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Theoretical Investigation of Ferromagnetism and Optical Properties of $CuCr_2X_4$ (X = S, Se) Spinels via Ab-initio Calculations

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ABSTRACT

The spintronics technology improve the spin functionality which captivated the existence of ferromagnetism. The control of magnetic properties by electrons spin and transport effect have been illustrated in $CuCr_2X_4$ (X = S, Se) spinels DFT through Wien2k and BoltztraP codes. The negative formation of energy established the thermodynamic stability of the examined spinels. The half metallic ferromagnetism in the analyzed spinel's assures density of states. Magnetic moment (Integer value) and the insulating nature with down spin is the reaction of 100% spin polarization. The $\Delta(d)>(\Delta_{CF})$ and negative $\Delta(pd)$ attainment of the condition have presented the prevailing part of electrons spin to create ferromagnetism.

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1. Introduction

The half metallic ferromagnetism has been a theme of intense attention due to inherent technologically usage in significant spintronic, ferroelectric, and ferromagnetic applications displaying in spinels (Lunkenheimer, Fichtl, Hemberger, Tsurkan, & Loidl, 2005; Mahmood et al., 2020; C. Sun et al., 2010). Researchers have fascinated in view of the attention of CMR (Colossal Maneto-resistance) between studied spinels due to transition metal ferro-spinels among these spinels (Baltzer, Wojtowicz, Robbins, & Lopatin, 1966; von Helmolt, Wecker, Holzapfel, Schultz, & Samwer, 1993). $CdCr_2S_4$ and $CdCr_2Se_4$ are technically the two vital transition of temperatures at 84.5K and 129.5K separately in ferromagnetic semiconductors (Hemberger et al., 2005). In these type of materials S ions (in $CdCr_2S_4$) or six Se ions (in $CdCr_2Se_4$) forms the surrounding and crystallize in cubic spinel structure. In ferro-magnets, electrostriction has been discovered for it (Lunkenheimer et al., 2005; C. P. Sun et al., 2010). By using electric field CMR may be stimulated in these spinels as it has been reported besides it (C. Sun et al., 2010). Magnetic properties of such materials has extended the significance by application view point in the study of field induced electrical characteristics (Kim, Myung, Yoon, Kang, & Sun, 2004). $CuCr_2S_4$ has been investigated by Wustrow et al investigated to exploit $CuCr_2S$ couple at high voltage which belongs to Cu thiospinels family (Wustrow et al., 2018). In this presumed research work $CuCr_2S_4$ comprises of the synthesis, structural and electrochemical examinations.$CuCr_2S_4$ testified studies displays that stable compound with normal distribution of cations indicates that compound is stable (Zhang, Stevanović, d'Avezac, Lany, & Zunger, 2012). Pyrochlore lattice created at tetrahedral positions by the combination of Cr ions in which antiferromagnetic interaction among closest neighbors that restricts the spin alignment as well as magnetic prevention (Anderson, 1956). Though, the SOC effect reduces the ferromagnetism by producing balance states and least free energy, but this energy simultaneously helps the magnetic ordering. The least energy creates net magnetic ordering in it. Particularly magnetic frustrations due to Cr bonded by tetragonal contraction which surprised by creating it valuable contender in spintronics and other electronic devices by $ZnCr_2O_4$ and $CdCr_2O_4$ (Dutton, Huang, Tchernyshyov, Broholm, &

Cava, 2011; Kumar, Fennie, & Rabe, 2012; Tran & Blaha, 2009). The $MgCr_2O_4$ and $ZnCr_2O_4$ studied ensure their sensitivity to ferromagnetism. Instead of limiting literature the ferromagnetic ordering and high magnetic moment had been explored in $CuCr_2X_4$ (X = S, Se). Furthermore, the insulting band gaps 0.938 eV and 0.638 eV for $CuCr_2S_4$ and $CuCr_2Se_4$ also reported which make them significant materials for transport applications (Madsen & Singh, 2006).

