Study of magnetic interactions in a geometrically frustrated compound, Sr₃NiPtO₆, using density functional approach

SUDHIR K. PANDAY and KALOBARAN MAITI(a)

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research
Homi Bhabha Road, Colaba, Mumbai - 400 005, India

received 8 July 2009; accepted in final form 8 October 2009
published online 6 November 2009

PACS 75.30.Et – Magnetic properties and materials: exchange and superexchange interactions
PACS 75.50.Mm – Magnetic properties and materials: magnetic liquids
PACS 71.70.Gm – Electronic structure of bulk materials: exchange interactions

Abstract – We investigate the electronic structure of Sr₃NiPtO₆ using ab initio calculations. This compound is a geometrically frustrated insulator and does not show long-range order down to 1.8 K measured; a signature of spin-liquid-like behavior. Electronic band structure calculation within the local spin density approximations in our study reveals an insulating ground state in Sr₃NiPtO₆ unlike analogous compounds in this family. The Ni moment is found to be large and the intra-chain coupling favors antiferromagnetic ordering. These results establish the importance of intra-chain antiferromagnetic interaction in addition to geometrical frustration to derive the ground-state properties.

Copyright © EPLA, 2009

Introduction. – A new class of compounds, AE₃M′M″O₆ (AE = alkaline earths, M and M′ are transition metals) have been found to possess geometrical frustration that led to varied interesting properties [1–18]. The crystal structure of this class of materials is rhombohedral, K₄CdCl₆ type (space group R3c) as shown in fig. 1. It contains one-dimensional (1D) chains along the c-axis consisting of alternating MO₆ trigonal prisms and M′O₆ octahedra connected by face sharing. In the ab-plane, the chains form a triangular lattice. Thus, these systems exhibit fascinating electronic and magnetic properties characteristic of 1D chains as found in various integer and half-integer spin chain systems involving divalent Ni and Cu [19–21]. In addition, they possess properties due to geometrical frustration in the ab-plane. Many compounds in this class are synthesized and studied extensively due to the finding of varieties of interesting properties involving geometrical frustration [1–18].

Most of these compounds are reported to contain one or two types of magnetic ions possessing finite magnetic moments [3–6]. The magnetic interactions between these ions lead to different kinds of magnetic ordering such as ferromagnetic, antiferromagnetic, ferrimagnetic etc. [1,7–9]. Interestingly, Sr₃NiPtO₆ exhibits an anomalous behavior; signature of long-range magnetic order was not observed down to 1.8 K measured. The temperature dependence of magnetic susceptibility is similar to that of a spin-liquid-like ground state [1]. This is the only compound in this class exhibits such a behavior. Analogous compounds Sr₃NiRhO₆ [1] and Sr₃CuPtO₆ [2] exhibit long-range order similar to the other compounds in this family [3–6]. In these later systems, geometrical frustration in the ab-plane is manifested as a partially disordered antiferromagnetic phase, where two third of these magnetically ordered chains couple antiferromagnetically and the rest is incoherent.

(a)E-mail: kmaiti@tifr.res.in

Fig. 1: (Color online) The crystal structure of Sr₃NiPtO₆. Quasi-one-dimensional chains are shown by shaded regions.
Several contrasting suggestions exist in the literature to explain the absence of magnetic order in Sr$_3$NiPtO$_6$. For example, comparison of Sr$_3$NiPtO$_6$ and Sr$_3$CuPtO$_6$ indicated that Ni$^{2+}$ could be in a singlet state [2]. However, Ni$^{2+}$ in a similar compound, Sr$_3$NiRhO$_6$ possess large magnetic moment ($S = 1$ state) [1,6], which is puzzling. Moreover, the anomalous behavior observed in Sr$_3$NiPtO$_6$ needs serious attention.

In this paper, we report the electronic structure of Sr$_3$NiPtO$_6$ calculated using ab initio band structure calculations within the local spin density approximations (LSDA) with an emphasis on the issue of magnetic moment formation and the nature of coupling among them. Calculated results within the local spin density approximations reveals an insulating ground state unlike that observed in analogous compounds in this family [6]. The Ni moment is found to be large and couple antiferromagnetically along the chain.

