Compensated half-metallicity in the trigonally distorted perovskite NiCrO_{3}

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Compensated Half-metallicity in the Trigonally Distorted Perovskite-type $NiCrO_3$

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Using first principles calculations, we investigate the electronic and magnetic properties of the trigonally distorted ($R\bar{3}c$) perovskite-derived $NiCrO_3$. Within the local spin density approximation (LSDA), our calculations show that this system is an exactly compensated half-metal (CHM). The local spin moments of Cr 2.04, and antialigned Ni –1.41 and three oxygens –0.63 (in the units of μ_B), indicate high spin $S=\frac{3}{2}$ Cr^{3+} and $S=\frac{3}{2}$ $(NiO_3)^{3-}$ units. Considering reasonable values of the on-site Coulomb repulsion U on both Ni and Cr ions with LDA+U approach, this system becomes an insulator (as reported by Chamberland and Cloud) having a narrow gap in the spin-up channel, while the other channel has a large gap of ∼3 eV. Although inclusion of U seemingly leads to the transition Ni^{2+}→high spin $S=\frac{3}{2}$ Ni^{3+}, consistent with the experimentally observed effective moment, the zero net moment remains unchanged due to either reduction of oxygen local moments or enhancement of Cr local moment. Compression of volume by 10% leads to CHM even when correlation effects are included. These results suggest the possibility of a CHM state in $NiCrO_3$ and provide another route to search for CHM, which is a property sought by many.

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Introduction. A half-metallic antiferromagnet, more properly called a compensated half-metal (CHM), is half-metallic, having one conducting and the other insulating spin channels, but vanishing (compensating) net magnetic moment, hence no macroscopic magnetic field. Since proposed by van Leuken and de Groot[1] fifteen years ago, the CHM has been considered as an encouraging candidate for spintronics – fully polarized carriers without a macroscopic magnetic field to deal with – and a possible single spin superconductor.[2] However, a true CHM has not yet been established.

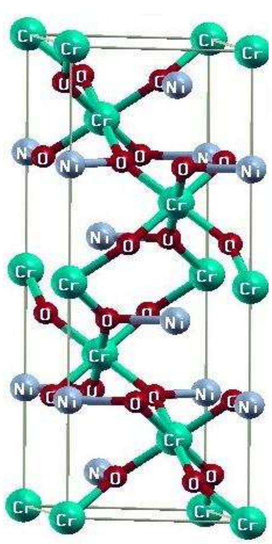

FIG. 1: (Color online) Crystal structure of the trigonally distorted $NiCrO_3$, having the corner-sharing CrO_6 octahedra.

Since at least two different kinds of magnetic ions are necessary for vanishing moment, the double perovskite systems were investigated in several theoretical researches.[3–9] However, preparing an ordered sample has been frequently failed.[10,11] The Heusler structures, which have produced many half-metals, also have been considered as another promising candidate.[12–14] Nakao has suggested CHM in tetrahedrally coordinated chalcopyrites[15] and in their monolayer superlattices.[16]

In this study, we will extend the search for CHMs to the trigonally distorted perovskite-related systems having two different transition metals. Several systems of this class were synthesized about forty years ago.[17–19] Here we will investigate $NiCrO_3$ with a corundum-related structure, synthesized by Chamberland and Cloud.[17] Their procedure involved preparation at high (60-65 kbar) pressure at 1200 °C, followed by quenching to room temperature, so intermixing on the Ni and Cr sites cannot be ruled out. The susceptibility measurements showed a Curie-Weiss behavior in the high T regime and discontinuities at 250 K and 120 K, proposed to be canted antiferromagnetism. The value of the effective moment was p_{eff}=5.8 μ_B, close to the value for Cr^{3+} and Ni^{3+}, both carrying high spin $S=\frac{3}{2}$, implying a possibility of CHM. This system was proposed to be semiconducting with an activation energy of 0.11 eV, though no detailed information was provided. More recently, this compound has been obtained as a minority during the oxidization process by a few groups,[20,21] who measured only the space group and lattice constants consistent with those of Chamberland and Cloud.[17]

