First-principles study of crystal and electronic structures and magnetic property for $NaFe_xCr_{1-x}(WO_4)_2$ compounds

N. Tsogbadrakh[1*], L. Nyam - Ochir,[1] Kh.Tsookhuu[1] and S. C. Hong[2]

[1]*Department of Physics, School of Science,*

National University of Mongolia, University Street, Ulaanbaatar 14200, Mongolia

[2]*Department of Physics and Energy Harvest Storage Research Center, University of Ulsan,*

93, Daehak-ro, Namgu, Ulsan 680-749, Republic of Korea

E-mail address: Tsogbadrakh@num.edu.mn

We have first studied the crystal and electronic structures, and magnetic property for sodium double tungstate $NaFe_xCr_{1-x}(WO_4)_2$ (x = 0, 0.50 and 1.0) compounds using the plane wave self -consistent method within the framework of density functional theory (DFT). We show that the ground state of sodium double tungstate compounds is the antiferromagnetic (AFM) state. We emphasize that the AFM coupling on the *bc* plane is generated by the 90^0 superexchange mechanism. While the AFM coupling of the long range magnetic interaction between the layers along the a − axis is generated by the Na mediated super - superexchange mechanism.

Keywords: double tungstate, antiferromagnetism, superexchange, PWscf

1. Introduction

The crystal structure of double tungstates of the general formula $NaM(WO_4)_2$ (M = Cr and Fe) are closely related to the transition metal tungstate (MWO_4) compounds, which crystallizes in monoclinic space group P2/c (#13). The sodium compounds, however, a doubled a lattice parameter due to additional layers of Na − O polyhedra instead of each second layer with zigzag chains of MO_6 octahedra.[1,2] Therefore, they are called sodium double tungstates.

The magnetic and electron spin resonance (ESR) studies of $NaCr(WO_4)_2$ compound show the AFM ordering and strong exchange interactions.[3] Nyam - Ochir et al. experimentally showed that the $NaCr(WO_4)_2$

and $NaFe(WO_4)_2$ compounds in the AFM state provide a suitable test for the super − superexchange mechanism by the Cr^{+3}/Fe^{+3} − $O − O − Cr^{+3}/Fe^{+3}$ bonds on the *bc* plane.[4] However the mechanism of long range magnetic interaction between the layers along the a axis is not completely explained still now. But the magnetic ordering of $NaFe_xCr_{1-x}(WO_4)_2$ compounds with x = 0.25, 0.50 and 0.75 disappears by the magnetization and neutron diffraction experiments.[4]

In recent years, the theoretical studies for crystal, electronic and magnetic properties in the transition metal tungstate (MWO_4) compounds have been done using the first - principles method.[5-11]

In this paper we present the first results of crystal and electronic structures and magnetic

property for sodium double tungstate $NaFe_xCr_{1-x}(WO_4)_2$ compounds using the plane wave self - consistent method within the framework of DFT.

2. Calculation method

Our calculations are based on the plane wave self - consistent field (PWscf) method using the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE)[12] within the framework of DFT,[13,14] as implemented in the QUANTUM ESPRESSO package.[15] The interaction between the ions and valence electrons is expressed as the ultrasoft pseudopotential.[16] The following electronic states are treated as valence states: $Na(2s^2, 2p^6, 3s^1)$, $O(2s^2, 2p^4)$, $W(5s^2, 5p^6, 5d^4, 6s^2)$, $Cr(3s^2, 3p^6, 3d^5, 4s^1)$ and $Fe(3s^2, 3p^6, 3d^6, 4s^2)$ for atoms. The wave functions are expressed as plane waves up to a kinetic

