Probing magnetoelastic coupling and structural changes in magnetoelastic gallium ferrite

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Abstract

Temperature dependent x-ray diffraction and Raman spectroscopic studies were carried out on flux-grown single crystals of gallium ferrite with a Ga:Fe ratio of 0.9:1.1. Site occupancy calculations from the Rietveld refinement of the x-ray data led to an estimated magnetic moment of $\sim 0.60 \, \mu_B/\text{f.u.}$ which was in good agreement with the experimental data. A combination of these two measurements indicates that there is no structural phase transition in the material between 18 and 700 K. A detailed line shape analysis of the Raman mode at $\sim 374 \, \text{cm}^{-1}$ revealed a discontinuity in the peak position data indicating the presence of spin–phonon coupling in gallium ferrite. A correlation of the peak frequency with the magnetization data led to two distinct regions across a temperature $\sim 180 \, \text{K}$ with appreciable change in the spin–phonon coupling strength from $\sim 0.9 \, (T < 180 \, \text{K})$ to 0.12 cm$^{-1}$ ($180 \, \text{K} < T < T_c$). This abrupt change in the coupling strength at $\sim 180 \, \text{K}$ strongly suggests an altered spin dynamics across this temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Gallium ferrite (GaFeO$_3$ or GFO) is a room temperature piezoelectric [1, 2] and a ferri-/paramagnet [3]. It possesses a non-centrosymmetric orthorhombic structure with space group $Pc2_1\text{m}$ [4]. Its magnetic transition temperature ($T_c$) is sensitive to the stoichiometry of the material i.e. Ga:Fe ratio [5]. Initial interest in GFO arose from a report by Rado [6] showing a large magnetoelastic coupling in stoichiometric GFO ($\alpha_{\text{ac}} \approx 1 \times 10^{-11} \, \text{S m}^{-1}$ at 77 K). In recent years, multiferroics and the study of the magnetoelastic phenomenon has gained prominence after illustration of this effect in perovskite oxides such as BiFeO$_3$ [7] and TbMnO$_3$ [8]. In GFO, recently Ogawa et al [9] demonstrated large magnetoelastic coupling as shown by magnetization induced second harmonic generation and large angle Kerr rotation of the second harmonic light in the ferrimagnetic state. In another study, Jung et al [10] reported optical absorption in the presence of a magnetic field of 500 Oe suggesting a large optical magnetoelectric effect below $T_c$. Moreover, in materials exhibiting large magnetoelectric coupling [11, 12], one may expect structural and magnetic degrees of freedom behaving in tandem. However, while GFO’s magnetoelectric characteristics are reasonably well demonstrated, its magnetoelastic behavior demands studies on high quality samples to elucidate structure–property correlations in GFO.

A recent structural study [10] on single crystal GFO using neutron and synchrotron scattering reported the absence of any structural change across the magnetic transition. In addition, significant distortion of the FeO$_6$ octahedra in the unit cell resulted in the shift of Fe ions from the center of FeO$_6$ octahedra, leading to a spontaneous polarization along the crystallographic $b$-direction [5]. In the context of structure
related studies of GFO, we note that many such studies have been conducted using tools which yield information at a rather macroscopic scale. It would, therefore, be interesting to examine the structure of GFO at nanometer-length scales using techniques such as Raman spectroscopy. Further, to the best of our knowledge, there is no report on the structural study of GFO beyond room temperature. Such a study, both at macroscopic and microscopic length scales, could shed light on the possible temperature driven structural phase transformation imparting higher symmetry to the system.

Raman spectroscopy has been used extensively to probe intricate structural details of various multiferroic materials such as structural distortion [13], spin dynamics [14] and any kind of coupling between structure and magnetic degrees of freedom [15, 16]. In particular, Raman spectroscopy has been used to elucidate the spin–phonon coupling in a variety of materials: in rare-earth manganites [17] showing large phonon softening across magnetic $T_c$, in TbMnO$_3$ [15] and in BiFeO$_3$ [18]. In rare-earth manganites, it was also shown that the manganites with smaller rare-earth ions show negligible spin–lattice coupling [17]. All these reports conclusively prove the utility of Raman spectroscopy to investigate multiferroic materials.

