Electronic and Microscopic Properties of Spin ½ System, $CuInO(VO_4)$

Dilruba Khanam[1], Asif Iqbal [1], and Badiur Rahaman [1]*

[1]Department of Physics, Aliah University, Kolkata-700160

Email: badiur.rahaman@gmail.com

Abstract

We present first principles density functional theory (DFT) calculations within the generalized gradient approximation for the exchange-correlation functional in order to gain microscopic understanding, electronic and microscopic properties of $CuInO(VO_4)$. We discuss explicitly the electronic properties, nature of the exchange paths and estimate magnetic exchange interactions. Focusing on the calculated magnetic interactions and electronic structure of $CuInO(VO_4)$ puts it in the class of weakly coupled low dimensional antiferromagnetic tetramer with spin S=1/2.

Keywords: Electronic Structure, Magnetic Exchange Interaction, Wannier Function, Microscopic Modelling

1. Introduction

The importance of low dimensional quantum spin systems is due to quantum fluctuation in the low energy regime. Spin fluctuation is large for small spin and low dimensional systems. Odd- and even-leg ladders, dimer, alternating chain, spin-peierls are the different class of low dimensional quantum spin systems. Out of these dimer[1], spin ½ or spin 1 alternating Heisenberg antiferromagnetic (AFM) chains[2,3], even-leg ladders[4], spin-peierls[5] are spin gap systems whereas odd leg ladders[6], spin ½ uniform Heisenberg AFM chain[2,3] are spin gapless systems. Like dimer, tetramer chain systems have a finite gap between singlet ground state and triplet exited state. $CuInO(VO_4)$ is the class of low dimensional quantum spin system with spin S=1/2. The first-principles modelling of materials, which takes into account the chemistry and structural information accurately, turns out to be a useful tool in this context. This approach has been immensely successful in the modelling of various different spin compounds[7]. In this study, considering the case of $CuInO(VO_4)$, through first-principles calculations we establish that $CuInO(VO_4)$ behaves as weakly coupled spin tetramer with alternating nearest-neighbour.

2. Crystal Structure

$CuInO(VO_4)$ has monoclinic symmetry with space group $P2_1/c$ (No. 14). Unit cell of $CuInO(VO_4)$ consisting of 8 formula units. There are two inequivalent Cu atoms, Cu1 and Cu2 which are at the centre of a distorted octahedra constructed by six O-atoms. The lattice parameters of the compound are a=8.793Å, b=6.1542Å and c= 15.262Å, β=106.69º.[8] In $CuInO(VO_4)$, Cu1O6 and Cu2O6 octahedra share a common edge and form a tetramer Cu2-Cu1-Cu1-Cu2 chain. The tetramers are connected by VO4 tetrahedra. The voids and channels are occupied by In atoms. The different atoms are represented by

different colours as shown in the Figure 1. The various Cu-O distances (in Å) and angles (in degree) in Cu1O6 & Cu2O6 distorted octahedral of $CuInO(VO_4)$ is shown in Figure 2.

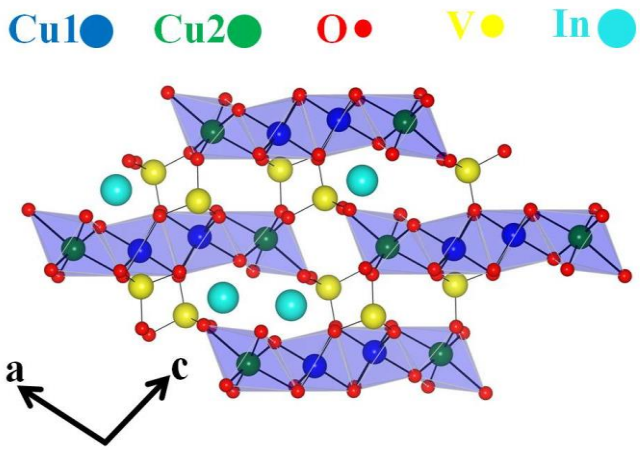

Figure 1: The crystal structure of $CuInO(VO_4)$ in distorted octahedral representation in ac-plane. The octahedral are connected by edge sharing.

