



Origin of the different multiferroism in BiFeO₃ and GaFeO₃

S. G. Bahoosh and J. M. Wesselinowa

Citation: *Journal of Applied Physics* **113**, 063905 (2013); doi: 10.1063/1.4791586

View online: <http://dx.doi.org/10.1063/1.4791586>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/113/6?ver=pdfcov>

Published by the [AIP Publishing](#)



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



Origin of the different multiferroism in BiFeO_3 and GaFeO_3

S. G. Bahoosh¹ and J. M. Wesselinowa²

¹Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

²Department of Physics, University of Sofia, Blvd. J. Bouchier 5, 1164 Sofia, Bulgaria

(Received 1 December 2012; accepted 28 January 2013; published online 11 February 2013)

We have proposed microscopic models for describing the multiferroic properties of BiFeO_3 and GaFeO_3 . It is shown that the mechanisms of the multiferroism are different. In BiFeO_3 , the magnetoelectric coupling is biquadratic, whereas in GaFeO_3 it is linear. The site disorder between Ga and Fe is a primary source of the net magnetic moment in GaFeO_3 . The temperature and magnetic field dependence of the polarization is calculated in order to show that the proposed models for these two multiferroics are correct. Near the magnetic phase transition temperature T_N we obtain a kink in the electric properties. © 2013 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.4791586>]

I. INTRODUCTION

There has been increasing recent interest in magnetoelectric (ME) multiferroics,^{1,2} which are materials that show spontaneous magnetic and electric ordering in the same phase. In multiferroics, it is possible that the spontaneous magnetization can be switched by an electric field or the polarization by a magnetic field. Although a certain number of materials with ferroelectricity and ferromagnetism exists, the coupling between those two properties is not always large enough. The nontrivial spin lattice coupling in these multiferroics has been manifested through various forms such as linear and bilinear ME effects, polarization change through field-induced phase transition, ME effect and dielectric anomalies at magnetic transition temperatures. Typically, the ferroelectric transition temperature is much higher than the magnetic one and the coupling between the two order parameters is weak, for example, in the transition metal perovskites BiFeO_3 (BFO) and the hexagonal RMnO_3 compounds. For potential applications of multiferroics, it is very important to establish general mechanisms that give rise to a strong coupling of ferroelectricity and magnetism. More specifically, one would like to construct situations where the two ordering temperatures can become close or even coincide: in that case one expects strong multiferroic behavior with a pronounced interdependence of the ferroelectric and magnetic order parameters. Such compounds are, for example, the orthorhombic RMnO_3 , RMn_2O_5 , MnWO_4 . It should be emphasized that various mechanisms of this ME coupling were predicted for both single-phase multiferroics and composite materials involving ferroelectric and magnetic phases. It is of fundamental interest to understand how such a coupling comes about and what is the microscopic mechanism behind the ME coupling in multiferroics. The aim of the present paper is to clarify the different origins of multiferroism in GaFeO_3 and BFO.

Most ferroelectrics are transition metal oxides, in which transition ions have empty d shells. These positively charged ions like to form “molecules” with one (or several) of the neighboring negative oxygen ions. This collective shift of cations and anions inside a periodic crystal induces bulk electric

polarization. The mechanism of the covalent bonding (electronic pairing) in such molecules is the virtual hopping of electrons from the filled oxygen shell to the empty d shell of a transition metal ion. Magnetism, on the contrary, requires transition metal ions with partially filled d shells, as the spins of electrons occupying completely filled shells add to zero and do not participate in magnetic ordering. The exchange interaction between uncompensated spins of different ions, giving rise to long-range magnetic ordering, also results from the virtual hopping of electrons between the ions. In this respect, the two mechanisms are not so dissimilar, but the difference in filling of the d shells required for ferroelectricity and magnetism makes these two ordered states mutually exclusive. Still, some compounds, such as BFO with magnetic Fe^{3+} ions, are ferroelectric. Here, however, it is the Bi ion with two electrons on the $6s$ orbital (lone pair) that moves away from the centrosymmetric position in its oxygen surrounding.³ Because the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak. For example, BFO shows a ferroelectric transition at $T_C = 1100$ K and a ferromagnetic transition at $T_N = 650$ K, below which the two orders coexist.¹ The multiferroic properties of BFO are investigated by many authors experimentally⁴⁻⁶ and theoretically.⁷⁻¹⁰ The influence of the magnetic (or electric) external field on the spontaneous polarization (magnetization) is observed. There is a biquadratic ME coupling in BFO⁹ similar to the hexagonal RMnO_3 multiferroics with $T_C \gg T_N$.¹¹