**Calculational details.** – The non-magnetic and magnetic GGA (generalized gradient approximation) electronic structure calculations were carried out using state-of-the-art full potential linearized augmented plane wave (FPLAPW) method [22]. The spin orbit coupling was considered in the calculations following a variational procedure, where the eigenenergies and eigenvectors were computed using scalar relativistic wavefunctions from LAPW calculations. The lattice parameters and atomic positions used in the calculations are taken from the literature [2]. The Muffin-Tins sphere radii were chosen to be 2.33, 2.19, 2.01, and 1.78 a.u. for Sr, Ni, Pt, and O, respectively. For the exchange correlation functional, we have adopted recently developed GGA form by Wu et al. [23]. The convergence was achieved by considering 512 $k$ points within the first Brillouin zone and the error bar for the energy convergence was set to be smaller than $10^{-4}$ Rydberg/cell.

**Results and discussions.** – Electronic structure is calculated for non-magnetic, ferromagnetic and antiferromagnetic arrangements of Ni moments. At first, we compare the calculated energy bands corresponding to the non-magnetic and ferromagnetic solution that provides information about the crystal field induced effects and the influence of exchange splitting on them. Calculated energy bands are shown in fig. 2; the left and right panels show the band dispersions corresponding to non-magnetic and ferromagnetic solutions, respectively. Contrary to experimentally observed insulating ground state, the non-magnetic solution converges to a metallic ground state with large contribution at the Fermi level, $\epsilon_F$ represented by “zero” in the energy scale. There are four bands lying within $\pm 0.1$ eV of $\epsilon_F$. At the $\Gamma$ and $M$ points, the bands just above and bellow the $\epsilon_F$ are two fold degenerate. The separation of these bands are largest at $\Gamma$ point ($\sim 0.16$ eV) and lowest at $M$ point ($\sim 0.04$ eV). The degeneracy of these bands is lifted along $MK$ direction.

![Fig. 2: (Color online) Band dispersions along different symmetry directions of the first Brillouin zone for non-magnetic and ferromagnetic solutions. The Fermi level is denoted by zero in the energy scale.](image)

The ferromagnetic solution corresponds to an insulating ground state. The up-spin energy bands move away from the Fermi level, towards lower energies. The Fermi level appears at the top of the down-spin bands. The energy gap in the down-spin channel is about 0.8 eV, which is much smaller than the gap of $\sim 2.5$ eV in the up-spin channel. The insulating gap of about 0.8 eV appears along the $MK$ and $\Gamma K$ directions. The band gaps at $\Gamma$, $K$ and $M$ points are found to be about 0.96, 1 and 1.1 eV, respectively.

Interestingly, consideration of finite exchange interactions leads to insulating phase in this compound. It is observed that antiferromagnetic phase may lead to metallic-insulator transition due to the change in lattice translational symmetry (supercell symmetry), thereby splitting the Brillouin zone. The other effect observed (e.g., in giant magnetoresistive materials) is a transition from paramagnetic insulating phase to ferromagnetic metallic phase where parallel spins favor a metallic conduction. Here, we observe opening of a large band gap leading to insulating state in a metal when spin polarization is switched on. Emergence of such insulating phase in a narrow band system can easily be realized. For example, in a half-filled band system, if the exchange splitting $J$ is larger than the bandwidth $W$ ($J/W > 1$) the system becomes insulating. $J/W < 1$ corresponds to a metallic ground state.
The character of various energy bands is shown in fig. 3. The degeneracy of Ni 3d in NiO6 trigonal prisms and Pt 5d orbitals in PtO6 octahedra is lifted due to the corresponding crystal field effect. We have defined the axis system such that the z-axis lies along the c-axis, and x and y axes are in the ab-plane (see fig. 1). The crystal field splitting of the Ni 3d and Pt 5d levels is evident in fig. 3(a), where we show the Ni 3d, Pt 5d and O 2p partial density of states (PDOS) obtained from the non-magnetic solution. Pt 5d dominated bonding and antibonding energy bands appear in the energy ranges from −7 to −5 eV and from −2.5 to −1 eV, respectively. O 2p contributions appear primarily between −2 and −5 eV. Energy bands having dominant Ni 3d character shown by thin solid lines appear in the vicinity of the Fermi level. The trigonal prismatic crystal field around the Ni site leads to three distinct energy bands having Fermi level. The trigonal prismatic crystal field around O2− shows by thin solid lines appear in the vicinity of the Fermi level.