energy cutoff of 30 Ry. The unit cell of $NaM(WO_4)_2$ (M = Cr and Fe) has 2 Na, 16 O, 4 W and 2 M atoms. We used the unit cell, ($2a$, b, c) and ($2a$, $2b$, c) supercells including the 24, 48 and 96 atoms respectively [See Fig. 1]. The summation of charge densities for both the unit cell and ($2a$, b, c) supercell, and ($2a$, $2b$, c) supercell is carried out using the special k-points generated by the (2x3x4) and (1x2x3) of Monkhorst - Pack meshes respectively.[17] We used the tetrahedral method[18] when we evaluate the electronic density of state (DOS). For the self - consistent cycle the total energy convergence is 10^{-8} eV. The occupation numbers of electrons are expressed Gaussian distribution function* with an electronic temperature of kT = 0.001 Ry. We performed the variable cell optimization and fixed the crystallographic angles. The atomic ionic positions are relaxed until the residual forces are less than 0.05 eV/Å.
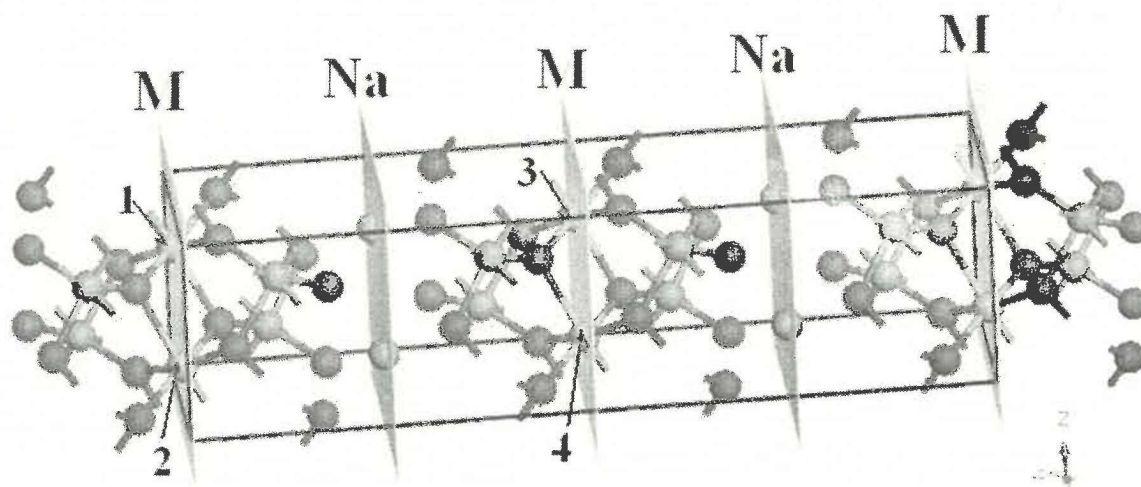

Fig.1. The (2a, b, c) supercell of NaM(WO₄)₂ (M = Cr and Fe) compounds. The greens are magnetic ions (M), The blues are tungsten atoms, The reds are oxygen atoms. The blue violets are sodium atoms.

3. Results and discussion

3.1. The unit cell of NaCr(WO₄)₂ and NaFe(WO₄)₂ compounds

The sodium double tungstate $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds contain of two magnetic ions in the unit cells. In order to determine the magnetic ground state of these compounds, we have performed the spin polarized calculations to find the magnetic energy gain ($\Delta E_{AFM-FM} = E_{AFM} - E_{FM}$) between the AFM and ferromagnetic (FM) states in all the unit cells. Our results are shown that the AFM state is favored in these sodium double tungstate compounds [Table 1], and agree with the experimental results. But the difference between the predicted and experimental values of magnetic moment for magnetic ions is large in the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds. It is therefore shown that the structural unit cell is different from the magnetic unit cells. For the structural unit cells we predicted the lattice parameters and crystallographic angle [Table 2]. The lattice parameter on the b axis increases from the experimental value up to 2%. The other lattice parameters increase up to 1%.

