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Magnetic ordering and exchange interactions in multiferroic $GaFeO_3$

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We report our first-principles calculations on multiferroic $GaFeO_3$. The total energy results for different spin and structural configurations reveal that the ground state of $GaFeO_3$ in its ideal structure is antiferromagnetic but it is likely to have a possible site disorder of Fe and Ga atoms between octahedral Ga sites and Fe sites, which is consistent with previous experimental observations. Examining the exchange interactions among Fe atoms at either Ga or Fe sites in $GaFeO_3$, we conclude that the net magnetic moments observed in experiments may arise from Fe atoms occupying the Ga sites. Despite the d^5 configuration of Fe ions in $GaFeO_3$, significant orbital magnetic moments are found to exist and their origin is attributed to the local distortion of oxygen octahedra as well as the Fe off-centering present in the system.

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Multiferroic materials have attracted lots of attention due to their intriguing magnetoelectric properties and potential applications to a new type of memory devices.[1] Among them, $GaFeO_3$ is one of the promising candidates due to its large magnetoelectric effect and the unique magnetoelectric, magneto-optic, and piezoelectric properties. Indeed there have been several experiments showing interesting characters of this material such as magnetization-induced second-harmonic generation,[2] x-ray directional dichroism,[3] and optical magnetoelectric effect.[4] More recently Kim *et al.*[5] reported an unusually large orbital magnetic moment in this material while Fe in $GaFeO_3$ has a formal valence of 3+ with the d^5 configuration, the orbital moment of which is supposed to be zero. Although the origin of magnetoelectric couplings and multiferroicity appears to be diverse depending on the systems, the mechanism behind the orbital moment in this material can give a clue to an understanding of the magnetoelectric coupling in other multiferroic materials.

There have been several suggestions to explain the magnetism in $GaFeO_3$ such as ferromagnetic (FM),[6] ferrimagnetic,[7] or canted-antiferro-type magnetic orderings.[8] However, due to the absence of theoretical studies on $GaFeO_3$, the detailed picture for the electronic and magnetic structures remains unclear. Although the Mössbauer experiment by Frankel *et al.*[7] and a recent experiment by Arima *et al.*[9] support the idea that Fe substituted at the Ga site may be an origin of the observed magnetic signal, there is no direct information on the exchange interactions as well as the magnetic configurations. Even the latest x-ray photoemission experiment[5] had difficulty in distinguishing the electronic structures of Fe atoms at different sites.

In this Rapid Communication, we report the results of our first-principles calculations on the electronic structure and magnetic properties of $GaFeO_3$. The ground-state magnetic configuration, orbital magnetic moment, and electronic structure are presented. Ideal $GaFeO_3$ without any site disorder is found to have an antiferromagnetic (AFM) spin configuration in its ground state. In reality, on the other hand, it is reported to have excess Fe atoms or defects,[9] which have complicated the understanding of magnetism in $GaFeO_3$. Indeed our calculations reveal that 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. The calculated orbital moment turns out to be nonzero due to the distorted local structure despite the d^5 configuration, but its magnitude is smaller than that of the experimental observation by Kim *et al.*[5]

We carried out electronic structure calculations for a unit cell containing 8 f.u. of $GaFeO_3$ based on density-functional theory[10] (DFT) within a local spin-density approximation plus Hubbard U (LDA+U) (Refs. 11 and 12) by employing a linear combination of localized pseudoatomic orbital (LCPAO) method.[13] We used $4\times4\times4$ k points for the k-space integration and the Ceperley-Alder exchange-correlation energy functional as parametrized by Perdew and Zunger.[14] The test calculations for FeO and α-Fe_2O_3 showed that the effective on-site Coulomb interaction parameter U_{eff}=4 eV describes the band gap as well as the detailed band structures, which compared well with previous studies.[12,15] Double-valence and polarization orbitals were included to check the basis set dependence. We confirmed that the orbital moment and other magnetic properties are not sensitive to the choice of Fe basis orbitals, while the inclusion of polarization orbitals for O and Ga is important to achieve well-converged results. Orbitals are generated by a confinement potential scheme[13] with a cutoff radius of 4.5 a.u. for oxygen and 5.5 a.u. for gallium and iron, respectively. In the pseudopotential generation, the semicore $3p$ electrons for transition-metal atoms were included as valence electrons in order to take into account the contribution of the semicore states to the electronic structures. The relativistic effect as well as spin-orbit coupling terms is also included to perform the orbital moment calculation. The real-space grid technique[16] was used with an energy cutoff of 280 Ry in numerical integrations and solution of the Poisson equation using the fast Fourier transformation (FFT) algorithm. All DFT calculations were performed using our DFT code, OPENMX, which is designed for the realization of large-scale DFT calculations.[17]