In this paper, we report a detailed x-ray diffraction and Raman study on flux-grown GFO single crystals to investigate the structure evolution, polyhedral distortion and magnetic moments on the basis of site occupancy and the role of low energy excitations across different transitions as a function of temperature in the temperature range 18–700 K.

2. Experimental details

Single crystals of GFO were synthesized by the flux growth process using $\beta$-Ga$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ as constituents and B$_2$O$_3$ and B$_2$O$_3$ as flux in the weight ratio 1:1.5:4:0.6 using a methodology similar to that reported in [1]. Dark brown crystals with dimensions $\sim 2\text{ mm} \times 4\text{ mm} \times 1\text{ mm}$ were extracted. Compositional analysis of the samples was carried out using energy dispersive spectroscopy (EDS) using an Oxford EDS spectrometer in a Zeiss scanning electron microscope. Average EDS data indicate that crystals are chemically homogeneous with a Ga to Fe molar ratio of 0.93:1.11 vis-à-vis initial mixing stoichiometry of 0.93:1.09 (Ga:Fe). Therefore, we specify our samples as Ga$_{2-x}$Fe$_x$O$_3$ with $1.09 \leq x \leq 1.11$. Temperature dependent powder x-ray diffraction (XRD) of the crushed single crystals was carried out using a high resolution Philips X’Pert PRO MRD diffractometer with an angular resolution of 0.0001°. A micro-Raman study was carried out in back scattering geometry using an optical fiber microscope coupled to a PI-Acton monochromator having a grating with 1800 grooves mm$^{-1}$ (resolution $\sim 0.6$ cm$^{-1}$/pixel) and a liquid nitrogen cooled CCD detector. An argon ion 514.5 nm laser line was used as an excitation source. The sample temperature was varied between 18 and 450 K using a closed cycle cryostat for the low temperature region while a hot–cold Linkam THMS600 stage was used for the high temperature region. Magnetization data as a function of temperature were acquired using a Quantum Design SQUID magnetometer.

3. Results and discussions

3.1. X-ray diffraction analysis

XRD data of the crushed single crystals were acquired over the temperature range 300–700 K at 50 K intervals within the 2θ range 26°–120°. Figure 1(a) shows representative XRD plots of the data taken at 300 and 700 K. The spectra were indexed to GFO ICDD data card no. 76-1005 and the peak match suggests single phase formation with no signature of secondary phase(s). The same holds true for all other intermediate temperatures whose plots are not shown here. Further, to understand any subtle change in the structure as well as to quantify the occupancy of lattice sites, we carried out Rietveld refinement of the XRD data using the FULLPROF 2000 package [19]. We used orthorhombic $Pc2_1n$ (Pna2$_1$; notation used in international tables of crystallography) symmetry of GFO in our refinements at all temperatures. The resolution of our measurements is better than 0.003 Å for all the d-values, well within the instrumental resolution. To avoid ambiguities, we excluded the 2θ region between 30.2° and 32.45° consisting of a peak of the high temperature dome material (PEEK). For refinements, we kept the anion site occupancies fixed to 1 for all the temperatures and the y-coordinate of the Ga1 ion was fixed to 0. The cation site occupancies were determined from the refinement of the 300 K data and these were kept constant in subsequent refinements for higher temperatures. Our refinements, as shown in figure 1(a), do not suggest any change in the peak profiles or relative intensities and thus rule out the existence of any anomalous structural change or distortion in GFO over the temperature range of our study. Further we analyzed the refined XRD data to understand the effect of temperature on the unit cell parameters, bond lengths and polyhedral distortion.