GaFeO_3 (GFO) has magnetic and piezoelectric properties and has been intensively studied recently for its potential application as a magnetoelectric ferrimagnet. The ferrimagnetic Curie temperature T_N for GFO is about 225 K.¹² Magnetic ordering occurs due to cation-oxygen-cation superexchange antiferromagnetic interactions. The multiferroic properties are studied experimentally^{12,13} and theoretically.¹⁴⁻¹⁷ Disorder plays a significant role in determining the magnetic and dielectric properties of GFO.¹⁵ There are two different Ga ions, Ga(1) and Ga(2), which have a formal valence of 3+ with a d^{10} nonmagnetic configuration. There are also two different iron sites which are categorized into Fe(1) and Fe(2) with a strong antiferromagnetic interaction. Fe ions are expected to

have the same valence of 3+ as Ga ions but with a d^5 magnetic configuration. The excess Fe atoms occupying the octahedral Ga sites are ferromagnetically coupled with the Fe atom at one of the two Fe sites, which can explain the origin of the net magnetic moment observed in experiments. Fe(1) and Fe(2) sites are surrounded by oxygen octahedra. It must be noted that each oxygen octahedron is significantly distorted. The distorted network of oxygen leads to the distortion of Fe positions and forms a noncentrosymmetric structure for each individual octahedron, which is considered to be responsible for the electric polarization. In conclusion, the origin of the magnetoelectric couplings and multiferroicity in GFO is influenced by the site disorder from Ga/Fe atoms. An anomaly on the permittivity as a function of temperature has been observed near its magnetic transition point T_N , which could be induced by the magnetoelectric coupling between its electric and magnetic orders.¹³ At low temperature, $T < T_N$, the permittivity variation $\Delta\epsilon$ depends on magnetization M and shows clearly a linear relationship between $\Delta\epsilon$ and M^2 , which indicates that a dielectric and magnetic correlation exists in the compound. GFO crystallizes in the non-centrosymmetric orthorhombic structure. In this structure, polarization along z -axis can be non-zero because the inversion symmetry is broken and there is no symmetry that involves a reflection in xy plane. GFO compounds exhibit strong spin-phonon coupling,¹⁸ which is manifested in anomalies in their Raman spectra close to magnetic transitions. Due to the unequal magnetic moments developed on the Fe ions in the presence of anti-site defects, the spin-phonon coupling locally changes the structure. These displacements of the ions are expected to contribute additionally to non-zero P_x and P_y . Such magnetostriction is expected to give rise to observable electromagnons¹⁹ in these compounds.

II. MODEL AND GREEN'S FUNCTIONS

Taking into account, these differences in the two multiferroic compounds we propose the following microscopic models in order to describe their properties. The Hamiltonian for BFO can be written as:⁹

$$H = H^e + H^m + H^{me}. \quad (1)$$

H^e is the Hamiltonian of the transverse Ising model (TIM) for the electric subsystem. Blinc and de Gennes²⁰ proposed the TIM for the description of order-disorder KDP-type FE. Further the TIM is applied to displacive type FE such as BaTiO_3 ,^{21,22} too. In the case of a tunneling frequency very small with respect of the interaction constant one may use the TIM as a model for order-disorder FE without tunneling motion (e.g., for NaNO_2 , TGS). Therefore, the TIM can be applied to describe the electric polarization in all type FE:

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (2)$$

where S_i^x , S_i^z are the spin-1/2 operators of the pseudo-spins, $J_{ij} > 0$ denotes the nearest-neighbor pseudo-spin interaction, Ω is the tunnelling frequency. In the ordered phase, we have the mean values $\langle S^x \rangle \neq 0$ and $\langle S^z \rangle \neq 0$, and it is appropriate

to choose a new coordinate system rotating the original one used in Eq. (2) by the angle θ in the xz plane. The rotation angle θ is determined by the requirement $\langle S^x \rangle = 0$ in the new coordinate system.

H^m is the Heisenberg Hamiltonian for the magnetic subsystem:

$$H^m = -\frac{1}{2} \sum_{\langle ij \rangle} A_1(i,j) \mathbf{B}_i \cdot \mathbf{B}_j - \frac{1}{2} \sum_{\langle ij \rangle} A_2(i,j) \mathbf{B}_i \cdot \mathbf{B}_j - \sum_i D_i (B_i^z)^2 - g\mu_B H \sum_i B_i^z, \quad (3)$$

where \mathbf{B} is the Heisenberg spin operator for the Fe ion, the exchange integrals A_1 and A_2 represent the coupling between the nearest and next-nearest neighbors, respectively, D_i ($D < 0$) is the single-site anisotropy parameter, $|D| < A_1$, H is an external magnetic field.

