Half-metallic Ferrimagnetism Driven by Coulomb Enhanced Spin-Orbit Coupling in PdCrO$_3$

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Recently, in the seemingly narrow gap insulating NiCrO$_3$ with the trigonally distorted (R$ar{3}$c) perovskite-like structure, a compensated half-metal (CHM) is predicted, as applying a modest pressure. Using $ab$ initio calculations including both Coulomb correlations and spin-orbit coupling (SOC), we investigate the as-yet-unsynthesized PdCrO$_3$, isostructural and isovalent to NiCrO$_3$. Upon applying the on-site Coulomb repulsion $U$ to both Pd and Cr ions, the Cr spin moment is precisely compensated with the antialigned spin moments of Pd and oxygens. Coincidentally only one spin channel remains metallic due to the twice larger width of the Pd 4$d$ bands than the Ni 3$d$ bands in NiCrO$_3$, indicating CHM in ambient pressure. Inclusion of SOC as well as correlation effects (LDA+U+SOC) produces a SOC constant enhanced twice over the value of LDA+SOC, leading to unusually large orbital moment of $-0.25 \mu_B$ on Pd. However, the half-metallicity still survives, so that a transition of CHM to a half-metallic ferrimagnet occurs due to Coulomb enhanced SOC. On the other hand, an isovalent, but presumed cubic double perovskite La$_2$PdCrO$_6$ is expected to be a half-metal ferrimagnet with tiny orbital moments.

A half-metal shows spin-dependent transport phenomena, ideally 100% spin polarization defined as

$$P = \frac{N_{\uparrow}(E_F) - N_{\downarrow}(E_F)}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)},$$

where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ are the spin up and down densities of states at the Fermi energy $E_F$, respectively. This is extremely interesting as a promising candidate of a spin injector in spintronics. In the early 1980’s, de Groot and coworkers suggested a half-metallic ferromagnet (HMFM). Focusing on stoichiometric compounds, HM has an integral net moment due to the nature of HM. Additionally, half-metallic ferrimagnets (HMFI) have been searched, since a higher Curie temperature has been expected. However, application of these kinds of HMs to spintronics has confronted some problems, in particular due to the presence of stray-field. Thus, for about the last 20 years, HMs with zero net magnetic moment, compensated half-metals (also so-called half-metallic antiferromagnets) have been sought. Since a compensated half-metal (CHM) was suggested in a Heusler compound, double perovskites, tetrahedrally coordinated chalcopyrites, and iron-pnictides have been theoretically studied. In spite of a number of theoretical predictions, no true CHM has been synthesized yet.

Very recently, Lee and Pickett suggest that applying moderate pressure leads to CHM in trigonally distorted perovskite-type NiCrO$_3$, which seems to be a semiconductor with the very small gap in the spin up channel in ambient pressure. In this paper, we will investigate an isostructural and isovalent PdCrO$_3$, but unsynthesized yet, using first principles calculations including both Coulomb correlations and spin-orbit coupling (SOC). Since strength of correlation of Pd ions is much weaker than that of Ni ions, a (half) metallic PdCrO$_3$ is expected even in ambient pressure. Although a Pd ion is often non-magnetic, a spin ordered Pd ion has not been rarely observed.

Compared with 5$d$ or 4$f$ systems, 3$d$ and 4$d$ systems show relatively small SOC. Combined with Coulomb correlations, however, SOC is sometimes amplified, so called “Coulomb enhanced SOC”. In the spinel compounds $TV_2O_4$ ($T$=Zn, Mn), Coulomb enhanced SOC leads to an orbital ordering on V ions with large orbital moments of 0.34 or 0.75 $\mu_B$. In another spinel FeCr$_2$S$_4$, a considerable orbital moment of 0.14 $\mu_B$ on Fe ions was obtained in LDA+U+SOC calculations.