In fig. 3(b), we show the spin-polarized Pt 5d PDOS obtained from ferromagnetic solution where all the spins are considered to be parallel. Both the spin channels of Pt 5d states are partially occupied and the insulating gap in the up-spin channel is decided by the 5d states, which is found to be about 2.5 eV. From the total electron count, we find that Pt has 6 electrons in the 5d bands indicating that the valence state is close to 4+. These 6 electrons occupy t2g orbitals making it completely filled. Since all these energy bands appear at much lower energies, an exchange splitting of about 0.6 eV observed for Pt 5d states does not push the down-spin bands energy levels about 5eV in all the spin-orbitals corresponding to Ni 3d electronic states. Such a large exchange correlation does not affect the insulating state of the d_{xz}, (d_{x^2−y^2}, d_{xy}) and (d_{xz}, d_{yz}) character as seen in figs. 3(c). Clearly, the ground state is metallic and the electronic density of states at the Fermi level are primarily contributed by Ni (3d_{xz} + d_{yz}) states.

In (b) and (c), we show d_{z^2} (upper panel), d_{xz} + d_{yz} (middle panel) and d_{x^2−y^2} + d_{xy} (lower panel) PDOS for Pt 5d and Ni 3d states, respectively. Up- and down-spin PDOS are shown by dashed and thick solid lines, respectively. In each case, the half intensity of the non-magnetic PDOS is shown by thin solid line for comparison.

Ferromagnetic solution exhibits large exchange splitting (about 1 eV) in all the spin-orbitals corresponding to Ni 3d electronic states. Such a large exchange correlation does not affect the insulating state of the d_{xz} and (d_{x^2−y^2}, d_{xy}) energy bands. The spin degeneracy lifting of (d_{xz}, d_{yz}) bands leads to a gap of about 0.8 eV at ϵ_F. Since, Ni^{2+} has 8 electrons in the d band, the down-spin band becomes completely empty due to spin polarization.

It is important to note that capturing insulating ground state in most of the oxides containing 3d transition metals requires consideration of on-site Coulomb interaction strength, U among 3d electrons. Correlation effect is also important in higher d systems [24,25]. This is the case in Sr3NiRhO6 [6]. However, in the present case, on-site Coulomb correlation among d electrons is not necessary to derive the insulating phase of Sr3NiPtO6. This comes naturally as Pt^{4+} has 6 electrons filling t2g bands and 8 electrons in Ni^{2+} leads to an empty (d_{xz}, d_{yz}) down-spin band making all other 3d bands filled.

The influence of U on the electronic structure is verified by including U in our calculations (GGA+U). U corresponding to Ni 3d electrons was varied up to 7 eV and that corresponding to Pt 4d electrons up to 4 eV. In all these cases, the ground state remains insulating as observed for U = 0; the increase in U leads to an enhancement in the energy separation between occupied and unoccupied bands. The Ni moment is found to be very close to the ferromagnetic GGA result. This is consistent with the expectations for an insulating system. Here it is important to note that although the inclusion of U does not change the total magnetic moment of the system, it would affect the strength of magnetic interaction.

The total converged energy for the ferromagnetic solution is found to be ~781 meV/f.u. lower than that for the non-magnetic solution. This clearly provides evidence against the non-magnetic phase as ground state for this system [2]. The magnetic moment centered at Ni sites is significantly large (≈1.5 μB). The magnetic moment at Pt site turns out to be negligible small (∼0.02 μB) that corresponds to low spin state in the octahedral symmetry. The total magnetic moments per formula unit