3.2. The electronic structure and magnetic property of NaFe_xCr_{1-x}(WO_4)_2 compounds

Nyam – Ochir et al. shown that the magnetic unit cell of $NaCr(WO_4)_2$ compound is the *(2a, 2b, c)* supercell and the magnetic experiments were performed on the polycrystal $NaFe_xCr_{1-x}(WO_4)_2$ compounds.[4] A single crystal has an atomic structure that repeats periodically across its whole volume. While a polycrystal is comprised of many individual grains. Each grain can be thought of as a single crystal, within which the atomic structure has long range order. In an isotropic polycrystal, there is no relationship between neighboring grains. Therefore there is no periodicity across a polycrystalline sample on a large enough length scale.

Therefore we first performed the spin polarization calculations of polycrystal $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds on *(2a, b, c)* supercell [Fig. 1.]: (i) $Fe_1/Cr_1(\downarrow)$, $Fe_2/Cr_2(\uparrow)$, $Fe_3/Cr_3(\uparrow)$ and $Fe_4/Cr_4(\downarrow)$ [denoted as AFM-1]; (ii) $Fe_1/Cr_1(\uparrow)$, $Fe_2/Cr_2(\downarrow)$, $Fe_3/Cr_3(\uparrow)$ and $Fe_4/Cr_4(\downarrow)$ [AFM-2]; (iii) $Fe_1/Cr_1(\uparrow)$, $Fe_2/Cr_2(\uparrow)$ $Fe_3/Cr_3(\downarrow)$ and $Fe_4/Cr_4(\downarrow)$ [AFM-3]. We have found that the most stable spin orientation is energetically AFM1 state in both the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds. The ground states of AFM2 and AFM3 states are energetically higher than that of AFM1 state by the energy difference of 4.45 (1.42) and 48.13 (26.59) meV respectively in the $NaCr(WO_4)_2$ ($NaFe(WO_4)_2$) compound. For the *(2a, b, c)* supercell approach the total energy calculations show that the magnetic energy gains ($\Delta E_{AFM-FM} = E_{AFM} - E_{FM}$) between the AFM and FM states are 23.91 and 12.88 meV/cell respectively in the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds. These values are consistent with the estimated values in the Table 1.

We extended the spin polarization calculations of polycrystal $NaFe_xCr_{1-x}(WO_4)_2$ compounds on *(2a, 2b, c)* supercell, as shown the spin orientations in the paper by Nyam – Ochir et al.[4] In this case the magnetic unit cell of $NaCr(WO_4)_2$ compound is created and the

magnetic moments are averaged. We have shown the predicted and experimental lattice parameters in the Fig. 2. For the magnetic couplings of the magnetic ions on the bc – plane, the distance between the Cr^{+3} and Cr^{+3} (Fe^{+3} and Fe^{+3}) ions is found to be 3.01 (3.21) Å in the $NaCr(WO_4)_2$ ($NaFe(WO_4)_2$) compounds. These distances are 3.04 and 3.19 Å in the experiment.[4] The experimental angles of $M^{+3} - O - M^{+3}$ couplings are 97.3 and 99.3^0 in the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ respectively. In our calculation the angles of $M^{+3} - O - M^{+3}$ couplings are determined to be 96.2 and 98.5^0 in the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ respectively. For the $NaFe_{0.5}Cr_{0.5}(WO_4)_2$ compound the distance between the Cr^{+3} and Fe^{+3} ions is found to be 3.1 Å. While the two angles of $Cr^{+3} - O - Fe^{+3}$ coupling are different and found to be 95.7 and 98.0^0.

Table 1. For the sodium double tungstate NaM(WO₄)₂ (M = Cr and Fe) compounds the magnetic energy gain (ΔE$_{AFM-FM}$ = E$_{AFM}$ - E$_{FM}$), the spin state and the magnetic moments for magnetic ions in the unit cells.

