P H Y S I C A L   R E V I E W   L E T T E R S

Charge Order and the Origin of Giant Magnetocapacitance in $LuFe_2O_4$

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The nature of the charge order in the charge frustrated compound $LuFe_2O_4$ and its effect on magnetocapacitance were examined on the basis of first-principles electronic structure calculations and Monte Carlo simulations of electrostatic energy. Our work shows that two different types of charge order of almost equal stability (i.e., $\sqrt{3} \times \sqrt{3}$ and chain types) occur in the Fe_2O_4 layers of $LuFe_2O_4$, and that the ground state of $LuFe_2O_4$ has a ferrielectric arrangement of the Fe_2O_4 layers with $\sqrt{3} \times \sqrt{3}$ charge order. The giant magnetocapacitance effect of $LuFe_2O_4$ at room temperature is accounted for in terms of charge fluctuations arising from the interconversion between the two types of charge order, that becomes hindered by an applied magnetic field.

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Ferroelectric oxides are essential components in a large number of applications [1]. In traditional ferroelectric materials like $BaTiO_3$, the ferroelectricity is driven by the hybridization of the empty d orbitals of Ti^{4+} with the occupied p orbitals of the oxygen anions [2]. Recently, a mixed-valence compound $LuFe_2O_4$ with the average valence $Fe^{2.5+}$ was found to exhibit ferroelectricity associated with the charge order (CO) leading to Fe^{2+} and Fe^{3+} ions [3]. Subramanian *et al.* reported that at room temperature the dielectric constant of $LuFe_2O_4$ decreases sharply when a small magnetic field is applied [4]. This suggests a strong coupling between spin moment and electric dipole at room temperature, and hence potential applications of $LuFe_2O_4$ in which the charge and spin degrees of freedom of electrons can be controlled.

At room temperature $LuFe_2O_4$ has a hexagonal layered structure (space group $R\bar{3}m$, $a = 3.44$ Å, and $c = 25.28$ Å) in which all Fe sites are crystallographically equivalent [5]. $LuFe_2O_4$ is an insulator [6], and undergoes a three-dimensional (3D) CO below 330 K [5,7,8] as well as a two-dimensional (2D) ferrimagnetic order below 240 K [8]. In $LuFe_2O_4$, layers of composition Fe_2O_4 alternate with layers of Lu^{3+} ions, and there are three Fe_2O_4 layers per unit cell [Fig. 1(a)]. Each Fe_2O_4 layer (referred to as the W layer) is made up of two triangular sheets of corner-sharing FeO_5 trigonal bipyramids [Figs. 1(b)–1(d)].

$LuFe_2O_4$ exhibits apparently puzzling physical properties, and the nature of its CO is not unequivocal. It is generally believed that lattice distortions accompany a CO [9]. Thus, it is unclear why $LuFe_2O_4$ is insulating above room temperature despite that $LuFe_2O_4$ adopts the structure in which all Fe sites are equivalent in this temperature region. The giant magnetocapacitance effect found for $LuFe_2O_4$ can be understood by supposing that the charge fluctuation of $LuFe_2O_4$ arising from its charge frustration is sharply reduced by an external magnetic field. However, it is unclear by what mechanism this happens. As to the nature of the CO in $LuFe_2O_4$, there is a controversy. By analogy with the stable long-range order of Ising spins

in a triangular lattice antiferromagnet (TLA), Yamada *et al.* proposed a model CO structure in which the two triangular sheets of a W layer do not have the same number of Fe^{2+} and Fe^{3+} ions, i.e., $[Fe^{2+}]:[Fe^{3+}] = 1:2$ in one triangular sheet, and 2:1 in another triangular sheet [i.e., the CO-I structure in Fig. 1(b)] [10]. The $\sqrt{3} \times \sqrt{3}$ superstructure of this CO model is compatible with the experimental observation. Subramanian *et al.* proposed a different CO structure in which one triangular sheet of a W layer has only Fe^{2+} ions and the other triangular sheet has only Fe^{3+} ions [i.e., the CO-II structure in Fig. 1(c)] [4], on the basis of the fact that the closest Fe-Fe distances in $LuFe_2O_4$ occur between adjacent triangular sheets of a W layer rather than within each triangular sheet.