The literature analysis about these materials show the experimental research work is very limiting on $CuCr_2Se_4$ but few theoretical reports exist on $CuCr_2X_4$ (X=S, Se) which support to analyze them for spintronic applications. Therefore, in the view of above discussion, the theoretical studies of transport and magnetic behaviors of $CuCr_2X_4$ (X=S, Se) have been incorporated in this article.

For this task, the DFT based Wien2K code, and BoltzTraP code has been practiced exploring the structures of studied spinels (Perdew et al., 2008). These exact band gap structures are run for the transport analysis by BoltzTraP code (Tran, Blaha, & Schwarz, 2007). The existence of structures of spinels reveals their diverse applications in the field of spintronic. Therefore, the results are discussed step by step below for the complete of the studied spinels.

2. Method of Calculation

The thiospinels $CuCr_2X_4$ (X=S, Se) magnetism and transport characteristics have been done by FP-L(APW+lo) method through the Wien2K code. The structural analysis and ground state study has been done by PBE-GGA (Koller, Tran, & Blaha, 2011). The optimizations of studied structures done until the all the strain forces becomes zero. In addition, for true electronic structures and band gap analysis, the TB-mBJ has been done through exchange and correlation configuration. The TB-mBJ improve the band gaps this high precision and less time (Blaha, Schwarz, Madsen, Kvasnicka, & Luitz, 2001; Rashid et al., 2019; Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, & Sofo, 2003). By using TB-mBJ exchange potential results achieved from thermoelectric as well as electronic band structures conveyed. The K-mesh of order 12 × 12 × 12 have been selected in first Brillion zone. Furthermore, the product $R_{MT}\times K_{max}$= 8, G_{max} = 16 and l_{max} are adjusted in the in put of the software.

3. Analysis Section

3.1. Electronic Characteristics

The spinel's $CuCr_2X_4$ (X=S, Se) with cubic structure and and space group Fd-3m#227 are optimized to in ferromagnetic state and compared its energy released with nonmagnetic state. The energy is taken the default units (Ry) in both the FM and NM states. The relative investigation depicts that the more energy released in FM state than NM states, which approve the FM state is much stable than the NM states. The thermodynamic stability of the deliberate spinel's, and also associated with the enthalpy formation which has been computed and reported in the Table 1.The thermodynamic stability guarantees the negative establishment of energy that declines from -1.46 eV to -0.34 eV as S is changed with Se. The stability, decreasing trend as we go down the group the exit of energy lessens by the substitution of S with Se. When structures optimized the lattice constantsa_0 (Å) by Murnaghan equation of states and shown in Table 1. Bulk modulus decreases by increasing the S/Se size and distance among atoms whereas the lattice constant increase from $CuCr_2S_4$ to $CuCr_2Se_4$. The computed magnetic and electronic and electronic characteristics are illustrated to see the effect of electrons spin. Thorough explanation of band structures (BS) is essential to recognize the electronic behavior. Hence, the examined compounds are plotted in Fig.2. For the computation of band structures. At Γ-symmetry point direction the valence band maxima exist, and conduction band minima exists at X direction having E_F on VB in up spin (↑) which depict the indirect band gap.

