths in full calculations shows that in LiCrO₂ most of the total bandwidth is due to the direct overlap, while in LiNiO₂ it mainly comes from the indirect hopping via oxygen. Note that in some crude approximation this means that the direct exchange due to d - d overlap is an order of magnitude stronger in LiCrO₂ compared to LiNiO₂.

Let us now look at the O- p -metal- d energy separation. Again, in the LMTO method there is a gauge that can be readily used: separation between the corresponding band-center quasiatomic parameters. In LiCrO₂ this separation appears to be 5.5 eV, while in LiNiO₂ it was 1.6 eV, 3.5 times smaller. This leads to a suppression (albeit not by the same factor) of the ferromagnetic superexchange in the former compound, as proposed by Khomskii.⁹ It is somewhat hard to estimate the actual reduction of this interaction, because the more diffuse character of the Cr d orbitals leads to some enhancement of the p - d hopping compared to the Ni compounds. Since the p - d overlap is already strong in the nickelate, this enhancement is not nearly as dramatic as that of the direct d - d hopping, but it should be present.

The summary of this part is that, while in the late $3d$ metal layered oxides, such as (Li,Na)NiO₂, and (Li,Na)CoO₂, the relatively strong ferromagnetic interactions (90° superexchange, but also Stoner ferromagnetism, discussed below) is largely, but not entirely compensated by the AFM superexchange (due to deviation from 90°) and by the direct d - d AFM exchange. In the early $3d$ metal oxides, like (Li,Na)CrO₂, the latter is greatly (up to an order of magnitude) enhanced, while the former is suppressed.

I will now address the question of the relative importance of several factors favoring AFM in-plane interactions in the early $3d$ oxides. Two have already been mentioned, stronger deviation of the metal-oxygen-metal angle from 90° (e.g., in LiCrO₂ this angle is 9.46° , while in NaNiO₂ is close to 92°), and stronger direct d -orbital overlap. There is a third important factor: the Stoner magnetism. Indeed, in such a system as NaNiO₂, where Ni is a Jahn-Teller ion with an orbital

degeneracy, the Fermi level falls inside the e_g band, which is wider in the FM case, and, correspondingly, has lower kinetic energy. In other words, itinerant e_g electrons have more freedom to move in the crystals on a background of parallel magnetic moments (one can also call this a d - d double exchange; the difference is purely terminological). Note that it does not matter if a small Jahn-Teller gap opens up in the e_g band; as long as this gap is smaller than or comparable to the bandwidth, kinetic energy will still favor the FM arrangement. LiCrO₂ does not display any orbital degeneracy, thus lacking this contribution to the magnetic interactions.

It is tempting to try to get an idea of the relative importance of the two FM interactions. I attempted to address this issue by doing calculations for a hypothetical LiCrO₂ with oxygen octahedra unsqueezed so as to have the Cr-O-Cr angle exactly 90° , while keeping the intraplane Cr-Cr distance constant (otherwise the calculations proceeded exactly as for the experimental structure, as described above in Table I and Fig. 2). One may think that this procedure would substantially enhance the 90° FM superexchange, hopefully keeping other magnetic interactions unchanged. The result seems, on the first glance, unusual: the exchange interaction becomes more antiferromagnetic (by about 17 meV). A closer look, however, reveals that this can be traced to the fact that the equilibrium O-Cr bond length in the AFM structure appears to be longer than in the FM structure (see Fig. 3), providing less hybridization and slightly smaller exchange splitting; note that the AFM energy gain due to the Cr-Cr direct exchange inversely depends on the exchange splitting. The total energy curves in Fig. 3 are almost rigidly shifted with respect to each other: the curvature is the same within the computational accuracy, corresponding to the frequency of the A_{1g} phonon of 567 cm^{-1} .

Finally, although one can expect that the role of the on-site Mott-Hubbard correlations should be small, given the large widths of the Cr d bands, it is of interest to estimate it using a standard implementation of the LDA+ U technique.¹⁰ The latter is most often used in one of two flavors:¹⁶ one is designed to reproduce the fully localized limit (FLL), the other simulates fluctuations around the mean-field solution (AMF). The former is believed to be more appropriate for large- U systems, and the latter for small U 's (admittedly, in this regime the very concept of LDA+ U becomes questionable). I have estimated the parameters using the LMTO internal quasiatomic loop¹⁷ to be $U=2.3 \text{ eV}$, $J=0.96 \text{ eV}$. This is a moderate U , probably more on the AMF side. Because of that, I have performed LDA+ U calculations in both limits, in order to compare them with each other and with the LDA. The results (assuming the FM structure) are shown in Fig. 4.