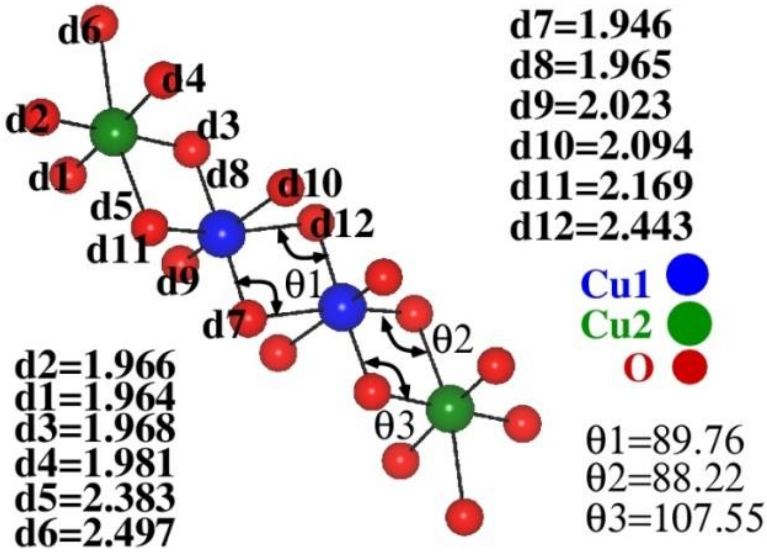

Figure 2: The various Cu-O distances (in Å) and angles (in degree) in Cu1O6 & Cu2O6 distorted octahedral in $CuInO(VO_4)$.

3. Electronic Structure

We used first principles density functional theory (DFT)[9] calculations within the GGA [10] for the exchange-correlation functional to investigate the microscopic understanding of $CuInO(VO_4)$. We have

used Vienna An initio Simulation Package (VASP)[11] based on plane wave basis as well *N*-th order MTO (NMTO) [12] and linear MTO (LMTO) [13] which are based on muffin-tin orbital (MTO).

The non-spin polarized density of state (DOS) of the compound $CuInO(VO_4)$ is shown in Figure 3. The black colour at Fermi level in the DOS represents Cu-d_{x2-y2} which is pronouncedly mixed with O-p and V-d states. Therefore, the electronic and magnetic properties of the title compound are mainly depending on the Cu-d_{x2-y2} state.

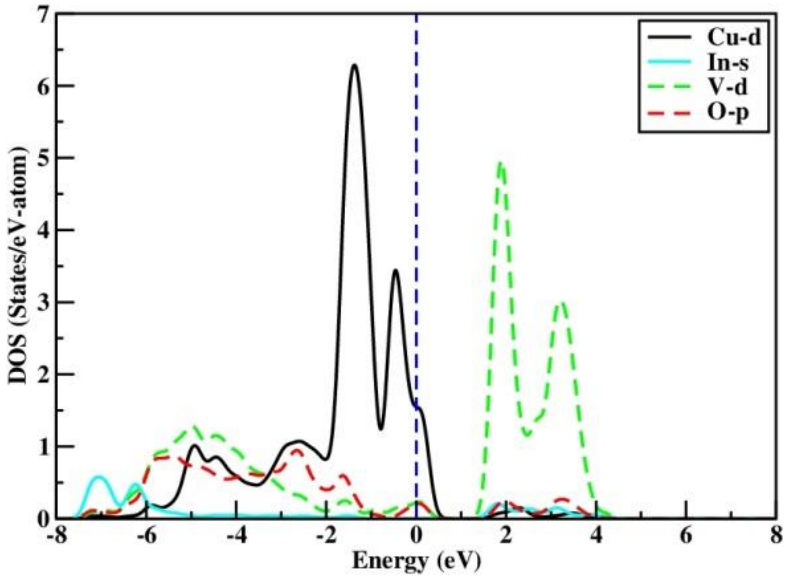

Figure 3: Electronic density of states (DOS) within GGA of exchange-correlation has been calculated using density functional theory of $CuInO(VO_4)$. Energy axis is plotted with respect to Fermi energy.

The corresponding spin-polarized density of state is shown in Figure 4 where Cu-d, O-p, V-d and In-s states are represented by black, red, green and cyan colours respectively and energy axis is plotted with respect to Fermi energy. All the d-states of Cu are completely filled in the majority and minority spin-channels except the minority channel of Cu-d_{x2-y2} which is half filled due to the crystal-field splitting of the distorted octahedra. Therefore, Cu has the nominal Cu^{2+} or d^9 valence. The O has also nominal O^{2-} valence states because O-p state is found to be mostly occupied. The finite hybridization of O-p and V-d states with Cu-d states close to Fermi level suggesting that the super-exchange path of magnetic interaction between two Cu sites are mediated by O and V atoms. The oxidation state of In and V ions are 3+ and 5+ respectively. The magnetic moment at Cu, O and V sites are found to be 0.72 μ_B, 0.18μ_B and 0.1μ_B respectively with a total magnetic moment of 1 μ_B per formula unit.