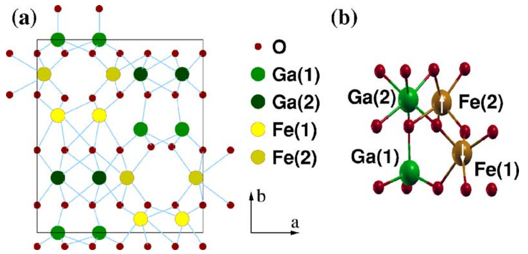

FIG. 1. (Color online) (a) Schematic drawing of the $GaFeO_3$ crystal structure. Light green, dark green, bright yellow, dark yellow, and red spheres correspond to Ga(1), Ga(2), Fe(1), Fe(2), and O, respectively. The unit cell contains 40 atoms and has the P_c2_1n space group. (b) Local environments of Fe(1), Fe(2), Ga(1), and Ga(2) sites and their magnetic configurations assuming that Fe occupies either of the Ga sites.

Figure 1 shows a schematic drawing of the $GaFeO_3$ crystal structure. $GaFeO_3$ crystal is known to be orthorhombic with lattice constants $a \simeq 8.75$ Å, $b \simeq 9.40$ Å, and $c \simeq 5.08$ Å and space group $Pc2_1n$ (or, equivalently, $Pna2_1$).[18] In Fig. 1(a), light and dark green spheres represent two different gallium ions Ga(1) and Ga(2), respectively. All Ga ions have a formal valence of 3+ with a d^{10} nonmagnetic configuration. Iron sites are also categorized into Fe(1) and Fe(2) represented by bright and dark yellow colors, respectively. Fe ions are expected to have the same valence of 3+ as Ga ions but with a d^5 magnetic configuration. Ga(2), Fe(1), and Fe(2) sites are surrounded by oxygen octahedra (marked by a red color) in contrast to the tetrahedral Ga(1) site. It is noted that each oxygen octahedron is significantly distorted. The distorted network of oxygens 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. Due to the complex nature of the coupling between structural and electronic degrees of freedom, the origin of the electric polarization and its coupling to the local magnetic ordering is not understood yet.

To determine the ground-state magnetic configuration of $GaFeO_3$, we carried out total energy calculations for various spin configurations in an ideal structure. As a result, the ground state is found to be antiferromagnetic with local moments at each site as listed in the upper panel of Table I. In order to probe the effect of spin-orbit interactions on the ground-state configuration, the calculations are done by both the semirelativistic treatment "without spin-orbit couplings (SOC)" and the fully relativistic one "with SOC." Both results are listed in Table I. As illustrated in Fig. 1(b), the magnetic moment of Fe(1) is antiparallel to that of Fe(2). In the noncollinear spin calculations with SOC, the spin moment direction of Fe(1) and Fe(2) is set to the [001] direction as suggested by experiment.[5] The magnitude of the magnetic moments of Fe(1) and Fe(2), estimated by using the Voronoi analysis,[19] ranges from 3.8 to 4.1, which compares well with the d^5 high-spin configuration. The differences in their magnitude between "with SOC" and "without SOC" are due to the noncollinear distribution of spin moments for the "with SOC" case. In the ideal structure, the magnetic moments of Ga(1), Ga(2), and O are negligible whereas the relatively large moments at the O(9) site are regarded as asymmetric tails of the neighboring Fe moments.

