Multiferroics and magnetoelectric effects in charge ordered compounds

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The coexistence of magnetic ordering and ferroelectricity, known as multiferroics, has drawn a lot of research effort. Depending on the origin of ferroelectricity, multiferroic materials can be classified into different groups. In this paper, we review recent progress in the field of multiferroics induced by different forms of charge ordering. In addition to a general description of charge order and electronic ferroelectricity, we focus on two specific systems: (1) charge order with frustration in RFe_2O_4 (R=Lu, Yb) system; (2) charge ordered perovskite manganites of the type $(R_{1-x}Ca_x)MnO_3$ (R=La, Pr). The charge ordering can be tuned by external electric fields, which results in pronounced magnetoelectric effects and strong dielectric tunability. Other materials and possible candidates with charge order induced multiferroics are also briefly summarized.

multiferroics, charge order, magnetoelectric effects

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The interplay between electricity and magnetism has been a core topic in modern condensed matter physics. For instance, the large field of spintronics relies primarily on the effects of spins on the electric transport properties (and vice versa) in conductors. The coupling of magnetic and electric degrees of freedom in insulators yields another new and exciting field: multiferroics and magnetoelectric (ME) effects [1–5].

Ferroelectrics and ferromagnets are both widely used in modern life. Ferroelectrics are materials that display a spontaneous electric polarization and the direction of the electric polarization can be reversed by electric fields. Ferroelectric order can only exist in a material with broken inversion symmetry. Ferromagnets in which all the magnetic moments are aligned in the same direction in zero magnetic field require the breaking of time-reversal symmetry and the magnetization is controlled by magnetic fields.

Multiferroics originally refers to the coexistence of both ferromagnetic and ferroelectric orders. However, by this strict definition, multiferroics would be rarely realized in a single-phase material. Nowadays, the scope of multiferroics has been extended to include any case in which spontaneous magnetic and dielectric orders coexist (Figure 1). In multiferroic materials, researchers may expect a strong cross coupling between ferroelectricity and magnetism that provides additional freedom for magnetization and polarization manipulation, that is, the control of polarization by a magnetic field and of magnetization by an electric field [6–10]. Therefore, the field of multiferroics and ME effects has attracted research focus because of their great potential for technological applications as well as the intriguing fundamental physics.

Although the investigation of the ME effects has a long history, the field remained flat till the beginning of this century because the ME effects observed were quite weak. In 2003 there were several breakthroughs: the discovery of

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magnetic-field-controllable ferroelectric polarization in $TbMnO_3$ [7] and $TbMn_2O_5$ [8], and the realization of giant ferroelectric polarization in $BiFeO_3$ thin films [11]. Since then, this field has evolved rapidly. Many new materials are being discovered and new concepts and theories are being developed. Thus far a number of single-phase materials have been reported to exhibit multiferroics and ME effects. Depending on the origin of ferroelectricity, multiferroic materials can be classified into different groups [12]: (1) multiferroics induced by a lone pair such as $BiFeO_3$; (2) geometric multiferroics such as $YMnO_3$; (3) magnetically induced multiferroics such as $TbMnO_3$; (4) exchange striction induced multiferroics such as Ca_3CoMnO_6; (5) charge order induced multiferroics.

In this paper, we review recent progress in the field of multiferroics induced by different forms of charge order (CO). After a general description of the concepts of CO and electronic ferroelectricity, we focus on two spectacular systems: (1) charge order with frustration in RFe_2O_4 (R=Lu, Yb) system; (2) charge ordered perovskite manganites of the type $(R_{1-x}Ca_x)MnO_3$ (R=La, Pr). The manipulation of the CO by external electric fields may induce phase transitions as well as pronounced magnetoelectric effects. Finally, a variety of other candidates for the CO induced multiferroics are summarized.

1 Charge order and electronic ferroelectricity

In conventional ferroelectrics, the covalent bond between the anions and cations or the orbital hybridization of electrons on both ions has a key role in establishing the dipolar arrangement [13–15]. The polarization is because of the relative displacement of positive and negative ions and a lattice distortion is generally accompanied with the ferroelectric transition. In contrast, a new class of ferroelectricity termed as "electronic ferroelectricity" in which the electric dipole depends on electron correlations rather than the displacement of cation and anion pairs, has been theoretically proposed and experimental discovered in the past two decades. The first theory of electronic ferroelectricity was proposed by Portengen et al. [16] for mixed-valent compounds.
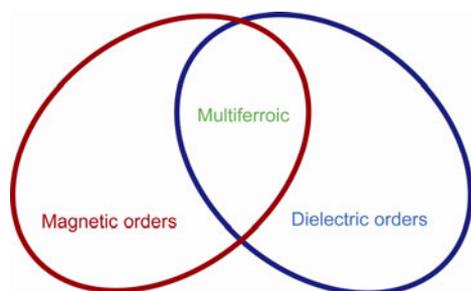
Now the concept has been developed to refer to the phenomena where spin and charge degrees of freedom of electrons are directly responsible for ferroelectricity [17]. In general, there are two types of electronic ferroelectricity: (1) charge driven ferroelectricity where the polarization is induced by different forms of charge order; (2) spin driven ferroelectricity where magnetic interactions and specific spin ordering (for example, spiral spin ordering) can cause a net polarization. The spin driven ferroelectricty and multiferroic has been intensively studied in the past decade, and several review articles have been published [18,19]. Here we focus on the charge driven electronic ferroelectricty and multiferroics in charge ordered compounds.