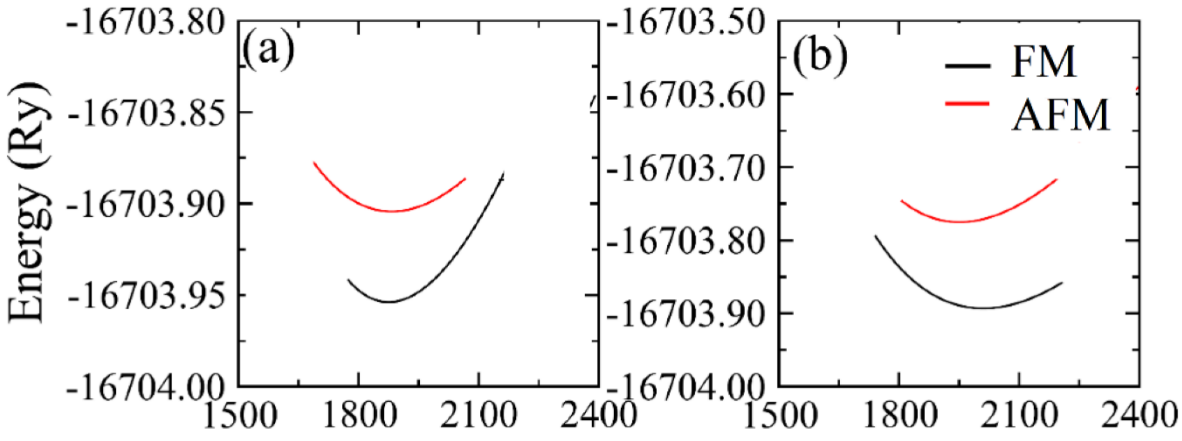

Figure 1: Optimized Energy Versus Volume Plots of (a) $CuCr_2S_4$, and (b) $CuCr_2Se_4$ in FM and NM States