Structure and methods. In this trigonally distorted system, Chamberland and Cloud reported only the space group $R\bar{3}c$ (No. 167) with the hexagonal lattice constants $a = 4.9252$ Å and $c = 13.504$ Å,[17] leading to a distortion factor $\frac{a\sqrt{6}}{c}$ of 0.89 (unity for the ideal perovskite). We have optimized the structure parameters in the cubic and the trigonally distorted structures. In both structures, the one in which the Ni ion sits on the A site and the Cr ion on the B site is much favored over reversed site occupation. Consistent with the experiments, our optimizations show that the cubic phase with optimized lattice constant $a = 3.602$ Å has much higher energy, by a few eV, than the distorted phase. Hence we will consider only the distorted structure.

In the $R\bar{3}c$ structure, using the experimental lattice parameters,[17] our optimizations indicate that Ni, Cr, and O ions lie on the $6a$ $(0,0,\frac{1}{4})$, $6b$ (0,0,0), and $18e$ $(x,0,\frac{1}{4})$ sites, respectively, with the oxygen internal parameter x of 0.3748. As displayed in Fig. 1, the Cr-O bond length of 1.915 Å is about 3% larger than the Ni-O bond length of 1.85 Å. The CrO_6 octahedra consist of a nearly square base and equilateral triangular faces, with only 1.8% difference between the O-O bond lengths. Thus the CrO_6 unit remains close to an ideal octahedron. The O-O-O bond angles are 60°, 2×60.6°, and 58.8°. The O-Cr-O bond angles are either 91° or 89°. The Ni ions lie at the center of mass of the equilateral triangle framed by in-plane oxygens. This trigonal planar symmetry D_{3h} of the NiO_3 leads to the crystal field splittings: doublet e_{1g} (d_{yz}, d_{zx}), doublet e_{2g} $(d_{xy}, d_{x^2-y^2})$, and singlet a_{1g} (d_{z^2}).

These calculations were carried out within the local spin density approximation (LSDA) followed by the LDA+U approach, as implemented in the all-electron full-potential code FPLO-9.[22] In the LDA+U approach, two popular double-counting schemes, the so-called around mean field (AMF) and the fully localized limit (FLL),[23,24] were used, showing similar results for this compound. In our calculations, a rhombohedral cell containing two formula units was used. The convergence was checked with a regular mesh containing up to 781 irreducible k-points.

LSDA electronic structure. The Cr local moment (2.04 μ_B) is precisely canceled by the moments of antialigned Ni (–1.41 μ_B) and three oxygens (–0.63 μ_B). The oxygen moment is unusually large for a $3d$ system, though not unprecedented. (In the PBE generalized gradient approximation,[25] the CHM configuration also results but with somewhat larger moments: Cr 2.26 μ_B, Ni –1.54 μ_B, three oxy-

