

Electronic and magnetic properties of a quasi-one-dimensional spin chain system, $\text{Sr}_3\text{NiRhO}_6$

S. K. Pandey and Kalobaran Maiti*

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

(Dated: April 17, 2008)

We investigate the electronic structure of $\text{Sr}_3\text{NiRhO}_6$, a quasi-one-dimensional spin chain system using *ab initio* band structure calculations. Spin polarized calculations within GGA reveal that Ni and Rh have finite moments and they are antiferromagnetically coupled along the chain axis in the ground state. While these results obtained within the local spin density approximations provide remarkable representation of the magnetic phase, the experimentally observed insulating behavior could not be captured within this method. GGA+ U calculations show that opening up of an insulating gap requires on-site Coulomb interaction among the Rh $4d$ electrons, $U_{dd}^{Rh} \approx 2.5$ eV and the correlation among Ni $3d$ electrons, $U_{dd}^{Ni} \approx 4.5$ eV suggesting this system to be a Mott insulator. Electron correlation among d electrons leads to significant enhancement of the O $2p$ character in the energy bands in the vicinity of the Fermi level and the d bands appear at lower energies. Energy gap in the up spin density of states appears to be significantly small (~ 0.12 eV) while it is > 2 eV in the down spin density of states suggesting possibility of spin polarized conduction in the semiconducting phase.

PACS numbers: 71.27.+a, 71.20.-b, 75.20.Hr

I. INTRODUCTION

Recently, quasi-one-dimensional compounds, $AE_3MM'O_6$ (AE = alkaline earth metals such as Ca, Sr *etc.*; M and M' are transition metals) possessing rhombohedral K_4CdCl_6 structure (space group $R\bar{3}C$) have attracted a great deal of attention due to their fascinating magnetic properties.^{1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16} In this structure (see Fig. 1), MO_6 forms in trigonal prismatic geometry and $M'O_6$ forms in octahedral geometry. These two units appear alternatively along the chain direction, c -axis and are connected via face sharing as shown in the figure. It is evident that the interchain interaction is significantly weak making these compounds a quasi-one-dimensional system. It is observed that antiferromagnetic, ferromagnetic or ferrimagnetic long-range ordered phases can be achieved by tuning the intrachain magnetic coupling in these one dimension chains.^{5,6,7} In addition to such interesting properties of the quasi-one-dimensional chains, the whole system can be viewed as made off antiferromagnetic or ferromagnetic chains arranged in a triangular lattice. Numerous studies based on tailoring the composition of these geometrically frustrated systems reveal plethora of novel phases such as spin liquid phase, partially disordered antiferromagnetic phase *etc.*^{2,3,4,5,6}

In this paper, we report our results on the electronic structure of $\text{Sr}_3\text{NiRhO}_6$ using full potential linearized augmented plane wave method. This compound exhibits ferrimagnetic intrachain ordering below 45 K. Further lowering in temperature leads to partially disordered antiferromagnetic phase below 10 K.⁶ Interestingly, analogous compound $\text{Sr}_3\text{NiPtO}_6$ exhibits spin-liquid behavior. While it is difficult to capture disorder effect and/or spin liquid phase using such *ab initio* band structure calcula-

tions, $\text{Sr}_3\text{NiRhO}_6$ is a good starting point to understand the intrachain coupling and associated ground state properties.

Our results clearly establish that the ground state of this compound consists of magnetic Ni and Rh ions which are antiferromagnetically coupled along the c -axis. To capture the insulating transport consistent with experimental observations, one needs to consider the on-site Coulomb interaction among Ni $3d$ and Rh $4d$ electrons in addition to the intrachain antiferromagnetic (IAFM) coupling, which suggests that this compound is a Mott insulator. On-site Coulomb interaction among Rh $4d$ electrons is found to be lower (about 60%) than that found for Ni $3d$ electrons as expected due to larger radial extension of the Rh $4d$ orbitals.