TABLE I. Calculated magnetic moment at two Ga, two Fe, and six O sites in μ_B units per Fe atom. The values of "without SOC" are obtained the calculation with pseudopotentials without spin-orbit coupling or relativistic effect.

		Without SOC Spin (μB) moment	With SOC Spin (μ_B) moment	Orbit moment (μ_B)
	Ga(1)	0.01	0.01	0.00
	Ga(2)	0.06	0.03	0.00
Ideal	Fe(1)	5.02	4.27	0.02
	Fe(2)	−5.11	−4.34	−0.02
	O	−0.03−0.06	−0.07−0.06	0.00
	Total	0.00[a]	0.00[a]	0.00[a]
Site disordered	Fe at Ga(2)	−5.17	−4.40	0.02

[a]The total moment in a unit cell without the Fe substitution at the Ga sites.

The site disorder between Ga and Fe has recently been suggested to be a primary source of the net magnetic moment in $GaFeO_3$.[5,9] In order to investigate the possible site disorders and their role in the determination of the magnetic properties of $GaFeO_3$, we examined the possible site disorder by carrying out total energy calculations for the interchanged positions of Ga and Fe atoms within an 8-f.u. cell of $GaFeO_3$,[20] where the atomic positions are kept as determined by experiments.[9,18] Among the configurations studied, it is confirmed that the ideal structure of $GaFeO_3$ with AFM order is the most stable energetically. The energy of the Fe interchanged with the Ga(1) site is higher than the ideal one by 74−171 meV per formula unit depending on the internal locations, whereas the total energy difference between the ideal $GaFeO_3$ and the configuration with the Fe interchanged with the Ga(2) site can be as small as 1 meV per formula unit. This implies that the site disorder involving the interchange of Fe and Ga(2) sites is highly probable and is consistent with the presence of Fe disorder with the Ga(2) site as observed in experiments.[9,21]

Early studies including the original one by Remeika[6] suggested $GaFeO_3$ to be ferromagnetic.[18,22,23] There were experiments[5,6,8,9,22] reporting that the net magnetic moment is parallel or almost parallel to the c axis and its magnitude ranges from $0.67\mu_B$/Fe to $0.87\mu_B$/Fe. However, Rado suggested a canted antiferromagnetic structure as a way to explain the nondiagonal character of the magnetoelectric susceptibility.[8] The Mössbauer data[7] supported a ferrimagnetic picture where the magnetic moment aligned along the c axis has about $5\mu_B$ per Fe atom—i.e., a high-spin configuration. The ferrimagnetic picture has been suggested to be reasonable by considering that some of the Fe at the Ga(2) site can contribute to the net magnetic moment. However, since the unit cell contains four different Ga(2), Fe(1), and Fe(2), respectively, one should note that there are several different oxygen paths from one cation to another. Due to the highly distorted structure, it is hard to predict the types of exchange

TABLE II. Heisenberg exchange interaction parameters J_{ij} between the Fe atoms at the site i and the site j in units of kelvin.

$i \backslash j$	Ga(2)	Fe(1)	Fe(2)
Ga(1)	0.14	−1.80	28.92
Ga(2)		−19.50	16.42
Fe(1)			−105.75

couplings based on the bond angles only. For example, our results demonstrate that the angle 104° between Ga(2) and Fe(1) through O′(6) corresponds to the AFM coupling while the angle 102° between Ga′(2) and Fe′(2) through O′(7) corresponds to FM.[24] Moreover the magnetic coupling between Fe atoms at the Ga(1) site and at the other sites has not yet been examined at all because of the relatively small amount of Fe atoms residing at the Ga(1) sites compared to the amount at the Ga(2) site.