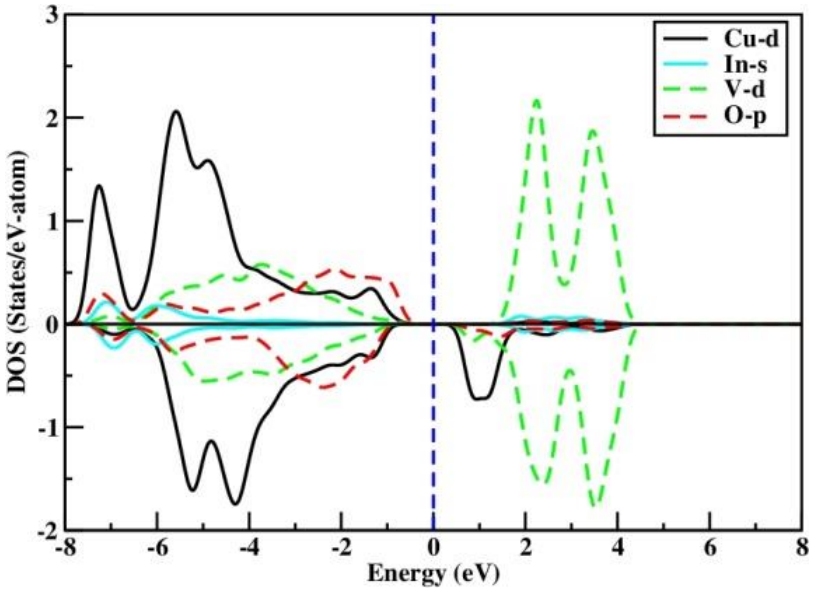

Figure 4: The spin polarized density of state for $CuInO(VO_4)$. The up channel of Cu-d is completely filled while the down channel of Cu-d is partially filled. Energy axis is plotted with respect to Fermi energy.

4. Magnetic Interactions

We have used Nth order Muffin Tin Orbital (NMTO) based downfolding technique to find out the various Cu-Cu magnetic exchanges in the compound. Using this technique, Cu-d_{x2-y2} only wannier function is constructed by keeping active only the Cu-d_{x2-y2} degrees of freedom and downfolding all the degrees of freedom associated with O, V, In and the Cu. This procedure gives renormalization of Cu-d_{x2-y2} orbital due to hybridization from O-p, V-d and In-s and the other Cu-d orbitals. The real space representation of the Hamiltonian in the effective Cu-d_{x2-y2}wannier function basis provides the effective Cu-d_{x2-y2} –Cu-d_{x2-y2} hopping interactions. Figure 6 represents the effective Cu-d_{x2-y2} wannier function of $CuInO(VO_4)$. The central part is shaped according to d_{x2-y2} symmetry whereas the tail sitting at the neighbouring oxygen sites are shaped according to O-p_x/p_y symmetries, indicating strong pd_σ bonding between Cu and O. Relatively large contribution of wannier orbitals on O- and V-sites indicate that the intrachain Cu1-Cu1 interaction is strongly mediated by the O atoms while intercahin Cu1-Cu2 interaction is mediated by the V atoms respectively. pdπ antibonds formed between Cu-d_{x2-y2} & O-p with somewhat stronger weights at O sites compared to that at V sites implies larger hybridization with O than V.

The paths for dominant magnetic interactions for $CuInO(VO_4)$ is shown in Figure 5. We see that in $CuInO(VO_4)$, the intra-tetramer nearest neighbour interaction t1 is mediated by Cu1 d-O p-Cu1 d and Cu1 d-O p-V d-O p-Cu1 d super-exchange paths while t2 is mediated by Cu1 d-O p-Cu2 d super-exchange path. The inter-tetramer interactions t3 and t4 are mediated by Cu d-O p-V d-O p-Cu d and Cu d-O p-In s-O p-Cu d super super-exchange paths respectively.