Charge order (CO) in solids is often observed in systems with ions that formally have a mixed valence [20]. Typically, two general types of charge order has been proposed: site-centered CO and bond-centered CO in which mirror planes of the CO structure can be marked at ions or bond centers (Figure 2). Because both types of CO structure do not break spatial inversion system, a net polarization is not induced. In order to realize ferroelectricity induced by the CO, it is necessary to combine the site-centered and bond-centered CO, that is, the simultaneous presence of inequivalent sites and bonds in the system. In some materials bonds are inequivalent because of the crystallographic structure, and a spontaneous CO that occurs below a certain ordering temperature drives the inequivalence of the sites. It can also occur in reverse, where the material can contain ions with different valences, which after a structural dimerization transition induces ferroelectricity. These two effects may also occur simultaneously, in which case there is one common phase transition.

2 Multiferroics in charge ordered RFe_2O_4

The RFe_2O_4 family, where R represents rare-earth elements from Dy to Lu and Y [21], is a good example of charge order induced ferroelectricity. The RFe_2O_4 system has a rhombohedral space group ($R\bar{3}m$) with a crystal structure

Figure 1 Generalized definition of multiferroics in which spontaneous magnetic and dielectric ordering coexist.
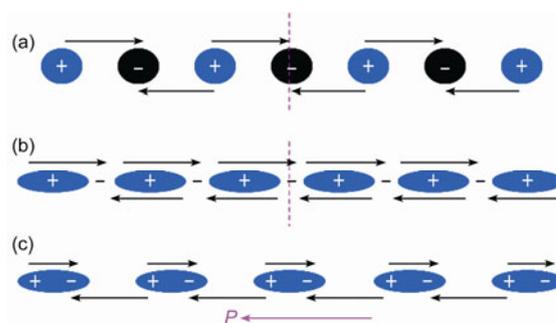

Figure 2 (a) Scheme of one-dimensional site-centered charge order; (b) bond-centered charge order; and (c) a linear combination of these two which induces a net polarization.

consists of the alternate stacking of triangular lattices of rare earth elements, iron and oxygen (Figure 3). An equal amount of Fe^{2+} and Fe^{3+} coexists at the same site in the triangular lattice. Compared to the average Fe valence of 2.5+, Fe^{2+} and Fe^{3+} ions are considered as having an excess and a deficiency of half an electron, respectively. Thus the interaction between Fe^{2+} and Fe^{3+} is accompanied by a frustration on the triangular lattice.

The competing interactions between frustrated charges are settled by a superstructure of Fe^{2+} and Fe^{3+} arrangements on the bilayer structure. As shown in Figure 4, within each bilayer of the iron triangular lattice, the lower layer presents the ratio 2:1 (Fe^{2+}:Fe^{3+}) but the upper layer gives the ratio 1:2 (Fe^{2+}:Fe^{3+}). This site centered charge redistribution is closely associated with the bilayer crystallographic structure and frustrated triangular geometry of RFe_2O_4. As a result, an electric dipole oriented from the upper layer to the lower layer within each iron bilayer is formed [22,23].

The CO in RFe_2O_4 has been confirmed by many experiments such as neutron scattering, electron diffraction, X-ray scattering, etc. [24–28]. For example, $LuFe_2O_4$ exhibits a three-dimensional (3D) charge ordered state below 330 K. Above 330 K, the 3D charge ordering transforms into a 2D ordering state. In 2005, I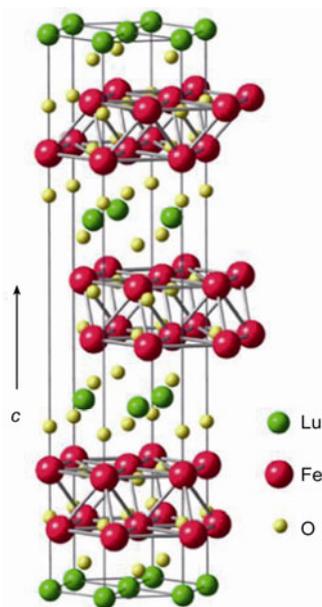keda et al. [22] first reported the discovery of ferroelectricity in $LuFe_2O_4$ and concluded that the electric polarization arises from the ordered arrangement of electrons on a triangular lattice. Figure 4 presents a similar result in $YbFe_2O_4$. The plot is the integration of the pyroelectric current measurement. The current flow from the sample was recorded on heating after electric field poling along the *c* axis. A spontaneous electric polarization appears immediately below the CO transition temperature T_{CO} ~ 330 K, which indicates the close correlation between the CO and ferroelectricity. The dielectric constant shows a strong dispersion (frequency dependence) at high temperature, consistent with order-disorder type ferroelectric materials [22].