The lower panel of Table I shows the magnetic moments for the case of Fe substituted at the Ga(2) site close to those of Fe at the original sites and the moment direction is parallel to that of Fe(2). It implies that the extra Fe atoms occupying the Ga(2) site always point to the same direction as Fe(2), thereby contributing to the net magnetic moment. This is quite an extraordinary case where the net moment is derived from the site disorder.

The origin of such magnetic ordering can be understood by examining the magnetic exchange couplings between Fe atoms at different atomic sites in the $GaFeO_3$ structure. Table II summarizes the calculated effective Heisenberg exchange interaction parameters J_{ij} defined by $\mathcal{H}=-\Sigma_{\langle ij\rangle}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$ where $\langle ij\rangle$ denotes a sum over all neighboring pairs of spins at sites i and j. To calculate the exchange parameter between Fe atoms at different atomic sites, we used the ϵ-Fe_2O_3 structure,[25] which is isomorphic to the $GaFeO_3$ with a full Fe substitution into all Ga sites. The effective interaction parameters were calculated by using the rigid-spin noncollinear perturbation method.[26] As shown in Table I, the ideal $GaFeO_3$ without any Fe substitution has an AFM ground state giving no net magnetic moment, which is consistent with the experiments by Frankel *et al.*[7] and Arima *et al.*[9] It is clear from Table II that Fe at the Ga(2) site is ferromagnetically coupled to Fe(2) and antiferromagnetically to Fe(1). Since Fe at the Ga(1) site also has a FM coupling with Fe at the Ga(2) and Fe(2) sites, it also contributes to the magnetization and magnetoelectric coupling. The strongest exchange interaction exists between Fe(1) and Fe(2), which plays an important role in stabilizing the AFM magnetic structure of $GaFeO_3$ as shown in Table I.

One of the intriguing issues in $GaFeO_3$ is an unexpectedly large orbital moment (M_O) reported in a recent x-ray magnetic circular dichroism (XMCD) measurement.[5] When the crystal has a sufficiently low symmetry to remove all of the orbital degeneracy, the orbital angular momentum is supposed to vanish at least to the lowest order. This is so-called orbital quenching,[27] which is derived by assuming the presence of time reversal symmetry. If the time reversal symmetry is broken or a local distortion is present, however, a non-negligible orbital momentum may arise. Indeed, as shown in

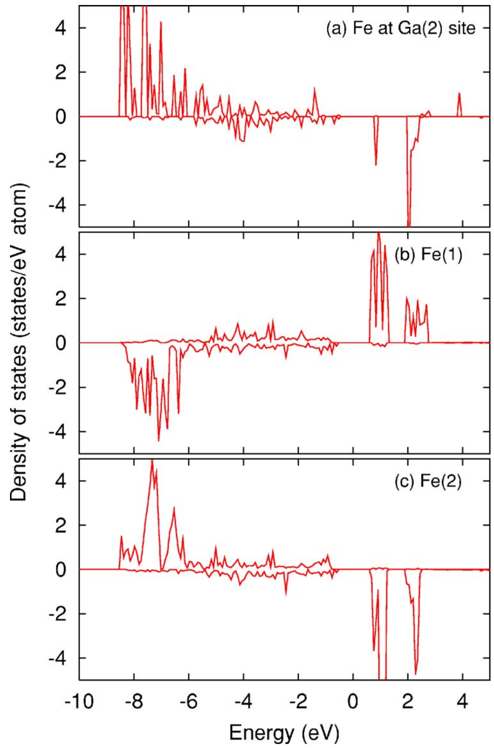

FIG. 2. (Color online) PDOS of Fe atoms (a) at Ga(2), (b) Fe(1), and (c) Fe(2) sites of $GaFeO_3$. Fermi level is set to be zero.