From the refinements, we obtained the atomic positions of the constituent ions and refinement parameters which are listed in table 1, showing the data for 300 and 700 K. Further, we estimated the lattice parameters at 300 K: $a = 8.744$ Å, $b = 9.395$ Å, $c = 5.079$ Å and unit cell volume, $V_{cell}$, of 417.26 Å$^3$. These values are in excellent agreement with those reported previously [4, 5]. Similarly, at 700 K the unit cell parameters and volume, calculated for the refined structure are $a = 8.769$ Å, $b = 9.422$ Å, $c = 5.097$ Å and $V_{cell} = 421.12$ Å$^3$, respectively. From these data, we then investigated the variation in the lattice parameters and unit cell volume between 300 and 700 K and a plot of these parameters versus temperature is shown in figure 1(b). As can be seen from the plot, the lattice parameters vary linearly with temperature. From the linear fitting of the above data, the coefficients of thermal expansion ($\alpha$, K$^{-1}$) of GFO along three principal axes ($\alpha$, $b$ and $c$) were calculated to be $7.2 \times 10^{-6}$, $7.5 \times 10^{-6}$ and $8.8 \times 10^{-6}$, respectively. Negligible difference among the three values suggests that GFO is a thermally isotropic material. From the slope of the unit cell volume versus temperature plot, the thermal coefficient for volume expansion ($\gamma$) was calculated to be...
2.37 × 10^-5 K^{-1} which follows the relation γ = 3α, true for an isotropic material. Further we estimated the GFO lattice parameters at low temperature by extrapolation and the estimated lattice parameters at 4 K, a ~ 8.725 Å, b ~ 9.374 Å and c ~ 5.066 Å, are in excellent agreement with those reported by Arima et al [5], (a ~ 8.71932(13) Å, b ~ 9.36838(15) Å c ~ 5.06723(8) Å). From the fact that the extrapolated lattice parameters agree with the reported low temperature data, it can be concluded that there is no structural transition or lattice parameter anomaly in GFO down to 4 K.

Next, to estimate the polyhedral distortions, we used the refined structural data to calculate the bond lengths using an approach proposed by Quentrec and Brot [20]. For clarity, a simulated crystal structure [21] of GFO has been shown in figure 1(c) where positions of Fe and Ga ions are marked: Ga1 is tetrahedrally coordinated while Ga2, Fe1 and Fe2 are octahedrally coordinated by oxygen atoms (shown clearly in figure 1(d) using data at 300 K). Here, we find that the Ga1–O tetrahedron is corner linked with the surrounding cation octahedra while the octahedra share their edges with each other. The estimated average bond lengths for Ga1–O, Ga2–O, Fe1–O and Fe2–O ions at 300 K are 1.860 Å, 2.023 Å, 2.033 Å and 2.039 Å, respectively. It is observed that upon increasing the temperature from 300 to 700 K, Ga1–O, Ga2–O and Fe1–O bonds stretch by 0.3%, 0.23% and 1.25%, respectively, while the Fe2–O bonds contract by 0.21%. This translates to a 0.54% reduction in the volume of Fe2–O octahedron, and an increase of 0.75%, 0.45% and 2.9% in Ga1–O tetrahedron, Ga2–O and Fe1–O octahedra volume, respectively. Further, changes in the bond lengths result in polyhedral distortion which is quantified by calculating the distortion index (Δ) as defined by Baur [22];