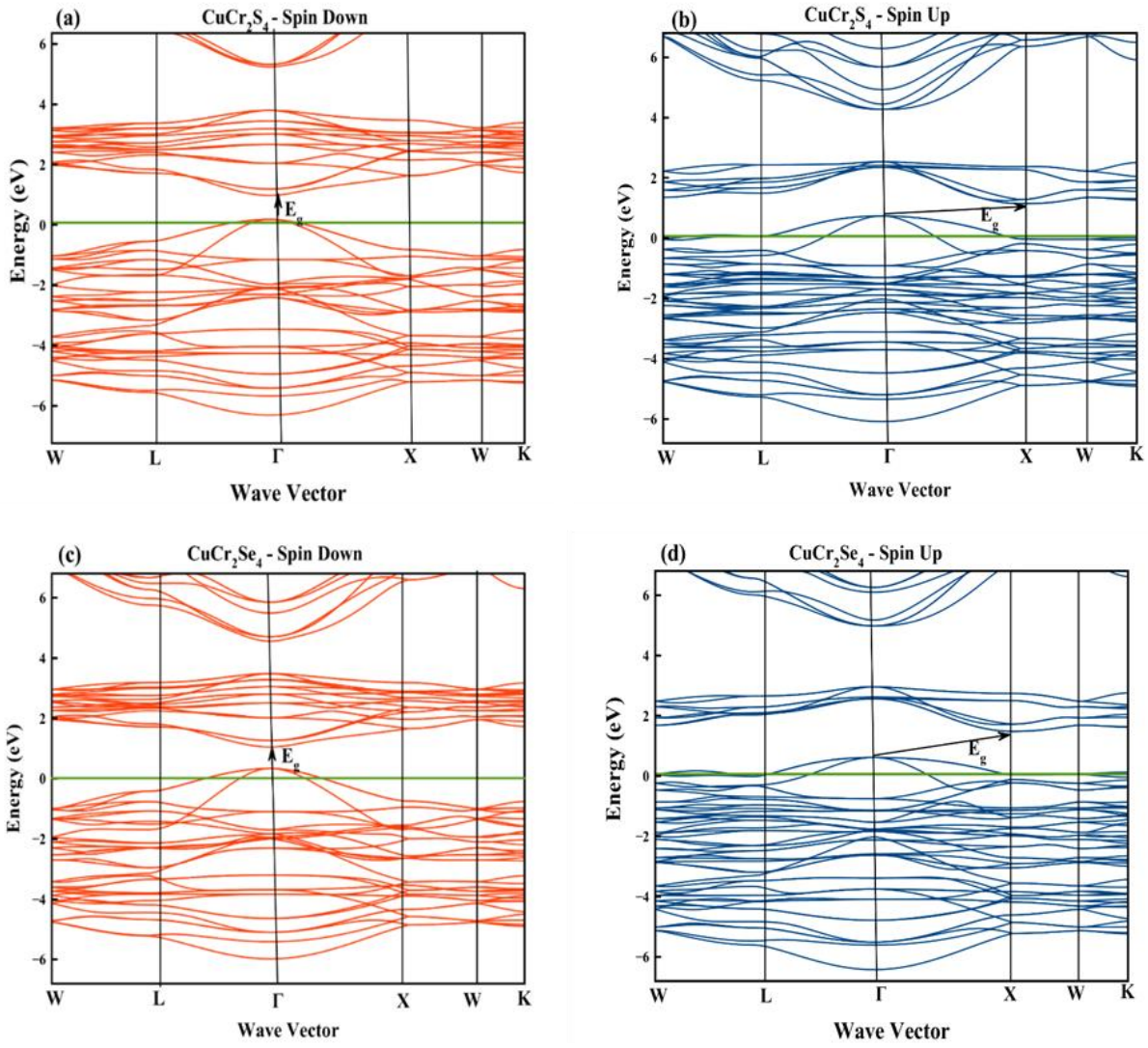

Figure 2: The Band Structures for Spin Up and Spin Down of (a, b) $CuCr_2S_4$ and (c, d) $CuCr_2Se_4$

While in down spin (↓) medium, both VBM and CBM exist at the Γ direction having Fermi level inside them which persuades the insulting gap because of exchange mode. Hence, the formation of ferromagnetic semiconductors results as the incorporation of up spin (↑) and down spin (↓) medium by insulting properties.

Table 1
The calculated lattice constant a_0 (Å), bulk modulus B_0 (GPa), Ground state energy difference ($\Delta E = E_{NM}-E_{FM}$), enthalpy of formation ΔH(eV) for $CuCr_2X_4$ (X = S, Se, Te).

Compound	a_0 (Å)	B_0(GPa)	ΔE (eV)	ΔH(eV)
$CuCr_2S_4$	10.22	82.74	5.74	-1.46
Exp.	10.24[a], 10.1[b]			
$CuCr_2Se_4$	10.76	65.35	6.74	-0.84
Exp.	-----			

[a]Ref (Tran & Blaha, 2009), Ref (Mahmood, Hassan, et al., 2019)[b]

The density of states (DOS) shows identical functioning and shown in Figs.3 The $SP = \frac{N\downarrow - N\uparrow}{N\downarrow + N\uparrow} X100$ is the equation computed for spin polarization in which N↑ showing the total density of states in the up-spin mode while N↓ is the total density of states in the down spin mode? Densities of states exist at Fermi level in up spin (↑) mode however energy gaps are forbidden inside the Fermi level. Consequently, SP has been found hundred percent (Choi, Shim, & Min, 2006; Walsh et al., 2007). The SP can be maintained by the integer value of total MM of the studied compounds is 100% as presented in Table 2. Partial density of states (PDOS) Cu, Cr and S/Se demonstrates further the exchange mechanism and ferromagnetism and are examined thoroughly as shown in Fig.3. The hybridize in the energy interval -4.0 to -0.5 eV between 3d states of Cr/Cu and O-2p states exist near E_F in up spinel mode. Whereas in down spin mode the range is from -3.0 to -1.0 eV for Cr-3d states, Cu-3d and S-3p states. Moreover, in the hybridization range for Cr-3d states, Cu-3d states and S-3p states in the conduction band in the range of 1.5 to 2.4 eV and 2 to 3.2 eV for spin up and down modes. Consequently, ferromagnetic semiconducting nature, generated by the interaction inside the valence band and separating of states in the down spin mode.

