Three Dimensional Magnetism and Coupling to the Conduction Electrons in PdCrO$_2$

Khuong P. Ong  
Institute of High Performance Computing, 1 Fusionopolis Way, Singapore 138632

David J. Singh  
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056  
(Dated: November 18, 2011)

We report density functional calculations addressing the electronic structure and magnetic properties of delafossite PdCrO$_2$. We find substantial magnetic interactions in the $c$-axis direction as well as beyond first nearest neighbors in-plane, so that PdCrO$_2$ is a 3D frustrated antiferromagnet. We also find substantial coupling between the Cr moments and the Pd derived conduction electrons.

PACS numbers: 75.10.Lp,75.30.Et

I. INTRODUCTION

Recent discoveries pointing to novel ground states and unusual behaviors in field and temperature dependent magnetic and thermodynamic properties have led to renewed interest in the physics of frustrated spin systems. Delafossite structure PdCrO$_2$ has attracted recent attention in this context. Importantly, like the sister compound PdCoO$_2$, it can be grown in high quality form facilitating experimental investigation of its physical properties. This material can be described as a stacking of 2D CrO$_2$ layers, separated by Pd, with the Cr ions arranged on a triangular lattice. In a standard nearest neighbor Heisenberg picture, the ground state would be expected to be a non-collinear 120° spin structure below the Neel temperature, $T_N=37.5$ K, but the actual magnetic structure of PdCrO$_2$ could be more complex. Takatsu and co-workers find that the magnetic Bragg peaks in neutron scattering are rather broad and half-integral $l$ (1/3,1/3,l) and (2/3,2/3,l) peaks are found in addition to the integer $l$ peaks. In any case, PdCrO$_2$ is a particularly interesting system because like its sister compound PdCoO$_2$ it is conducting and has a very large conductivity anisotropy. This offers an opportunity to study the interplay between frustrated magnetism and charge carriers in a near two dimensional metal. Furthermore, recent experiments have revealed an unconventional anomalous Hall effect in this material.

Doumerc and co-workers reported susceptibility data up to $\sim 450$ K. They obtained an effective moment of 4.1 $\mu_B$ and a Weiss temperature of -500 K, in a Curie-Weiss fit, although they qualify these values as approximate. The data show a poor fit except over a relatively small temperature range above $\sim 300$ K, in contrast to the other compounds they report: CuCrO$_2$, AgCrO$_2$ and CuFeO$_2$, which show very good Curie-Weiss behavior over a wide temperature range extending to below 100 K. In fact, in their data, there is still an apparent upward curvature to $\chi^{-1}(T)$ at the highest $T$, suggesting that the Weiss temperature could be lower in magnitude or that the system may have itinerant character.

Takatsu and co-workers show more details of the susceptibility below 350 K. There is no plausible Curie-Weiss fit to the data, but they do state that their data are consistent with the values extracted by Doumerc and co-workers. Interestingly, the data shows a broad maximum above $T_N$. However, in contrast to strongly 2D magnetic systems, $\chi$ just above $T_N$ is only slightly lower than the maximum value, and there are strong signatures of the ordering in $\chi(T)$ as well as resistivity and specific heat. This is not really consistent with expectations for a strongly 2D Heisenberg system. On the other hand, Takatsu and co-workers do observe a sublinear resistivity, $\rho(T)$ above $T_N$, which they attribute to short range magnetic correlations, and an unusual behavior in the specific heat also above $T_N$.

Motivated by this we performed density functional calculations of electronic structure and energetics of PdCrO$_2$ in order to address the nature and role of the metallic conduction electrons in PdCrO$_2$ and the extent to which the system is a realization of a 2D nearest neighbor Heisenberg magnet. We find in contrast to previous assumptions that (1) there is a considerable interplay between the Cr moments and the metallic electrons, and (2) there are strong magnetic interactions along the $c$-axis direction, so that even though PdCrO$_2$ is very two dimensional as an electron gas, it is a very three dimensional magnetic system. Finally, there is metal-metal bonding, consistent with previous studies of delafossite compounds.