Using superexchange formula $4t^2/U$, we can estimate the magnetic interactions between the magnetic ions from the values of hopping interaction with a choice of Hubbard parameter *U*. However, this provides

information of only the antiferromagnetic contributions. So, we used total energy calculation of different spin arrangements[14] and found out the magnetic exchange interactions by mapping the DFT energies to that of the Heisenberg model. Beyond GGA, the missing missing correlation energy at Cu sites is taken in terms of GGA+U calculations[15]. We have calculated the dominant magnetic exchanges of $CuInO(VO_4)$ compound using U=6eV[16], which is shown in Table I. The positive sign of interactions indicates antiferromagnetic whereas negative sign implies ferromagnetic nature of exchange interactions.

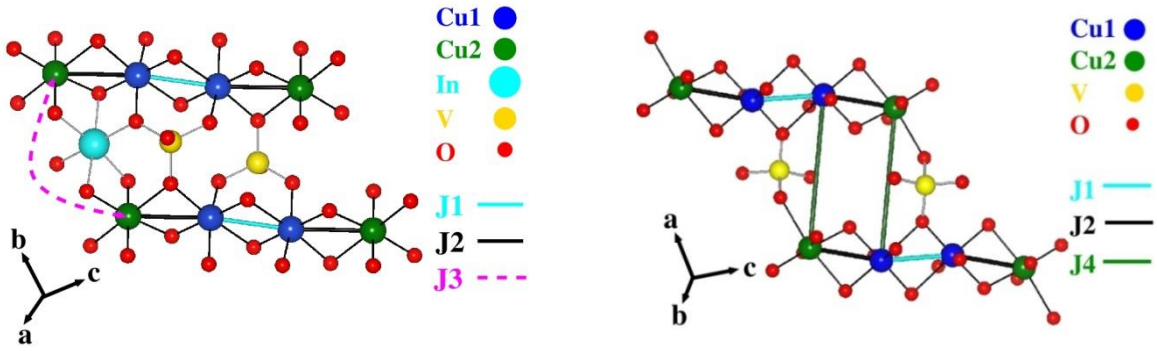

Figure 5: The exchange paths for various magnetic interactions.

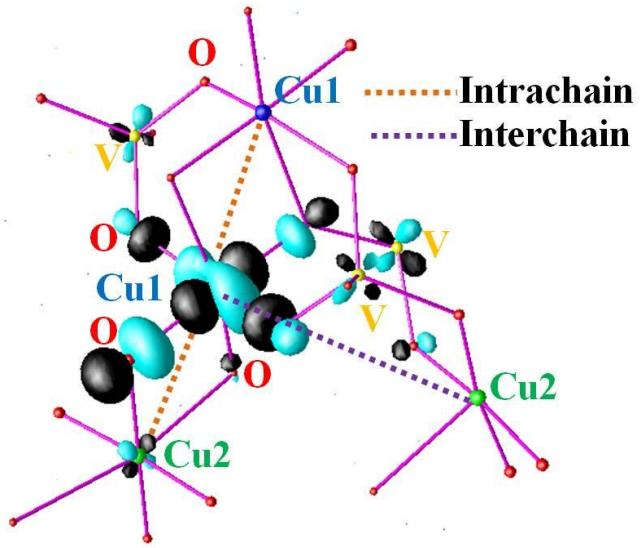

Figure 6: Wannier orbital for $CuInO(VO_4)$ compound**.**

TABLE 1: The values of dominant hopping and magnetic exchange interactions in $CuInO(VO_4)$

Interaction Type	Bond-distance (Å)	Path and Bond-angle	Hopping Intn. t's (meV)	$J=4t^2/U$ (meV)	Exchange Intn. J's (meV)
Intrachain	3.117	Cu1-O-Cu1; 89.76°	t1=150	J1=14.9	J1=22.8
	3.17	Cu1-O-Cu2; 88.22° & 107.55°	t2=136	J2=12.3	J2=7.7
Interchain	6.15	via In	t3=30	J3=0.6	J3= −0.06
	6.58	via V	t4=60	J4=2.4	J4=3.1

5. Conclusion

From microscopic investigations we conclude that the system appears weakly coupled Cu2-Cu1-Cu1-Cu2 AFM tetramer. The strongest intrachain interaction, J1=22.8 meV between Cu1-Cu1 is an order of magnitude stronger than that of Cu1-Cu2 intrachain interaction, J2=7.7 meV. Inter-tetramer interactions are J3= −0.06meV and J4=3.1meV which are weak compared to intra-tetramer interactions. We note that calculated small value of J3 is beyond the DFT accuracy limit, and the precise numerical value may not be trustworthy. Spin fluctuation prevent the long the long rage order because the system is low dimensional. Therefore, Neel temperature (T_N) should not be very high for this system.