	ΔE_{AFM-FM} (meV)	Spin state	magnetic moments (μ_B)		
			m(M₁)	m(M₂)	exp[4]
Cr	-22.907	AFM	2.8212	-2.8212	1.9(3)
Fe	-12.382	AFM	4.0194	-4.0194	3.31(6)

Table 2. For the sodium double tungstate NaM(WO₄)₂ (M = Cr and Fe) compounds the lattice parameters and the crystallographic angle in the AFM state. The experimental values are measured from low temperature neutron powder diffraction.[4]

	a (Å)		b (Å)		c (Å)		β (⁰)	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
Cr	9.803	9.876	5.699	5.797	4.942	4.985	90.300	90.336
Fe	9.863	9.886	5.730	5.826	4.957	4.976	90.607	90.678

For the magnetic couplings between the layers, the distance between the $Cr^{+3} - Cr^{+3}$ ($Fe^{+3} - Fe^{+3}$) ions along the a – axis is found to be 9.88 (9.95) Å in the $NaCr(WO_4)_2$ ($NaFe(WO_4)_2$) compounds. These values are close to 10 Å.[5] For the $NaFe_{0.5}Cr_{0.5}(WO_4)_2$ compound the distance between the Cr^{+3} and Fe^{+3} ions is found to be 9.92 Å.

The electronic DOS of the sodium double tungstate $NaFe_xCr_{1-x}(WO_4)_2$ (x = 0, 0.50 and 1.0) compounds are shown in the Fig. 3. We found that the $NaCr(WO_4)_2$ and $NaFe(WO_4)_2$ compounds have a band gap of 1.04 and 1.10 eV respectively [See Fig. 3]. The Na-3s, W-6s, Cr-4s and Fe-4s states become a full empty, and their peaks are not observed in the valence band. An electron in these states is transferred to the 2p state for nearest neighbor O atoms as the selection rules. Therefore these peaks are not observed in the spectra by X-ray Emission Spectroscopy (XES) and X-ray Photoemission Spectroscopy (XPS) in experiments. For the $NaM(WO_4)_2$ (M = V and Cr) the valence band mainly consists of the O-2p state sited from -8 eV to -2 eV below the Fermi level. While for the $NaFe(WO_4)_2$ the O-2p state, which sited from -6 eV to the Fermi level.
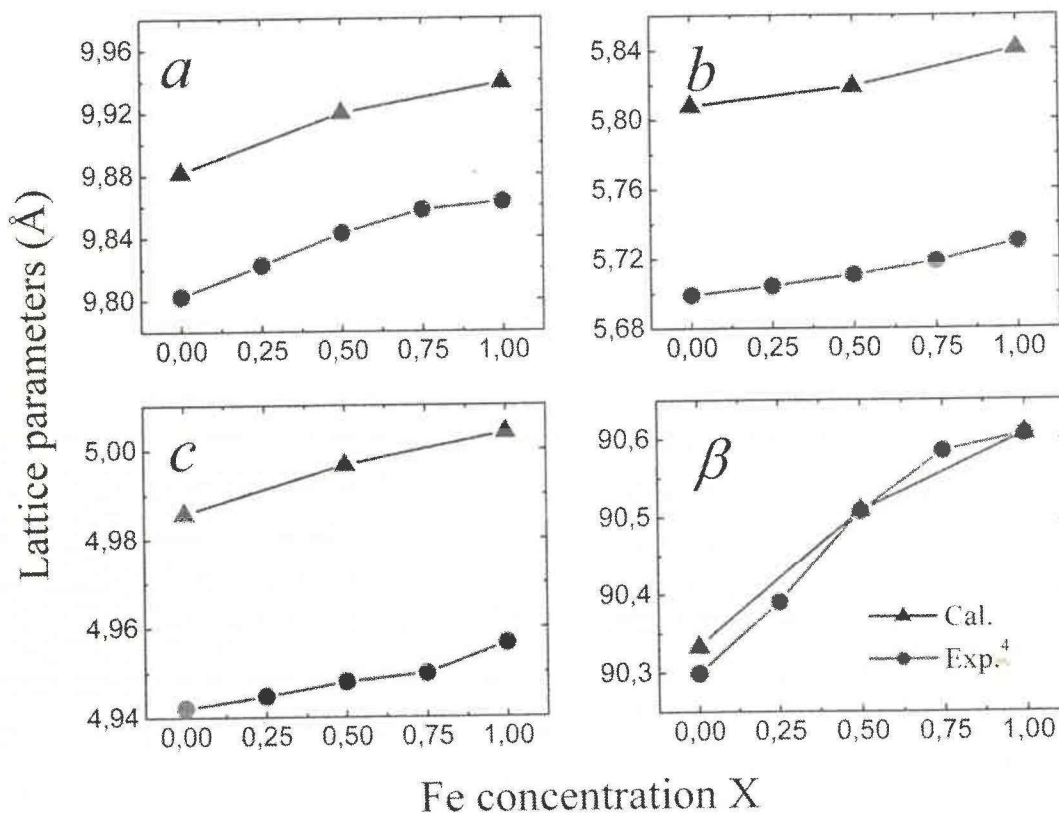