In this Letter, we probe the nature of the CO and the origin of the magnetocapacitance in $LuFe_2O_4$ on the basis of first-principles electronic structure calculations and Monte Carlo (MC) simulations of electrostatic interactions. Our study shows that the ground state of $LuFe_2O_4$ has the CO-I structure, the CO-II structure is unstable, and another CO structure different from CO-I and CO-II is very close in energy to the CO-I structure. The presence of two different CO structures close in energy is found crucial for the magnetocapacitance effect of $LuFe_2O_4$.

Our first-principles spin-polarized density functional theory calculations were performed on the basis of the frozen-core projector augmented wave method [11] encoded in the Vienna *ab initio* simulation package [12] using the generalized-gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [13] and the plane-wave cutoff energy of 400 eV. To properly describe the strong electron correlation in the $3d$ transition-metal oxide, the GGA plus on-site repulsion U method (GGA + U) was employed [14] with the effective U value ($U_{eff} = U - J$) of 4.61 eV. Calculations with various U_{eff} values show that our main results remain valid when U_{eff} is varied between ~3.6 and ~5.6 eV. In the following we report only those results based on $U_{eff} = 4.61$ eV. To simplify our discussion and reduce the computational task, we explore the CO
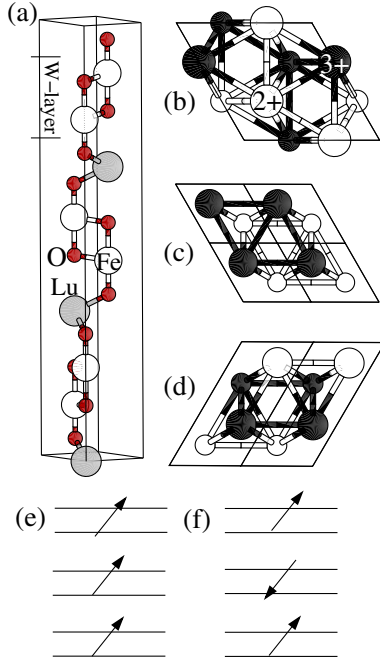
FIG. 1 (color online). (a) Hexagonal unit cell structure of $LuFe_2O_4$, where large gray, medium white, and small red circles represent the Lu, Fe, and O atoms, respectively. Schematic representations of the (b) CO-I, (c) CO-II, and (d) CO-III structures, where the small and large circles refer to the Fe ions in the upper and lower triangular sheets of a W layer, respectively. The Fe^{2+} and Fe^{3+} ions are represented by open and closed circles, respectively. Schematic representations of the (e) ferroelectric and (f) ferrielectric arrangements of the dipoles of the W layers in the CO-I structure.
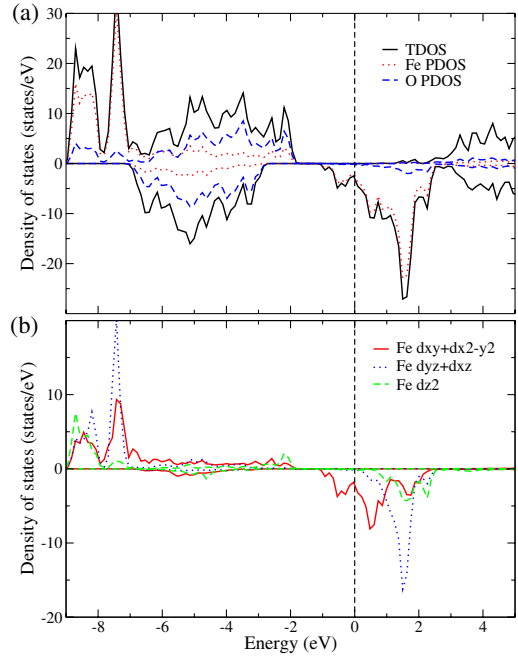

FIG. 2 (color online). Density of states of $LuFe_2O_4$ calculated for the room-temperature structure without CO. The DOS was calculated with 0.1 eV broadening.

structures of $LuFe_2O_4$ under the assumption that the spins of $LuFe_2O_4$ have a ferromagnetic ordering. This assumption is reasonable because the energy scale associated with different spin arrangements is much smaller than that associated with different COs. An additional restriction of our calculations is the use of the experimental lattice constants. Our full geometry optimization of $LuFe_2O_4$ with GGA calculations leads to the lattice constants that are very close to the experimental values.