$$\Delta = \frac{1}{n} \sum_{i=1}^{n} \frac{(l_i - l_{avg})}{l_{avg}}$$  \hspace{1cm} (1)
Experimental studies show a large magnetic moment in GFO in a zero net magnetic moment [5, 23, 24]. In contrast, as \( \sim \) partial occupancies, we calculated the Ga to Fe ratio in GFO found to be 0.14, 0.32, 0.83 and 0.89, respectively. From the occupancies of iron at Ga1, Ga2, Fe1 and Fe2 sites are \( \sim \) of stoichiometric GaFeO\(_3\), as \( \sim \) 0.67 \( \mu_B \) at 4 K. A previous neutron diffraction study [5] showed that Fe at Ga2 and Fe2 sites are ferromagnetically coupled while no comments were made on the spin configuration of Fe at the Ga1 site. Assuming ferromagnetic coupling of Fe at Fe1 and Ga1 sites and high spin moment of Fe [3] and, using the cation partial occupancies from our Rietveld data, we estimated the net magnetic moment of GFO to be \( \sim \) 0.60 \( \mu_B \)/f.u. which is in excellent agreement with our experimental observation. In contrast, if we assume Fe at Ga1 and Fe1 are antiferromagnetically coupled, the estimated moment is \( \sim \) 1.3 \( \mu_B \)/f.u. which is very large in comparison with our experimental data. Thus, we would expect Fe at the Ga1 site to be ferromagnetically aligned with respect to Fe at the Fe1 site and antiferromagnetically aligned to Fe at the Fe2 (and also Fe at Ga2) site. We also calculated net magnetic moment using partial occupancies and magnetic moments determined by Arima et al [5]. These results are tabulated in table 2. Based on our assumption that Fe at Fe1 and Ga1 sites are ferromagnetically and using the site occupancy data in stoichiometric GFO as reported by Arima et al [5], we estimated the net magnetic moment of stoichiometric GaFeO\(_3\), as \( \sim \) 0.55 \( \mu_B \)/f.u. which is very close to their experimental observation (\( \sim \) 0.65 \( \mu_B \)/f.u.). Here, the moment of Fe at the Ga1 site was taken to be the same as the moment of Fe at the Fe1 site. Finally, we calculated the net magnetic moment of GFO (0.86 \( \mu_B \)/f.u.) using partial occupancies of our Rietveld data and the magnetic moments from Arima et al [5]. The observed difference between the calculated and experimental moments might be attributed to the difference in the magnetic moments of Fe at cation sites (with respect to Arima et al [5]) due to nonstoichiometry of our sample. From this discussion, we conclude that the magnetism in GFO is highly sensitive to the cation site

| Ion (Wyckoff position) | 300 K | 700 K |
|------------------------|-------|-------|
| x | y | z | x | y | z |
| Ga1 (4a) | 0.1590(6) | 0 | 0.1617(2) | 0.1592(6) | 0 | 0.1649(4) |
| Ga2 (4a) | 0.1642(6) | 0.3124(8) | 0.8033(9) | 0.1644(5) | 0.3143(9) | 0.8084(4) |
| Fe1 (4a) | 0.1337(2) | 0.5791(5) | 0.1948(5) | 0.1357(7) | 0.5832(5) | 0.2053(9) |
| Fe2 (4a) | 0.0371(1) | 0.7910(4) | 0.6698(3) | 0.0376(8) | 0.7900(5) | 0.6712(9) |
| O1 (4a) | 0.3259(7) | 0.4360(9) | 0.9781(9) | 0.3283(7) | 0.4252(9) | 0.9810(1) |
| O2 (4a) | 0.4981(5) | 0.4226(3) | 0.5238(7) | 0.5014(2) | 0.4252(2) | 0.5367(4) |
| O3 (4a) | 0.9944(5) | 0.2094(7) | 0.6578(5) | 0.9964(2) | 0.2030(9) | 0.6539(2) |
| O4 (4a) | 0.1601(8) | 0.1998(3) | 0.1518(1) | 0.1583(3) | 0.1993(8) | 0.1474(1) |
| O5 (4a) | 0.1687(9) | 0.6624(5) | 0.8517(2) | 0.1713(5) | 0.6616(6) | 0.8541(9) |
| O6 (4a) | 0.1638(1) | 0.9319(6) | 0.5065(2) | 0.1630(7) | 0.9326(5) | 0.5055(5) |