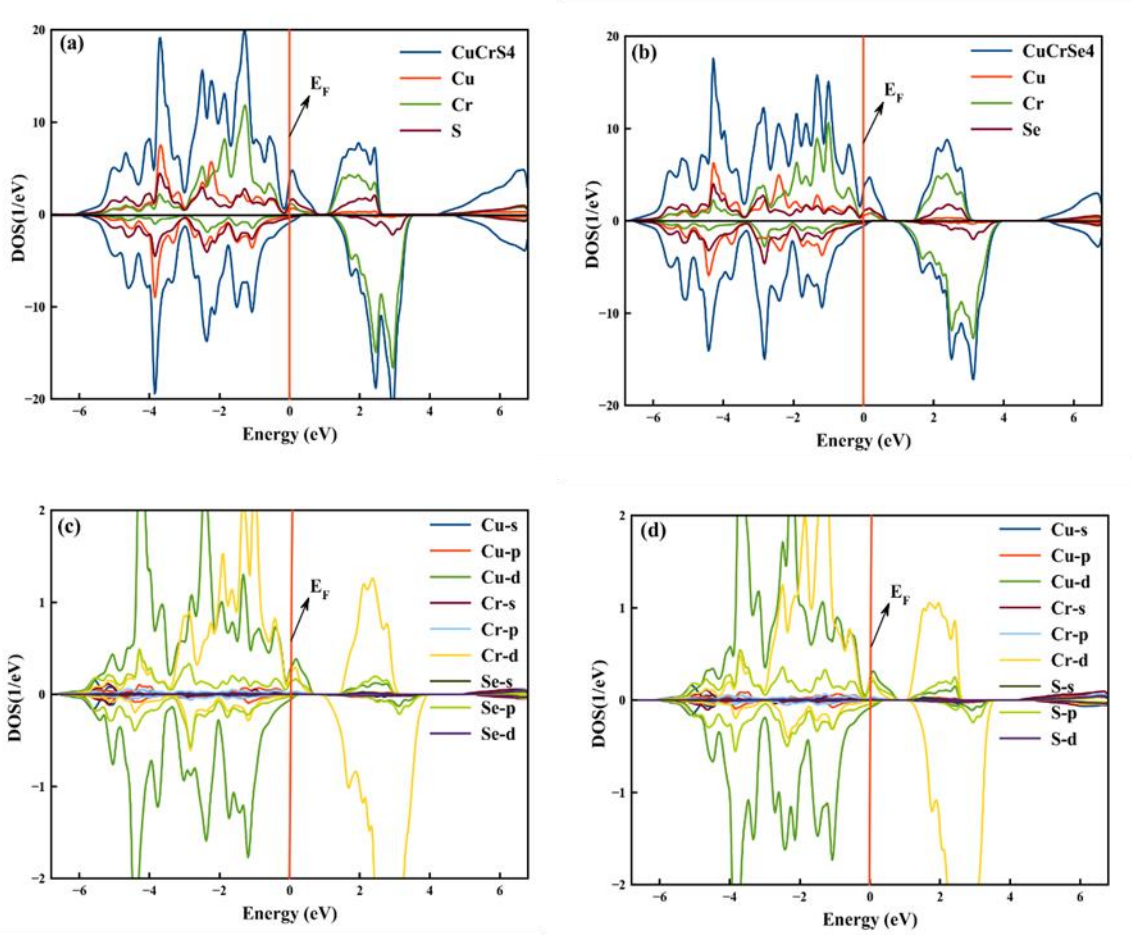

Figure 3: The total and Partial DOS for spin up and spin down of (a, b) $CuCr_2S_4$ and (c, d) $CuCr_2Se_4$

Table 2
The Total and The Local Magnetic Moments (in Bohr Magneton) Calculated for $MgCr_2X_4$ (X = S, Se, Te)

	Total (μ_B)	Int. (μ_B)	Mg (μ_B)	Cr (μ_B)	(Xμ_B)
$CuCr_2S_4$	3.0000	0.43	0.006	3.02	-0.06
$CuCr_2Se_4$	3.0000	0.54	0.002	3.05	-0.09

3.2. Magnetic Properties

The materials structures elaborated in this material generates crystal field and exchange energies by hybridization in distinct states. Tetrahedral arrangement of S/Se atoms effect the Cu site with valency +2, whereas Cr site having +3 valency is captured by the octahedron of S/Se atoms.