II. APPROACH

We performed density functional calculations with the Perdew, Burke, Ernzerhof (PBE) generalized gradient approximation using the all electron linearized augmented plane wave (LAPW) method as implemented in the WIEN2k code similar to our previous calculations for PdCoO$_2$. We carefully tested the convergence of our results against the various parameters, including tests with different sphere radii and different choices of the augmentation including both LAPW and so-called APW+lo basis sets. We found the results to be stable. We used the experimental lattice parameters, $a=2.923$ Å.
FIG. 1. (color online) Density of states and projections on Cr and Pd LAPW spheres of radius 2.05 bohr for ferromagnetic ordering.

and $c=18.087$ Å (delafossite structure, space group $R3m$, Pd at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Cr at $(0,0,0)$, O at $(\pm z, \pm z, \pm z)$, in rhombohedral coordinates). Refinement of the internal parameter corresponding to the O height above the Cr plane has not been reported in literature to our knowledge. As such, we calculated this parameter for a ferromagnetic and used it in the other calculations. We obtained $z=0.6111$, which yields a Cr-O distance of 1.962 Å. This is in accord with the expected bond length for high spin Cr$^{3+}$ (the Shannon radii are 1.22 Å for O$^{2-}$ and 0.755 Å for octahedral Cr$^{4+}$, summing to 1.975 Å). We also note that the Pd-Pd distance of $a=2.923$ Å is not much longer than the Pd-Pd distance of 2.75 Å in Pd metal. The Cr-O-Cr bond angles in the layers are 96.3°. Considering the Cr lattice, the O atoms directly connect the nearest neighbor Cr atoms in plane. There are no direct O connections to second neighbors. Secondly, in the out-of-plane direction, the shortest hopping paths are Cr-O-Pd-O-Cr. The Cr-O-Pd bond angles along this path are 120.7° with this O position.

III. MOMENT FORMATION AND ELECTRONIC STRUCTURE

We find that PdCrO$_2$ is strongly unstable against Cr moment formation regardless of the arrangement of the moments with an energy of $\sim 1$ eV/Cr. We also find all arrangements are metallic in accord with experiment. Therefore, PdCrO$_2$ should be described as a metal containing Cr local moments. We start our description with the calculated electronic structure with ferromagnetic alignment of these moments. The calculated energy is 0.92 eV lower than the non-spin-polarized (no Cr moments) case, and the magnetization is 2.87 $\mu_B$ per formula unit. The magnetization inside a Cr LAPW sphere (radius 2.05 bohr) is 2.57 $\mu_B$.

The calculated electronic density of states (DOS) is given in Fig. 1. It clearly shows crystal field split Cr $d$ states with the majority spin $t_{2g}$ states occupied, and the $e_g$ unoccupied, as are all the minority spin Cr states. The DOS at $E_F$ is Pd derived. These states provide a simple very two dimensional Fermi surface (Fig. 2), consistent with the observed strong conductivity anisotropy and reminiscent of PdCoO$_2$, which is also a highly anisotropic metal. As discussed previously, the states giving rise to the Fermi surface arise from Pd-Pd metal-metal bonding as in other delafossites. Additionally, two additional features are seen: (1) The Fermi surface has very little rounding, which is the condition for maximizing nesting (but note that density of states is Pd derived and low, $N(E_F)=0.7$ eV$^{-1}$, per formula unit on a both spins basis for this ferromagnetic ordering), and (2) While both the majority and minority spin Fermi surfaces are similar in shape, they are not identical, implying an interplay between the metallic, largely Pd derived, conduction band, and the Cr derived magnetic moments. In fact, the minority spin Fermi surface is 13% larger in volume than the majority spin surface. This interplay between Cr moments and the conduction electrons provides a mechanism for spin scattering, that will increase the resistivity as $T$ disorders the spins and also a mechanism for long range Cr-Cr interactions in-plane, as well as interactions in the $c$-axis direction.

IV. MAGNETIC INTERACTIONS

We studied the magnetic interactions through a series of supercell calculations with different magnetic orderings. These calculations and their energetics are summarized in Fig. 3. One may immediately note from the top panel of the figure that the out-of-plane magnetic interactions are large. Specifically, an antiferromagnetic stacking of ferromagnetic layers is found to be 18 meV/Cr lower in energy than a ferromagnetic stacking. This is large compared with the ordering temperature, $T_N = 38$ K, i.e. $kT_N = 3.3$ meV.