Fig. 3: (Color online) (a) The partial density of states (PDOS) corresponding to Ni3d (thin solid lines), O2p (dashed lines) and Pt 5d (thick solid lines) states for the non-magnetic solution. In (b) and (c), we show d_{z^2} (upper panel), d_{xz} + d_{yz} (middle panel) and d_{x^2−y^2} + d_{xy} (lower panel) PDOS for Pt 5d and Ni 3d states, respectively. Up- and down-spin PDOS are shown by dashed and thick solid lines, respectively. In each case, the half intensity of the non-magnetic PDOS is shown by thin solid line for comparison.
is found to be about \(2 \mu_B\) (effective total spin, \(S = 1\)). One can compare the magnetic moment with the experimental value obtained in the paramagnetic phase. Estimated effective paramagnetic moment, \(\mu = 2\sqrt{S(S+1)}\) is about 2.8 \(\mu_B\) which is less than the experimentally estimated value of about 3.4 \(\mu_B\). There could be two possible reasons for the discrepancy between calculated and measured effective moments: i) small paramagnetic impurity in the sample would enhance the effective magnetic moment and ii) there may be contribution from orbital part of the magnetic moment.

In order to investigate the later possibility we considered the effect of spin-orbit coupling (SOC) on the magnetic states of the Ni and Pt. We performed ferromagnetic GGA calculations including SOC for both the atoms. This calculation converges again to the insulating ground state. The spin part of the magnetic moments do not get affected by the SOC. However, SOC induces about 0.16 \(\mu_B\) orbital magnetic moments centered at Ni site. The direction of orbital and spin parts of magnetic moments are same, which is as per Hund’s rule. The orbital part of magnetic moment for Pt atom is found to be very small (0.02 \(\mu_B\)). The small orbital moment for heavier Pt atom in comparison to lighter Ni atom may be attributed to the fully filled electronic configuration of \(t_2g\) bands. Consideration of orbital part of magnetic moment improves the effective magnetic moment which is found to be about 3 \(\mu_B\). The relatively small value of orbital part of magnetic moment in comparison to spin part clearly indicates that the magnetic properties of \(\text{Sr}_3\text{NiPtO}_6\) compound are primarily determined by the spin dynamics associated to Ni 3d electrons.

The above results establish that the Ni possess large magnetic moment and the ground state of \(\text{Sr}_3\text{NiPtO}_6\) should also be decided by the magnetic interaction between the Ni ions. The magnetic susceptibility data have shown negative sign for Curie temperature, which indicates the effective antiferromagnetic interaction between the magnetic atoms [1].

It is already well known that magnetic interactions can be captured well via \textit{ab initio} calculations [26]. In order to learn the nature of magnetic interaction among Ni atoms, we calculated the electronic structure for antiferromagnetic coupling among neighboring intra-chain Ni atoms. The energy of this solution is found to be about 5 meV/f.u. less than that for the FM solution indicating that antiferromagnetic interaction provides more stability to the system, which is consistent with magnetization data [1]. The calculation gives almost the same magnetic moments (\(\sim 1.5 \mu_B\)) as observed before; the net magnetic moment is close to zero. This Ni moment is very close to that found in \(\text{Sr}_3\text{NiRhO}_6\) [6]. The rough estimate of Heisenberg exchange parameter between nearest Ni moments can be estimated by mapping the energies of ferromagnetic and antiferromagnetic solutions to Heisenberg Hamiltonian. The exchange parameter thus obtained is found to be about 13 K.

![Fig. 4: (Color online) Up- and down-spin PDOS corresponding to (a) Ni 3d_{z^2}, (b) Ni 3(d_{xz} + d_{yz}), (c) Ni 3(d_{x^2−y^2} + d_{xy}), and (d) Pt 5d states for the antiferromagnetic solution.](image-url)
(M-O-O-M super superexchange interaction), intra-chain interactions become important in deriving the ground state properties. Thus, the anomalous behavior of Sr$_3$NiPtO$_6$ may be attributed to aniferromagnetic coupling of Ni moments.

***

The authors acknowledge Prof. E. V. Sampathkumaran, TIFR, India for drawing our attention towards this compound and useful discussions.