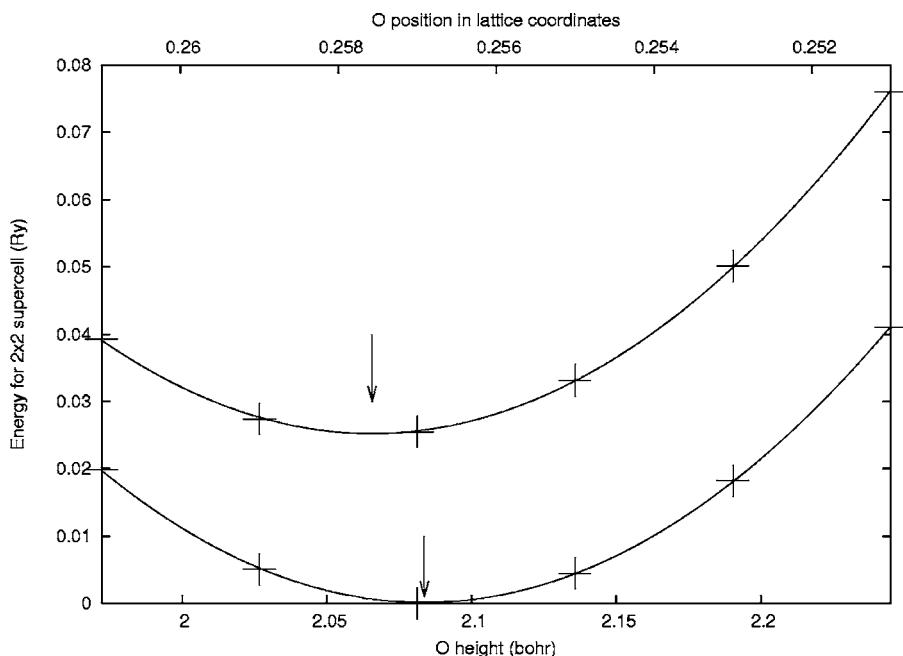


FIG. 3. Total energy as a function of oxygen position. The upper curve is for the ferromagnetic, the lower for the ferrimagnetic case (see Table I). The range of positions spans the experimental structure from Ref. 4 on the left to the structure with the Cr-O-Cr angle equal to 90° on the right. Calculated equilibrium positions are indicated by arrows.

As expected, LDA+ U does not introduce any new physics: the minimal gap is still the spin-flip gap between t_{2g} and e_g , enhanced by 0.5 eV in the AMF solution, due to a shift of the occupied band by $\approx(U-J)/2$, and by 1 eV in the FLL, due to an additional shift of the unoccupied states by the same amount. Note that these shifts are smaller than those expected in a typical band insulator due to the well-known density-derivative discontinuity,¹⁸ related to an unscreened long-range exchange interaction.¹⁹ For example, for ZnS, which has a gap of 3.8 eV, the LDA gives a gap of 1.7–1.8 eV. While I was not able to locate data for the experimental gap in LiCrO₂, the optical gap in NaCrO₂ was reported to be about 3.5 eV,²⁰ thus making comparison with ZnS rather meaningful. Note that the numbers in Fig. 4 are for the FM ordering; introduction of antiferromagnetism of course increases the gap (cf. Table I).

To conclude, one can describe LiCrO₂ as a weakly correlated band insulator with the minimal gap being the spin-flip t_{2g} - e_g gap. Magnetically it is a frustrated nearest-neighbor two-dimensional triangular antiferromagnet, with a sizable exchange constant of the order of 20 meV.

I would like to acknowledge many useful discussions with Michelle Johannes and Daniel Khomskii.