Of the small collinear cells that we studied, the lowest energy belongs to AF-2 (see Fig. 3 for notation), which corresponds to the ordering in CuFeO$_2$. The
This interplay between magnetic order and the conduction electrons is also seen in the calculated densities of states. As mentioned, for the ferromagnetic order, we obtain \( N(E_F) = 0.70 \, \text{eV}^{-1} \) on a per formula unit both spins basis. For the AF-z (see Fig. 3) order, we obtain \( N(E_F) = 0.69 \, \text{eV}^{-1} \) on the same basis, while we obtain \( N(E_F) = 0.81 \, \text{eV}^{-1} \), for AF-1, \( N(E_F) = 0.76 \, \text{eV}^{-1} \), for AF-2, and \( N(E_F) = 0.77 \, \text{eV}^{-1} \), for AF-3. The bare specific heat coefficient \( \gamma \) inferred from these values is 1.6-1.9 mJ/mol K\(^2\), comparable to the specific heat value of Takatsu and co-workers of 1.4\( \pm \)0.2 mJ/mol K\(^2\) in the ground state. This leaves little room for any renormalization at low \( T \).

The variability of the electronic structure at \( E_F \) depending on magnetic state provides a qualitative framework for understanding why the resistivity of high quality crystals of PdCrO\(_3\) is so much higher than that of PdCoO\(_2\), even though the Fermi surface, structure and band character at the Fermi surface are very similar\(^{13,19}\) and also why the resistivity shows a strong signature of the magnetic ordering, with a pronounced decrease in resistance as \( T \) is lowered through \( T_N \). Specifically, this connection between magnetic order and the electrons at the Fermi surface indicates that strong spin-fluctuation scattering is expected above the ordering temperature, freezing out as \( T \) is lowered below \( T_N \).

Materials with this type of coupling between magnetism and electrons at the Fermi surface tend to be the ones that display unusual properties, such as superconductivity (as in e.g. the Fe-pnictides where the coupling is very strong) when the magnetism is suppressed. Therefore, this coupling of spin fluctuations to electrons at the Fermi surface suggests that it will be of considerable interest to experimentally examine what happens as the magnetic order is suppressed, e.g. by pressure or alloying.

We now turn to the energetics (Fig. 3) in more detail. To do this we write a short range model with interactions to nearest and next-nearest neighbors in-plane and to the out-of-plane nearest neighbor position (out of six), respectively.

\[
E = E_F + j_1 N_{1\up} + j_2 N_{2\up} + j_3 N_{z\up}
\]

where \( E \) is the energy per Cr, \( E_F \) is the energy of the ferromagnetic ordering, \( N_{1\up} \) is the average number of opposite spin first nearest neighbors in the structure, and similarly for next nearest neighbors and neighbors along the \( c \)-axis direction. While this could be converted into a three neighbor Heisenberg model, we write it this way because the moments in the Cr LAPW spheres vary between the different configurations (in the range 2.48 \( \mu_B \) to 2.57 \( \mu_B \)).

In any case, if we match the energies of the ordered structures, F, AF-z, AF-1 and AF-3, we obtain \( j_1 = -16 \) meV, \( j_2 = +2 \) meV and \( j_3 = -3 \) meV. The energies cannot be reasonably reproduced without all three parameters (note that each shell has 6 atoms, so e.g. the difference between ferromagnetic and AF-z is \( 6j_z = -18 \) meV, which
is not small, etc.) Use of these values, yields the energy for the AF-2 state to within 1 meV / Cr atom. While the model is perhaps too simple to capture all aspects of the magnetic interactions in PdCrO$_2$, it does clearly show that the material cannot be reasonably understood as a simple 2D nearest neighbor Heisenberg model.

V. DISCUSSION AND CONCLUSIONS

Considering the ordering temperature $kT_N=3.3$ meV, it would seem that none of these interactions can be neglected, i.e. at least first and second in-plane neighbors and crucially c-axis interactions need to be included when discussing the magnetism of PdCrO$_2$.