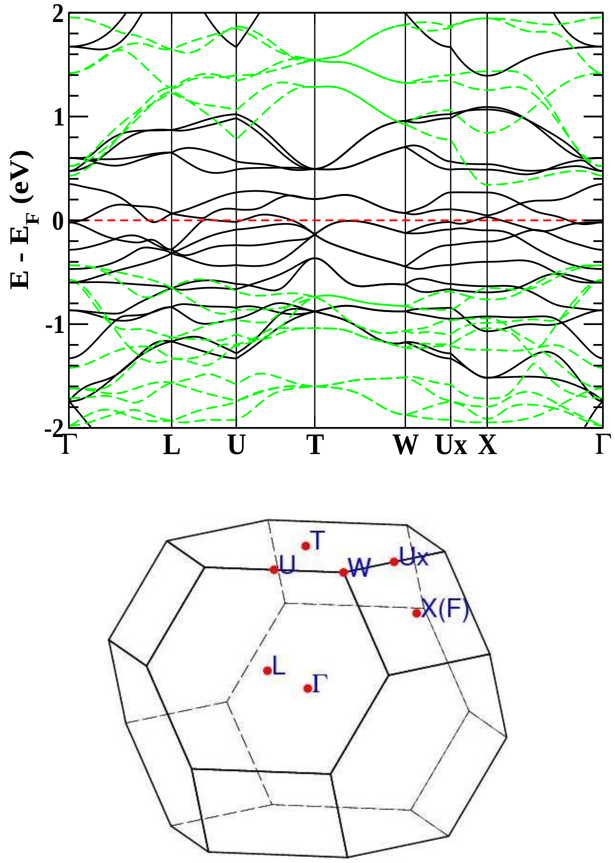

FIG. 2: (Color online) Top: LSDA band structure near the Fermi energy E_F, where the bands arise only from d orbitals of Ni and Cr ions. The dashed horizontal line indicates E_F, which is taken as the zero of energy. Bottom: Brillouin zone and high symmetry points of the rhombohedral structure, which has similarity to the fcc Brillouin zone with a 3-fold axis oriented along the z-axis.

gens totaling to –0.72 μ_B .) This CHM state with zero net moment is favored by 300 meV/f.u. over the nonmagnetic state. Thus $NiCrO_3$ is a compensated half-metal within LSDA,[26] regardless of the choice of exchange-correlation functional.

The LSDA band structure near E_F is displayed in Fig. 2, illustrating the 0.8 eV gap in the spin-down channel leading to the half-metallic state. In the spin-up (metallic) channel, the Ni e_{2g} bands lying in the range of 0.6–1 eV are separated from the mixture of the other Ni d and Cr t_{2g} bands spread out over the regime of –1.8 eV to 0.4 eV. In the spin-down bands, the Ni $3d$ (majority) states are fully occupied with small (1.4 eV) bandwidth, and Cr $3d$ (minority) states are empty. The corresponding densities of states in the full energy range and with enlargements emphasizing Ni and Cr separately, are displayed in Fig. 3. The oxygen bands in the range of –7.5 to –2 eV are separated from the d bands by 0.5 eV. How-

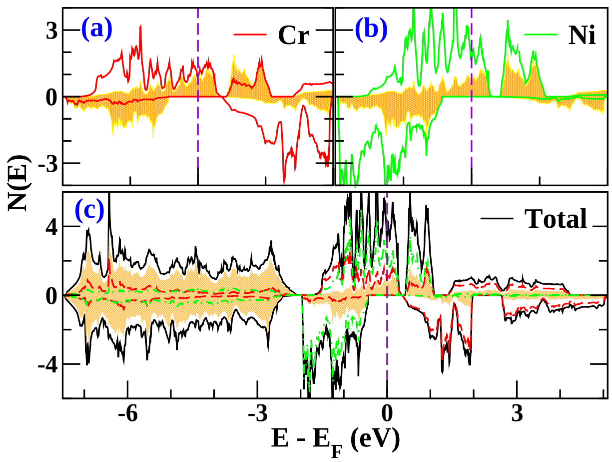

FIG. 3: (Color online) Total and atom-projected LSDA densities of states, which shows the half-metallic aspect, expressed per eV-formula unit. In all panels, the shaded regions indicate three oxygens-projected DOS. The total density of states $N(E_F)$ at E_F is 3.80 states per eV per a formula unit, decomposed of 50% Ni, 30% Cr, and 20% three oxygens characters. (a) Cr $3d$ DOS in solid line, from -2 eV to 2 eV; (b) Ni $3d$, on same scale as in (a); (c) total DOS in the entire O $2p$ - metal $3d$ region. The unoccupied Cr e_g states with the exchange splitting of 1.5 eV lie on 1.5–4 eV and 2.5–5 eV in the spin-up and spin-down channels, respectively. The exchange splitting of Cr t_{2g} states is about 2 eV. The t_{2g}-e_g crystal field splitting of Cr in the spin-up channel is 3.5 eV, 1 eV larger than in the spin-down channel. The vertical dashed line indicates E_F.

ever, the mixture of O $2p$ character into both Ni and Cr bands indicates strong $p-d$ hybridization.