II. COMPUTATIONAL DETAILS

The spin polarized GGA (generalized gradient approximation) and GGA+ U (U = on-site Coulomb repulsion strength) electronic structure calculations were carried out using *state-of-the art* full potential linearized augmented plane wave (FPLAPW) method.¹⁷ The lattice parameters and atomic positions used in the calculations are taken from literature.⁸ The Muffin-Tin sphere radii were chosen to be 2.33, 2.19, 2.01, and 1.78 a.u. for Sr, Ni, Rh, and O atoms, respectively. For the exchange correlation functional, we have adopted recently developed GGA form of Wu *et al.*¹⁸ The on-site Coulomb interactions were considered within LSDA+ U (LSDA = local spin density approximation) formulation of Anisimov *et al.*¹⁹ The calculations were performed by varying on-site Coulomb interaction among Ni $3d$ electrons, U_{dd}^{Ni} and Rh $4d$ electrons, U_{dd}^{Rh} . The convergence was achieved by con-

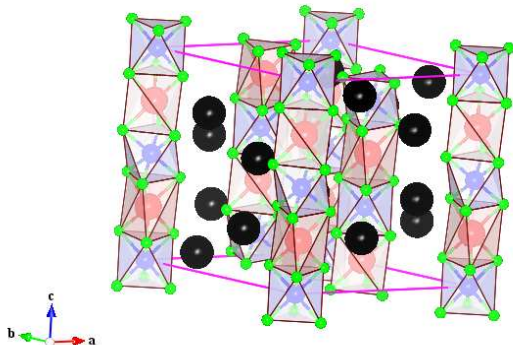


FIG. 1: (Color online) The unit cell of $\text{Sr}_3\text{NiRhO}_6$. Sr is represented by largest symbols (black). Gradually decreasing sized symbols represent Ni (pink), Rh (blue) and O (green), respectively.

sidering 512 k points within the first Brillouin zone and the error bar for the energy convergence was set to be smaller than 10^{-4} Ryd/cell.

III. RESULTS AND DISCUSSIONS

The crystal structure of $\text{Sr}_3\text{NiRhO}_6$ is hexagonal as shown in Fig. 1, where the Sr, Ni, Rh, and O ions are denoted by spheres of decreasing size. It is evident from the figure that the Ni and Rh ions are surrounded by six oxygen ions forming trigonal prism and octahedron, respectively. The trigonal prisms and octahedra are connected by face sharing and form the chains along the c -axis. If the axis system is defined such that z -axis is along c -axis and x - and y -axis are in the ab -plane, both Ni 3d and Rh 4d orbitals defined in this axis system will not be degenerate due to the corresponding crystal field effect. There will be three bands consisting of d_0 , $d_{\pm 1}$ and $d_{\pm 2}$ orbitals. The energy separation and the location of the bands in the energy axis will depend on the type of crystal field is applicable as discussed later in the text.

In Fig. 2, we show the partial density of states (PDOS)

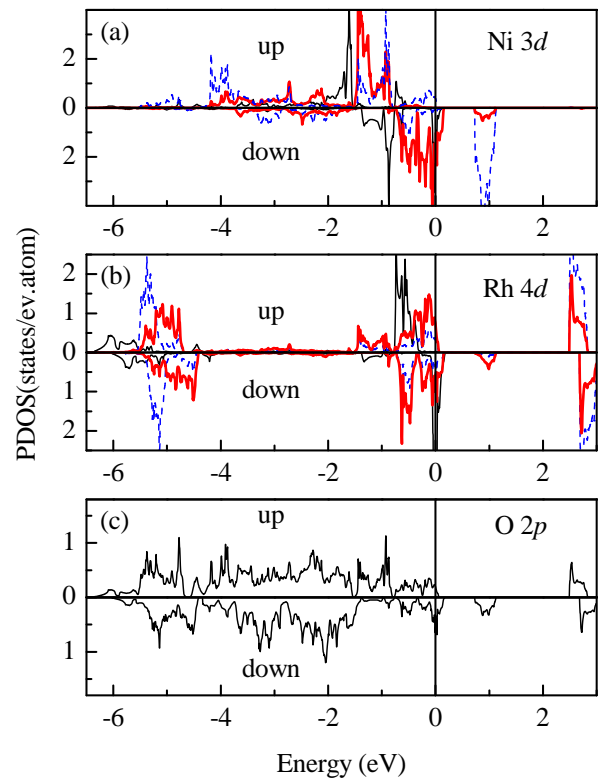


FIG. 2: Color online) The partial density of states (PDOS) corresponding to d_0 (thin solid lines), $d_{\pm 1}$ (dashed lines) and $d_{\pm 2}$ (thick solid lines) orbitals for (a) Ni and (b) Rh obtained from spin-polarized GGA calculation when Ni and Rh are ferromagnetically coupled. (c) O 2p PDOS.

corresponding to Ni 3d, Rh 4d and O 2p electronic states obtained from GGA calculations, where Ni and Rh are ferromagnetically coupled. The band splitting due to the crystal field as discussed above is visible clearly in the figure. In Fig. 2(a), the energy range above -2 eV is essentially contributed by Ni 3d electronic states. The lower energy region (-4 to -2 eV) contains very low intensity of Ni 3d PDOS and has dominant O 2p contributions. The energy distributions of the density of states (DOS) corresponding to both Ni 3d and O 2p states appear similar. These results suggest that the DOS in -4 to -2 eV range can be attributed to bonding states arising from Ni 3d and O 2p hybridizations and the antibonding states with dominant Ni 3d character appear above -2 eV.