where \( l_i \) is the distance from the central atom to the \( i \)th coordinating atom, \( n \) is the number of bonds and \( l_{avg} \) is the average bond length. It is observed that, at 300 K, the Ga1–O tetrahedron is least distorted (\( \Delta = 0.0065 \)) among all the polyhedra and remains close to its ideal shape, while, both Fe1–O and Fe2–O octahedra are significantly distorted with \( \Delta = 0.0650 \) and 0.0760, respectively, and the Ga2–O octahedron is comparatively less distorted (\( \Delta = 0.0182 \)). Upon increasing the temperature to 700 K, the distortion indices of the above polyhedra change to 0.0051, 0.0806, 0.0701 and 0.0260, respectively. This shows that with increasing temperature, the shape of the Ga1–O tetrahedron tends to become more regular (\( \Delta = 0.0 \)), the shape of the Fe2–O octahedron remains the same as at 300 K and Ga2–O and Fe1–O octahedra become further distorted. Such details on the structural distortion of GFO can be crucial to understand the temperature dependence of microscopic polarization in GFO. Previous first-principles studies have shown an important correlation between the structural distortion and polarization in GFO [23].

Structural refinement of the XRD data also gives an estimate of the cation occupancies which can be used to explain the observed magnetic behavior as cation site disordering can lead to significant changes in the magnetic properties [3, 5]. Site disordering in GFO is expected due to the fact that, in addition to being isovalent, the ionic radii of Fe and Ga are quite close to each other (0.645 and 0.62 Å, respectively). From the data at 300 K, we refined the cation occupancies keeping anion occupancies fixed at 1.0. The occupancies of iron at Ga1, Ga2, Fe1 and Fe2 sites are found to be 0.14, 0.32, 0.83 and 0.89, respectively. From the partial occupancies, we calculated the Ga to Fe ratio in GFO as \( \sim \) 0.93:1:11 which is in very good agreement with the EDS data, as mentioned in section 2. In the following paragraph, we discuss the correlation between cation site occupancies and the observed magnetic behavior of the GFO samples.

If GFO was to behave as a perfect antiferromagnet, the Fe spins on two octahedral sites would be antiparallel, resulting in a zero net magnetic moment [5, 23, 24]. In contrast, experimental studies show a large magnetic moment in GFO below \( T_c \) [5, 25]. It has been suggested that this observed magnetic moment at low temperatures can be attributed to the cation site disorder, i.e. the presence of octahedral Fe ions predominantly, on the octahedral Ga sites [5].
occupancies. Moreover, it is possible to tune the magnetic behavior of GFO by careful compositional tailoring.

### 3.2. Temperature dependent Raman spectroscopy

In a recent theoretical work, Fennie et al. [26] predicted that the combination of strain, spin–phonon coupling and optical modes can play an important role in simultaneously stabilizing both ferroelectric and ferromagnetic phases. The veracity of Fennie et al.’s work was demonstrated in a recent report by Lee et al. [11] in which tuning of bi-axial strain in EuTiO$_3$ thin films led to a large spin–lattice coupling, resulting in simultaneous ferroelectricity and ferromagnetism. Further, since Raman spectroscopy can probe lattice excitations, i.e. phonons, and magnetic excitations, i.e. magnons as well as their interactions, it is an ideal tool to investigate the spin–lattice coupling in materials. Spin correlation among the nearest neighbors, i.e. ($S_i$, $S_j$), can be used to relate the behavior of the phonons to determine the spin–lattice coupling strength [27].

In GFO, while the neutron studies conducted by Arima et al. did not make any mention of the first-order spin–lattice coupling [5], a recent Raman study on polycrystalline bulk stoichiometric GFO [28] speculated the existence of spin–lattice coupling based on the discontinuity in the line width of one of the phonons at 200 K. However, the poor quality of Raman spectra, possibly due to the polycrystalline nature of the samples, does not exude the confidence to draw these conclusions. In contrast, our temperature dependent Raman measurements have been carried out on high quality single crystals of GFO to investigate the temperature dependent behavior of Raman modes from the perspective of understanding the role of phonons across the phase transitions in this material.