Usually, strong SOC induces mixing of states to the opposite spin channel, resulting in undermining half-metallicity. On the contrary, in the case of PdCrO$_3$ showing Coulomb enhanced SOC, a considerable orbital moment is induced, but the mixing of states is tiny. Considering only correlation effects, PdCrO$_3$ is a precise CHM. Our LDA+U+SOC calculations produce substantial orbital moment of $-0.25 \mu_B$ on Pd ion, resulting in nonzero net moment ($-0.29 \mu_B$/f.u.). However, the half-metallicity remains unchanged. As a result, this system be-
FIG. 1: (Color online) Our optimized crystal structure \((R\bar{3}c)\) of the trigonally distorted \(\text{PdCrO}_3\), consisting of \(\text{CrO}_6\) octahedra and \(\text{PdO}_3\) triangular planes: the small (red) spheres for \(\text{O}\) and the large (blue) spheres for \(\text{Pd}\). The \(\text{PdO}_3\) triangular planar symmetry leads to the crystal field splittings: doublets \(e_1g (d_{yz}, d_{zx})\), \(e_2g (d_{xy}, d_{x^2−y^2})\), and singlet \(a_1g (d_{z^2})\). This figure was produced by VESTA.

As observed in \(\text{NiCrO}_3\), our relaxations show that the distorted structure \((R\bar{3}c)\) is energetically favored by 0.3 eV per formula unit (f.u.) over the cubic structure. The lattice parameters in the distorted phase are \(a=4.9597\ \text{Å} \) and \(c=13.5985\ \text{Å}\), close to the volume of the cubic phase. Thus, we will address only the distorted phase. In the \(R\bar{3}c\) structure, \(\text{O}\) ions lie on 18\(e\) \((x, 0, 1/4)\) sites with the optimized internal parameter \(x=0.5845\). \(\text{Pd}\) and \(\text{Cr}\) ions sit on the 6\(a\) \((0,0,1/4)\) and 6\(b\) \((0,0,0)\), respectively. As displayed in Fig. 1 the Cr-O bond length of 1.87 Å is about 9% shorter than the Pd-O bond length. The O-Cr-O bond angles are either 87° or 93°. The O-O-O bond angles are 60°, 2×56.9°, and 61.6°, indicating nearly ideal \(\text{CrO}_6\) octahedral structure.

Our calculations were carried out with the local spin density approximation (LSDA) and spin-orbit coupling scheme, implemented in two all-electron full-potential codes FPLO-9 and Wien2k. (Since both results are similar, we will show only ones obtained from Wien2k unless stated otherwise.) Additionally, the correlation effects were treated using LDA+U approach with the double-counting scheme of the fully localized limit. The structural parameters were optimized until forces were smaller than 1 meV/Å. The Brillouin zone was sampled with \(20×20×20\) \(k\)-mesh.

**TABLE I:** Magnetic moments in units of \(\mu_B\). The net moment includes the moment of the interstitial regime not given here. \(U=3\) eV for \(\text{Pd}\) and 4 eV for \(\text{Cr}\) were used in the LDA+U and LDA+U+SOC calculations.

|                  | Cr  |   | Pd  |   | 3O  |   | net |   |
|------------------|-----|---|-----|---|-----|---|-----|---|
| **LSDA**         | 0.54| -0.42| -0.24| -0.24|     |   |     |   |
| **LSDA+U**       | 2.08| -1.26| -0.90| 0.00|     |   |     |   |
| **LSDA+SOC**     | 0.35| -0.01| -0.27| -0.05| -0.15| -0.22|     |   |
| **LSDA+U+SOC**   | 2.13| -0.07| -1.24| -0.25| -0.90| -0.29|     |   |

**LSDA electronic structure.** Our LSDA calculations show that the Cr moment 0.54 \(\mu_B\) is antialigned to the Pd moment -0.42 \(\mu_B\), consistent with low spin \(S = 1/2\) configurations in both \(d^5\) \(\text{Cr}^{3+}\) and \(d^7\) \(\text{Pd}^{3+}\) ions. Note that these moments...
FIG. 3: (Color online) LDA+U densities of states (DOSs) per eV per f.u. at \( U = 3 \) eV for Pd and 4 eV for Cr. Top: total and atom-projected DOSs. The unoccupied manifolds lying above \( \sim 2 \) eV are Cr \( e_{2g} \) in the spin up and Cr \( t_{2g} \) in the spin down. The inset shows the compared LDA+U DOS (dashed line) with LDA+U+SOC DOS (solid line). Bottom: orbital-projected DOS of Pd \( d \) states. The \( e_{1g}-e_{2g} \) crystal field splittings are \( \sim 3 \) eV for the spin up and 2 eV for the down. The \( a_{1g} \) bands spread throughout the regime of Pd \( d \) states, though the center is midway between the \( e_{1g} \) and \( e_{2g} \) manifolds.