The spin-up channel is more interesting, being a mixture of Cr majority and Ni minority states. To balance the five occupied Ni (majority) spin-down bands (per f.u.) there must be five spin-up bands occupied (on average through the zone, due to the metallic nature). Three bands, around 0.5 eV and above, are separated from the other intermixed seven bands, so the filling is 5/7. These can be identified as Cr e_g and a substantial admixture of Ni (and of O $2p$ as noted earlier). The occupied spin-up bands are Cr t_{2g} admixed with Ni d_{yz}, d_{zx}, and d_{z^2} bands. Being strongly hybridized and metallic, formal valences become a murky concept. $S = \frac{3}{2}$ Cr^{3+} seems to be the clearest feature; presuming O^{2-} ions with their formal valence one would obtain $S = \frac{3}{2}$ Ni^{3+}. We emphasize that the strong $p-d$ hybridization and metallicity make these assignments of limited use.

Inclusion of correlation effects. We have used the LDA+U approach to model the observed insulating state. The proper U values for this system are unclear, but values that have been widely used in oxides are 3–4 eV for Cr[27] and 6–8 eV for Ni,[28] having been obtained from comparison with experimental data or calculated from the constrained LDA approach.[30] The Hund's exchange integral J=1 eV has been fixed for all values of U, after some variation of J indicated results are insensitive to values

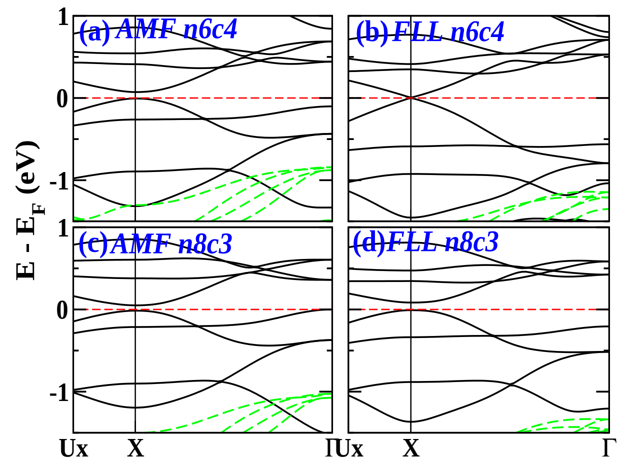

FIG. 4: (Color online) Blowup band structures along the Ux-X-Γ line near E_F for various values of U in both schemes of LDA+U. Here, $n6c4$ denotes U=6 and 4 eV for Ni and Cr ions, respectively. In panel (b), the gap of 5 meV separates nearly degenerate linear bands similar to what has been observed (at the Γ point) in $CoSb_3$.[29]

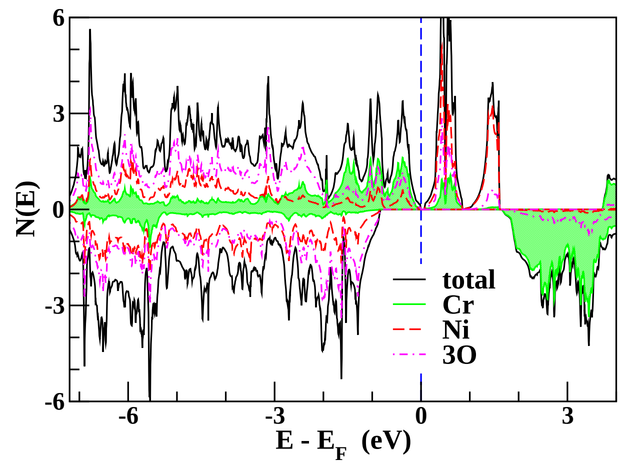

FIG. 5: (Color online) Total and atom-projected densities of states per formula unit in the AMF scheme of LSDA+U using U= 4 and 6 eV for Cr and Ni ions, respectively. Near E_F the occupied part has mostly Cr d character, but the bottom of the unoccupied part has Ni d character even though the strong O characters also exist. In particular, the O characters are nearly the same as the d character in the range of -0.1– 0.1 eV. This indicates a nearly compensated half-semimetal.

around this one.