APPENDIX: DIRECT EXCHANGE IN THE LDA

Consider two overlapping orbitals $\phi_1 \equiv \phi(r)$, $\phi_2 \equiv \phi(|\mathbf{r} - \mathbf{R}|)$ centered at the points separated by R . The corresponding atomic (on-site) energy we shall call E , and we assume that there is intraatomic exchange splitting such that the spin-up state has the energy E , but the spin-down state has

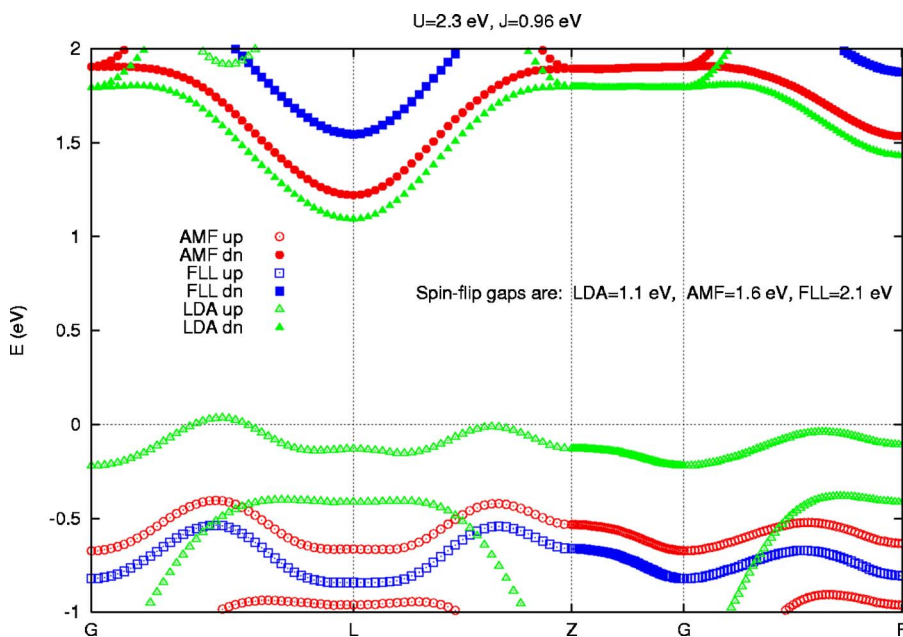


FIG. 4. (Color online) Band structure of ferromagnetic LiCrO₂ in the LDA and in two different LDA+ U flavors.

the energy $E+I$. The intraatomic exchange parameter I in the LSDA is known as the Stoner parameter. For strongly correlated systems the Hubbard $U \gg I$ plays the leading role instead. One may expect that in an intermediate regime the cost of flipping a spin is intermediate between the LSDA I and Hubbard U . The so-called Andersen force theorem¹⁴ states, among other things, that in the LSDA the total energy difference between the ferro- and antiferromagnetic arrangements can be computed as the difference in one-electron energy plus the difference in magnetic (Stoner) energy. The one-electron part favors antiferromagnetism. Indeed, the occupied levels in the ferromagnetic case are not shifted with respect to the on-site energy for the spin-up state, but in the antiferromagnetic case, in the second-order perturbation theory, they shift down by t^2/I each, where t is the hopping integral, $t = \langle \phi_1 | -\nabla^2 + V_{\text{eff}}(\mathbf{r}) | \phi_2 \rangle$ (in Ry).

The magnetic part favors ferromagnetism, since the corresponding energy in the LSDA is $E_{\text{St}} = -\int I m^2(\mathbf{r})/4$, where $m^2(\mathbf{r})$ is the total spin density. For the ferromagnetic align-

ment $m(\mathbf{r}) = \phi_1^2 + \phi_2^2$, $E_{\text{St}} = -\int I(\phi_1^2 + \phi_2^2)^2/4$. For the antiferromagnetic one $m(\mathbf{r}) = \phi_1^2 - \phi_2^2$, $E_{\text{St}} = -\int I(\phi_1^2 - \phi_2^2)^2/4$. Thus this term favors ferromagnetism by $I \langle \phi_1^2 | \phi_2^2 \rangle$ and is the LSDA counterpart of the textbook direct ferromagnetic exchange. Note that in transition metals I is on the order of 0.5–1 eV. Assuming that the tails of the d -wave function decay as $\exp(-r/r_d)$, we see that the ferromagnetic exchange is of the order of $I \exp(-R/r_d)$. In t , for weak overlaps, the main role is played by the kinetic energy, $t \sim \langle \phi_1 | -\nabla^2 | \phi_2 \rangle \sim \langle \phi_1 | \phi_2 \rangle / r_d^2 \sim \exp(-R/2r_d) / r_d^2$. The ratio $J_{\text{FM}}/J_{\text{AFM}}$ is thus $I^2 \exp(-R/r_d) / [\exp(-R/2r_d) / r_d^2]^2 = I^2 r_d^4$. Recalling that in solids the internuclear distance R is of the order of the lattice parameter a , while the Fermi vector is of the order of the Brillouin zone radius π/a , we can estimate $J_{\text{FM}}/J_{\text{AFM}} \sim (I^2/m_d^2 E_F^2)(\pi r_d/a)^4$, where $m_d \sim 5-10$ is the effective d -band mass, $E_F \sim 3-5$ eV is the d -band width, $r_d \sim 1$ (in Bohr radii), $a \sim 5-10$. Thus $J_{\text{FM}}/J_{\text{AFM}} \sim 10^{-3}$.