The GGA + U calculation for the non-CO state of $LuFe_2O_4$ with the room-temperature crystal structure and hence the hexagonal symmetry shows that all Fe ions are in the high spin state. The plots of density of states (DOS) calculated for the non-CO state [Fig. 2(a)] predict a metallic behavior for $LuFe_2O_4$, in disagreement with experiment. This is not surprising because the Fe ions are in the valence state of 2.5+ in the absence of CO. We found it impossible to produce an insulating band gap for any CO structure as long as the structure keeps the hexagonal symmetry. For a transition-metal ion in a trigonal bipyramidal crystal field, the five d states are split in three groups, i.e., $\{d_{xy}, d_{x^2-y^2}\}$, $\{d_{xz}, d_{yz}\}$, and $\{d_{z^2}\}$. The partial DOS plots shown in Fig. 2(b) indicates that the down-spin bands leading to a metallic character arise from the d_{xy} and $d_{x^2-y^2}$ orbitals; i.e., the $\{d_{xy}, d_{x^2-y^2}\}$ states have a lower

energy than do the $\{d_{xz}, d_{yz}\}$ states for the FeO_5 trigonal bipyramids in $LuFe_2O_4$.

To search for possible low-energy CO patterns, we resort to the classical MC method by considering only the inter-site Coulomb repulsion. This simplified approach is reasonable for the purpose of finding stable CO patterns. As the energy reference of this calculation, each $Fe^{2.5+}$ site of the non-CO state is assumed to carry zero charge, so that, after a CO takes place, Fe^{3+} and Fe^{2+} sites will carry 0.5δ ($0 < \delta < 1$) and -0.5δ charges, respectively, (δ denotes the degree of the charge transfer). For simplicity, we assume that the charge on oxygen is independent of δ. We perform MC simulations using a $2\sqrt{3} \times 2\sqrt{3}$ supercell with periodic boundary conditions and evaluate the long-range Coulomb interaction using the Ewald sum method. There occur two different low-energy CO patterns. The most stable one is a chainlike CO structure (hereafter the CO-III structure) with energy $-1.601\delta^2$ eV per formula unit (f.u.), in which chains of Fe^{2+} ions alternate with those of Fe^{3+} ions in each triangular sheet [Fig. 1(d)]. Given the trigonal symmetry of each W layer, there are three different, but equivalent, ways of choosing the chain direction in each W layer. When the three different chain orientations occur randomly, the overall superlattice diffraction pattern will exhibit a $\sqrt{3} \times \sqrt{3}$ structure. The CO-I structure proposed by Yamada *et al.* is found to have a slightly higher energy, i.e., $-1.379\delta^2$ eV/f.u.. (The stability of this CO cannot be deduced by analogy with the $\sqrt{3} \times \sqrt{3}$ spin configuration of Ising spins that occurs in a TLA when the nearest-neighbor spin exchange is antiferromagnetic and the next-nearest-neighbor spin exchange is ferromag-

netic. This spin configuration becomes the ground state only when the next-nearest-neighbor interactions are stabilizing. In the CO-I structure, the next-nearest-neighbor interactions are destabilizing due to Coulomb repulsion.) Our MC simulations show that the CO-II structure proposed by Subramanian *et al.* is found to be highly unstable, namely, its energy is even higher than the non-CO structure by $0.496\delta^2$ eV/f.u.. The instability of the CO-II structure is due to the large positive electrostatic energy between the ions of the same charge in each triangular sheet. We also consider MC simulations using another model that takes into consideration only the nearest-neighbor electrostatic interactions within each triangular sheet and between adjacent triangular sheets of every W layer. Qualitatively, this model leads the same results as described above.