Figure 4 displays the enlarged band structures along the Ux-X-Γ line (which is where the gap opens) near E_F (set to zero), for these ranges of U and using both commonly used LDA+U schemes. The energy gap in the spin-down channel increases to about 2.6 eV in AMF and 3.6 eV in FLL (not shown in the figure). In the spin-up channel, the bottom of the conduction bands and the top of the valence bands both consist of the mixture of the O p_z and Ni e_{2g} bands, in particular near the X point, with little Cr d character. However, about 50% at the bottom of the conduction bands and the top of the valence bands are oxygen and Ni characters, respectively. The second highest valence band, which is nearly flat, is one of the Cr t_{2g} bands. In AMF, at $n6c4$ (denoting $U_{Ni} = 6$ eV, $U_{Cr} = 4$ eV) a small gap in the spin-up channel opens at the X point, whereas in FLL two bands almost touch at E_F. For $n8c3$, in FLL the band structure is similar with that of $n6c4$, except for a slight increase in the energy gap. In AMF, however, Cr t_{2g} bands at the Γ point are raised, leading to an small indirect gap of the Γ to X point almost equal to the direct gap at X. This indirect gap is observed only in the case of U=3 eV for Cr ions in AMF.

The FLL and AMF methods are known to encourage magnetism differently.[31] Here we find that applying U on the metal atoms leads to significantly different induced moments on the oxygen ions. In FLL, applying U enhances the magnitudes of all local moments, and the combined moment of three oxygens is still about 40% of the Ni moment. In AMF, on the other hand, both Ni and Cr moments are increased by applying U, but the moment of three oxygens becomes only 20% of the Ni moment. These different moments can be ascribed to an energy penalty for magnetism in AMF that is not present in FLL, as discussed previously.[31] On balance, however, the moment compensation remains unchanged when varying U in the range studied here.

Since differences in the overall DOS curves are small, we show only that for $n6c4$ in AMF in Fig. 5. In the spin-up channel, the Fermi energy lies between the occupied Cr d bands and the unoccupied Ni e_{2g} bands. Just above 1.5 eV, narrow unoccupied Ni a_{1g} bands, *i.e.* mixing slightly with O states, exist. As a result, in the insulating phase, the Ni ion is apparently trivalent, even though the local moment of -1.90 μ_B is considerably reduced due to strong $p-d$ hybridization. However, the charge difference of Ni ions, obtained by the Mullikan charge decomposition, between in LSDA and LDA+U is only ∼0.2e, similar to that observed in charge disproportionated $Na_{1/2}CoO_3$.[32]

Discussion and Summary. Given the very small gap in the up channel, modest pressure should close the gap, giving a CHM state, as we now show. At 10% compression in volume, the zero moment is slightly degraded within LSDA, but inclusion of U in the same range as in the ambient pressure restores the state of the zero moment. In the spin-up channel, which is insulating at ambient pressure, Ni a_{1g} bands of W ≈0.6 eV cross E_F along the L-Γ-X line, resulting in being metallic and a precise compensated half-metal. (Below ∼ 10% compression, the electronic structures are very similar with those at ambient pressure.) This suggests that applying pressure will lead to a CHM state even though this system is insulating at ambient pressure.

In summary, we have investigated $R\bar{3}c$-structure $NiCrO_3$, using both LSDA and LDA+U approaches. Within LSDA, this system is a precise compensated half-metal with the energy gap of 0.8 eV in the spin-down channel. Considering the on-site Coulomb repulsion U of both Ni and Cr ions, we obtained an insulating phase, but retaining zero net moment regardless of the magnitude of U. Interestingly, the energy gap is substantial (2.6 − 3.6 eV) in the spin-down channel, whereas it is tiny or vanishing in the spin-up channel. Application of pressure provides a likely route to a CHM state in this compound. These findings provide another structure class that may be favorable for synthesis of a compensated half metal.

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