

A First-Principles Study of Structure-Property Correlation and the Origin of Ferrimagnetism in Gallium Ferrite

Amritendu Roy¹, Ashish Garg¹, Rajendra Prasad², Sushil Auluck³

¹Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, India

²Department of Physics, Indian Institute of Technology Kanpur, Kanpur, India

³National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi, India
Email: rprasad@iitk.ac.in

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ABSTRACT

A first-principles study of structure property correlation and the origin of ferrimagnetism is presented based on LSDA+U method. In particular, the results for the ground state structure, electronic band structure, density of states, Born effective charges, spontaneous polarization and cationic disorder are discussed. The calculations were done using Vienna ab-initio simulation package (VASP) with projector augmented wave method. We find that the ground state structure is orthorhombic and insulating having A-type antiferromagnetic spin configuration. The cationic disorder is found to play an important role. Although the cationic site disorder is not spontaneous in the ground state, interchange of octahedrally coordinated Ga2 and Fe2 sites is most favored. We find that ferrimagnetism in gallium ferrite is primarily due to this exchange between Ga-Fe sites such that Fe spins at Ga1 and Ga2 sites are antiferromagnetically aligned while maintaining ferromagnetic coupling between Fe spins at Ga1 and Fe1 sites as well as between Fe spins at Ga2 and Fe2 sites. Further, the partial density of states shows noticeable hybridization of Fe 3d, Ga 4s, Ga 4p and O 2p states indicating some covalent character of Ga/Fe-O bonds. However, the charge density and electron localization functions show largely the ionic character of these bonds. Our calculation predicts spontaneous polarization of $\sim 59 \mu\text{C}/\text{cm}^2$ along *b*-axis.

Keywords: Gallium Ferrite; LSDA+U; Spontaneous Polarization; Ferrimagnetism; Cation Site Disorder

1. Introduction

Gallium ferrite (GaFeO_3 or GFO) is a room temperature piezoelectric and a ferrimagnet whose magnetic transition temperature (T_C) is slightly lower than room temperature [1] but tunable to room temperature and beyond by tailoring the composition [1,2] and processing conditions.[1-3] Thus, compositionally modulated GFO is a promising candidate for room temperature magnetoelectric applications.

Early studies on GFO [2] predicted simultaneous piezoelectricity and ferromagnetism. Structural characterization using x-ray [1,4,5] and neutron [1,4,6] diffraction techniques concluded an orthorhombic structure (Space Group: $Pc2_1n$) with eight formula units per unit cell, is stable over a wide temperature domain (4K-700K)[1,7]. The unit cell comprises of two types of Ga (Ga1 and Ga2) and Fe (Fe1 and Fe2) ions and six types of O (O1, O2,...O6) ions.[1] The above studies also suggest substantial cationic site disorder *i.e.* some of the Ga sites are always occupied by Fe ions and *vice-versa*.[1] However, magnetic behavior of GFO had been a matter of uncertainty for a long time. Initial prediction of ferromagnetic ordering [2] was challenged by Frankel *et al.*[8] who using high field Mössbauer spectroscopy and macroscopic magnetic measurements proved collinear ferrimagnetism in GFO. Ferrimagnetic ordering has been further demonstrated by almost all subsequent studies using neutron diffraction technique.[1,4] Piezoelectricity in GFO, on the other hand, has been hardly studied with few exceptions showing that the piezoelectric constants are almost double to that of quartz [9] which is attributed to the

asymmetric Ga1-O tetrahedron in the GFO unit cell. [10]

In spite of extensive experimental studies, first-principles calculations on GFO, have not been carried out much, partly due to the complex crystal structure with substantially large number of ions in the unit cell having partial site occupancies of the cations. However, such type of studies have been quite successful in predicting and analyzing structure-property correlations in complex material systems and in this regard, a detailed study on GFO would be particularly interesting to probe the hitherto disputed issues such as the ground state structure, magnetic structure and the piezoelectric response of the material. Our study, using first-principles calculations, shows that the ground state structure of GFO is A-type antiferromagnetic. The calculations indicate the presence of large spontaneous polarization (P_s) of $\sim 59 \mu\text{C}/\text{cm}^2$ along crystallographic *b*-axis. Finally, we predict that the observed ferrimagnetism is solely due the inherent cation site disorder in the material.