Group theoretical methods predict that there are a total of 120 normal modes (117 Raman and 8 IR active) of vibration in GFO considering 8 f.u. in a primitive cell and $Pna2_1(C_{2h}^5)$ space group [28]. Since the above space group does not contain an inversion center, the IR active modes are simultaneously Raman active and these modes are non-degenerate [29]. In the present study, we acquired Raman spectra of single crystals and observed 32 Raman active modes in the spectral range 90–900 cm$^{-1}$ at 300 K. It is likely that while some modes are below our detection limit on the lower wave number side, orientation of the crystal may also restrict the observation of some other modes due to selection rules.

As can be seen from figure 2(a), 32 distinct Raman peaks occur at 99, 106, 118, 121, 129, 138, 149, 154, 173, 199, 211, 219, 240, 257, 270, 303, 329, 349, 359, 374, 394, 438, 465, 521, 575, 604, 655, 674 688, 723, 743 and 759 cm$^{-1}$. In contrast, the report by Sharma et al. [28] on polycrystalline GFO samples showed a rather broad spectrum with a fewer number of Raman modes. The representative spectra measured from our samples at various temperatures between 18 and 450 K are shown in figure 2(a). A first glance suggests that the Raman modes harden with the lowering of temperature accompanied by a narrowing of the peak widths. Moreover, upon cooling across the magnetic transition ($T_c \sim$ 290 K), the number of Raman peaks remains the same suggesting the absence of a structural change near $T_c$, consistent with the temperature dependent neutron diffraction studies reported earlier [5]. For further analysis of the Raman data to examine any subtle change in the structure, we divided the entire spectrum into two ranges, i.e. 275–550 cm$^{-1}$ and 620–820 cm$^{-1}$. The spectra in these two ranges were deconvoluted into a sum of nine and six Lorentzians, labeled as M1 to M9 and X1 to X6, respectively, as shown in figures 2(b) and (c) along with the fitted curves. The extracted line shape parameters characterizing a Lorentzian function, i.e. peak positions and line widths or FWHM increase with increasing temperature. Similar behavior also holds true for X1–X6 modes. Such a behavior is an expected outcome of lattice expansion and an increase in the phonon population as a result of increasing temperature.

This hardening of phonons with decreasing temperature can be described by the following relation [30],

$$\omega_j(T) = \omega_j(0) + (\Delta\omega_j)_\text{el-ph}(T) + (\Delta\omega_j)_\text{anh}(T) + (\Delta\omega_j)_\text{el-ph}(T) + (\Delta\omega_j)_\text{sp-ph}(T)$$

where $\omega_j(T)$ and $\omega_j(0)$ are the phonon frequencies of the $j$th mode at any temperature $T$ and at 0 K, $(\Delta\omega_j)_{\text{el-ph}}$,
Figure 2. Temperature dependent Raman spectra of a GFO single crystal (a) at selected temperatures between 18 and 450 K and in the frequency range (b) 275–550 cm\(^{-1}\) and (c) 620–820 cm\(^{-1}\). Each spectrum was fitted with a sum of Lorentzian line shapes and fitted spectra are superimposed.

\(\Delta \omega_j\)\(_{\text{anh}}\), \(\Delta \omega_j\)\(_{\text{el-ph}}\) and \(\Delta \omega_j\)\(_{\text{sp-ph}}\) are the changes in phonon frequencies, respectively due to change in the lattice parameters of the unit cell (quasi-harmonic effect), intrinsic anharmonic interactions, electron–phonon coupling and spin–phonon coupling in magnetic materials caused by the modulation of exchange integral by lattice vibrations [30].

