Frustration and charge order in $LuFe_2O_4$

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The nature of a transition from two- to three-dimensional charge order (2D-CO→3D-CO) in the multiferroic material $LuFe_2O_4$ is discussed. It is shown that a high-temperature ordered phase of the Ising model with antiferromagnetic or antiferroelectric (AF) interactions on a triangular bilayer (W layer) is a dimer partially disordered AF (DPDA) state, which is a generalization of a well-known partially disordered AF structure for the triangular lattice. The DPDA state is stable against a variation of interaction parameters in a wide range. It is demonstrated that the transition of W layers to the DPDA state gives rise to the 2D-CO phase in $LuFe_2O_4$ at a high temperature.

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Multiferroic materials with strong magnetoelectric coupling have inspired a tremendous interest due to the great potential applications to memory elements, filtering devices, and high-performance insulators.[1–4] Among other multiferroics, $LuFe_2O_4$ has drawn substantial attention due to a mechanism of the ferroelectricity originating from charge order (CO).[5,6] At low temperatures the CO is assumed to be coupled with ferrimagnetic order.[7] Geometric frustration in both charge and spin systems of $LuFe_2O_4$ as well as low dimensionality lead to complex behavior of this substance: a rich phase diagram,[8] incommensurate ordered states,[9,10] giant magnetodielectric response,[11] and magnetic coercivity.[7]

$LuFe_2O_4$ has a hexagonal layered structure with the space group $R\bar{3}m$. All iron sites are crystallographically equivalent and form triangular bilayers called W layers.[6] Since a formal average charge of the iron ions is equal to +2.5, the same numbers of Fe^{2+} and Fe^{3+} ions are distributed over the lattice. An observation of lattice deformations around the iron ions with the different charges by means of x-ray and neutron diffraction[9,10] as well as a high effective mass of charge carries[8] support the localized description of this mixed-valence system. Below 500 K a two-dimensional charge order (2D-CO) appears; that is, the Fe^{2+} and Fe^{3+} ions form a 2D superstructure within individual W layers although the W layers remain uncorrelated between each other. This high-temperature 2D-CO is characterized by the wave vector $\mathbf{k} = (\frac{1}{3}, \frac{1}{3})$.[9,10] That is why a six-sublattice (6-SL) model of CO was proposed: in each layer of the W layers, two-thirds of all iron ions form the honeycomb structure with alternating Fe^{2+} and Fe^{3+} positions. A state of the other one-third has not been clearly identified.[9,10]

At approximately 320 K a transition from the 2D-CO to three-dimensional charge order (3D-CO) takes place.[5,12] The internal structure of the W layers remains similar to the 2D-CO but the 3D-CO demonstrates incommensurability.[9,10] The 3D-CO phase gives evidence of the bulk ferroelectric state.[5,6] The CO plays a crucial role in the ferroelectricity of $LuFe_2O_4$ because it breaks the inversion symmetry of the W layer and generates the electric dipole moment.[13] It was supposed that in $LuFe_2O_4$ the W layers are stacked up in the ferroelectric order which causes the bulk ferroelectric state.[6] X-ray scattering[12] and very recent measurements of ac permittivity[14,15] have cast doubt on the bulk nature of the ferroelectricity in $LuFe_2O_4$ assuming antiferroelectric arrangement of the W layers.

Various types of ordered charge structures in $LuFe_2O_4$ were proposed and investigated theoretically.[12,16–18] Since the iron ions have the two charge states their arrangement can be described by the Ising model. The Coulomb interaction between iron ions at zero temperature leads to a stripe charge structure of W layers.[16,17] When charge carriers in $LuFe_2O_4$ are considered as small polarons, the Ising model with short-range interactions is applied.[10,18] The first-principal calculations with lattice relaxation produce the 6-SL CO with broken inversion symmetry and a nonzero electric dipole moment of the W layer.[12,17] It was also found that the W layers should be stacked rather than in the antiferroelectric arrangement.[12]

Below $T_N = 240$ K a complex magnetic order develops and at $T_L = 170$ K another magnetostructural transition takes place.[19] Various phenomena were observed at low temperatures in different samples of $LuFe_2O_4$: a phase separation,[20] spin-glass behavior related to an oxygen content,[21] and interplay between magnetic and charge orders.[13]

In this paper we investigate the nature of the 2D-CO and 3D-CO phases as well the transition between them. The AF Ising model on the triangular lattice was thoroughly investigated theoretically,[22–25] and a lot of Ising triangular magnetic systems were studied experimentally.[23,25,26] If the nearest-neighbor AF interactions only are taken into account, a highly frustrated state appears.[22] The next-nearest-neighbor and other interactions partially lift the degeneracy and fix three-sublattice ferrimagnetic, stripe, or other low-temperature phases. There is a universal high-temperature phase, namely the partially disordered AF (PDA) state proposed by Mekata.[23] In this case two-thirds of the lattice sites are ordered to the honeycomb AF structure and one-third is disordered. One can note that this structure is similar to the 2D-CO state. The PDA state has a large entropy that lowers its free energy and leads to an entropy-driven phase transition at high temperatures.[23,27]