2. Calculation Methodology

We used Vienna ab-initio simulation package (VASP) [11] with projector augmented wave method (PAW) [12] in our work. The Kohn-Sham equation [13] was solved using local spin density approximation (LSDA+U) [14] with Hubbard parameter, $U = 5 \text{ eV}$, and the exchange interaction, $J = 1 \text{ eV}$. Our calculations for the determination of the ground states structure are based on the stoichiometric GFO assuming no partial occupancies of the constituent ions with starting parameters taken from previous literature.[1] We considered 3 valence electrons of Ga

($4s^2 4p^1$), 8 for Fe ($3d^7 4s^1$) and 6 for O ($2s^2 2p^4$) ions. Structural optimization was carried out using Monkhorst-Pack [15] $7 \times 7 \times 12$ mesh. Born effective charges, and spontaneous polarization for the ground state structure were calculated using Berry phase method. [16]

3. Results and Discussions

3.1. Structural Optimization: Ground State Structure

Though previous literature predicts the ground state structure of GFO to be antiferromagnetic [1,17], possible antiferromagnetic configurations have not been explored. Therefore, we started with four possible antiferromagnetic spin configurations as shown schematically in **Figure 1(a)-(d)** i.e. AFM-1, AFM-2, AFM-3 and AFM-4, to arrive at the ground state spin ordering. It should be noted that other possible antiferromagnetic spin configurations were found to be equivalent to one of the above configurations. Computation of the total energies of the above structures shows, that the energetically, AFM-3 > AFM-4 > AFM-2 > AFM-1. Therefore, we can conclude that AFM-1 spin configuration is the most favored configuration and all the further calculations were performed on AFM-1 structure.

Structural optimization by relaxing the ionic positions, lattice parameters and unit cell shape further reveals that the ground state structure retains the original $Pc2_1n$ symmetry observed experimentally [1,18]. The calculated ground state lattice parameters: $a = 8.6717 \text{ \AA}$, $b = 9.3027 \text{ \AA}$ and $c = 5.0403 \text{ \AA}$ are in good agreement with previous experimental results.[1,7,18] Calculated ionic positions show that Fe1 and Fe2 ions are located on alternate planes parallel to ac -plane. Since Fe1 and Fe2 have antiparallel spin configurations and are situated on alternate parallel planes, we conclude (see **Figure 1**) that the ground state magnetic structure of GFO is A-type antiferromagnetic. Using the ground state structural data, we further calculated cation-oxygen bond length and Fe/Ga-O-Fe/Ga bond angles. We found that cation-oxygen polyhedra are significantly distorted which could contribute to the observed piezoelectric behavior. Calculation of Fe-O-Fe, on the other hand, could be linked with the super-exchange interaction between O and neighboring Fe^{3+} ions. In general, larger the Fe-O-Fe bond angle results in stronger antiferromagnetic super-exchange.[19] The maximum value of Fe1-O1-Fe2, bond angle is $\sim 168.54^\circ$ while other angles are: Fe1-O3-Fe2, 123.13° and Fe1-O5-Fe2, 126.23° , respectively. Such large Fe-O-Fe bond angles (larger than 90°) results in antiferromagnetic ordering of Fe1 and Fe2 ions and lead to noticeable super-exchange interaction between Fe and O ions which is reflected in significantly large magnetic moments of O. Similar large bond angles among Fe1-O-Ga2 and Fe2-O-Ga1 ensure that Fe ions occupying Ga sites due to site disorder would therefore form strong antiferromagnetic spin arrangement between Fe at Ga1 with Fe2 and Fe at Ga2 with Fe1, respectively. Therefore we can conclude that any Fe ion, due to partial site occupancy, occupying Ga1 site would have antiferromagnetic ordering with Fe2 and Fe at Ga2 site and would be antiferromagnetically coupled with Fe1 site.

3.2. Electronic Band Structure, Density of States and Bonding

Figure 2 shows the electronic band structure along high sym-

metry directions and total density of states of GFO. It is found that GFO possesses a direct band gap (E_g) of $\sim 2.0 \text{ eV}$ ($\Gamma - \Gamma$). However, experimental studies reports a band gap of 2.7-3.0 eV.[20] The difference between our results and the experimental results is primarily due to underestimation of band gap by the LSDA technique which is very common in electronic structure calculation of oxides. [21] Cation site disorder, inherent to the experimental structure of GFO might also contribute to the effect of enhancing the band gap. [22] The angular momentum character of the bands over different energy domains can be identified by computing the partial density of states. Our calculations shows that the upper most part of the valence band is mainly composed of Fe $3d$ and O $2p$ states. Beyond the Fermi level, a narrow energy band (1.77 eV to 2.45 eV) comprises mainly of Fe $3d$ character, while the highest energy window has contributions from Fe $3d$, Ga $4s$, Ga $4p$ and O $2p$ states. Calculations of the partial density of states demonstrate significant hybridization of Fe $3d$ and O $2p$ states throughout the uppermost part of the valence band which further indicates presence of significant covalent character between Fe-O bonds.