Table I, Fe atoms in $GaFeO_3$ possess an orbital magnetic moment of a significant size, $0.02\mu_B$/Fe, which is a nontrivial value obtained from the noncollinear spin calculations of $GaFeO_3$ including SOC.[28] In XMCD measurements, Kim *et al.*[5] observed that Fe has an orbital magnetic moment of $0.017\mu_B$/Fe at 190 K, which corresponds to 4.6% of the spin moment (M_S) at that temperature. Then they extrapolated M_O to a zero-temperature value of about $0.23\mu_B$/Fe in comparison to the M_S of $5\mu_B$/Fe. Interestingly our calculated value of M_O is quite close to the experimental value observed at 190 K, whereas the zero-temperature expectation is much higher than ours. Although thermal fluctuations can reduce the spin moment significantly, they may not affect the orbital moment if the distortion of the oxygen octahedra remains below 190 K. Our calculation results suggest that the structure itself, especially the distorted nature of oxygen octahedra and the Fe off-centering, does not change significantly at 190 K and the asymmetric charge transfer between O $2p$ and Fe $3d$ at 0 K survives even at the higher temperature.

Figure 2 shows the projected density of states (PDOS) of Fe atoms at (a) Ga(2), (b) Fe(1), and (c) Fe(2) sites, respectively. The overall features of the Fe $3d^5$ electronic levels as obtained from the LDA+U calculations are reasonable and consistent with x-ray absorption spectroscopy (XAS) results in terms of the Fe $3d$ bandwidth (2–3 eV).[5] It is noted that the electronic structure of Fe in $GaFeO_3$ is very similar to that of the hematite α-Fe_2O_3. Previous LDA+U studies of α-Fe_2O_3 by using the different types of basis sets and U_{eff} =2–5 eV (Ref. 15) show that the energy separation between the occupied and unoccupied d levels is about 7–9.5 eV and the oxygen states prevail in the valence band, which is also observed in $GaFeO_3$ (Fig. 2). From the point of energy levels of Fe d states, the local environment of Fe atoms in $GaFeO_3$ is not much different from one of the most conventional iron oxides: e.g., α-Fe_2O_3. Therefore the states of the Fe atom substituted into the Ga(2) site are rather close to those of the original Fe sites. Further various distortions of the surrounding oxygen octahedra as well as the different Fe off-centerings make such a variance in Fig. 2. Thus the XAS results can be understood as an average of the Fe spectra from three different sites whereas the Fe at the Ga(2) site plays an important role in the determination of the magnetic properties.

In summary we have presented the results of our first-principles calculations of $GaFeO_3$ including the ground-state magnetic configuration, orbital and spin magnetic moments, effective exchange interactions, and electronic structure. $GaFeO_3$ in its ideal structure is determined to have an antiferromagnetic order with no net moment. Fe substituted into the Ga(2) site, being ferromagnetically aligned with Fe(2), is shown to be an origin of the observed net magnetic moment. From the total energy results, we showed that the net moment can be derived from the site disorder of Fe and Ga atoms between the octahedral Ga site and the Fe sites, which is consistent with experimental observations. The calculated value of orbital moment is $0.02\mu_B/\mathrm{Fe}$ which is close to the value of the XMCD data at 190 K, $0.017\mu_B/\mathrm{Fe}$. Finally we have discussed the detailed electronic structures of Fe atoms at three different atomic sites, which vary slightly from one to another due to complex distortions of the oxygen octahedra.

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[28] From the calculations of the orbital moment for MnO, which has neither off-centered TM ions nor distorted oxygen octahedra, we obtained an orbital moment of less than $0.002\mu_B/\mathrm{Mn}$ which is consistent with previous studies on MnO. On the other hand, the orbital moment of α-Fe_2O_3 is found to be $0.03\mu_B$, comparable to that of $GaFeO_3$. While rocksalt MnO is highly symmetric in its structure, α-Fe_2O_3 has a so-called corundum structure where the Fe atom is off-centered in the distorted oxygen octahedra just like in $GaFeO_3$. Therfore we conclude that M_O of about $\sim 0.01\mu_B$ is meaningful and it comes from the orbital and bond anisotropy due to the distorted structure.