In addition to the electronic ferroelectricity below 330 K, the strong magnetic interactions between localized Fe moments develop as a ferrimagnetic ordering [25]. Figure 6 shows the temperature dependence of magnetization of $YbFe_2O_4$. A magnetic transition is clearly seen at ~245 K. Therefore, the coexistence of ferrimagnetic order and electronic ferroelectricity makes RFe_2O_4 a new class of multiferroics. Since both the ferroelectricity and magnetism in the system originate from the same Fe ions, it holds the promise of strong magnetoelectric coupling [29].
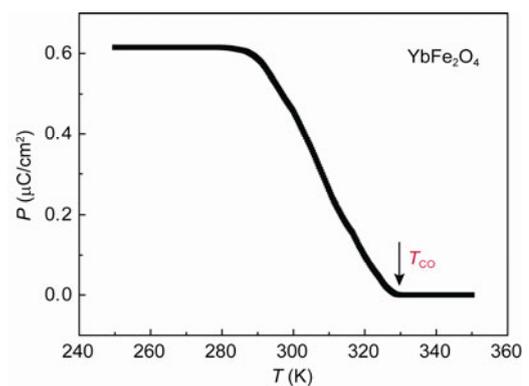

Figure 5   Charge order induced electric polarization in $YbFe_2O_4$. A ferroelectric transition is observed at the charge order transition temperature T_{CO}.
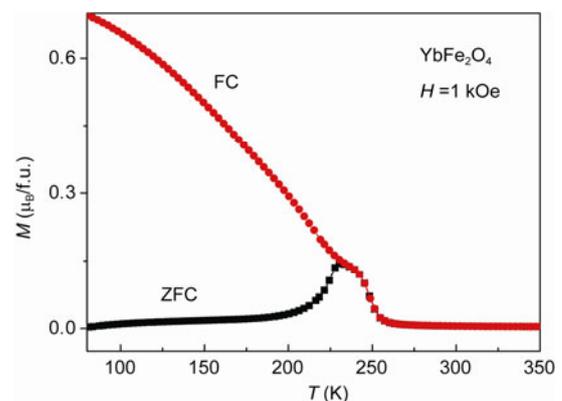

Figure 3   Crystal structure of the RFe_2O_4 family.
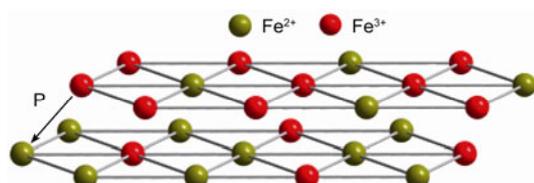
Figure 4   Charge order configuration in RFe_2O_4.

Figure 6   Temperature dependence of the magnetization of $YbFe_2O_4$. A ferrimagnetic ordering occurs below 245 K.

3   Modify charge ordering by external electric fields

The CO in many systems could be manipulated by external forces such as magnetic field, electric field, laser irradiation, and pressure [30–35]. For example, an electrically driven phase transition is realized in the CO perovskite manganites [35] and magnetite (Fe_3O_4) [31] below the T_{CO}. Similarly, the CO state in RFe_2O_4 can be modified by external electric fields [36–39]. Figure 7 demonstrates the electric field modification on the CO in a $LuFe_2O_4$ single crystal.

When a small electric current is applied in the *ab* plane of the crystal, the resistivity is high and remains constant because the CO is unaffected. However, once a high electric current is applied, which generates a high electric field in the order of several kV/cm, the measured voltage on the sample shows an abrupt drop and then stabilizes at a incremental value. This sharp transition is a sign of CO breakdown induced by a high electric field. The resistivity drops by more than three orders, indicating an electrically driven insulator-metal transition. In the CO state, the charge carriers are initially localized at each atomic site because of the repulsive electron-electron interaction. Sufficiently strong electric field may cause the breakdown of the CO state, which immediately releases a large number of mobile charge carriers, and consequently, a metallic state appears. This electrically driven phase transition leads to a giant electroresistance effect which could be used in memory devices [36,37].

As the CO induces the electronic ferroelectricity in RFe_2O_4, the modification of CO by external electric field would consequently influence the dielectric and ferroelectric properties. Figure 8 shows the dielectric constant of $LuFe_2O_4$ as a function of temperature under zero and a 50 V/cm dc bias field. A large difference between two curves appears above 250 K as the dielectric constant is greatly suppressed in a dc bias field, indicating a high dielectric tunability [40].
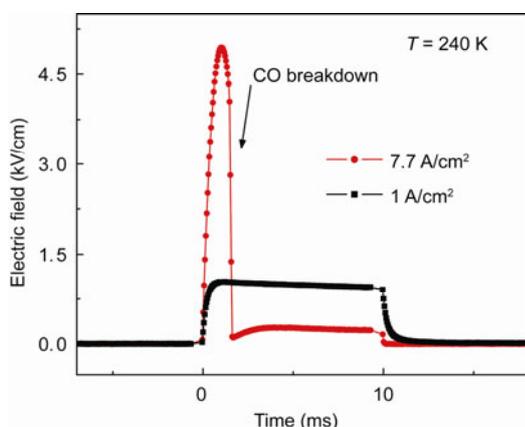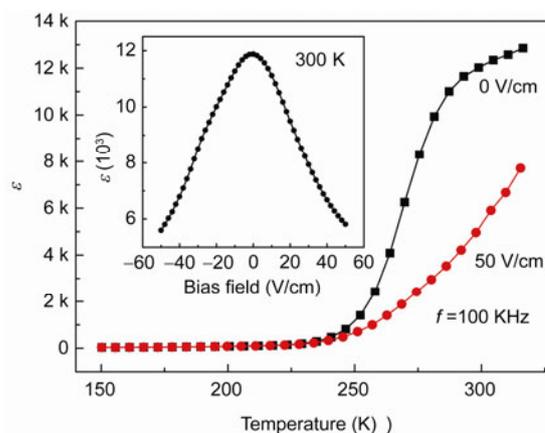

Figure 8   Giant dielectric tunability in $LuFe_2O_4$. The dc bias electric field significantly supresses the dielectric constant. Reprinted with permission from ref. [40]. Copyright 2008, American Institute of Physics.