H^{me} describes the coupling between the magnetic and the electrical subsystems in BFO which we take to be biquadratic:

$$H^{me} = -g \sum_{ij} \sum_{kl} S_k^z S_l^z \mathbf{B}_i \cdot \mathbf{B}_j. \quad (4)$$

Although many theoretical and experimental researches have been processed on coupling between the magnetic and electric subsystems, the form of the ME energy and the coupling mechanism is still an important issue for debate. Katsufuji *et al.*²³ found that the changes in dielectric and magnetic properties of the hexagonal ferroelectromagnet RMnO_3 are dominated by the pair correlation of the nearest-neighbor Mn ions, $\langle \vec{B}_i \vec{B}_j \rangle$. So, for the coupling of intrinsic spin and polarization, there are sufficient reasons for proposing such a biquadratic ME coupling term.⁶ The use of the TIM and biquadratic coupling between the pseudospins and magnetic moments, Eq. (4), implies that the magnetic and ferroelectric ordering have independent mechanism. In particular, this generally leads to different transition temperatures for the two subsystems. The model can be applied to multiferroic substances where $T_C \gg T_N$, for example, hexagonal RMnO_3 and BFO.

For the other multiferroic compound, GFO, the multiferroic nature in these oxides arises from the magnetically induced ferroelectricity in these materials. There are a few recent reports where ferroelectricity in certain oxides arises from magnetic interactions and related factors. Thus, in GdFeO_3 ferroelectric polarization is induced by striction through exchange interaction between the Gd and Fe spins.²⁴ Ferroelectricity in $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ arises from magnetic interactions involving the two transition metal ions,²⁵ while in $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ ferroelectricity is driven by the off-centering of magnetic Mn^{4+} ion in the antiferromagnetic insulator.²⁶ In SmFeO_3 , two non-equivalent spin pairs give rise to ferroelectric polarization.²⁷ The oxides, in this study, have only one magnetic ion (Fe^{3+}), but there is considerable disorder which can give rise to different spin states of the octahedral Fe^{3+} ions.¹⁶ Ferroelectricity caused by the presence of two such Fe^{3+} ions in simple oxides of the type GaFeO_3 or AlFeO_3 is indeed interesting. Therefore, the ME coupling

term H^{me} , Eq. (4) must be modified. In GFO, similar to the orthorhombic $RMnO_3$ and RMn_2O_5 ,²⁸ and in accordance to the results observed by Sun *et al.*¹³ for GFO, the leading ME interaction term is taken to be linear in the electrical dipole moment, due to the improper nature of its ferroelectricity. In a ferroelectromagnet, the difference in the dielectric constant $[\Delta\epsilon = \epsilon(H) - \epsilon(0)]$ below T_C is proportional to the square of the magnetization, i.e., $\Delta\epsilon \sim \gamma M^2$, where γ is the ME coupling constant.²⁹ Sun *et al.*¹³ have observed a linear relationship between $\Delta\epsilon$ and M^2 as an indication of the ME coupling. Therefore, the properties of GFO will be considered by the following coupling term H^{me} :

$$H^{me} = -g' \sum_{ij} \sum_k S_k^z \mathbf{B}_i \cdot \mathbf{B}_j. \quad (5)$$

Here g' is again the coupling constant between the magnetic and the electric order parameters. The ME coupling in this group of multiferroics should be invariant with respect to spatial inversion. Therefore, the actual coupling mechanism is more complicated and is proportional, e.g., to some vector, but the resulting coupling can be modelled by the form (5) where the coupling constant g' is a pseudoscalar. In the phenomenological treatment of Mostovoy,³⁰ this was taken by introducing one more vector in the ME coupling term, i.e., the coupling is not $S^z \mathbf{B} \mathbf{B}$, but rather $\mathbf{P} \cdot \mathbf{M} (\Delta \cdot \mathbf{M}) \dots$ in the notation of the author. In our model, the spins \mathbf{B} are even, but polarization, or pseudospins S are odd under reflection, i.e., S should change sign. For the total coupling term to be invariant, the coupling constant g' should change sign, i.e., it should be a pseudoscalar.