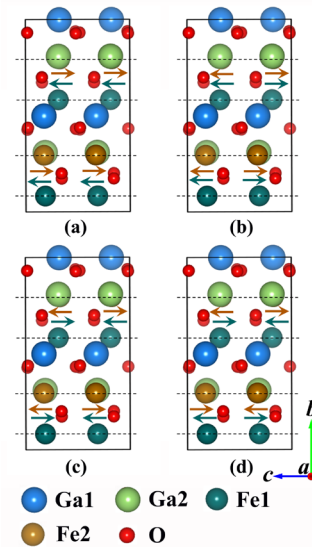


Figure 1. Schematic representation of different antiferromagnetic ordering (a) AFM-1, (b) AFM-2, (c) AFM-3 and (d) AFM-4

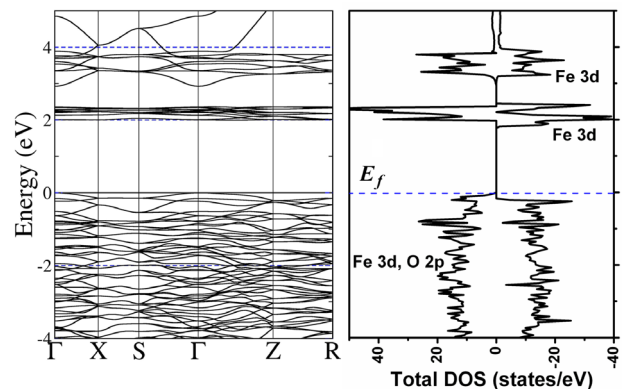


Figure 2. Electronic band structure (left) and total density of states of GFO with orthorhombic symmetry.

Analysis of the chemical bonding can further be carried out by plotting electron localization function (ELF) which gives a measure of the local influence of the Pauli repulsion on the behavior of the electrons. A large value of ELF function indicates space with anti-parallel spin configuration [23]. Our calculation of ELF distribution in GFO unit cell (not shown here) depicts maximum ELF value at O sites and small values at Fe and Ga sites indicating charge transfer from Fe/Ga to O sites. A complete charge transfer was found between Fe2 and O3 ions. Similar charge transfer was also noticed between Fe1 and O1, O2 ions. Thus, we can predict that Fe-O bonds in GFO are mostly ionic. In comparison, finite value of ELF between O and Ga1 and Ga2 indicate some degree of covalent characteristics.

3.3. Cation Site Disorder and Ferrimagnetism

Calculation of the magnetic moments of the constituent ions in the ground state shows that Fe1 and Fe2 ions have magnetic moments of $+4.05 \mu_B$ and $-4.04 \mu_B$, respectively. We find that the magnitude of moments agrees reasonably well with the experimental data. [1] It was also found that the oxygen ions surrounding the Fe ions manifest small but finite magnetic moments attributed to super-exchange interactions with the surrounding Fe ions.

Till now, our calculations have been based on the ground state structure containing no partial site occupancies of the cations which is however, in contrast with the experimental reports showing significant Fe occupancies at the Ga sites. Thus, to probe the effect of cation site disorder on the magnetic characteristics of GFO, we selectively interchanged Fe and Ga sites and computed total energy of the system. Since, GFO unit-cell contains four ions of each type of cation, such an interchange would result in $\frac{1}{4}$ th site occupancy of Fe ions at Ga sites and *vice-versa*. Calculations of total energy of these disordered structures show that partial site occupancy is not favored in the ground state, also observed previously by Han *et al.* [17]. However, it was found that among various possible cases of site disorders, Fe2 ions preferentially occupying Ga2 sites is most probable since ΔE , the energy difference with respect to the ground state in that case is minimum. Although these energy differences may be affected by the computational methodology, the magnitude of the available thermal energy at room temperature ($kT \sim 25$ meV) is of the order of the energy difference for Fe2-Ga2 site disorder indicating towards the role of thermally originated defects. An important observation of the inclusion of cation site disorder in the calculation would be on the modification of the local magnetic moments. It was observed that upon interchanging Fe1 and Ga1 sites, the average magnetic moment of Fe ion at Ga1 site becomes $3.99 \mu_B$. On the other hand, the magnetic moment of Fe ion at Ga2 site becomes $4.11 \mu_B$ when Fe2 and Ga2 sites are interchanged. In order to analyze the observed ferrimagnetism as against the antiferromagnetic ordering in the ground state, we further calculated the total magnetic moment of the disordered structure, using the partial site occupancies from the Rietveld refinement data [24] and taking the magnetic moments for different cation sites, from our calculation with site disorder. We estimated net magnetic moment of $0.24 \mu_B$ / Fe site which agrees quite well with experimental results. [25] Therefore, we conclude that ferrimagnetism in GFO is solely due to site disorder in the structure.