The DOS in the energy ranges -6.3 to -4.4 eV and -1.5 to 0 eV correspond to Rh 4d-O 2p bonding and antibonding bands, respectively. The intensity of Rh 4d PDOS is almost similar in these two regions, with negligible con-

tribution in the energy region of -4.4 to -1.5 eV (see Fig. 2(b)). Two distinct features are observed in Fig. 2. (i) The energy separation between bonding and antibonding bands arising due to Ni 3d-O 2p hybridizations is significantly smaller than the energy separation between the bonding and antibonding Rh 4d-O 2p bands. (ii) The bonding and antibonding Ni 3d-O 2p bands have dominant O 2p and Ni 3d character, respectively. However, the mixing of Rh 4d and O 2p characters in the Rh 4d-O 2p hybridization is much stronger. These observations clearly demonstrate the stronger O 2p-Rh 4d hybridization presumably due to larger radial extension of the 4d orbitals compared to the 3d orbitals. Such large overlap integral, t leads to larger separation of the bonding and antibonding bands. However, the bandwidth of the individual bands does not appear to increase.

In addition, it is evident from Fig. 2(a) that up-spin channel of Ni 3d states is almost fully occupied, whereas down-spin channel is partially occupied. Major contribution in the unoccupied level comes from $d_{\pm 1}$ orbitals. In the case of Rh 4d states, DOS corresponding to both the spin states are partially occupied and thus, contribute to the unoccupied DOS.

The GGA calculations for ferromagnetic (FM) intrachain coupling converged to the metallic ground state in sharp contrast to the experimentally observed insulating behavior in this compound. Moreover, the total magnetic moment per formula unit (fu) obtained from this calculation is about $2.85 \mu_B$, which is much larger than the experimentally estimated value of $\sim 1 \mu_B$.⁶ The magnetic moment centered at Ni and Rh sites are $1.55 \mu_B$ and $0.43 \mu_B$, respectively. Magnetic moment centered at the oxygen sites is found to be $0.13 \mu_B$, which is large and induced by the Ni 3d and Rh 4d moments.

It is evident from the magnetic moments that if Ni and Rh are antiferromagnetically coupled, the total magnetic moment would match with the experimental results. In order to investigate such possibility, we have calculated the ground state energies and wavefunctions corresponding to antiferromagnetic coupling between Ni 3d and Rh 4d moments. Interestingly, the calculated ground state energy is found to be 27 meV/fu lower than that of FM state. The calculated total magnetic moment comes out to be $1.04 \mu_B$ /fu. Both these findings provide remarkable representation of the experimental magnetization data.⁶ The calculated magnetic moments for Ni and Rh are $1.31 \mu_B$ and $-0.36 \mu_B$, respectively. The moment centered at oxygen site is almost negligible ($0.02 \mu_B$).

The calculated Ni 3d, Rh 4d and O 2p PDOS are shown in Fig. 3. It is evident from the figure that intrachain antiferromagnetic interaction leads to significant reduction in bandwidth of all the energy bands and redistribution in spectral weight. For example, Ni 3d up spin band is almost completely filled and the Fermi level, ϵ_F is pinned at the top of the down spin band having dominant $d_{\pm 2}$ contributions and a width of about 0.5 eV while Ni 3d down spin band in Fig. 2 has a width of about 1 eV and is partially filled. The occupancy of Rh 4d up spin and