We have calculated the polarization in BFO from the Green's function $G_{ij} = \langle \langle S_i^+; S_j^- \rangle \rangle$ using the method of Tserkovnikov:³¹

$$P = \frac{1}{2N} \sum_k \tanh \frac{E(\mathbf{k})}{2k_B T}, \quad (6)$$

where $E(\mathbf{k})$ is the transverse pseudo-spin wave energy:

$$E(\mathbf{k}) = 2\Omega \sin \theta + \frac{1}{2} P \cos^2 \theta J_{eff} - \frac{1}{4} P \sin^2 \theta J_{eff}(\mathbf{k}) - \frac{1}{NP} \sum_q (\cos^2 \theta J_{eff}(\mathbf{k} - \mathbf{q}) - \frac{1}{2} \sin^2 \theta J_{eff}(\mathbf{q})) \langle S_q^- S_q^+ \rangle \quad (7)$$

with $\sin \theta = 4\Omega / (PJ_{eff})$ and $J_{eff} = J_0 + 2g(\langle B^- B^+ \rangle + \langle B^z \rangle^2)$. The magnetic correlation function $\langle B^- B^+ \rangle$ and the magnetization $\langle B^z \rangle$ are calculated from the spin Green's function $G'_{ij} = \langle \langle B_i^+; B_j^- \rangle \rangle$. Due to the ME coupling, the exchange interaction constant is also renormalized to $A_{1eff} = A_1 + 2gP^2 \cos^2 \theta$. Analogically calculations are made for GFO.

III. NUMERICAL RESULTS

In this section, we shall present the numerical calculations of our theoretical results taking the following model parameters, which are appropriate for BFO with $T_N = 640$ K, $T_C = 1100$ K: $A_1(\text{Fe-Fe}) = 35$ K, $A_2(\text{Fe-Fe}) = -42$ K, $D = -5$ K, $\Omega = 20$ K,

$J = 2350$ K, $g = 80$ K, $S = 2.5$ for the magnetic spins, and $S = 0.5$ for the pseudospins; and for GFO with $T_N = 225$ K, $T_C = 330$ K: $A_1(\text{Fe(1)-Fe(2)}) = -18$ K, $A_2(\text{Ga(1)-Fe(2)}) = 11$ K, $D = -5$ K, $\Omega = 20$ K, $J = 265$ K, $g' = 50$ K. The values for the exchange interaction constants J , A_1 , and A_2 can be estimated from the expression in mean-field theory $J = 3k_B T_C / zS(S+1)$ ³² where z is the number of nearest neighbors, S is the spin value, and k_B is the Boltzmann constant. From this relation, we have obtained the exchange interaction constants of the multiferroic BFO and GFO.

First, we consider the multiferroic BFO which is one of the few multiferroics with both ferroelectricity and magnetism above room temperature. The rhombohedrally distorted perovskite structure can be indexed with $a = b = c = 5.633 \text{ \AA}$, $\alpha = \beta = \gamma = 59.4^\circ$ and space group $R3c$ at room temperature, owing to the shift of Bi ions along the [111] direction and distortion of FeO_6 octahedra surrounding the [111] axis.¹ The electric polarization prefers to align along the [111] direction. In BFO, the Fe spins order antiferromagnetically below 640 K, in a complex spin structure based on G-type antiferromagnetism (i.e., with each Fe ion surrounded by six antiparallel nearest neighbors). We have calculated the spontaneous polarization $P \parallel c$, P_c , in BFO and the temperature dependence of P_c for $H = 0$ (curve 1) and for $H \parallel c \neq 0$ (curve 2) is shown in Fig. 1. The Curie temperature T_C and the polarization P_c increase with increasing of H_c . Figure 1 clearly illustrates the ME coupling between the two order parameters below $T_N = 640$ K, which is manifested as a kink at the magnetic phase transition temperature (curve 1). This anomaly in P_c can be explained as an influence of vanishing magnetic ordering in the system. Because of $T_N \ll T_C$, the magnetic subsystem cannot influence the ferroelectric one above T_N , the two phases coexist only below T_N . Such a kink is observed in the dielectric function $\epsilon(T)$ in the vicinity of the magnetic transition point in BFO nanoparticles.^{33,34} With increasing of the magnetic field H_c the kink in P_c disappears (curve 2). The disappearance is a result of the T_N shift due to the applied magnetic field. The magnetic phase transition temperature depends on H_c , it shifts to higher values and for $H_c \neq 0$ it is larger than T_C . Jun *et al.*³⁵ have investigated the temperature dependence of the