The repulsive effect of 3d-Cr creates the octahedral of S/Se which in the near octahedron is powerful and weaker as move away. The increasing energy e_g of states as associated to t_{2g} states that extend the octahedron medium of S/Se atoms separate the 3d-Cr into high energy (e_g) and low energy (t_{2g}) (Kumar et al., 2012; Mahmood, Rashid, et al., 2019) [30]. Energies of the crystal field energies in both spin modes described by $(\Delta_{CF}^{\uparrow} = t_{2g}^{\uparrow} - e_g^{\uparrow})$ and $(\Delta_{CF}^{\downarrow} = t_{2g}^{\downarrow} - e_g^{\downarrow})$ are shown in Table 3.Furthermore the correlation of crystal energy with the exchange separating of 3d states of Cr determined by the relation $\Delta(d) = \Delta_d^{\downarrow} - \Delta_d^{\uparrow})$ Ferromagnetism domination results in the larger value of exchange energy besides the crystal field energy. By the measurement of indirect exchange energy $\Delta(pd)$ another kind of energy is produced by 3d states of Cr and p states of S/Se. Lower energy support ferromagnetism when $\Delta(pd)$ is negative. $CuCr_2S_4$ to $CuCr_2Se_4$ the value of $\Delta(pd)$ and $\Delta(d)$ increases presented in Table 3 where Δ_{CF} decreases that clearly indicates that later one is more promising for ferromagnetism. Ferromagnetism can be elaborated by exchange constant that calculated by the relations $N_0\alpha = \Delta E_C / x\langle S\rangle$ and $N_0\beta = \Delta E_V / x\langle S\rangle$, where $(\Delta E_V = E_V^{\downarrow} - E_V^{\uparrow})$ and $(\Delta E_C = E_C^{\downarrow} - E_C^{\uparrow})$ and the energies at valence band as well as on conduction bands, where x is the absorption of Cr and $\langle S\rangle$ is MM of Cr atom. In usual cases the $(N_0\alpha)$ retain positive values and $(N_0\beta)$ negative. Therefore, the similar effect of studied FM has been seen in Table 3.

Table 3
The calculated values spin down gap ($\uparrow E_g$ (eV)), crystal field energy ($\Delta E_{crystal}$), direct exchange $\Delta_x(d)$ and indirect exchange $\Delta_x(pd)$ and the exchange constants ($N_o\alpha$ and $N_o\beta$) for $CuCr_2X_4$ (X = S, Se, Te).

Compounds	$\uparrow E_g$	($\Delta E_{crystal}$)	$\Delta_x(d)$	$\Delta_x(pd)$	$N_o\alpha$	$N_o\beta$
$CuCr_2S_4$	1.45	3.70	3.98	-0.20	0.33	-0.14
$CuCr_2Se_4$	0.85	2.94	4.10	-0.25	0.52	-0.16

Zenger's exchange model supports the attraction of down spin mode whose energy reduces and shows the magnetic impurity operated have negative value $(N_0\beta)$ (Hassan, Arshad, & Mahmood, 2017; Kant, Deisenhofer, Tsurkan, & Loidl, 2010; Mahmood, Yaseen, Haq, Laref, & Nazir, 2019). Therefore, the source of ferromagnetism confirm that this is due to exchange energies. The examined compounds of magnetic moments and partial MM are reported in Table 2. The transporting of magnetic moment towards nonmagnetic sites indicates that the exchange interaction Cr-3*d* states and S/Se p states causes the decrease of magnetic moment of Cr. Because of unlike exchanges included in the structures may be due to transition of MM from magnetic to nonmagnetic sites.