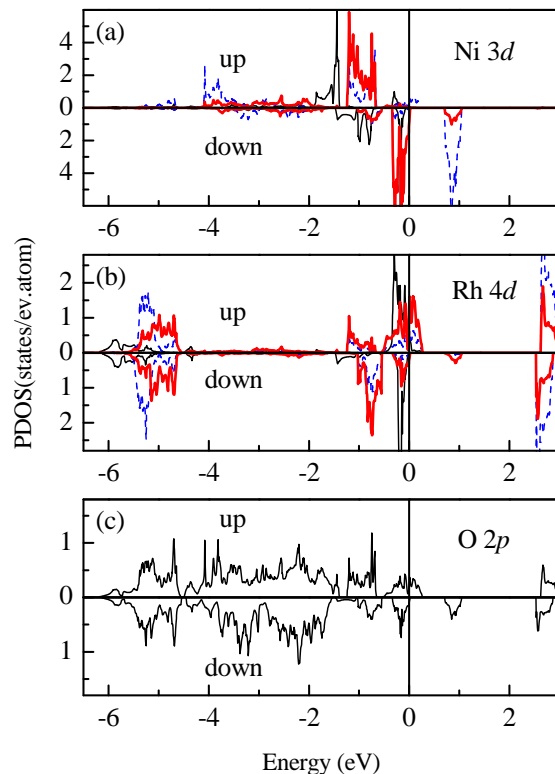


FIG. 3: (Color online) The partial density of states (PDOS) corresponding to d_0 (thin solid lines), $d_{\pm 1}$ (dashed lines) and $d_{\pm 2}$ (thick solid lines) orbitals for (a) Ni and (b) Rh obtained from spin-polarized GGA calculation when intrachain Ni and Rh are antiferromagnetically coupled. (c) O 2p PDOS.

down spin PDOS exhibit spectral distribution opposite to that observed in Fig. 2 as expected due to antiferromagnetic coupling. In this case also the bands are narrower than those observed in Fig. 2. The O 2p contribution at the Fermi level is dominant for up spin while in the ferromagnetic case it was down spin.

All the above results clearly establish that the LSDA approach is adequate to capture the magnetic phase in this system. Although, there is significant spectral weight redistributions observed for different magnetic configurations, both these calculations converge to metallic ground state in contrast to the experimental studies.

It is well known that such *ab initio* calculations often underestimate the on-site Coulomb correlation energy, which plays significant role in determining the electronic properties of d and f electron systems.²⁰ The consideration of on-site Coulomb interaction among the d electrons (U_{dd}) under GGA+ U formulation is expected to improve

the situation. Thus, we have carried out GGA+ U calculations for different values of U_{dd} corresponding to Ni 3d electrons, which is defined as U_{dd}^{Ni} and Rh 4d electrons, which is defined as U_{dd}^{Rh} . The calculations were carried out considering the intrachain antiferromagnetic coupling.

The calculated band gaps in the vicinity of ϵ_F for up spin and down spin density of states are shown in Fig. 4. It is evident from the figure that consideration of the electron correlation for both Ni 3d and Rh 4d electrons helps to achieve the insulating phase. We have shown two types of results in the figure, (i) the dependence of the band gap as a function of U_{dd}^{Ni} for a fixed value of $U_{dd}^{Rh} = 3$ eV and (ii) band gap as a function of U_{dd}^{Rh} for a fixed value of $U_{dd}^{Ni} = 5.5$ eV. In the up spin channel (see Fig. 4(a)), it is evident that an increase in U_{dd}^{Ni} does not lead to insulating phase till $U_{dd}^{Ni} = 4$ eV. An increase in U_{dd}^{Ni} above 4 eV provides an energy gap of about 0.12 eV. Interestingly, the band gap remains unchanged for further increase in U_{dd}^{Ni} . On the other hand, the calculations as a function of U_{dd}^{Rh} for $U_{dd}^{Ni} = 5.5$ eV, indicate gradual increase in band gap. Thus, the energy gap is essentially determined by U_{dd}^{Rh} when U_{dd}^{Ni} is kept large. The Fig. 4(a) suggests that the creation of insulating ground state requires U_{dd}^{Rh} to be at least 2.6 eV. Since the Coulomb repulsion strength depends inversely on the separation of the two electrons, the strength of on-site Coulomb interaction is sensitive to the radial extension of the wave functions. The present result of U_{dd}^{Ni} larger than U_{dd}^{Rh} is consistent with this behavior.

Calculations for the down spin channel exhibit gradual increase in band gap with the increase in U_{dd} for both Ni 3d and Rh 4d electrons. The magnitude of the gap in this case is always much higher (> 2 eV) than that (< 1 eV) observed for up spin density of states. It is thus clear that various electronic properties of this compound will essentially be controlled by electronic density of states in the up spin channel.

In order to investigate the character of the electronic states in the valence band, we show the calculated PDOS for $U_{dd}^{Ni} = 5$ eV and $U_{dd}^{Rh} = 3$ eV in Fig. 5. All the bands are significantly modified due to the spectral weight transfer from ϵ_F to the energy region away from it. Ni 3d $_{\pm 1}$ contributions exhibit significant band narrowing. The up spin bands appear around -5.8 eV and the down spin ones around 2.5 eV. The contributions from other Ni 3d orbitals appear between -2 eV to -5 eV. Interestingly, the consideration of U_{dd}^{Ni} leads to a significant increase of Ni 3d character at higher energies. Thus the O 2p contributions relative to Ni 3d become significantly high in the vicinity of the Fermi level.