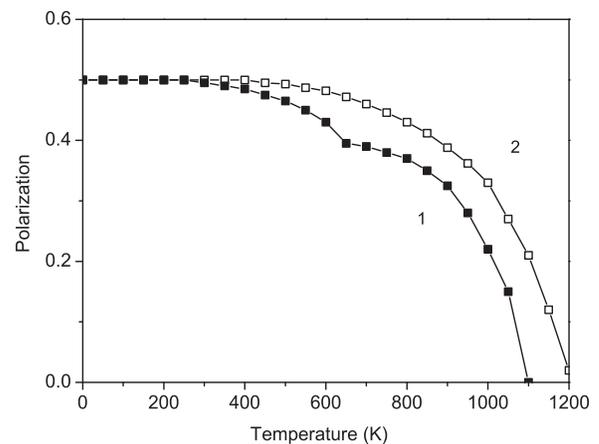


FIG. 1. Temperature dependence of the polarization P_c in BFO for (1) $H_c = 0$, kink at T_N , (2) $H_c \neq 0$, kink disappears.

dielectric constant in Nb-doped BFO ceramics for different magnetic fields. The anomaly in the dielectric constant disappears in the presence of high magnetic fields. Unfortunately, there are not so many experiments about the magnetic field influence in multiferroic BFO.

We will now discuss in more detail the effect of an applied magnetic field H_c on the polarization P_c . The ferroelectric properties strongly depend on the external magnetic field. This shows one of the important properties of multiferroics, that the polarization can be influenced by an external magnetic field. In Fig. 2, we present the magnetic field dependence of the polarization P_c . A continuous increase in the polarization P_c is seen with an increase of H_c , what would lead to increasing in the dielectric constant, too. This is indicative of the coupling between the order parameters - polarization and magnetization. The Curie temperature T_C and the pseudo-spin excitation energy increase with increasing of H_c , too. The increase of the polarization is stronger at high temperatures, at low temperatures the polarization is saturated and nearly independent on the applied magnetic field what is in qualitative agreement with the experimental data in polycrystalline BFO thin films of Naganuma and Okamura.³⁶ A stronger increase of the polarization at low temperatures including room temperatures could be obtained in BFO nanoparticles or thin films for example through ion doping or substrate effects. When a magnetic field is applied to a magnetoelectric material, the material is strained. This strain induces a stress on the piezoelectrics (all ferroelectrics are piezoelectrics), which generates the electric field. This field could orient the ferroelectric domains, leading to an increase in polarization value. Such magnetoelectric coupling and large polarization, i.e., large dielectric constant, could be useful in device applications. The obtained influence of an external magnetic field on the polarization is in agreement with the experimental data of Cheng and Wang³⁷ that the electrical polarization in an epitaxially BFO film grown on a SrTiO₃ substrate is greatly enhanced by a magnetic field. They proposed that due to the fact that both magnetic and ferroelectric domains are strongly coupled together in the BFO films the activation energy for the electrical polarization domains switching is reduced by the application of a magnetic field. As a result, the electrical polarization

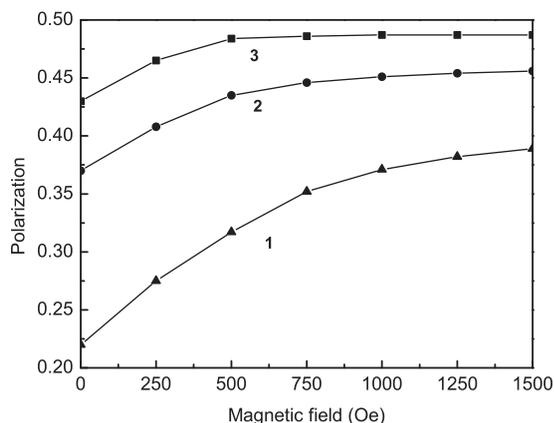


FIG. 2. Magnetic field dependence H_c of the polarization P_c in BFO for different temperature values: 1—1000; 2—800; 3—600 K.

that can be switched by an electrical field is increased by the magnetic field. A similar increase of the saturation polarization with an increase of the magnetic field is observed in Tb doped BFO by Palkar *et al.*³⁸