To more accurately probe the stabilities of the CO-I, CO-II, and CO-III structures with respect to the non-CO structure, we carry out GGA + U calculations for LuFe$_2$O$_4$ on the basis of its crystal structure determined at room temperature. Our GGA + U calculations for the CO-II structure, with an initial guess of the charge density expected for it, always converged to the non-CO structure. Therefore, it is concluded that the CO-II structure is not stable, as found from our MC simulation. Since there are three W layers per unit cell and since each W layer has a nonzero dipole moment in the CO-I structure, there are two different arrangements of the W layers in the CO-I structure, i.e., the ferroelectric arrangement [Fig. 1(e)] and the ferrielectric arrangement [Fig. 1(f)]. For the ferroelectric CO-I and the CO-III structures, our GGA + U calculations were carried out in two steps. In the first step, the ferroelectric CO-I or the CO-III structure was introduced in LuFe$_2$O$_4$ without allowing the crystal structure to relax. Such a CO induced solely by electrostatic interactions was first proposed by Attfield *et al.* [15] and later computationally realized by Leonov *et al.* [16] in their studies of the CO phenomenon in Fe$_2$OBO$_3$. In the second step, the crystal structure with the ferroelectric CO-I or the CO-III structure was completely optimized. Thus, the energy gain ΔE of the ferroelectric CO-I or the CO-III structure relative to the non-CO structure is written as $\Delta E = \Delta E_1 + \Delta E_2$, where ΔE_1 and ΔE_2 are the energy gains obtained in the first and second steps, respectively. ΔE_1 arises from electrostatic interactions, and ΔE_2 from the geometry relaxation.

Our GGA + U calculations of the first step show that the ferroelectric CO-I and the CO-III structures are stable in the absence of geometry relaxation [17] (with $\Delta E_1 = 239$ and 219 meV/f.u., respectively), and are an insulator (with band gap of 0.18 and 0.15 eV, respectively). The forces acting on the atoms calculated for both CO structures with no geometry relaxation are large hence indicating instability of the "frozen" structure. Our GGA + U calculations of the second step show that the ΔE_2 values of the ferroelectric CO-I and the CO-III structures are 163 and 165 meV/f.u., respectively. Thus, after structural relaxation, the ferroelectric CO-I structure remains only slightly more stable than the CO-III structure (by 19 meV/f.u.).

Another important finding of our calculations is that the energy gain resulting solely from electrostatic interactions is greater than that from geometry relaxation (i.e., $\Delta E_1 > \Delta E_2$), in contrast to the case of Fe$_2$OBO$_3$, for which our calculations showed that $\Delta E_1 \ll \Delta E_2$ (i.e., 77 vs 272 meV) [18]. Bond-valence-sum calculations [19] for the optimized structures of the ferroelectric CO-I and the CO-III structures show that the valence states of the Fe^{2+} and Fe^{3+} sites are close to the nominal $+2$ and $+3$, respectively. Both CO structures have a larger band gap after geometry optimization (i.e., 0.70 and 0.54 eV for the ferroelectric CO-I and the CO-III structures, respectively). The DOS plots calculated for the ferroelectric CO-I and the CO-III structures with the relaxed structures are presented in Fig. 3. All the occupied up-spin 3d bands of the Fe^{2+} ions lead to a spherical charge distribution, and so do those of the Fe^{3+} ions. It is the occupied down-spin 3d bands of the Fe^{2+} ions that provide an anisotropic charge distribution arising from the Fe 3d orbitals and hence information about the orbital order (OO). This is shown in the insets of Fig. 3, which reveal that the two triangular sheets of a W layer have an identical OO in the CO-III structure, but different OO's in the ferroelectric CO-I structure. In the ferroelectric CO-I structure, the orbitals of the $\{d_{xy}, d_{x^2-y^2}\}$ type are involved in the OO of the triangular sheet of containing fewer Fe^{2+} ions than Fe^{3+} ions, but those of the $\{d_{xy}, d_{x^2-y^2}\}$ and $\{d_{xz}, d_{yz}\}$ types in the other triangular sheet. In the CO-III structure, the orbitals of the $\{d_{xy}, d_{x^2-y^2}\}$ and $\{d_{xz}, d_{yz}\}$ types are involved in the OO
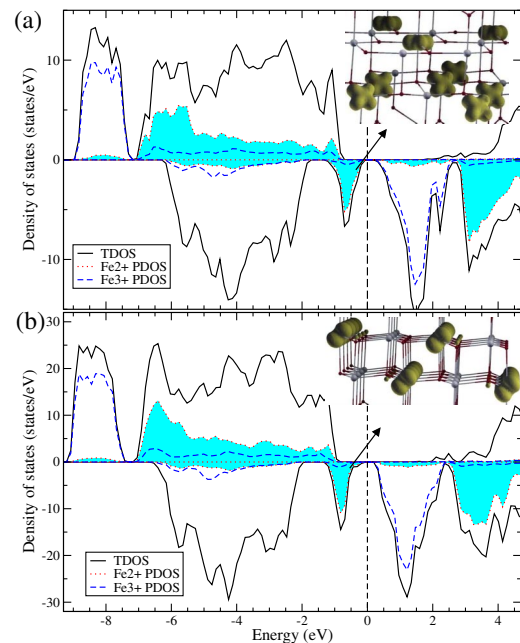