Ferroelectric materials with a high dielectric tunability, that is, a strong dependence of their dielectric constant on the applied dc bias electric field, have potential application for many devices [41–44]. A high tunability in ferroelectrics such as $Sr_{1-x}Ba_xTiO_3$ usually requires a large dc electric field in the order of tens of kV/cm. Besides, conventional ferroelectric materials usually exhibit a high tunability in a narrow temperature range around the ferroelectric transition. These drawbacks have strongly limited the applicability of dielectric tunability in tunable devices. In contrast, it was found that the electronic ferroelectric RFe_2O_4 system exhibits a low-field giant dielectric tunability over a broad temperature interval around room temperature. The required dc bias electric field is almost three orders less than those conventional ferroelectrics. The dielectric tunability can be further modified by the substitution of Fe^{2+} with other transition metal elements or making $LuFe_2O_4$ based composites [45,46].

4   The magnetoelectric effects in RFe_2O_4

Since both magnetic and ferroelectric ordering in RFe_2O_4 are established in the same Fe^{2+}/Fe^{3+} ions, one may expect that the two orders are closely coupled. Specifically, when the CO is modified by external electric fields, the magnetic ordering could be influenced, and consequently leads to the inverse ME effect. The magnetization of a $LuFe_2O_4$ single crystal as a function of applied voltage is shown in Figure 9. The magnetic field is applied along the *c* axis (the easy magnetization direction) while the voltage pulse is applied in the *ab* plane where the CO is easier to be broken down than the *c*-axis direction. With the increase of applied voltage, the magnetization changes slightly when the voltage is low. This initial change could be the normal magnetic relaxation with time. When the applied voltage is above a critical voltage, the magnetization exhibits a sizable jump.

Figure 7   Electric field modification of charge order in $LuFe_2O_4$.

In zero magnetic field, the magnetization jumps down. In contrast, the magnetization jumps up in a constant 0.1 T magnetic field. These results suggest that the magnetization of multiferroic RFe_2O_4 can be effectively controlled by electric fields. By simultaneously monitoring the current with applied voltage pulse, it was found that this dramatic magnetization change is related to the breakdown of the CO [47].

To further confirm the electrically driven magnetization change, we performed a series of magnetization measurements with single voltage pulses at different temperatures and magnetic fields. Figure 10 shows the results at 200 and 100 K. The curves marked with 0 T were measured as following: a 5 T magnetic field was applied along the *c* axis to magnetize the sample, then the field is removed and the
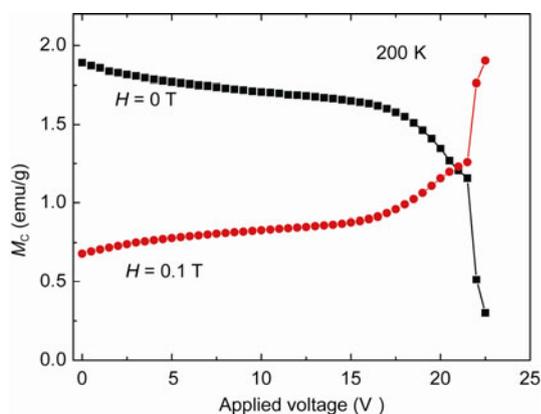

Figure 9 Magnetization as a function of applied voltage pulse in $LuFe_2O_4$. The curve with *H*=0 T was measured after filed cooling in a 5 T to 200 K and removing the field. Reprinted with permission from ref. [47]. Copyright (2009) by The American Physical Society.
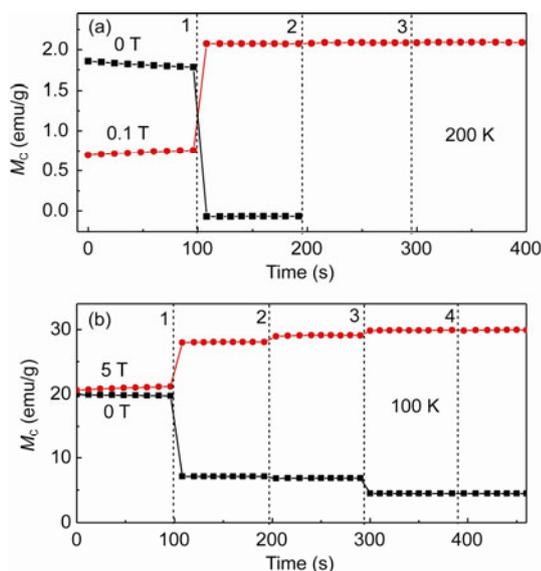