6. Acknowledgements

We are grateful to the authority of Aliah University for purchase and installation super-computer in the Department of Physics. We also heartily acknowledge the support of the WBDST through Grants No. 463 (Sanc.) / ST/ P/ S & T / 16G-5 / 2018 dated 14.03.2019.

REFERENCES

[1] G. S. Uhrig and H. J. Schulz, Phys. Rev. B 54, R9624 (1996).
[2] F. D. M. Haldane, Phys. Rev. Lett. 50, 1153 (1983).
[3] H. A. Bethe, Z. Phys. 71, 205 (1938).
[4] E. Dagotto, and T. M. Rice, Science 271, 618 (1996); M. Wang, M. Yi, S. Jin, H. Jiang, Y. Song, H. Luo, A.D. Christianson, C. de la Cruz, E. Bourret-Courchesne, D.-X. Yao, D.H. Lee, and R.J. Birgeneau, Phys. Rev. B 94, 041111(R) (2016).

[5] J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, Extended Linear Chain Compounds. 3, 353 (1983) (New York: Plenum).

[6] D. Schmidiger, K.Yu. Povarov, S. Galeski, N. Reynolds, R. Bewley, T. Guidi, J. Ollivier, and A. Zheludev, Phys. Rev. Lett. 116, 257203 (2016).

[7] O. S. Volkova, L. V. Shvanskaya, E. A. Ovchenkov, E. A. Zvereva, A. S. Volkov, D. A. Chareev, K. Molla, B. Rahaman, T. Saha-Dasgupta, and A. N. Vasiliev, Inorg. Chem. 55, 10692 (2016); K. V. Zakharov, E. A. Zvereva, M. M. Markina, M. I. Stratan, E. S. Kuznetsova, S. F. Dunaev, P. S. Berdonosov, V. A. Dolgikh, A. V. Olenev, S. A. Klimin, L. S. Mazaev, M. A. Kashchenko, Md. A. Ahmed, A. Banerjee, S. Bandyopadhyay, A. Iqbal, B. Rahaman, T. Saha-Dasgupta, and A. N. Vasiliev, Phys. Rev. B 94, 054401 (2016); A. N. Vasiliev, O. S. Volkova, E. A. Zvereva, A. V. Koshelev, V. S. Urusov, D. A. Chareev, V. I. Petkov, M. V. Sukhanov, B. Rahaman, and T. Saha-Dasgupta, ibid. 91, 144406 (2015); P. S. Berdonosov, E. S. Kuznetsova, V. A. Dolgikh, A. V. Sobolev, I. A. Presniakov, A. V. Olenev, B. Rahaman, T. Saha-Dasgupta, K. V. Zakharov, E. A. Zvereva, O. S. Volkova, and A. N. Vasiliev, Inorg. Chem. 53, 5830 (2014).

[8] P. Moser, V. Cirpus and W. Jung, CuInOVO4 - Single Crystals of a Copper(II) Indium Oxide Vanadate by Oxidation of Cu/In/V Alloys *Z. Anorg. Allg. Chem.* **625** 714 (1999).

[9] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[10] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[11] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).

[12] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B 62, R162 (2000).

[13] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. 53, 2571 (1984).

[14] H. J. Xiang, E. J. Kan, Su-Huai Wei, M.-H.Whangbo, and X. G. Gong, Phys. Rev. B 84, 224429 (2011).

[15] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czy˙zyk, and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993).

[16] Anatoly Koshelev et. al., Anatoly Koshelev, Elena Zvereva, Larisa Shvanskaya, Olga Volkova, Mahmoud Abdel-Hafiez, Andrey Gippius, Sergey Zhurenko, Alexey Tkachev, Dmitry Chareev, Norbert Büttgen, Martina Schädler, Asif Iqbal, Badiur Rahaman, Tanusri Saha-Dasgupta, and Alexander Vasiliev, *J. Phys. Chem. C* , 123, 29, 17933–17942 (2019).