4. Conclusion

In short, the present article, ensure the detailed analysis of electronic and magnetic characteristics of $CuCr_2X_4$ (X=S, Se) by Wien2k code. The examined compounds are ferromagnetic semiconductors, that validates the electronic band structures and density of

states. The optimization analysis confirms the more energy release in FM states than in NM states ensures the stability of FM states. The FM is elaborated in terms of electrons spin which show strong hybridization. The FM is favorable because $\Delta(d)$ has higher values as compared to (Δ_{CF}). The energy decreases in down spin mode have -Ve value of *pd*-exchange energy which is also the justification of FM and electrons spin. The p-*d* hybridization/exchange interaction is due to the growth of μ_{Cr} and shifting of MM on nonmagnetic sits. Therefore, the complete analysis of magnetic characteristics ensures importance of studied materials for spintronic applications.

References

Anderson, P. W. (1956). Ordering and antiferromagnetism in ferrites. *Physical review, 102*(4), 1008.

Baltzer, P., Wojtowicz, P., Robbins, M., & Lopatin, E. (1966). Exchange interactions in ferromagnetic chromium chalcogenide spinels. *Physical review, 151*(2), 367.

Blaha, P., Schwarz, K., Madsen, G. K., Kvasnicka, D., & Luitz, J. (2001). wien2k. *An augmented plane wave+ local orbitals program for calculating crystal properties, 60*.

Choi, H., Shim, J., & Min, B. (2006). Electronic structures and magnetic properties of spinel Zn Mn 2 O 4 under high pressure. *Physical Review B, 74*(17), 172103.

Dutton, S. E., Huang, Q., Tchernyshyov, O., Broholm, C., & Cava, R. J. (2011). Sensitivity of the magnetic properties of the ZnCr 2 O 4 and MgCr 2 O 4 spinels to nonstoichiometry. *Physical Review B, 83*(6), 064407.

Hassan, M., Arshad, I., & Mahmood, Q. (2017). Computational study of electronic, optical and thermoelectric properties of X3PbO (X= Ca, Sr, Ba) anti-perovskites. *Semiconductor Science and Technology, 32*(11), 115002.

Hemberger, J., Lunkenheimer, P., Fichtl, R., Krug von Nidda, H.-A., Tsurkan, V., & Loidl, A. (2005). Relaxor ferroelectricity and colossal magnetocapacitive coupling in ferromagnetic CdCr2S4. *Nature, 434*(7031), 364-367.

Kant, C., Deisenhofer, J., Tsurkan, V., & Loidl, A. (2010). *Magnetic susceptibility of the frustrated spinels ZnCr2O4, MgCr2O4 and CdCr2O4.* Paper presented at the Journal of Physics: Conference Series.

Kim, J.-H., Myung, S.-T., Yoon, C., Kang, S., & Sun, Y.-K. (2004). Comparative study of LiNi0. 5Mn1. 5O4-δ and LiNi0. 5Mn1. 5O4 cathodes having two crystallographic structures: fd 3ˉm and P 4332. *Chemistry of materials, 16*(5), 906-914.

Koller, D., Tran, F., & Blaha, P. (2011). Merits and limits of the modified Becke-Johnson exchange potential. *Physical Review B, 83*(19), 195134.

Kumar, A., Fennie, C., & Rabe, K. (2012). Spin-lattice coupling and phonon dispersion of CdCr 2 O 4 from first principles. *Physical Review B, 86*(18), 184429.

Lunkenheimer, P., Fichtl, R., Hemberger, J., Tsurkan, V., & Loidl, A. (2005). Relaxation dynamics and colossal magnetocapacitive effect in Cd Cr 2 S 4. *Physical Review B, 72*(6), 060103.

Madsen, G. K., & Singh, D. J. (2006). BoltzTraP. A code for calculating band-structure dependent quantities. *Computer Physics Communications, 175*(1), 67-71.

Mahmood, Q., Hassan, M., Ahmad, S., Bhamu, K., Mahmood, A., & Ramay, S. M. (2019). Study of electronic, magnetic and thermoelectric properties of AV2O4 (A= Zn, Cd, Hg) by using DFT approach. *Journal of Physics and Chemistry of Solids, 128*, 283-290.