Figure 10 Electrical switch of magnetization in LuFe2O4 at 200 and 100 K. Reprinted with permission from ref. [47]. Copyright (2009) by The American Physical Society.

remanent magnetization was measured with time in zero magnetic field. The curves marked with 0.1 and 5 T were measured in a constant 0.1 or 5 T field after a ZFC process. The dotted lines refer to the positions where a 22 V at 200 K or 100 V at 100 K voltage pulse was applied. In zero magnetic field, the remnant magnetization is immediately switched to zero after applying a single voltage pulse. In a constant 0.1 T magnetic field, the magnetization is immediately switched up after applying a voltage pulse and remains in the high state. The successive voltage pulses have negligible influence on the magnetization. These results demonstrate that a single electric pulse can cause a permanent change in the magnetization

Figure 11 shows the reversible switch of magnetic states at 200 K by employing the electrical control of magnetization in single crystal $LuFe_2O_4$. In State 1, the magnetization is set by applying a 0.1 T field; then the magnetization is switched up to a high level (State 2) by applying a voltage pulse; once the magnetic field is cutoff the magnetization drops to a remanent level (State 3); and finally, the magnetization is switched down to a very low level (State 4) by applying another voltage pulse. These four magnetic states can be repeatedly reproduced for many times. Therefore, a multiple-state memory could be constructed based on this type of electric switch of magnetization.

The electrical switch of magnetization can also be used for manipulating the magnetization hysteresis loop. Figure 11 shows the magnetization hysteresis loops measured at 100 K after a ZFC process. The normal hysteresis loop shows a large coercive field of 2.5 T. When a 100 V voltage pulse is applied at −1 T in the descending branch, the magnetization switches from positive to negative. Similarly, when a 100 V voltage pulse is applied at +1 T in the ascending branch, the magnetization switches from negative to positive. This result demonstrates that the magnetization reversal process can be electrically assisted.

The electrically induced magnetization change is related to the breakdown of CO and an intrinsic spin-charge coupling
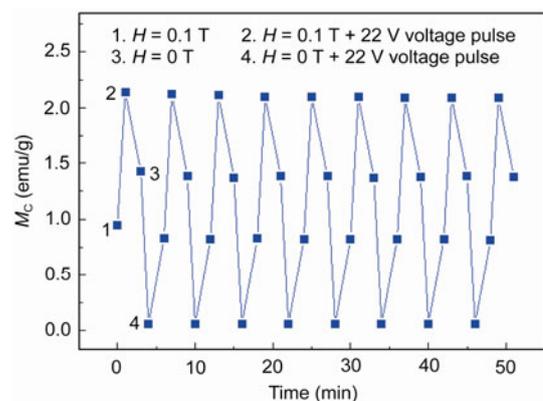

Figure 11 Reversible switch of multiple magnetic states at 200 K. Reprinted with permission from ref. [47]. Copyright (2009) by The American Physical Society.
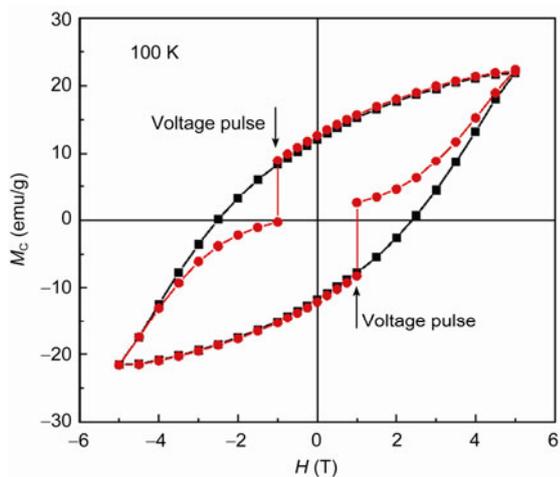
Figure 12 Electrical manipulation of magnetization hysteresis loop at 100 K. The black square curve is the normal hysteresis loop measured after ZFC to 100 K. The red circle curve is the hysteresis loop measured with voltage pulses. The arrows mark the positions where a 100 V voltage pulse is applied. Reprinted with permission from ref. [47]. Copyright (2009) by The American Physical Society.

Figure 14 Electric field driven magnetic relaxation in LuFe2O4. After a field cooling to 200 K, the magnetic field is cut off and the magnetization is measured as a function of time. The red solid curve is the normal relaxation. The dashed line is a schematic plot of relaxation with temporal heating. Reprinted with permission from ref. [48], IOP Publishing.

in LuFe$_2$O$_4$. The physical mechanism has been interpreted qualitatively by a three-temperature model in which the temperatures of the electron, spin, and lattice are considered separately [48]. The CO breakdown triggered by external stimulus leads to an immediate rise in the temperature of the electrons, and consequently drives a temperature rise in the spin system via a strong electron–spin coupling. This temporary temperature change in the spin system during the applied current pulse would accelerate the spin relaxation, and result in a macroscopic change in magnetization. This type of electrically assisted magnetic relaxation may be expected in other CO systems with a strong electron–spin coupling.