Fig. 2. The lattice parameters of $NaFe_xCr_{1-x}(WO_4)_2$ compounds as a function of Fe concentration.

The W-5d and M-3d states are splitting to the t_{2g} (d_{xy}, d_{xz} and d_{yz}) and e_g (d_{z2} and d_{x2-y2}) states around the Fermi level as a crystal field of the WO_6 and MO_6 octahedra. For the WO_6 octahedra the W-5d(t_{2g}) state is sited below the M-3d state and not full empty. The W-5d(t_{2g}) state is hybridized with the bonding states of O-2p state in the valence band. The W-5d(e_g) state is a full empty and hybridized with the nonbonding state of O-2p state in the conduction band [See Fig. 3]. For the $NaCr(WO_4)_2$ the localized Cr-3d(t_{2g}) state is full occupied and the Cr-3d(e_g) state is a full empty. For the $NaFe(WO_4)_2$ the Fe-3d(t_{2g}) and

Fe-$3d(e_g)$ states are full occupied and these states are strong hybridized with the O-$2p$ state.

The total charge densities of $NaFe_xCr_{1-x}(WO_4)_2$ (x = 0, 0.5 and 1.0) compounds presented in the Fig. 4 are shown the AFM coupling on the bc plane is generated by the 90^0 superexchange mechanism.[19] While the FM coupling is not generated on the bc plane.

The AFM coupling along the a axis is generated by the Na mediated super – superexchange ($M^{+3} - WO_6 - Na - WO_6 - M^{+3}$) mechanism.[20] It is also shown that the bond distance between the magnetic ions increases as inserted the Fe ion into the $NaCr(WO_4)_2$ compound, and the Fe containing AFM coupling becomes weakly compare with the Cr – Cr bond in the $NaCr(WO_4)_2$ compound.