We start with the Ising model of an individual W layer:

$$H_W = \frac{1}{2N} \sum_{i,j} J_{ij} q_i q_j, \tag{1}$$

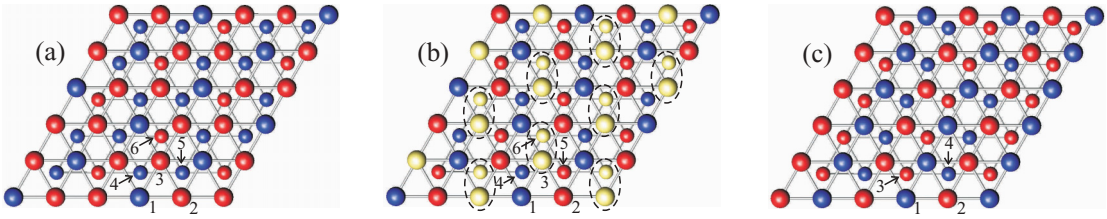

FIG. 1. (Color online) Charge order in W layer: (a) FI, (b) DPDA, and (c) stripe structures. The large and small spheres correspond to the two layers, the effective charges of iron ions are denoted by color, sublattices are shown by the numbers, and pairs of disordered sites in the DPDA phase are outlined by the dashed lines.

where $q_i = \pm 1$ denotes the effective charge of the ith iron ion, and N is the total number of sites. The summation in the Hamiltonian (1) is performed over all sites of the W layer. The Coulomb interaction constant is positive, $J_{ij} \geqslant 0$, and decreases with the distance r_{ij} as $J_{ij} \propto r_{ij}^{-1}$. This dependence is not correct at short distances, which is why models with other types of interactions were also considered previously.[16,18] As we show below the particular form of the spatial dependence of the interaction is not very important for further discussion.

We consider few charge configurations of the W layer in the framework of the mean-field theory developed earlier for the triangular lattice.[23] First, each triangular layer of the W layer can be divided into three sublattices [see Fig. 1(a)]. As a result we obtain the 6-SL charge structure. It is well suited for a description of 2D-CO and 3D-CO states.[9,10] Let the sublattices 1,2,3 and 4,5,6 belong to the first and second layers of the W layer, correspondingly. Our further investigation is limited to antisymmetric structures

$$\langle q\rangle_1 = -\langle q\rangle_4, \quad \langle q\rangle_2 = -\langle q\rangle_5, \quad \langle q\rangle_3 = -\langle q\rangle_6, \qquad (2)$$

where $\langle q\rangle_\lambda$ is the average charge of the λth sublattice. Conditions (2) lead to the zero total effective charge of the W layer $\langle q\rangle = \sum_{\lambda=1,\ldots,6}\langle q\rangle_\lambda = 0$.[28] The 6-SL model comprises configurations with the broken inversion symmetry: ferrielectric (FI) shown in Fig. 1(a) ($\langle q\rangle_1 < 0$, $\langle q\rangle_2 > 0$, $\langle q\rangle_3 > 0$) and ferroelectric (FE) ($\langle q\rangle_1 > 0$, $\langle q\rangle_2 > 0$, $\langle q\rangle_3 > 0$). They have a nonzero electric dipole moment. Its z component is proportional to $p = (1/3)\sum_{\lambda=1,\ldots,3}\langle q\rangle_\lambda \neq 0$. The electric dipole moment of W layers is supposed to cause the bulk ferroelectric state in $LuFe_2O_4$.[6,12,16]

Keeping in mind the remarks above on the PDA phase, we also consider the PDA state of the W layer; that is, each its layer is in the PDA state. To do this in the 6-SL model we assume two sublattices to be in disordered state ($\langle q\rangle_3 = \langle q\rangle_6 = 0$) and the four others to form the honeycomb ordered structures in the two layers ($\langle q\rangle_1 = -\langle q\rangle_2 = \langle q\rangle_5 = -\langle q\rangle_4$) as shown in Fig. 1(b).

A detailed investigation of the PDA structure of the W layer reveals that there are pairs of disordered iron sites in the neighboring layers. They are marked by the dashed ovals in Fig. 1(b). The pairs prove to be in zero effective field. On the other hand, ions making up the pairs are separated by the shortest distance in the system and the Coulomb coupling between them, J_0, is the strongest one. That is why the ions in the pairs should be strongly correlated or, in other words, they form dimers to lower the total energy. We also take the dimer PDA (DPDA) structure into consideration.