This analysis is consistent with the experiments as shown in Figure 14. After a field cooling in 1 T from 300 to 200 K,
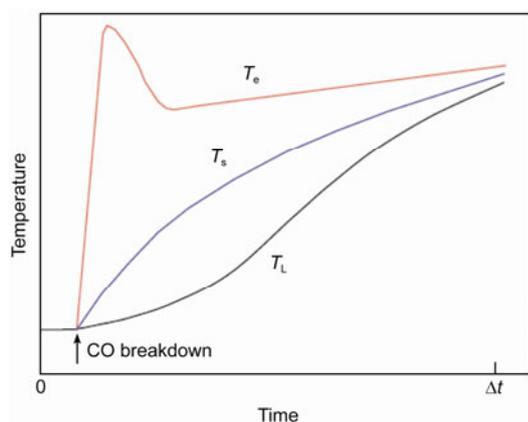

Figure 13 Schematic illustration of the temperature variation of electron, spin, and lattice systems, separately (the three-temperature model), during an applied electrical pulse. Reprinted with permission from ref. [48], IOP Publishing.
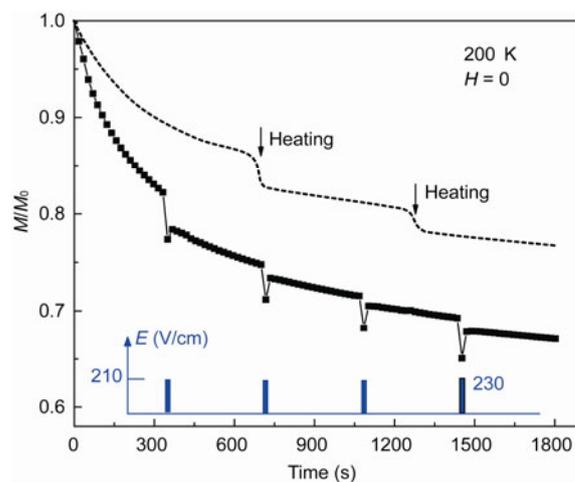
the magnetic field is removed and the magnetic relaxation is measured with time. At certain time, an electric field is applied on the sample and the magnetization in field is measured. The intensity of applied electric field is carefully selected so that the current is low enough to avoid Joule heating, whereas the induced magnetization change is easily detectable. After measuring the magnetization in electric field, the electric field was cut off and the magnetic relaxation was measured in the zero field. This process is repeated several times. As expected, the magnetization with applied electric field drops because the (partial) breakdown of CO also destroys magnetic ordering. When the electric field is removed, the CO is restored and the magnetic ordering is also recovered. This leads to a rise of magnetization. However, the magnetization does not return to the level before applying the electric field but to a lower level. The difference between the magnetic relaxation with electric field disturbances and the normal relaxation (the red solid curve) indicates that the magnetic relaxation is accelerated during the applied electric field so that a part of relaxed magnetization cannot recover after the electric field is off. The dashed line mimics the magnetic relaxation with simple heating. The clear distinction between magnetic relaxation with electric field disturbances and the relaxation with temporal heating further confirms that the electrically driven magnetization change in LuFe$_2$O$_4$ is not because of the heating effect.

The above experiments suggest that the electrical breakdown of CO can induce immediate and giant changes in magnetization. The physics of this electrical switch of magnetization could be related to an intrinsic spin-charge coupling. There have been some theoretical models predicting a spin-charge coupling in LuFe$_2$O$_4$ [23,29]. The magnetization switch in LuFe$_2$O$_4$ only requires a low cur-

rent density of 10^0 A/cm^2 or a small electric field of 10^2–10^3 V/cm, which is quite smaller than using spin-polarized current or electric fields, where a high current density [49] of 10^5–10^8 A/cm^2 or a high electric field [50] of 10^5–10^6 V/cm is usually required.

5   Multiferroics in charge ordered manganites

5.1 $Pr_{1-x}Ca_xMnO_3$

Among the various mixed-valence manganites, the R_{1-x}-Ca_xMnO_3 system is of great interest for the study of the CO and strongly correlated nature among spin, charge and lattice [51–56]. In these manganites CO typically extends over a large part of the doping phase diagram. For example, in $Pr_{1-x}Ca_xMnO_3$, CO exists for a wide doping range ($0.3 < x < 0.85$). For a long time, the CO in $Pr_{1-x}Ca_xMnO_3$ was thought to be the classical picture with a site-centered checkerboard pattern. However, Daoud-Aladine et al. [57] proposed an electronic ground state where one e_g electron is shared by two Mn ions, the so-called bond-centered Zener polaron picture which has been confirmed by recent experimental results [58]. Either the site-centered or bond-centered CO does not break the inversion symmetry, and thus would not induce a spontaneous polarization. Efremov et al. [59] proposed that the CO configuration in $Pr_{1-x}Ca_xMnO_3$ depends antiferromagnetic charge exchange (CE) double zig-zag state sets at $x=0.5$ and a pure bond-centered one appears at $x=0.4$.

In the range of $0.4 < x < 0.5$, the bond-centered and the site-centered CO pictures coexist and the result breaks the inversion symmetry, leading to the appearance of a spontaneous electric polarization (Figure 15). It had been difficult to show the predicted polarization in $Pr_{1-x}Ca_xMnO_3$ because of the relatively high conductivity of these compounds. Recently, some progress in experiments has been achieved. Jooss et al. [60] provides, by refinements of electron diffraction microscopy data, indirect evidence for canted antiferroelectricity in $Pr_{0.68}Ca_{0.32}MnO_3$.