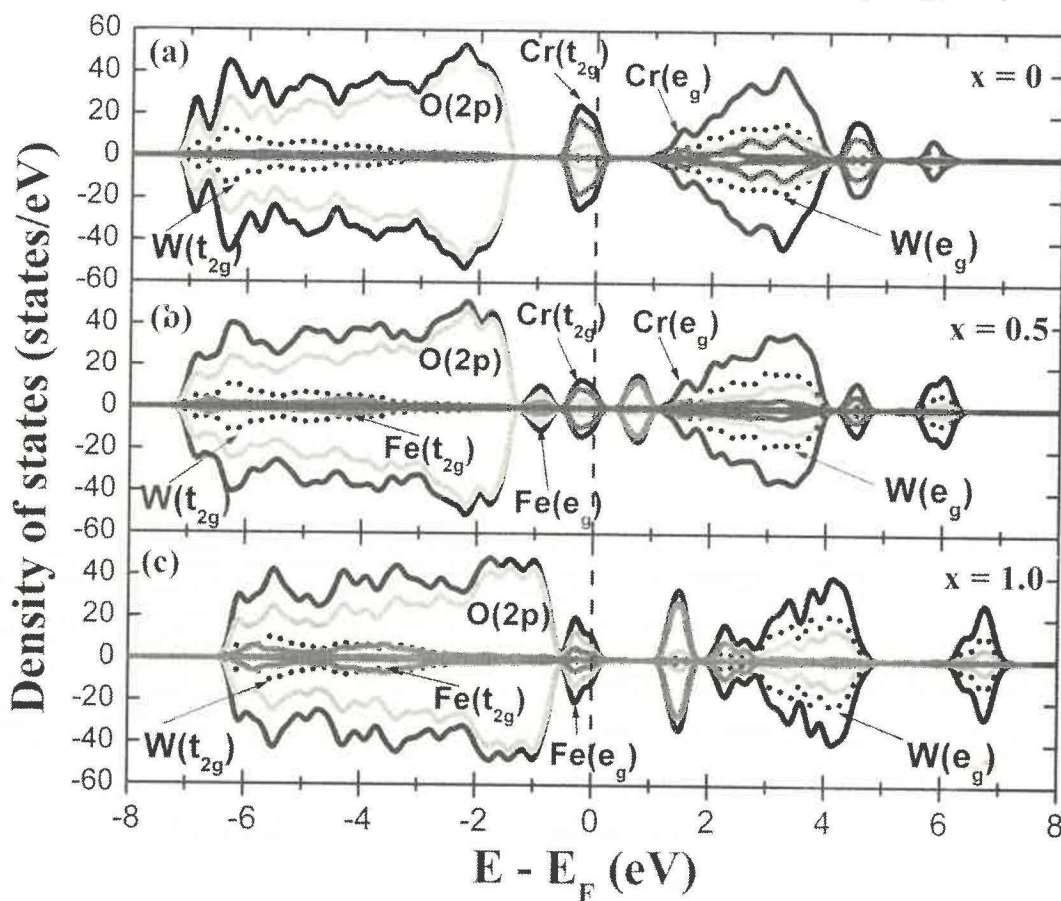**Fig. 3.** *The total and projected densities of states of $NaFe_xCr_{1-x}(WO_4)_2$ (x = 0 (a), 0.5 (b) and 1.0 (c)) compounds. The black is total DOS. The green is the PDOS for O-2p. The black short dot is the PDOS for W-5d. The red is the PDOS for Fe-3d ion. The blue is the PDOS for Cr-3d ion.*
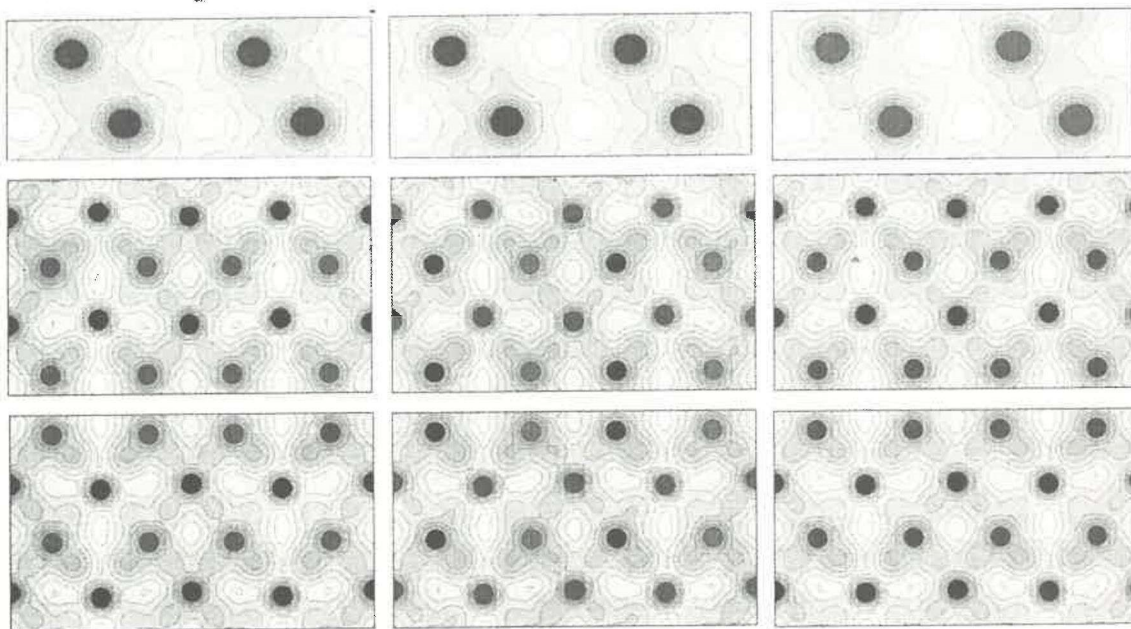
Fig. 4. *The total charge densities of NaCr(WO$_4$)$_2$ (first column), NaFe$_{0.5}$Cr$_{0.5}$(WO$_4$)$_2$ (second column) and NaFe(WO$_4$)$_2$ (third column) compounds. The top panel is in plane case, which is containing the 3 and 4 magnetic ions). The middle and bottom panels are low (2 and 4 magnetic ions containing) and upper (1 and 3 magnetic ions containing) inter planes respectively [See Fig. 1].*