The quasi-harmonic effect on the vibrational mode due to change in the unit cell volume triggered by the thermal effects can be approximated by Grüneisen’s law relating the change in the frequency to the change in the lattice volume [30], i.e. \(\Delta \omega_j/\omega_j\)\(_{\text{qh}}\) = \(\gamma_j\)\((\Delta V/V)\) \((\gamma_j\) is the Grüneisen parameter for the normal mode \(j\) and \(\Delta V/V\) is the fractional unit cell volume change due to thermal expansion). Since, XRD analysis shows minute change (<1\%) in the unit cell volume of GFO over the temperature range 18–450 K, it is expected that the contribution of quasi-harmonic effects on the mode frequency is negligible.

Next, we examine the contribution due to intrinsic anharmonic interactions, i.e. \(\Delta \omega_j\)\(_{\text{anh}}\). Let us consider only the contribution from cubic and quartic anharmonic processes and further assume that each phonon decays into lower energy phonons of equal energy, i.e. a phonon with frequency \(\omega\) decays into (three) phonons of frequency \(\omega/2\) (\(\omega/3\)) for the cubic (quartic) anharmonic process. Therefore, the temperature dependence of frequency of the \(j\)th mode can be represented by the following relation (equation (3)) [31],

\[
\omega_j(T) = \omega_j(0) - A_j \left[ 1 + \frac{2}{e^{\hbar \omega_j(0)/2k_BT} - 1} \right] - B_j \left[ 1 + \frac{3}{e^{\hbar \omega_j(0)/3k_BT} - 1} + \frac{3}{(e^{\hbar \omega_j(0)/3k_BT} - 1)^2} \right]
\]

where \(\omega_j(0)\) is 0 K frequency of the mode in harmonic approximation while \(A_j\) and \(B_j\) are anharmonicity coefficients, giving the strength of cubic and quartic anharmonic processes, respectively.
Figure 3. Temperature dependence of the line shape parameters of nine modes between 275 and 550 cm$^{-1}$. The solid and dotted lines represent the simulated peak position and line width data according to equations (3) and (4), respectively. The ferri- to paramagnetic transition temperature ($T_c = 290$ K) is marked for reference.

Similarly, the line width of a Raman mode has the following temperature dependence,

$$\Gamma_j(T) = \Gamma_j(0) + C_j \left[ 1 + \frac{2}{\beta \omega_j(0)/2k_B T - 1} \right] + D_j \left[ 1 + \frac{3}{\beta \omega_j(0)/3k_B T - 1} + \frac{3}{(\beta \omega_j(0)/3k_B T - 1)^2} \right]$$

(4)

where $\Gamma_j(0)$ is intrinsic broadening of the $j$th mode arising from factors other than phonon decay such as the presence of structural defects while $C_j$ and $D_j$ are parameters for cubic and quartic anharmonic processes, respectively.

Equations (3) and (4) have been used to fit the peak frequency and line width data for modes M1–M9 (shown in figure 3) and modes X1–X6 (not shown here). It was observed that the temperature dependence of the peak position of modes M1, M2, M3, M4, M6 (see figure 3) fits reasonably well to equation (3). However, the frequency shifts of modes M5, M7, M8 and M9 cannot be adequately described by equation (3) using one set of fitting parameters. Hence, the parameters $\omega_0(0)$, $A$ and $B$ for these modes were optimized by fitting the experimental data above $T_c$. Below $T_c$, the most pronounced deviation from the fit is found for modes M5 and M9, with M5 softening and M9 hardening. Figure 3 also shows the plot of variation of the line width (right axis) of the above nine modes (M1–M9) as a function of temperature along with the fits using equation (4). Here, the modes M2, M3, M4, M6 and M8 in figure 3 fit particularly well to equation (4) throughout the entire temperature range. As far as modes M1, M5, M7, M9 are concerned, the line widths of these modes follow the anharmonic interaction model reasonably well below $T_c$. However, above $T_c$, line widths of these modes become nearly temperature independent, resulting in significant deviation from the fit to equation (4). These changes in the line widths for some of the modes below $T_c$ indicate a spin–phonon interaction in GFO. The apparent temperature independent behavior of line widths of a few modes can be argued as a consequence of the competition between a decrease in the line widths due to the absence of magnon–phonon interaction above $T_c$ and an increase in the line widths with increased site disordering with increasing temperature. Since GFO is an insulator within the studied temperature range, electron–phonon interaction is unlikely to be temperature dependent and hence its contribution to change in line width with temperature can be neglected [30].