More recently, the measurement of the electric field gradient tensor provided clues to the predicted paraelectric to ferroelectric phase transition in the charge ordered $Pr_{1-x}Ca_xMnO_3$ manganites [61].
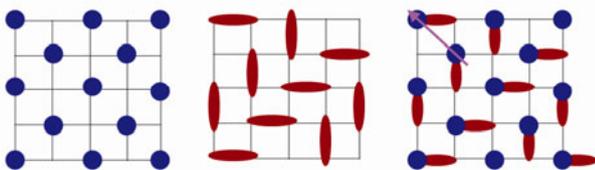
5.2   Half-doped manganite $La_{0.5}Ca_{0.5}MnO_3$

The half-doped manganite $La_{0.5}Ca_{0.5}MnO_3$ is another prototype of CO manganites. The ground state of $La_{0.5}Ca_{0.5}MnO_3$ has been proved to be inhomogeneous, consisting typically of metallic clusters trapped in an insulating charge ordered antiferromagnetic matrix [62]. The CO configuration in $La_{0.5}Ca_{0.5}MnO_3$ is still controversial even after extensive investigations [63]. A traditional checkerboard site-centered CO state has been proposed. Conversely, a bond-centered CO state based on the so-called Zener polaron has been suggested. In either case, the CO configuration does not break the spacial inversion symmetry and should not induce a ferroelectricity. Recently, theoretical work by Giovannetti et al. [64] illustrated that the combination of a peculiar charge-orbital ordering and a tendency to form spin dimmers in $La_{0.5}Ca_{0.5}MnO_3$ breaks the inversion symmetry and result in polar states with relatively strong ferroelectricity. Based on this theory, the CO induced ferroelectricity along with the antiferromagnetic ordering could make $La_{0.5}Ca_{0.5}$-MnO_3 a possible candidate for new multiferroics with strong ME effects. Recently, some experimental evidences supportting this theoretical prediction have been found [65].

The dielectric constant of $La_{0.5}Ca_{0.5}MnO_3$ as a function of temperature is shown in Figure 16. A pronounced peak appears just at 200 K where the CO transition occurs. Below the peak temperature T_P, the dielectric constant shows certain dispersion behavior (frequency dependence). The dielectric constant measured with different electrodes always shows a maximal at 200 K, suggesting that the dielectric peak is an intrinsic characteristic of $La_{0.5}Ca_{0.5}MnO_3$.

Since a peak in the dielectric constant was commonly observed at the ferroelectric transition, the dielectric peak at T_{CO} indicates that a polarization could be induced by the CO transition. The relaxor-like broad peak and the dispersion below T_P imply that the polar entities could be in the form of small polar clusters/domains. In addition to the dielectric

Figure 15   Charge ordering configuration in $Pr_{1-x}Ca_xMnO_3$. Site-centered (left), bond-centered (middle), and intermediate (right). A polarization is induced in the intermediate CO configuration.
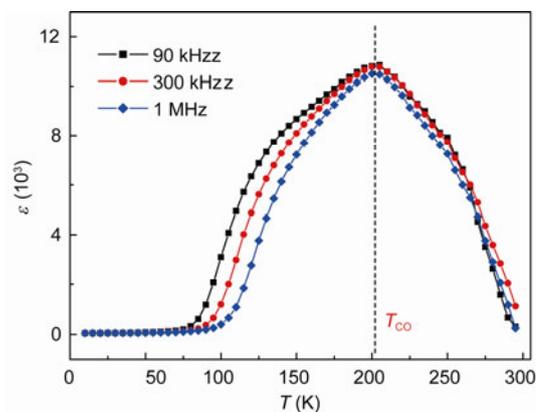
Figure 16   Temperature dependence of dielectric constant of $La_{0.5}Ca_{0.5}$-MnO_3. A pronounced peak is observed at the CO temperature T_{CO}. Reprinted with permission from ref. [40]. Copyright 2008, American Institute of Physics.

peak at T_{CO}, a strong magnetodielectric effect was observed in $La_{0.5}Ca_{0.5}MnO_3$. The dielectric constant measured in a 5 T magnetic field is much higher than that in the zero field (Figure 17). This strong magnetodielectric effect below T_{CO} seems to indicate a strong ME coupling in the antiferromagnetic CO state.

The measurements of ME coupling coefficient by a dynamic technique [66] provides further evidence for the CO induced multiferroics and ME effects. Figure 18 shows the temperature dependence of the longitudinal ME coefficient α in $La_{0.5}Ca_{0.5}MnO_3$. The ME coefficient is small at high temperature, indicating a weak ME coupling in the paramagnetic state. Just below the CO transition at 200 K, the ME coefficient increases rapidly and reaches 2.38 (mV/cm·Oe) at low temperature. These results directly show that the ME coupling is greatly enhanced in the CO state.