Consideration of the on-site Coulomb interaction among Rh 4d electrons reveals large effect on the density of states distribution. In the GGA calculation d_0 was almost fully occupied and there was a significant contribution of $d_{\pm 1}$ and $d_{\pm 2}$ orbitals within 0.28 eV of ϵ_F in the unoccupied up spin channel as evident from Fig. 3(b). This trend is reversed in GGA+ U calculations,

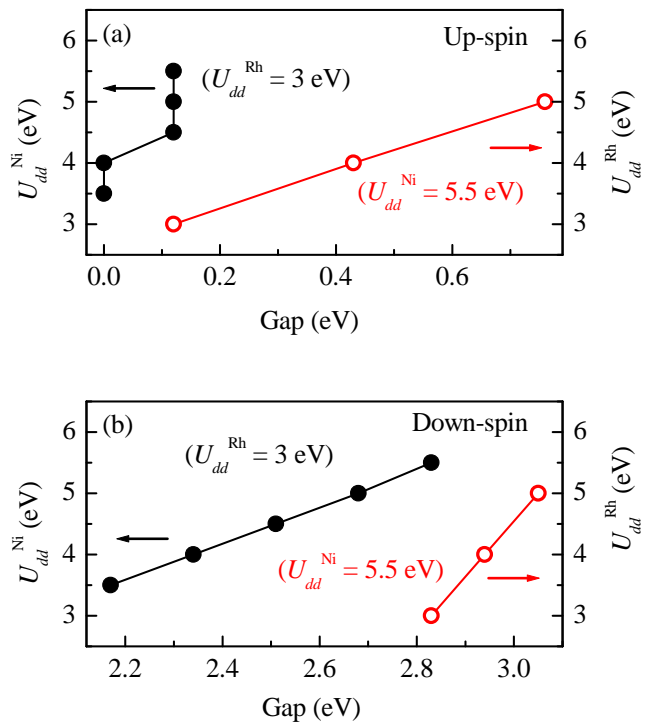


FIG. 4: (Color online) On-site Coulomb interaction among Ni 3d (U_{dd}^{Ni}) and Rh 4d (U_{dd}^{Rh}) electrons vs. insulating gap for (a) up-spin and (b) down-spin channels. Two cases are considered: (i) U_{dd}^{Rh} is fixed at 3 eV and U_{dd}^{Ni} varied from 3.5 to 5.5 eV (solid circles) and (ii) U_{dd}^{Ni} is fixed at 5.5 eV and U_{dd}^{Rh} varied from 3 to 5 eV (open circles).

where region within 0.75 eV above the ϵ_F is contributed by the electronic states having d_0 character. The electronic states below ϵ_F are contributed by $d_{\pm 1}$ and $d_{\pm 2}$ orbitals.

Despite the fact that the Ni 3d PDOS appear far away from ϵ_F , it has finite contribution in the vicinity of ϵ_F . This is evident in the rescaled Ni 3d PDOS ($\times 15 + 1$) shown in Fig. 5(a) by dot-dashed line. Interestingly, the energy distribution of these density of states closely follows the distribution observed in Rh 4d and O 2p PDOS. This clearly manifests the effect of hybridization between Ni 3d and Rh 4d states via O 2p states. Most interestingly, the gap in the up spin channel is much smaller than that found in down spin channel. Thus, this system provides an unique example of a semiconductor, where the electronic conduction is spin polarized. *While half-metallic materials have long been investigated due to spin polarized conduction of charge carriers in this system.*