This conclusion may seem unexpected considering the very two dimensional electronic structure at the Fermi energy, as found both in our calculations and as is clear from the experimental resistivity anisotropy. However, we note that a similar behavior is found in the layered cobaltate Na$_x$CoO$_2$. That materials has a related crystal structure, that is similar to the delafossite, except that the layer stacking differs and bridges between planes are O neighbors along $c$ instead of two O separated by a Pd (i.e. in Na$_x$CoO$_2$ the O in neighboring layers are directly on top of each other). The three dimensional magnetic behavior in Na$_x$CoO$_2$ arises in part because of this bonding topology, which provides many superexchange exchange paths between the neighboring Co$_2$ structure CoO$_2$ layers. Within this framework, the c-axis magnetic interactions and the coupling to the conduction electrons are inter-related since they are both mediated by or through Pd.

In any case, we note that the Kosterlitz-Thouless type of suppression of the ordering temperature is logarithmic in the anisotropy of the interactions. As such, very strong anisotropy is needed to obtain two dimensional, as opposed to three dimensional, magnetism. We can conclude that PdCrO$_2$ is a three dimensional frustrated antiferromagnet with an interesting interplay between magnetism and conduction electrons.

ACKNOWLEDGMENTS

Work at ORNL was supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Work at IHPC was supported by the Singapore Agency for Science Technology and Research (A*STAR). DJS is grateful for the hospitality of IHPC where a portion of this work was performed.

---

1. H. Takatsu, H. Yoshizawa, S. Yonezawa, and Y. Maeno, Phys. Rev. B 79, 104424 (2009).
2. H. Takatsu, S. Yonezawa, S. Fujimoto, and Y. Maeno, Phys. Rev. Lett. 105, 137201 (2010).
3. H. Takatsu and Y. Maeno, J. Cryst. Growth 312, 3461 (2010).
4. M. Mekata, T. Sugino, A. Oohara, Y. Oohara, and H. Yoshizawa, Physica B 213, 221 (1995).
5. E. Rastelli and A. Tassi, J. Appl. Phys. 81, 4143 (1997).
6. A. Wichainchai, P. Dordor, J. P. Doumerc, E. Marques-taut, M. Pouchard, P. Hagenmuller, and A. Ammar, J. Solid State Chem. 74, 126 (1988).
7. H. Takatsu, S. Yonezawa, C. Michioka, K. Yoshimora, and Y. Maeno, J. Phys. Conf. Ser. 200, 012198 (2010).
8. J. P. Doumerc, A. Wichainchai, A. Ammar, M. Pouchard, and P. Hagenmuller, Mat. Res. Bull. 21, 745 (1986).
9. R. Seshadri, C. Felsker, K. Thieme, and W. Tremel, Chem. Mater. 10, 2189 (1998).
10. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
11. D. J. Singh and L. Nordstrom, Planewaves, Pseudopotentials and the LAPW Method, 2nd Ed. (Springer Verlag, 2006).
12. P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (K. Schwarz, Tech. Univ. Wien, Austria)(2001).
13. K. P. Ong, D. J. Singh, and P. Wu, Phys. Rev. Lett. 104, 176601 (2010).
14. E. Sjostedt, L. Nordstrom, and D. J. Singh, Solid State Commun. 114, 15 (2000).
15. R. D. Shannon, D. B. Rogers, and C. T. Prewitt, Inorg. Chem. 10, 713 (1971).
16. N. Terada, S. Mitsuda, H. Oshumi, and K. Tajima, J. Phys. Soc. Jpn. 75, 023602 (2006).
17. F. Ye, Y. Ren, Q. Huang, J. A. Fernandez-Baca, P. Dai, J. W. Lynn, and T. Kimura, Phys. Rev. B 73, 220404(R) (2006).
18. T. Nakajima, A. Suno, S. Mitsuda, N. Terada, S. Kimura, K. Kaneko, and H. Yamauchi, Phys. Rev. B 84, 184401 (2011).
19. K. P. Ong, J. Zhang, J. S. Tse, and P. Wu, Phys. Rev. B 81, 115120 (2010).
20. S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Endrele, J. Mesot, D. P. Chen, C. T. Lin, and B. Keimer, Phys. Rev. Lett. 94, 157205 (2005).
21. L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, A. Stunault, G. J. McIntyre, and N. Kernavanois, Phys. Rev. B 75, 054405 (2006).
22. M. D. Johannes, I. I. Mazin, and D. J. Singh, Phys. Rev. B 71, 214410 (2005).