Now we will consider the multiferroic material GFO. It has an orthorhombic unit cell with $a \sim 8.8\text{\AA}$, $b \sim 9.4\text{\AA}$, $c \sim 5.1\text{\AA}$. The space group is $Pc2_1n$, which indicates the spontaneous polarization along the b axis, P_b , and behaves as ferrimagnetic with the spin moment along the c axis.³⁹ The origin of the polarization along the b axis is still discussed and there are two assumptions. Abrahams *et al.*⁴⁰ proposed that the piezoelectric effect in gallium iron oxide primarily originates in the Ga tetrahedron. Ga1-O4 bonds of the tetrahedron Ga1 is almost parallel to the axis b . Pressure along this direction may cause compression of this bond and induce a dipole. On the other hand, Arima *et al.*³⁹ assumed that each Fe atom is octahedrally surrounded by O atoms and slightly displaced from the center of the octahedron; the shift is 0.26\AA at Fe1 sites and -0.11\AA at Fe2 sites along the b axis. Thereby, the spontaneous electric polarization is generated along the b axis. Rado⁴¹ highlights the magnetoelectric coupling in GFO as an induced polarization P_b by a magnetic field along the c axis H_c . In Fig. 3 is demonstrated the temperature dependence of the polarization P_b in GFO. It decreases with increasing temperature T . At the ferrimagnetic transition temperature $T_N = 225\text{ K}$ (for $H = 0$) P shows a small kink (curve 1) which is an evidence for the ME effect in GFO. A similar behavior we observe also for the pseudo-spin wave energy E_b (Fig. 4), it decreases with increasing temperature and shows an anomaly at T_N which is stronger compared with that in P . So, we infer that this kind of anomaly could be attributed to a magnetic ordering from the super-exchange interaction between neighbouring Fe^{3+} ions. Recently, the electric polarization in GFO has been estimated by Mishra *et al.*⁴² using a simple ionic model and its value is found to decrease with increasing temperature. Moreover, we obtain that the kink in the polarization P_b and the pseudo-spin wave energy E_b is suppressed by an external magnetic field H_c and no cusp is observed (Figures 3 and 4, curve 2). This behavior is in qualitative agreement with the experimental results of Naik *et al.*¹² and Sun *et al.*¹³ The authors have studied the permittivity ϵ in GFO and observed

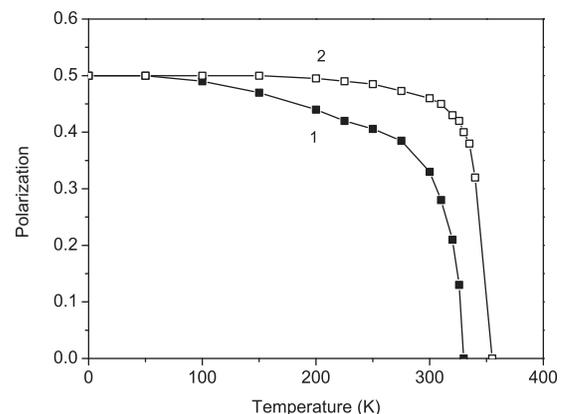


FIG. 3. Temperature dependence of the polarization P_b in GFO for (1) $H_c = 0$, kink at T_N , (2) $H_c \neq 0$, kink disappears.

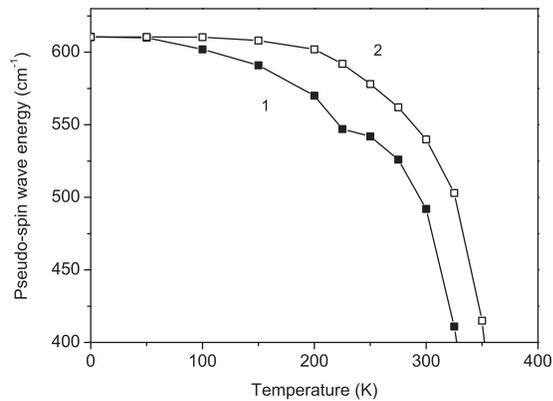


FIG. 4. Temperature dependence of the pseudo-spin wave energy E_b in GFO for (1) $H_c = 0$, kink at T_N , (2) $H_c \neq 0$, kink disappears.

a dielectric anomaly around the magnetic phase transition temperature T_N which disappears by applying of an external magnetic field H . Moreover, at low temperature, $T < T_N$, the permittivity variation $\Delta\epsilon$ depends on magnetization M and shows clearly a linear relationship between $\Delta\epsilon$ and M^2 ,¹³ which indicates that a dielectric and magnetic correlation exists in this compound. Analogous dielectric anomaly is observed in BiMnO_3 at T_N ,²⁹ which might be fully suppressed by a certain applied magnetic field, and then no dielectric cusp will be observed. Linear ME coupling is believed to operate also in multiferroics BaMnF_4 ⁴³ and FeTiO_3 .⁴⁴ For the case $H_c \neq 0$, the electric properties in b direction increase with H (curve 2). This is in agreement with the experimental data of Arima *et al.*³⁹ which explain the results as follows. In the H_c case where a magnetic field is parallel to the Fe spin moments, the Fe2 moment increases, while the Fe1 moment decreases. If the displacement along the b axis of Fe2 is enlarged by the modulation of the magnetic moment, that of Fe1 is reduced, conversely. Since the displacements of Fe1 and Fe2 are opposite in direction with each other, the magnetic field induced modulation of the displacement cooperatively affects the bulk polarization P_b as a result.