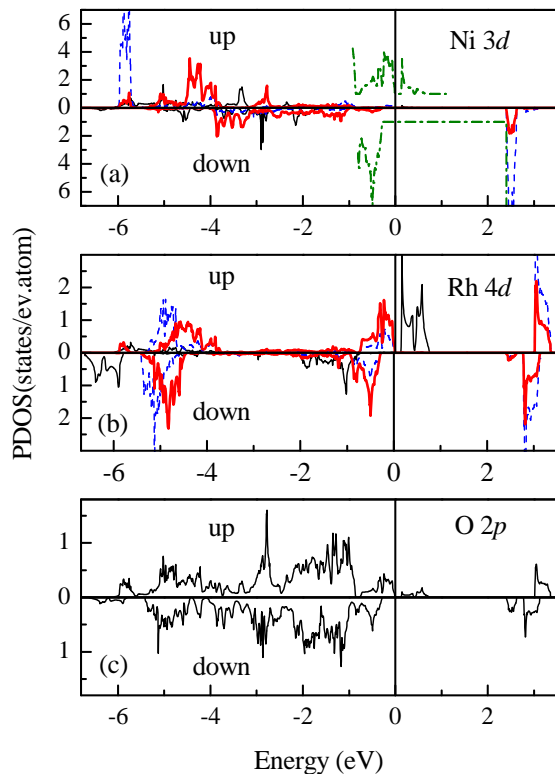


FIG. 5: (Color online) The partial density of states (PDOS) corresponding to d_0 (thin solid lines), $d_{\pm 1}$ (dashed lines) and $d_{\pm 2}$ (thick solid lines) orbitals for (a) Ni and (b) Rh obtained from spin-polarized GGA+ U calculation ($U_{dd}^{Ni} = 5$ eV and $U_{dd}^{Rh} = 3$ eV) when intrachain Ni and Rh are antiferromagnetically coupled. (c) O $2p$ PDOS.

This compound manifests properties that can be more useful in the semiconductor industry, where spin based technology is envisaged.

Now, we discuss the manifestation of intrachain antiferromagnetic coupling and Coulomb correlation in the band structure along different high symmetry directions of the Brillouin zone. The dispersion curves corresponding to different bands for FM, IAFM and IAFM considering $U_{dd}^{Ni} = 5$ and $U_{dd}^{Rh} = 3$ eV for both the spin channels are plotted in Fig. 6. The zero in the energy scale indicates ϵ_F . In the ferromagnetic solution, the up spin bands along ΓM and ΓA directions do not cross the Fermi level, while the down spin bands cross ϵ_F in all the directions indicating half metallicity along these directions. The antiferromagnetic coupling among Ni and Rh in the chains leads to narrowing of the bands and the up spin bands cross the Fermi level in all the directions. On the other hand the down spin bands in the vicinity of ϵ_F

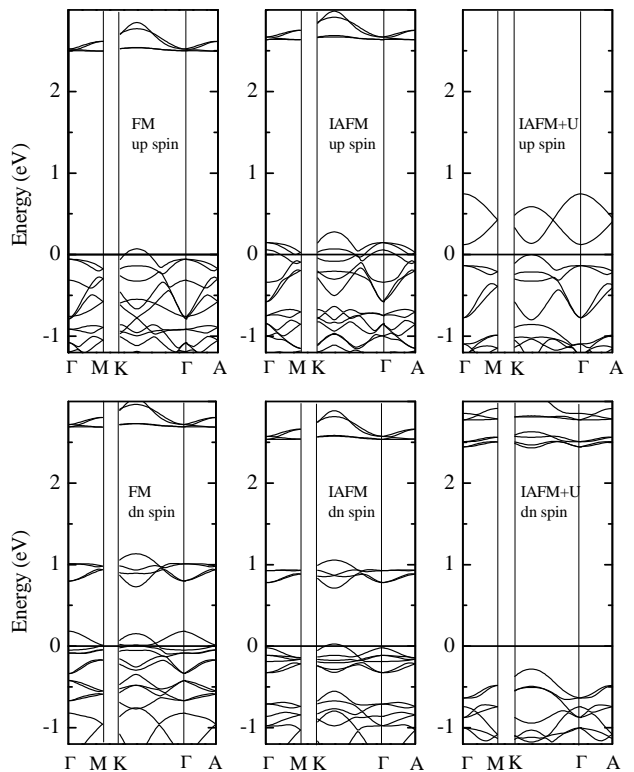


FIG. 6: Dispersion curves along different symmetry directions of the first Brillouin zone for both the spin channels. Fermi level is denoted by zero in the energy scale.

essentially appear below ϵ_F . Again, the band crossing of the down spin band is observed only along $K\Gamma$ direction suggesting half metallicity in other directions.

Inclusion of the electron correlation among the d electrons leads to significant change in the band structure. While, there is a hard gap in both the spin channels consistent with the transport behavior of this compound, the gap exhibit significant k -dependence. The gap at the high symmetry point, Γ is lower than that observed at M , K or A points. Interestingly, the dispersion of the bands close to ϵ_F appears to be larger than that observed in the uncorrelated case. This indicates that although electron correlation essentially tends to localize the electrons, the electronic states in the vicinity of the Fermi level are highly mobile.