4. Conclusion

In conclusion, we have shown that the ground state for sodium double tungstate NaFe$_x$Cr$_{1-x}$(WO$_4$)$_2$ (x = 0, 0.50 and 1.0) compounds is the AFM state using the first - principles approach within the framework of density functional theory. This result agrees with the experimental results. We emphasized that the AFM coupling on the *bc* plane is generated by the 90^0 superexchange mechanism. While the AFM coupling between the layers along the *a* – axis is generated by the Na mediated super - superexchange mechanism.

Acknowledgments

References

[1] P. V. Klevtsov and R. F. Klevtsova, J. Solid State Chem. **2**, 278 (1970).

[2] R. F. Klevtsova and N. V. Belov, Sov. Phys. – Crystallogr. **15**, 32 (1970).

[3] J. Hanuza, M. Maczka, K. Hermanowicz, P. J. Deren, W. Strek, L. Folcik and H. Drulis, J. Solid State Chem. **148**, 468 (1999).

[4] L. Nyam-Ochir, H. Ehrenberg, A. Buchsteiner, A. Senyshyn, H. Fuess and

D. Sangaa, J. Magn. Magn. Mater. **320**, 3251 (2008).

[5] O. Yu, V. L. Bekenev and Y. M. Solonin, J. Alloys and Compounds **480**, 184 (2009).

[6] K. V. Shanavas, D. Choudhury, I. Dasgupta, S. M. Sharma and D. D. Sarma, Phys. Rev. B **81**, 212406 (2010).

[7] S. Rajagopal, V. L. Bekenev, D. Nataraj, D. Mangalaraj and O. Y. Khyzhun, J. Alloys and Compounds **496**, 61 (2010).

[8] M. V. Lalic, Z. S. Popovic and F. R. Vukajlovic, Comput. Mater Sci. **50**, 1179 (2011).

[9] M. G. Brik, V. Nagirnyi and M. Kirm, Materials Chemistry and Physics **134**, 1113 (2012).

[10] A. Kuzmin, A. Kalinko and R. A. Evarestov, Acta Materialia **61**, 371 (2013).

[11] A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko and R. Kalendarev, Phys. Scr. **89**, 044005 (2014).

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

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

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

[15] P. Gianmozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazaaoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C.

Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovich, J. Phys.: Condens. Matter **21**, 395502 (2009).

[16] D. Vanderbilt, Phys. Rev. B. **41**, 7892 (1990).

[17] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[18] P. E. Blochl, O. Jepsen and O. K. Andersen, Phys. Rev. B. **49**, 16223 (1994).

[19] W. Geertsma and D. Khomskii, Phys. Rev. B **54**, 3011 (1996).

[20] A. Okazawa and T. Ishida, Chem. Phys. Lett. **480**, 198 (2009).