Recently, Saha *et al.*¹⁶ have shown that in GFO polarization along z -axis can be non-zero because the inversion symmetry is broken and there is no symmetry that involves a

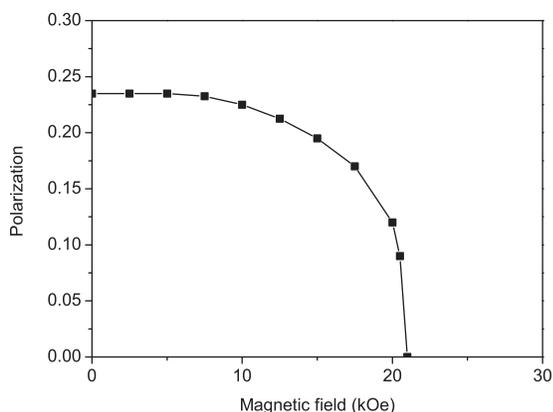


FIG. 5. The polarization P_c in dependence of the magnetic field H_c in GFO for $T = 150$ K.

reflection in xy -plane. They have noted that P_z is not switchable (cannot be reversed on the application of electric field of opposite polarity). We have calculated the electric polarization along the c axis induced by a magnetic field along the c axis. The results are shown in Fig. 5. It can be seen that the polarization decreases with increasing magnetic field. This behavior is in qualitative agreement with the experimental data of Naik *et al.*¹² and Saha *et al.*¹⁶ Suppression of polarization by magnetic fields indicates a strong magnetoelectric coupling.

IV. CONCLUSIONS

In conclusion, we have proposed microscopic models in order to explain the different origins of the ME effect in the multiferroic compounds BFO and GFO. In BFO, the ME coupling is taken to be biquadratic, whereas in GFO, it is linear. Disorder plays a significant role in determining the magnetic and dielectric properties of GFO. We have studied the temperature and magnetic field dependence of the polarization P and the pseudo-spin wave energy E . The appearance of an anomaly in the polarization P around T_N for zero magnetic field and its disappearance in a small magnetic field H suggest an active ME coupling in BFO and GFO. The behavior of the polarization in an external magnetic field is different in BFO and GFO and is dependent on the direction of P and H . The qualitative agreement with the experimental data is an evidence for the correct choice of our microscopic models.

ACKNOWLEDGMENTS

One of us (S.G.B.) acknowledges support by the International Max Planck Research School for Science and Technology of Nanostructures in Halle.

- ¹K. F. Wang, J.-M. Liu, and Z. F. Ren, *Adv. Phys.* **58**, 321 (2009).
- ²S.-W. Cheong and M. Mostovoy, *Nature Mater.* **6**, 13 (2007).
- ³R. Seshadri and N. A. Hill, *Chem. Mater.* **13**, 2892 (2001).
- ⁴Y.-H. Chu, L. W. Martin, M. B. Holcomb, and R. Ramesh, *Mater. Today* **10**, 16 (2007).
- ⁵R. Mazumder, S. Ghosh, P. Mondal, D. Bhattacharya, S. Dasgupta, N. Das, A. Sen, A. K. Tyagi, M. Sivakumar, T. Takami, and H. Ikuta, *J. Appl. Phys.* **100**, 033908 (2006).
- ⁶T.-J. Park, G. C. Papaefthymiou, A. J. Viescas, A. R. Moodenbaugh, and S. S. Wong, *Nano Lett.* **7**, 766 (2007).
- ⁷C.-W. Nan, G. Liu, Y. Lin, and H. Chen, *Phys. Rev. Lett.* **94**, 197203 (2005).
- ⁸J. Slutsker, I. Levin, J. Li, A. Artemev, and A. L. Roytburd, *Phys. Rev. B* **73**, 184127 (2006).
- ⁹St. Kovachev and J. M. Wesselinowa, *J. Phys.: Condens. Matter* **21**, 225007 (2009).
- ¹⁰A. Stroppa and S. Picozzi, *Phys. Chem. Chem. Phys.* **12**, 5405 (2010).
- ¹¹J. M. Wesselinowa and St. Kovachev, *J. Appl. Phys.* **102**, 043911 (2007).
- ¹²V. B. Naik and R. Mahendiran, *J. Appl. Phys.* **106**, 123910 (2009).
- ¹³Z. H. Sun, B. L. Cheng, S. Dai, L. Z. Cao, Y. L. Zhou, K. J. Jin, Z. H. Chen, and G. Z. Yang, *J. Phys. D: Appl. Phys.* **39**, 2481 (2006).
- ¹⁴A. N. Kalinkin and V. M. Skorikov, *Inorg. Mater.* **45**, 189 (2009).
- ¹⁵M. J. Han, T. Ozaki, and J. Yu, *Phys. Rev. B* **75**, 060404(R) (2007).
- ¹⁶R. Saha, A. Shireen, S. N. Shirodkar, U. V. Waghmare, A. Sundaresan, and C. N. R. Rao, *Solid State Commun.* **152**, 1964 (2012).
- ¹⁷D. Stoeffler, *J. Phys. Condens. Matter* **24**, 185502 (2012).
- ¹⁸R. Saha, A. Shireen, A. K. Bera, S. N. Shirodkar, Y. Sundarayya, N. Kalarikkal, S. M. Yusuf, U. V. Waghmare, A. Sundaresan, and C. N. R. Rao, *J. Solid State Chem.* **184**, 494 (2011).