The occupancies of different d orbitals corresponding to Ni and Rh obtained from GGA+ U ($U_{dd}^{Ni} = 5$ and $U_{dd}^{Rh} = 3$ eV) calculation are shown in Table 1. In up spin channel, all the Ni $3d$ orbitals are almost completely filled and in down spin channel, only d_0 orbital is completely

filled. The small deviations (~ 0.05) from the completely filled values can be attributed to the hybridization of Ni $3d$ orbitals with the neighboring O $2p$ orbitals. Total number of electron in the Ni $3d$ is found to be 7.91, which suggests that the valency of Ni is close to $2+$.

Table 1: The electron occupancies of d_0 , $d_{\pm 1}$, and $d_{\pm 2}$ orbitals for Ni and Rh obtained from spin polarized GGA+ U calculation.

	d_{-2}	d_{-1}	d_0	d_1	d_2	Total
Ni-up	0.95	0.98	0.94	0.98	0.95	4.8
Ni-down	0.8	0.28	0.95	0.28	0.8	3.11
Rh-up	0.65	0.5	0.21	0.5	0.65	2.51
Rh-down	0.66	0.52	0.82	0.52	0.66	3.18

In the case of Rh $4d$ orbitals, both the spin channels are partially occupied. Our calculations exhibit 5.69 electrons in the Rh $4d$ orbitals. If we consider O in $2-$ and Sr in $2+$ states, then charge neutrality condition demands Rh to be in $4+$ state, which corresponds to 5 electrons in the $4d$ orbitals. The extra 0.69 electrons can be attributed to strong hybridization of Rh $4d$ orbitals with the neighboring O $2p$ orbitals.

The calculated magnetic moments for Ni and Rh ions are $1.69 \mu_B$ and $-0.68 \mu_B$, respectively, with almost negligible contribution from oxygen ($0.01 \mu_B$). The total magnetic moments per formula unit, including the contribution of $-0.07 \mu_B$ from the interstitial region, is found to be about $1 \mu_B$ consistent with the experimental results.⁶

In order to understand the possible cause for IAFM interaction between Ni and Rh spins, we show the schematic crystal field split energy level diagram for both Ni and Rh obtained from spin unpolarized GGA calculation by considering centers of gravity of d_0 , $d_{\pm 1}$, and $d_{\pm 2}$ PDOS is shown in Fig. 7. It is evident from the figure that d_0 orbital has lowest energy for both Ni and Rh. However, next energy levels consist of different orbitals. In Ni, next level corresponds to $d_{\pm 1}$ orbitals, whereas in Rh it is $d_{\pm 2}$ orbitals. The separation of Rh $d_{\pm 2}$ and $d_{\pm 1}$ is found to be ~ 0.7 eV, which is about double of the Hund's coupling energy (J_H) of Rh $4d$ electrons estimated from spin polarized GGA calculation. On the other hand the energy separation of Ni d_0 , $d_{\pm 1}$, and $d_{\pm 2}$ orbitals are found to be ~ 0.3 eV, which is about one fifth of the estimated value of J_H for Ni $3d$ electrons.

As discussed above, Ni is in $2+$ state leading to $S = 1$ state. Rh^{4+} has 5 electrons in the $4d$ orbitals. The schematic diagram clearly shows that Rh atoms will be in low-spin ($S=1/2$) state with 2 electrons occupying d_0 orbital and the other 3 electrons will occupy $d_{\pm 2}$ orbitals making them more than half-filled. It is well known that in such a case, the interacting electrons via oxygen $2p$ orbitals (superexchange interaction) favor antiparallel coupling in the ground state.²¹

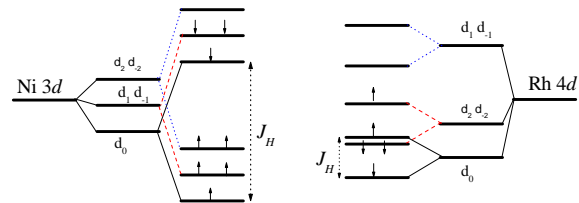


FIG. 7: (Color online) Schematic energy level diagram of d_0 , $d_{\pm 1}$, and $d_{\pm 2}$ orbitals for Ni^{2+} and Rh^{4+} showing antiferromagnetic coupling as the possible ground state.

IV. CONCLUSIONS

In conclusion, we studied the electronic and magnetic properties of $\text{Sr}_3\text{NiRhO}_6$ using *ab initio* spin polarized band structure calculations within GGA and GGA+ U . The calculations for intrachain antiferromagnetic coupling exhibit the lowest energy. The magnetic moments of Ni and Rh ions were found to be $\sim 1.7 \mu_B$ and $-0.7 \mu_B$, respectively, with a total moment of about $1 \mu_B$. All these results corresponding to the magnetic phase provide a remarkable representation of the experimental results.