FIG. 3 (color online). DOS of LuFe$_2$O$_4$ calculated for (a) the relaxed CO-I and (b) the relaxed CO-III structures. The blue regions highlight the PDOS of the Fe^{2+} ion. The inset shows the charge density plot calculated for the occupied down-spin d states. The DOS was calculated with 0.1 eV broadening.

of both triangular sheets of a W layer. The OO's found for the unrelaxed structure are quite similar to those found for the optimized structures described above.

Experimentally, a large spontaneous electric polarization was found in $LuFe_2O_4$ [3]. Of the two stable CO structures, CO-I and CO-III, only the CO-I structure has a nonzero electric polarization. For our calculations of the spontaneous electric polarization of the ferroelectric CO-I structure, we use the Berry phase method [20]. The calculated electric polarization should be compared with the experimental one measured at a low temperature where there is no charge fluctuation. The spontaneous electric polarization along the c-axis is calculated to be 52.7 $\mu C/cm^2$, which is much greater than the experimental value of about 25 $\mu C/cm^2$ measured at 77 K [3]. To resolve this discrepancy, we consider the ferrielectric CO-I structure [Fig. 1(f)]. Our GGA + U calculations with complete geometry optimization show that the ferrielectric CO-I structure is more stable than the ferroelectric CO-I structure by 12 meV/F.U.. The spontaneous electric polarization along the c-axis calculated for the ferrielectric CO-I structure is 26.3 $\mu C/cm^2$, in excellent agreement with experiment. Thus, from the viewpoint of the total energy and the spontaneous electric polarization, it is concluded that $LuFe_2O_4$ has the ferrielectric CO-I structure. Note that the spontaneous electric polarization for the ferrielectroc CO-I structure is smaller than that of ferroelectric CO-I structure by a factor of approximately two, instead of three expected from Figs. 1(e) and 1(f). This is due to the fact the two crystal structures, which are each separately optimized, are slightly different.

Now we turn attention to the probable origin of the giant magnetocapacitance effect of $LuFe_2O_4$ at room temperature. According to our electronic structure calculations, the two different CO structures, CO-I and CO-III, are very close in energy. Given the room-temperature structure of hexagonal symmetry, the ferroelectric CO-III state is higher in energy than the ferroelectric CO-I state only by 20 meV/f.u.. Thus, at room temperature, there should occur charge fluctuations associated with the interconversion between the two different CO states, which should form different domains separated by domain boundaries. Then, due to the large polarizability caused by the charge fluctuations, the dielectric constant of $LuFe_2O_4$ should be very large. Under an external magnetic field the Zeeman effect should preferentially stabilize one of the two CO states because the two states are most likely to have different total spin moments. Consequently, an external magnetic field will reduce the extent of charge fluctuation and hence decrease the electric polarization. The ac dielectric dispersion observed for $LuFe_2O_4$ can be understood in terms of the dielectric response and the motion of the ferroelectric domain boundaries between the CO-I and CO-III states [3]. At present we cannot answer the question of which CO state will be preferentially stabilized by an external magnetic field, because only the ferromagnetic spin arrangement was considered in the present work. Further studies are necessary to address this question.

We note that the spontaneous EP of $LuFe_2O_4$ is much greater than that of the recently discovered multiferroic materials (such as $TbMnO_3$ [21]), so $LuFe_2O_4$ represents a promising candidate for novel magnetoelectric devices.

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