FIG. 4: (Color online) Comparison between band structures of LDA+U (black solid and dotted lines for the spin up and down characters, respectively) and of LDA+U+SOC (red dashed lines), near \( E_F \). In the spin down channel, the top of the valence and the bottom of the conduction bands shift up by 0.1 eV and 0.3 eV, respectively, leading to a gap of 2.5 eV.

are considerably reduced from the formal values due to strong hybridization and metallic character. \( N(E_F) = 4.03 \) states/eV-f.u. is decomposed into 15% Cr, 35% Pd, and 50% three oxygens characters (not shown here). As shown in Table II substantial oxygen moment \((-0.24 \mu B\) for three O’s) results in the net moment of \(-0.24 \mu B/\text{f.u.}\). This simple ferrimagnetic state has a little lower energy than the non-magnetic state.

Note that the width of 3 eV of the partially occupied Pd \( 4d \) bands is twice wider than the Ni \( 3d \) bands in NiCrO\(_3\).\(^{18}\) This suggests that PdCrO\(_3\) remains metallic in ambient pressure, as considering even correlation effects, in contrast to NiCrO\(_3\) (see below).

Effects of correlation. Now we will address results as considering correlation effects. We applied the on-site Coulomb repulsion \( U \) to both transition metals. The proper values of \( U \) are unclear in this system, yet. In our calculations, values of \( U \) were varied in the range of \( U = 2-7 \) eV for both ions, while the Hund’s exchange parameter \( J = 1 \) eV remained fixed. Regardless of strength of \( U \) in this range, inclusion of \( U \) leads to a transition of the low spin to high spin configurations on both ions, and coincidently a net moment exactly compensated (see below). Besides, from comparison with experimental data, 3–4 eV for Cr and \( \sim 3 \) eV for Pd in oxides have been widely used.\(^{18,22,34}\) Thus, we will focus on results obtained at \( U = 4 \) eV for Cr and 3 eV for Pd.

The corresponding band structure and DOSs displayed in Figs. 2 and 3 show a half-metal. The orbital-projected DOS of Pd \( 4d \) is given in the bottom panel of Fig. 3. In the spin down (insulating) channel, a gap of 2.3 eV between the occupied Pd \( d \) and the unoccupied Cr \( t_{2g} \) manifolds is open. The occupied Pd \( d \) states lie in the range of \(-2.8 \) to \(-0.3 \) eV. The spin up (conducting) channel shows more interesting features due to metallicity. The occupied
enhanced SOC is due to orbital polarization enforced by site spin. This is also observed in the small change in the spin moments, implying tiny mixing with states of the opposite spin. As given in Table I, the nearly unchanged spin moments indicate negligible effects result in a large orbital moment of Pd ions on Pd ion driven by Coulomb repulsion, leading to a precisely compensated half-metallic state in LDA+U+SOC calculations. This may be due to the difference in crystal field splittings between both systems, leading to different orbital polarization. Our calculations show that this HMFM state is stable for small distortion in structure, as observed in the other double perovskites.

In summary, we investigated the as-yet unsynthesized PdCrO$_3$, isostructural and isovalent to the trigonally distorted perovskite-derived NiCrO$_3$, using ab initio calculations considering both Coulomb correlations and spin-orbit coupling (LDA+U+SOC). Inclusion of $U$ leads to a precisely compensated half-metal, but unusually large orbital moment of $-0.25 \mu_B$ on Pd ion driven by Coulomb enhanced SOC destroys CHM. Nevertheless, the half-metallicity still survives, so that this system becomes HMFI. Our findings suggest that HM is possible even for the system with substantial SOC and large orbital moments.

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34 In the metallic Sr\(_2\)RhO\(_4\), \( U=2 \) eV for Rh ions showed consistent results with the ARPES band structure.\(^{22}\) So, in a metallic system, \( U \approx 3 \) eV seems to be reasonable for Pd ions. One may expect a higher value of \( U \) for an insulating system. However, even for \( U=7 \) eV, PdCrO\(_3\) remains a compensated half-metal.