The insulating phase observed in transport measurements could not be captured within GGA suggesting importance of electron correlation. GGA+ U calculation reveals that the critical values of Coulomb correlation strength to open up the insulating gap are ~ 4.5 and ~ 2.5 eV for Ni $3d$ and Rh $4d$ electrons, respectively. The inclusion of electron correlation leads to significant change in character of the energy bands. The feature close to ϵ_F exhibits enhancement of O $2p$ character, while the d character enhances at higher energies. Interestingly, the band gap in up spin channel is found to be significantly small (~ 0.12 eV) compared to that observed (> 2 eV) in the down spin channel indicating possibilities of spin polarized conduction in the semiconducting phase.

V. ACKNOWLEDGEMENTS

The authors acknowledge Prof. E.V. Sampathkumar, TIFR, India for drawing our attention towards

this compound and useful discussions.

-
- * Electronic mail: kbmaiti@tifr.res.in
- ¹ S. Niitaka, H. Kageyama, M. Kato, K. Yoshimura, and K. Kosuge, *J. Solid State Chem.* **146**, 137 (1999).
 - ² E. V. Sampathkumaran and A. Niazi, *Phys. Rev. B* **65**, 180401(R) (2002).
 - ³ D. Flahaut, S. Hébert, A. Maignan, V. Hardy, C. Martin, M. Hervieu, M. Costes, B. Raquet, and J.M. Broto, *Eur. Phys. J B* **35**, 317 (2003).
 - ⁴ S. Agrestini, C. Mazzoli, A. Bombardi, and M.R. Lees, arXiv:0801.2495v1.
 - ⁵ S. Niitaka, K. Yoshimura, K. Kosuge, M. Nishi, and K. Kakurai, *Phys. Rev. Lett.* **87**, 177202 (2001).
 - ⁶ N. Mohapatra, K. K. Iyer, S. Rayaprol, and E. V. Sampathkumaran, *Phys. Rev. B* **75**, 214422 (2007).
 - ⁷ H. Wu, Z. Hu, D. I. Khomskii, and L. H. Tjeng, *Phys. Rev. B* **75**, 245118 (2007).
 - ⁸ K. E. Stitzer, W. H. Henley, J. B. Claridge, H. -C. zur Loye, and R. C. Layland, *J. Solid State Chem.* **164**, 220 (2002).
 - ⁹ K. Sengupta, S. Rayaprol, K. K. Iyer, and E. V. Sampathkumaran, *Phys. Rev. B* **68**, 012411 (2003).
 - ¹⁰ M. -H. Whangbo, D. Dai, H. -J. Koo, and S. Jovic, *Solid State Commun.* **125** 413 (2003).
 - ¹¹ R. Vidya, P. Ravindran, H. Fjellvåg, and A. Kjekshus, *Phys. Rev. Lett.* **91**, 186404 (2003).
 - ¹² E. V. Sampathkumaran, N. Fujiwara, S. Rayaprol, P. K. Madhu, and Y. Uwatoko, *Phys. Rev. B* **70**, 014437 (2004).
 - ¹³ R. Frésard, C. Laschinger, T. Kopp, and V. Eyert, *Phys. Rev. B* **69**, 140405(R) (2004).
 - ¹⁴ H. Wu, M. W. Haverkort, Z. Hu, D. I. Khomskii, and L. H. Tjeng, *Phys. Rev. Lett.* **95**, 186401 (2005).
 - ¹⁵ K. Takubo, T. Mizokawa, S. Hirata, J.-Y. Son, A. Fujimori, D. Topwal, D. D. Sarma, S. Rayaprol, and E.-V. Sampathkumaran, *Phys. Rev. B* **71**, 073406 (2005).
 - ¹⁶ J. Sugiyama, H. Nozaki, Y. Ikedo, P. L. Russo, K. Mukai, D. Andreica, A. Amato, T. Takami, and H. Ikuta, *Phys. Rev. B* **77**, 092409 (2008).
 - ¹⁷ P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2.
 - ¹⁸ Z. Wu and R. E. Cohen, *Phys. Rev. B* **73**, 235116 (2006).
 - ¹⁹ V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk and G. A. Sawatzky, *Phys. Rev. B* **48**, 16929 (1993).
 - ²⁰ V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).
 - ²¹ J. B. Goodenough, in *Magnetism and the Chemical Bond* (Interscience Publishers, New York-London, 1963).