In the framework of the mean-field theory[23] all the interactions in the Hamiltonian (1) are reduced to three inter- and intrasublattice coupling parameters for the 6-SL structure,

$$A_n = \sum_{j\in L_n} J_{ij}, \qquad (3)$$

where $n = 1,2,3$, the set L_1 consists of the sites j belonging to the same sublattice as the ith site ($i \neq j$), and the sets L_2 and L_3 contain the sites of other sublattices in the same layer as the ith site or another layer, correspondingly. The values of these parameters diverge while r_{ij} increases. However, only their differences $(A_1 - A_3,\ A_2 - A_3)$ have physical meaning and they converge to constant values. An evaluation of these quantities for the Coulomb interaction can be performed by means of Ewald summation for systems with planar periodicity.[29] The effective field for the λth sublattice has the form

$$\phi_\lambda = (A_1 - A_3)\langle q\rangle_\lambda + (A_2 - A_3)(\langle q\rangle_{\lambda'} + \langle q\rangle_{\lambda''}), \qquad (4)$$

where $\langle q\rangle_{\lambda'}$ and $\langle q\rangle_{\lambda''}$ denote other sublattices in the same or another layer, correspondingly.

Apart from the parametrization (3), the system of equations for the average charges of sublattices is the same as that for the triangular AF Ising model:[23]

$$\langle q\rangle_i = -\tanh[\beta(\alpha\langle q\rangle_i + \langle q\rangle_j + \langle q\rangle_k)], \qquad (5)$$

where indexes $i \neq j \neq k \neq i$ take values 1, 2, 3; $\beta = (A_2 - A_3)/T$; $\alpha = (A_1 - A_3)/(A_2 - A_3)$; and T is the temperature.

A general form of the free energy for the 6-SL model is

$$F_6 = -\frac{T}{3}\left\{3\ln 2 + \beta\left[\frac{\alpha}{2}\sum_i \langle q\rangle_i^2 + \sum_{i>j}\langle q\rangle_i\langle q\rangle_j\right] + \sum_{i\neq j\neq k\neq i}\ln\cosh[\beta(\alpha\langle q\rangle_i + \langle q\rangle_j + \langle q\rangle_k)]\right\}, \qquad (6)$$

where the low indices are again limited by the values 1, 2, and 3. The free energy for the PDA structure is obtained when one of sublattices proves to be disordered, $\langle q\rangle_i = 0$. The free energy of the DPDA phase is obtained by subtracting from F_{PDA} the part corresponding to the disordered sublattices and addition of the free energy of the sublattices of disordered dimers. Finally it takes the form

$$F_{\mathrm{DPDA}} = F_{\mathrm{PDA}} - \frac{T}{3}\ln\cosh\frac{J_0}{T}. \qquad (7)$$

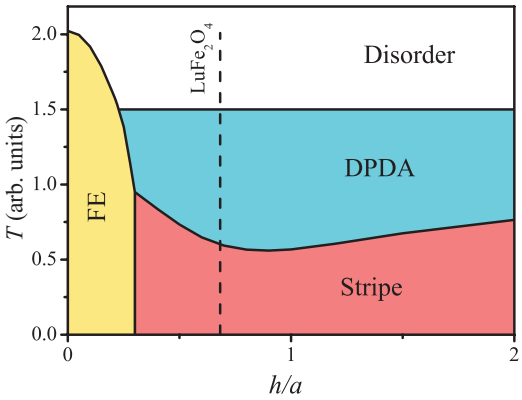

FIG. 2. (Color online) Phase diagram of the Ising model with Coulomb coupling on the W layer. The dashed line denotes the interlayer distance (h/a) corresponding to $LuFe_2O_4$.

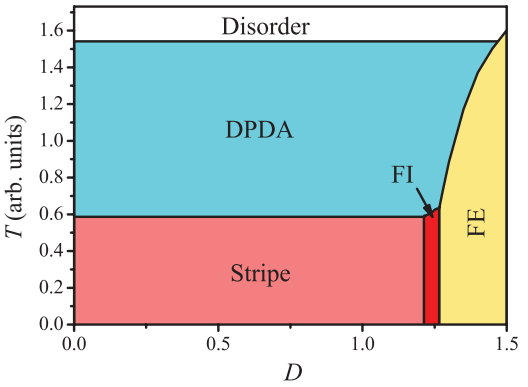

FIG. 3. (Color online) Phase diagram of stacked W layers with the coupling between W layers in the form of Eq. (8).

From Eq. (7) one can see that the free energy of the DPDA phase is lower than that of the PDA phase at any finite temperature.