Mahmood, Q., Noor, N., Jadan, M., Addasi, J. S., Mahmood, A., & Ramay, S. M. (2020). First-principle investigation of ferromagnetism and thermoelectric characteristics of MgCr2X4 (X= S, Se) spinels. *Journal of Solid State Chemistry, 285*, 121261.

Mahmood, Q., Rashid, M., Noor, N., Ashiq, M. G. B., Ramay, S. M., & Mahmood, A. (2019). Opto-electronic and thermoelectric properties of MgIn2X4 (X= S, Se) spinels via ab-initio calculations. *Journal of Molecular Graphics and Modelling, 88*, 168-173.

Mahmood, Q., Yaseen, M., Haq, B. U., Laref, A., & Nazir, A. (2019). The study of mechanical and thermoelectric behavior of MgXO3 (X= Si, Ge, Sn) for energy applications by DFT. *Chemical Physics, 524*, 106-112.

Perdew, J. P., Ruzsinszky, A., Csonka, G. I., Vydrov, O. A., Scuseria, G. E., Constantin, L. A., . . . Burke, K. (2008). Restoring the density-gradient expansion for exchange in solids and surfaces. *Physical Review Letters, 100*(13), 136406.

Rashid, M., Alghamdi, A. S., Mahmood, Q., Hassan, M., Yaseen, M., & Laref, A. (2019). Optoelectronic and thermoelectric behavior of XIn2Te4 (X= Mg, Zn and Cd) for energy harvesting application; DFT approach. *Physica Scripta, 94*(12), 125709.

Scheidemantel, T., Ambrosch-Draxl, C., Thonhauser, T., Badding, J., & Sofo, J. O. (2003). Transport coefficients from first-principles calculations. *Physical Review B, 68*(12), 125210.

Sun, C., Huang, C., Lin, C., Her, J., Ho, C., Lin, J.-Y., . . . Yang, H. (2010). Colossal electroresistance and colossal magnetoresistance in spinel multiferroic CdCr 2 S 4. *Applied physics letters, 96*(12), 122109.

Sun, C. P., Huang, C. L., Lin, C. C., Her, J. L., Ho, C. J., Lin, J.-Y., . . . Yang, H. D. (2010). Colossal electroresistance and colossal magnetoresistance in spinel multiferroic CdCr2S4. *Applied physics letters, 96*(12), 122109. doi:10.1063/1.3368123

Tran, F., & Blaha, P. (2009). Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Physical Review Letters, 102*(22), 226401.

Tran, F., Blaha, P., & Schwarz, K. (2007). Band gap calculations with Becke–Johnson exchange potential. *Journal of Physics: Condensed Matter, 19*(19), 196208.

von Helmolt, R., Wecker, J., Holzapfel, B., Schultz, L., & Samwer, K. (1993). Giant negative magnetoresistance in perovskitelike La 2/3 Ba 1/3 MnO x ferromagnetic films. *Physical Review Letters, 71*(14), 2331.

Walsh, A., Wei, S.-H., Yan, Y., Al-Jassim, M., Turner, J. A., Woodhouse, M., & Parkinson, B. (2007). Structural, magnetic, and electronic properties of the Co-Fe-Al oxide spinel system: Density-functional theory calculations. *Physical Review B, 76*(16), 165119.

Wustrow, A., Key, B., Phillips, P. J., Sa, N., Lipton, A. S., Klie, R. F., . . . Poeppelmeier, K. R. (2018). Synthesis and characterization of MgCr2S4 thiospinel as a potential magnesium cathode. *Inorganic chemistry, 57*(14), 8634-8638.

Zhang, X., Stevanović, V., d'Avezac, M., Lany, S., & Zunger, A. (2012). Prediction of A 2 B X 4 metal-chalcogenide compounds via first-principles thermodynamics. *Physical Review B, 86*(1), 014109.