3.4. Born Effective Charge and Spontaneous Polarization

Born effective charges (BEC or Z^*), are important quantities in characterizing the piezoelectrics, ferroelectrics and multiferroics since they relate the lattice displacements and electric field and therefore give a measure long range Coulomb interaction, whose competition with the short range forces leads to the ferroelectric transition. Recent first-principles calculations show anomalously large BECs for some ions in common ferroelectrics [21] which are often explained as manifestation of strong covalent character of bonds between the specific ions. In GFO, from the ELF plots, we find that charge sharing between the Ga/Fe and O ions in cation-oxygen bonds is insignificant while the structural data indicates large distortion of the cation-oxygen polyhedra. Since ferroelectric and/ piezoelectric responses are combined manifestations of structural distortions and effective charges of constituent ions [26] it is imperative to calculate the Born effective charges of ions in GFO. Here we calculate the BEC tensors of nonequivalent ions of GFO by slightly displacing each ion, one at a time, along three axes of Cartesian co-ordinates and then calculating the resulting difference in polarization, using Berry phase method. **Table 1** lists the diagonal elements of BEC tensor for each ion. It is noticed that the principal elements of BEC tensor for Ga1 are close to the nominal ionic charge of Ga *i.e.*, +3. Thus we predict that all the Ga1-O bonds are mainly ionic in nature. On the other hand, Ga2 develops a maximum effective charge of 3.53, $\sim 18\%$ higher with respect to its nominal charge. In contrast, both Fe1 and Fe2 ions show much higher increase in the effective charges, 36% and 27% respectively. Oxygen ions show a maximum reduction of 39.5% with respect to the nominal ionic charge.

Structural analysis of GFO shows that while the constituent ions possess inversion symmetry in the crystallographic *a* and *c* directions, the inversion symmetry is lost in crystallographic *b*-direction. Since existence of spontaneous polarization (P_s) is manifestation of the lack of inversion symmetry, we argue that the direction of spontaneous polarization in GFO is only along the *b*-direction. Using the Born effective charges from **Table 1**, we further calculated the magnitude of P_s of GFO as $\sim 58.63 \mu C/cm^2$ along the *b*-direction which is an order of magnitude larger than that predicted by Arima *et al.*[1] who neglected the role of effective charges and other ions in determining the magnitude of P_s . A calculation on the relative contribution of

Table 1. Principal elements of Born effective charge tensors of constituent ions along with their nominal charges, in GFO.

Ion	Nominal ionic charge (e)	Z^* (e)		
		Z_{xx}	Z_{yy}	Z_{zz}
Ga1	+3	3.01	3.11	2.99
Ga2	+3	3.57	3.16	3.53
Fe1	+3	3.66	3.78	4.08
Fe2	+3	3.68	3.38	3.82
O1	-2	-2.29	-2.58	-2.79
O2	-2	-2.45	-2.29	-2.41
O3	-2	-2.54	-2.30	-2.75
O4	-2	-2.27	-2.85	-2.17
O5	-2	-2.50	-2.16	-2.79
O6	-2	-2.32	-2.08	-2.40

individual ions shows that the contribution of Ga1 is largest. However, it is balanced by opposite contributions from Fe1, O1, O2 and O6. Structural data further substantiate that these ions are the most asymmetrically placed around the inversion center whereas Ga2 and Fe2 cations maintain nearly centrosymmetric configuration and contribute minimum to the total polarization. Therefore, we predict that P_s in GFO is primarily contributed from Ga1, Fe1, O1, O2 and O6 ions.