¹K.-S. Kim, S.-W. Lee, H.-S. Moon, H.-J. Kim, B.-W. Cho, W.-I. Cho, J.-B. Choi, and J.-W. Park, *J. Power Sources* **129**, 319 (2004); L. Zhang and H. Noguchi, *J. Electrochem. Soc.* **150**, A601 (2003); P. Arora, D. Zhang, B. N. Popov, and R. E. White, *Electrochem. Solid-State Lett.* **1**, 249 (1998).

²E. Cauda, D. Mescia, D. Fino, G. Saracco, and V. Specchia, *Ind. Eng. Chem. Res.* **44**, 9549 (2005).

³C. Delmas, G. Le Flem, C. Fouassier, and P. Hagenmuller, *J. Phys. Chem. Solids* **29**, 55 (1978).

⁴J. L. Soubeyroux, D. Fruchart, C. Delmas, and G. Le Flem, *J. Magn. Magn. Mater.* **14**, 159 (1979).

⁵H. Kadowaki, H. Takei, and K. Motoya, *J. Phys.: Condens. Matter* **7**, 6869 (1995).

⁶S. Angelov, J. Darriet, C. Delmas, and G. Le Flem, *Solid State Commun.* **50**, 345 (1984).

⁷V. R. Galakhov, E. Z. Kurmaev, St. Uhlenbrock, M. Neumann, D. G. Kellerman, and V. S. Gorshkov, *Solid State Commun.* **95**, 347 (1995).

⁸A. Olariu, P. Mendels, F. Bert, B. G. Ueland, P. Schiffer, R. F. Berger, and R. J. Cava, *Phys. Rev. Lett.* **97**, 167203 (2006).

⁹D. I. Khomskii (unpublished).

¹⁰P. Blaha *et al.*, computer code WIEN2K (Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001).

¹¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

¹²The O-O hopping between the layers is partially enhanced by assisted O-Li-O hopping. Detailed analysis in the isostructural NaCoO₂ [M. D. Johannes, I. I. Mazin, and D. J. Singh, *Phys. Rev. B* **71**, 214410 (2005)] shows that both direct and indirect paths yield comparable contributions.

¹³For ferromagnetically ordered layers the effective interlayer hopping is considerably enhanced because hopping to six second neighbors in the next layer is comparable to the hopping to the first neighbor located right above the atom in question (see Ref. 12). In-plane antiferromagnetism suppresses already weak interplanar hopping.

¹⁴A. K. Mackintosh and O. K. Andersen, in *Electrons at the Fermi Surface*, edited by M. Springford (Cambridge University Press, Cambridge, U.K., 1975).

¹⁵M. J. Johannes, I. I. Mazin, and N. Bernstein (unpublished).

¹⁶A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Lichtenstein, *Phys. Rev. B* **67**, 153106 (2003).

¹⁷I. I. Mazin and S. L. Molodtsov, *Phys. Rev. B* **72**, 172504 (2005).

¹⁸J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983); L. J. Sham and M. Schluter, *ibid.* **51**, 1888 (1983).

¹⁹E. G. Maksimov, I. I. Mazin, S. Y. Savrasov, and Y. A. Uspenski, *J. Phys.: Condens. Matter* **1**, 2493 (1989).

²⁰P. R. Elliston, F. Habbal, N. Saleh, G. E. Watson, K. W. Blazey, and H. Rohrer, *J. Phys. Chem. Solids* **36**, 877 (1975).