REFERENCES

[1] Mohapatra N., Iyer K. K., Rayaprol S. and Sampathkumaran E. V., Phys. Rev. B, 75 (2007) 214422.
[2] Claridge J. B., Layland R. C., Henley W. H. and zur Loye H.-C., Chem. Mater., 11 (1999) 1376.
[3] Wu H., Haeverkort M. W., Hu Z., Khomskii D. I. and Tjeng L. H., Phys. Rev. Lett., 95 (2005) 186401.
[4] Wu H., Hu Z., Khomskii D. I. and Tjeng L. H., Phys. Rev. B, 75 (2007) 245118.
[5] Flahaut D., Hébert S., Maignan A., Hardy V., Martin C., Hervieu M., Costes M., Raquet B. and Broto J. M., Eur. Phys. J. B, 35 (2003) 317.
[6] Pandey S. K. and Maiti K., Phys. Rev. B, 78 (2008) 045120.
[7] Sampathkumaran E. V. and Niazi A., Phys. Rev. B, 65 (2002) 180401(R).
[8] Agrestini S., Mazzoli C., Bombardi A. and Lees M. R., Phys. Rev. B, 77 (2008) 140403(R).
[9] Niitaka S., Yoshimura K., Kosuge K., Nishi M. and Kakurai K., Phys. Rev. Lett., 87 (2001) 177202.
[10] Niitaka S., Kageyama H., Kato M., Yoshimura K. and Kosuge K., J. Solid State Chem., 146 (1999) 137.
[11] Stitzer K. E., Henley W. H., Claridge J. B., zur Loye H.-C. and Layland R. C., J. Solid State Chem., 164 (2002) 220.
[12] Sengupta K., Rayaprol S., Iyer K. K. and Sampathkumaran E. V., Phys. Rev. B, 68 (2003) 012411.
[13] Whangbo M.-H., Dai D., Koo H.-J. and Jobic S., Solid State Commun., 125 (2003) 413.
[14] Vidy R., Ravindran P., Fjellvåg H. and Kjekshus A., Phys. Rev. Lett., 91 (2003) 186404.
[15] Sampathkumaran E. V., Fujihara N., Rayaprol S., Madhu P. K. and Uwatoko Y., Phys. Rev. B, 70 (2004) 014437.
[16] Frésard R., Laschinger C., Kopf T. and Eyert V., Phys. Rev. B, 69 (2004) 140405(R).
[17] Takubo K., Mizokawa T., Hirata S., Son J.-Y., Fujimori A., Topwal D., Sarma D. D., Rayaprol S. and Sampathkumaran E.-V., Phys. Rev. B, 71 (2005) 073406.
[18] Sugiyama J., Nozaki H., Ikedo Y., Russo P. L., Mukai K., Andreica D., Amato A., Takami T. and Ikuta H., Phys. Rev. B, 77 (2008) 092409.
[19] Maiti K. and Sarma D. D., Phys. Rev. B, 58 (1998) 9746.
[20] Maiti K., Sarma D. D., Mizokawa T. and Fujimori A., Europhys. Lett., 37 (359) 1997; Phys. Rev. B, 57 (1998) 1572.
[21] Maiti K., Mahadevan P. and Sarma D. D., Phys. Rev. B, 59 (1999) 12457.
[22] Blaha P., Schwarz K., Madsen G. K. H., Kvasnicka D. and Luitz J., WIEN2k An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlsruhe Schwarz Technische Universität Wien, Austria) 2001, ISBN 3-9501031-1-2.
[23] Wu Z. and Cohen R. E., Phys. Rev. B, 73 (2006) 235116.
[24] Maiti K. and Singh R. R., Phys. Rev. B, 71 (2005) 161102(R); Maiti K., Singh R. R. and Medicherla V. R., Phys. Rev. B, 76 (2007) 165128.
[25] Singh R. S., Medicherla V. R. R., Maiti K. and Sampathkumaran E. V., Phys. Rev. B, 77 (2008) 201102(R).
[26] Sarma D. D., Shanthi N., Barman S. R., Hamada N., Sawada H. and Terakura K., Phys. Rev. Lett., 75 (1995) 1126; Maiti K., Phys. Rev. B, 75 (2006) 235110; 115119; 77 (2008) 212407.