Finally, to quantify the spin–phonon coupling strength as given by the last term in equation (2), we utilize the formalism proposed by Granado et al [30] suggesting a mechanism for phonon renormalization due to spin–phonon interactions. The spin–phonon coupling strength for a given mode can be estimated by relating the change in the peak position from the conventional anharmonic behavior below $T_c$ to the
 nearest neighbor spin–spin correlation function as given by \( \Delta \omega_{\text{sp-ph}} \approx \eta \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \). Here, \( \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = 2 \left( M(T)/M_s \right)^2 \); \( M(T) \) is the magnetization of GFO per Fe site below \( T_c \), \( M_s \) is the saturation magnetization and \( \eta \) represents the spin–phonon coupling strength. The factor of two on the right arises due to two nearest neighbors in the ferromagnetic \( ac \)-plane for each type of Fe ion in the unit cell. Since, mode M5 at 374 cm\(^{-1} \) exhibits the largest deviation from the conventional anharmonic behavior below \( T_c \), this should correspond to possibly the largest value of \( \eta \). As per the above relation, a plot between \( \omega(T) \) versus \( [M(T)/M_s]^2 \), as shown in figure 4, is used to estimate the value of \( \eta \) (1/2 of the slope, \( m \)) for GFO. The figure shows two distinct regions across a temperature \( \sim 180 \) K, defined as \( T_1 \), as depicted by the sharp change of slope: a region on the low temperature side below \( T_1 \) with a relatively large value of \( \eta \sim 0.9 \) cm\(^{-1} \) and another region above \( T_1 \) but below \( T_c \) with a much smaller value of \( \eta \sim 0.12 \) cm\(^{-1} \). Such an abrupt change in \( \eta \) across \( T_1 \) is a strong indication of change in the spin dynamics in GFO. Moreover, these values of \( \eta \) obtained for GFO are comparable to the earlier estimates reported for other systems using Raman scattering. For instance, on antiferromagnetic rutile structured MnF\(_2\) and FeF\(_2\), Lockwood et al [27] showed the spin–phonon coupling strength for different modes in the range from 1.3 to \( \sim 0.4 \) cm\(^{-1} \) while Gupta et al [32] found a very large spin–phonon coupling strength (\( \sim 5.2 \) cm\(^{-1} \)) for Sr\(_2\)Ru\(_3\)O\(_{10}\). Therefore, our measurements suggest that the spin–phonon coupling of GFO is rather weak immediately below \( T_1 \) until \( T_1 \) before increasing substantially below \( T_1 \). It would be interesting to further examine this phenomenon across \( T_1 \) by carrying out ac magnetic measurements as a function of temperature and frequency to understand the spin dynamics and to probe deeper into the nature of this transition.

4. Conclusions

In conclusion, temperature dependent x-ray and Raman studies of GFO single crystals ruled out any structural transition between 18 and 700 K. Rietveld refinement of the XRD data showed a thermally isotropic nature of the material. Calculated magnetic moments based on the cation occupancies, determined from Rietveld refinement, matched very well with the experimentally measured values and supported cationic site disorder as a mechanism for the observed ferrimagnetic behavior. The variation of the peak position for the Raman mode at \( \sim 374 \) cm\(^{-1} \) with temperature suggested spin–phonon interactions in the material with a coupling strength of \( \sim 0.9 \) cm\(^{-1} \) below \( \sim 180 \) K. The abrupt change in the slope of phonon frequency versus the square of normalized magnetization at \( \sim 180 \) K indicates a change in the nature of spin–lattice interactions across this temperature.

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