To take into consideration stripe CO we also investigate a four-sublattice (4-SL) model. The two layers of the W layer are separated into four sublattices as shown in Fig. 1(c). The average charges of the sublattices obey the conditions $\langle\tilde{q}\rangle_1 = -\langle\tilde{q}\rangle_2$, $\langle\tilde{q}\rangle_3 = -\langle\tilde{q}\rangle_4$, and $|\langle\tilde{q}\rangle_1| = -|\langle\tilde{q}\rangle_3|$. The 4-SL model also restricts the total effective charge to the zero value. The 4-SL model describes the two types of the stripe CO discussed in Refs. 16 and 17. Calculations of the effective charges and the free energy are performed similarly to the 6-SL model.

A phase diagram of the isolated W layer is plotted in Fig. 2 as a chart of temperature versus the interlayer distance h for the Coulomb coupling between effective charges in terms of the in-plane lattice constant a. There exist two phases at low temperatures. When h goes to zero the W layer transforms to the plane honeycomb lattice with the AF ground state. It corresponds to the FE order of the W layer $(\langle q\rangle_1 = \langle q\rangle_2 = \langle q\rangle_3)$. At large interlayer distances the stripe phase appears. The DPDA phase has the lowest free energy at high temperatures within a wide range of h. In addition we calculated the phase diagrams for the Ising model with two sets of short-range interactions proposed in (a) Ref. 16 and (b) Refs. 10 and 18 instead of the Coulomb coupling. The DPDA state persisted at high temperatures in both cases, which reveals a universal character of the DPDA state on the W layer.

A coupling between W layers results in the 3D-CO state in $LuFe_2O_4$. It is assumed to be due to the electric dipole moment of the W layers.[6,12,17] The interaction between W layers influences the internal charge structure of the W layers. To take it into consideration in the simplest form we extend the Hamiltonian (1) as follows:

$$H = H_W - Dp^2, \tag{8}$$

where D is a positive parameter. This produces an additional term in the effective field (4) of the form $\phi_\lambda \to \phi_\lambda - 2Dp$. For the 4-SL model and the DPDA state, $p = 0$. It should be mentioned that, in effect, this form of the interaction between W layers is approximate because of the following reason. The structure of neighboring W layers can be represented as -(AB)-(CA)-(BC)-, where A, B, and C are usual notations for the hexagonal layers in a closely packed lattice. The layers of the same W layer are in parentheses. Coupling of layers of different types, e.g., A and C in the first pair of W layers, corresponds exactly to the form in Eq. (8) from symmetry considerations because each ion from one layer interacts exactly with the average charge of the other layer. Coupling of the layers of the same type, e.g., A and A, is slightly different, which leads to an additional term independent of p in Eq. (8). A numerical estimation of this term has shown that it is extremely small and we neglect it hereinafter. It should be stressed that the coupling in the form of Eq. (8) allows us to study the effect of the interaction between W layers on the internal structure of the W layers but does not distinguish between ferro- and antiferroelectric stacking of the W layers.

A phase diagram of the systems of W layers with the interaction between neighboring layers is shown in Fig. 3. One can see that in the vicinity of $D = 1.2$ the FI order within W layers appears at low temperatures and the DPDA state is the high-temperature phase. This part of the phase diagram corresponds to the situation observed in $LuFe_2O_4$. Both the phases are characterized by the wave vector $\mathbf{k} = (\frac{1}{3}, \frac{1}{3})$. The FI state has a nonzero electric dipole moment. That is why the W layers turn out to be coupled at low temperatures and the 3D-CO exists. Since the electric dipole moment for the DPDA state is equal to zero the 2D-CO develops at high temperatures. Theoretical estimations of D in $LuFe_2O_4$ have a large spread in values. Thus, the Ewald summation over stacked W layers with the Coulomb interaction $(J_{ij} \propto r_{ij}^{-1})$ and the model with short-range coupling[18] give $D \approx 0.76$ and $D \approx 0.02$, correspondingly. The first-principle calculations with lattice relaxation produce $D \approx 1.4$,[17] $D \approx 0.77$,[12] and the antiferroelectric ordering of W layers. They also show that the stripe phase is suppressed in $LuFe_2O_4$. This means that in effect the area where the FI phase exists should be much large than that shown in Fig. 3. It should be mentioned that the simple mean-field form of the interaction between the W layers [Eq. (8)] does not allow the incommensurate charge order to be reproduced in the 3D-CO.

In conclusion, we have shown that the DPDA ordered state is a universal high-temperature phase for the AF Ising model on a W layer similarly to the PDA state on the triangular lattice;[23,25,27] that is, it exists in a wide range of

coupling parameters. Since the DPDA phase does not have the electric dipole moment, its occurrence in $LuFe_2O_4$ at high temperatures decouples W layers and gives rise to the transition to 2D-CO.

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