4. Summary

To summarize, we show, using first-principles calculations using LSDA+U that orthorhombic $Pc2_1n$ symmetry with A-type antiferromagnetic spin configuration is the ground state structure of gallium ferrite. The calculated ground state lattice parameters, bond strength and bond angles agree well with the reported as well as our experimental results. Electronic density of states showed hybridization among Fe $3d$, Ga $4s$, Ga $4p$ and O $2p$ states. From the electron localization function (ELF) calculation, we find almost complete charge transfer between Fe2 and O3 and Fe1 and O1, O2 ions suggesting that Fe-O bonds in GFO have mostly ionic character. Calculations also showed a spontaneous polarization of $\sim 59 \mu\text{C}/\text{cm}^2$ along b -direction i.e. [010]-axis of GFO, attributed to the non-centrosymmetry and effective charges of Ga1, Fe1, O1, O2 and O6 ions. We find that the cation site disorder, although not preferred in the ground state, is the most favored configuration in the disordered state. An examination of the role of cation site disorder on magnetic structure of GFO shows modification of the local magnetic structure with altered magnetic moments of Fe ions at Ga site. This suggests that ferrimagnetism in GFO is solely due to the site disorder.

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REFERENCES

- [1] T. Arima, D. Higashiyama, Y. Kaneko, J. P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, and Y. Tokura, *Physical Review B* 70 (6), 064426 (2004).
- [2] J. P. Remeika, *Journal of Applied Physics* 31 (5), S263 (1960).
- [3] C. H. Nowlin and R. V. Jones, *Journal of Applied Physics* 34 (4), 1262 (1963).
- [4] M. B. Mohamed, A. Senyshyn, H. Ehrenberg, and H. Fuess, *Journal of Alloys and Compounds* 492 (1-2), L20.
- [5] W. Kim, J. H. We, S. J. Kim, and C. S. Kim, *Journal of Applied Physics* 101 (9), 09M515 (2007).
- [6] Y. Kaneko, T. Arima, J. P. He, R. Kumai, and Y. Tokura, *Journal of Magnetism and Magnetic Materials* 272-276 (Part 1), 555 (2004).
- [7] S. Mukherjee, A. Garg, and R. Gupta, *Journal of Physics: Condensed Matter* 23 (44), 445403 (2011).
- [8] R. B. Frankel, N. A. Blum, S. Foner, A. J. Freeman, and M. Schieber, *Physical Review Letters* 15 (25), 958 (1965).
- [9] D. L. White, *Bull. Am. Phys. Soc.* 5, 189 (1960).
- [10] S. C. Abrahams and J. M. Reddy, *Physical Review Letters* 13 (23), 688 (1964).
- [11] G. Kresse and D. Joubert, *Physical Review B* 59 (3), 1758 (1999).
- [12] P. E. Blöchl, *Physical Review B* 50 (24), 17953 (1994).
- [13] W. Kohn and L. J. Sham, *Physical Review* 140 (4A), A1133 (1965).
- [14] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *Journal of Physics: Condensed Matter* 9 (4), 767 (1997).
- [15] H. J. Monkhorst and J. D. Pack, *Physical Review B* 13 (12), 5188 (1976).
- [16] R. D. King-Smith and D. Vanderbilt, *Physical Review B* 47 (3), 1651 (1993).
- [17] M. J. Han, T. Ozaki, and J. Yu, *Physical Review B* 75 (6), 060404 (2007).
- [18] S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, *The Journal of Chemical Physics* 42 (11), 3957 (1965).
- [19] J. B. Goodenough, *Physical Review* 100 (2), 564 (1955).
- [20] Z. H. Sun, S. Dai, Y. L. Zhou, L. Z. Cao, and Z. H. Chen, *Thin Solid Films* 516 (21), 7433 (2008).
- [21] A. Roy and et al., *Journal of Physics: Condensed Matter* 22 (16), 165902 (2010).
- [22] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, *Applied Physics Letters* 94 (4), 041903 (2009).
- [23] A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, *Angewandte Chemie International Edition in English* 36 (17), 1808 (1997).
- [24] A. Roy, S. Mukherjee, R. Gupta, S. Auluck, R. Prasad, and A. Garg, *Journal of Physics: Condensed Matter* 23 (32), 325902 (2011).
- [25] A. Roy, R. Prasad, S. Auluck, and A. Garg, *Journal of Applied Physics* 111 (4), 043915 (2012).
- [26] R. E. Cohen, in *Piezoelectricity* (Springer Berlin Heidelberg, 2008), Vol. 114, pp. 471.