- ¹⁹A. B. Sushkov, M. Mostovoy, R. V. Aguilar, S.-W. Cheong, and H. D. Drew, *J. Phys.: Condens. Matter* **20**, 434210 (2008).
- ²⁰R. Blinc and B. Zeks, *Soft Modes in Ferroelectric and Antiferroelectrics* (North-Holland, Amsterdam, 1974).
- ²¹R. Pirc and R. Blinc, *Phys. Rev. B* **70**, 134107 (2004).
- ²²H. X. Cao and Z. Y. Li, *J. Phys.: Condens. Matter* **15**, 6301 (2003).
- ²³T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, and H. Takagi, *Phys. Rev. B* **64**, 104419 (2001).
- ²⁴Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. Arima, and Y. Tokura, *Nature Mater.* **8**, 558 (2009).
- ²⁵P. Mandal, V. S. Bhadram, Y. Sundarayya, C. Narayana, A. Sundaresan, and C. N. R. Rao, *Phys. Rev. Lett.* **107**, 137202 (2011).
- ²⁶H. Sakai, J. Fujioka, T. Fukuda, D. Okuyama, D. Hashizume, F. Kagawa, H. Nakao, Y. Murakami, T. Arima, A. Q. R. Baron, Y. Taguchi, and Y. Tokura, *Phys. Rev. Lett.* **107**, 137601 (2011).
- ²⁷J. H. Lee, Y. K. Jeong, J. H. Park, M. A. Oak, H. M. Jang, J. Y. Son, and J. F. Scott, *Phys. Rev. Lett.* **107**, 117201 (2011).
- ²⁸J. M. Wesselinowa and I. Georgiev, *Phys. Status Solidi B* **245**, 1653 (2008).
- ²⁹T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, *Phys. Rev. B* **67**, 180401(R) (2003).
- ³⁰M. Mostovoy, *Phys. Rev. Lett.* **96**, 067601 (2006).
- ³¹Yu. A. Tserkovnikov, *Theor. Math. Phys.* **7**, 511 (1971).
- ³²N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).
- ³³R. Mazumder, P. S. Devi, D. Bhattacharya, P. Choudhury, A. Sen, and M. Raja, *Appl. Phys. Lett.* **91**, 062510 (2007).
- ³⁴G. L. Yuan, S. W. Or, J. M. Lu, and Z. G. Liu, *Appl. Phys. Lett.* **89**, 052905 (2006).
- ³⁵Y. K. Jun, W. T. Moon, C. M. Chang, H. S. Kim, H. S. Ryu, J. W. Kim, K. H. Kim, and S. H. Hong, *Solid State Commun.* **135**, 133 (2005).
- ³⁶H. Naganuma and S. Okamura, *J. Appl. Phys.* **101**, 09M103 (2007).
- ³⁷Z. Cheng and X. Wang, *Phys. Rev. B* **75**, 172406 (2007).
- ³⁸V. R. Palkar, D. C. Kundaliya, S. K. Malik, and S. Bhattacharya, *Phys. Rev. B* **69**, 212102 (2004).
- ³⁹T. Arima, D. Higashiyama, Y. Kaneko, J. P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, and Y. Tokura, *Phys. Rev. B* **70**, 064426 (2004).
- ⁴⁰S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, *J. Chem. Phys.* **42**, 3957 (1965).
- ⁴¹G. T. Rado, *Phys. Rev. Lett.* **13**, 335 (1964).
- ⁴²S. K. Mishra, R. Mittal, R. Singh, M. Zbiri, T. Hansen, and H. Schober, e-print arXiv:1211.0833v1.
- ⁴³D. R. Tilley and J. F. Scott, *Phys. Rev. B* **25**, 3251 (1982).
- ⁴⁴C. Ederer and C. J. Fennie, *J. Phys.: Condens Matter* **20**, 434219 (2008).