6   Multiferroics in other charger ordered materials

In addition to the RFe_2O_4 and charge ordered $(R_{1-x}Ca_x)$-

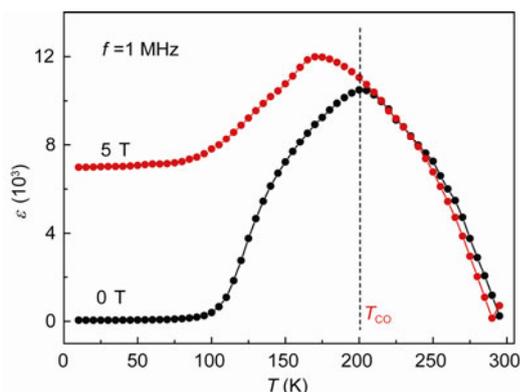**Figure 17**   Magnetodielectric effect in $La_{0.5}Ca_{0.5}MnO_3$. Reprinted with permission from ref. [40]. Copyright 2008, American Institute of Physics.
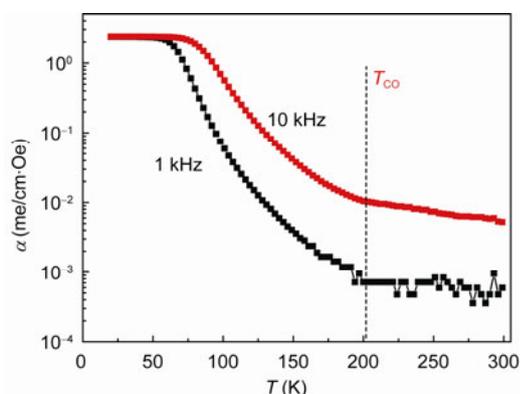

Figure 18   Temperature dependence of magnetoelectric coefficient in $La_{0.5}Ca_{0.5}MnO_3$. The coefficient increases rapidly below the CO transition temperature T_{CO}. Reprinted with permission from ref. [40]. Copyright 2008, American Institute of Physics.

MnO_3 perovskite manganites, there are a number of other materials showing the CO induced multiferroics [67]. A few possible candidates were also predicted by theoretical calculations. In the following, we present a brief summary of these CO materials.

Another intriguing and well known CO system is magnetite, Fe_3O_4, which exhibits the Verwey insulator–metal transition at $T_V = 120$ K and a ferrimagnetic ordering below ~ 860 K. The nature of the Verwey transition is related to the CO transition of Fe^{2+} and Fe^{3+} ions, though the exact pattern of CO in Fe_3O_4 is still a matter of controversy. Recent first-principles studies suggest that the noncentrosymmetric Fe^{2+}/Fe^{3+} charge-ordering in Fe_3O_4 may produce ferroelectricity [68,69]. Nevertheless, experimental evidence for this prediction is still lacking.

The bilayered perovskite manganites $Pr(Sr_xCa_{1-x})_2Mn_2O_7$ are also well known for the complex magnetic phase diagram as well as the CO and orbital order phenomena. In the past several years, there have been a few experiments showing signs of CO induced ferroelectricity in $Pr(Sr_x-Ca_{1-x})_2Mn_2O_7$ [70–72]. Particularly, CO induced polar domains and domain walls have been observed in a bilayered manganite $Pr(Sr_{0.15}Ca_{0.85})_2Mn_2O_7$ using second harmonic generation microscopy.

The rare earth nickelates of the type $RNiO_3$ could be another candidate for CO induced multiferroics. At high temperature, the valence of Ni is 3+, but below a certain temperature a charge disproportionation into formally Ni^{2+} and Ni^{4+} takes place, particularly when the rare earth is small (Y, Lu) [73,74]. The disproportionation leads to the formation of a rock-salt-like CO structure. It has been argued that the CO in combination with a specific magnetic structure would give ferroelectricity [67].

It is worthy to note that some organic materials may also exhibit the CO phenomenon. As a good example, the quasi-one-dimensional organic system (TMTTF)2X shows charge ordering at $T_{CO} \sim 50$–150 K, after which the molecules (sites) become inequivalent with alternating charges and the low-temperature phase becomes ferroelectric [75]. Moreover, a long-range antiferromagnetic ordering may be develop at low temperature, thus giving multiferroics.

7   Conclusions

We have introduced the concepts of charge ordering and electronic ferroelectricity, and reviewed recent progress in charge-order driven multiferroics. We focus on two specific systems: (1) strongly charge frustrated system RFe_2O_4 (R=Lu and Yb); (2) the $(R_{1-x}Ca_x)MnO_3$ (R=La and Pr) perovskite manganites. The ferroelectricity in RFe_2O_4 has been verified by both theoretical as well as experimental results. It originates from the peculiar CO on a frustrated triangular bilayer lattice. The CO state in RFe_2O_4 can be manipulated by external stimulus, which results in a variety of interesting

effects. The strong dielectric tunability and strong magneto-electric effects (electrical control of magnetization) are promising for applications. For the charge ordered manganites, theoretical work has been in the forefront of experimental work. Although some signs have been recently observed, more solid experimental evidence for electronic ferroelectricity in $(R_{1-x}Ca_x)MnO_3$ manganites are required.

Compared with conventional displacive ferroelectricity, the electronic ferroelectricity induced by CO is fragile and can be easily modified by external stimulus because the charge carriers are easier to fluctuate around localized sites than anion/ion displacement. This feature makes it difficult to realize a stable high polarization at high temperature. How to overcome this drawback is a key issue in future study. In comparison with magnetically induced multiferroics, the CO induced multiferroics is still relatively rare. In the future, more effort is needed in this field to find new multiferroics induced by different forms of CO.

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