TOPICAL REVIEW— Magnetism, magnetic materials, and interdisciplinary research

Structural changes concurrent with ferromagnetic transition*

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Ferromagnetic transition has generally been considered to involve only an ordering of magnetic moment with no change in the host crystal structure or symmetry, as evidenced by a wealth of crystal structure data from conventional X-ray diffractometry (XRD). However, the existence of magnetostriction in all known ferromagnetic systems indicates that the magnetic moment is coupled to the crystal lattice; hence there is a possibility that magnetic ordering may cause a change in crystal structure. With the development of high-resolution synchrotron XRD, more and more magnetic transitions have been found to be accompanied by simultaneous structural changes. In this article, we review our recent progress in understanding the structural change at a ferromagnetic transition, including synchrotron XRD evidence of structural changes at the ferromagnetic transition, a phenomenological theory of crystal structure changes accompanying ferromagnetic transitions, new insight into magnetic morphotropic phase boundaries (MPB) and so on. Two intriguing implications of non-centric symmetry in the ferromagnetic phase and the first-order nature of ferromagnetic transition are also discussed here. In short, this review is intended to give a self-consistent and logical account of structural change occurring simultaneously with a ferromagnetic transition, which may provide new insight for developing highly magneto-responsive materials.

Keywords: ferromagnetic transition, crystal structure, morphotropic phase boundary (MPB), magnetostriction, multiferroicity

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1. Introduction

Generally, a ferromagnetic or ferrimagnetic transition refers to an ordering of magnetic moment, and it stands as a central issue for both a fundamental understanding of ferromagnetism and the vast applications of ferromagnetic materials. Over the past decades, the crystal structures of various ferromagnetic materials have been determined by conventional X-ray diffractometry (XRD), building up a wealth of crystal structure data.[1] These XRD data indicate that in general there is no change in the host crystal structure or symmetry upon a ferromagnetic transition;[2,3] thus a cubic paramagnet has commonly been assumed to transform into a cubic ferromagnet upon a ferromagnetic transition. The best known examples are those typical cubic ferromagnets like Fe, Ni, $CoFe_2O_4$, Terfenol-D, etc.: the crystal structure remains the same, cubic, above and below the Curie temperature T_c.[1] A few exceptions exist (like Ni_2MnGa, Fe–Pt alloys, etc.), but their large structure change (1%–10%) is attributed to a simultaneous martensitic transition.[4,5] Therefore, from the available experimental evidence it seems that a ferromagnetic transitions generally involve no structural change.

However, the existence of the magnetostrictive effect in all known ferromagnetic systems suggests that the magnetic moment is invariably coupled to the crystal lattice;[6,7] hence magnetic ordering appears to have the potential to cause a change in crystal structure. Such a possibility was suggested by Callen and Callen in the year of 1963; they deduced a crystal symmetry change upon a magnetic transition by a phenomenological study.[8] Also from the group theory developed by Opechowski,[9] it can be inferred from the tables of magnetic symmetry listed in Ref. [9] that a change of crystal symmetry upon magnetic ordering is likely. But, direct evidence for the suggested structure change has remained obscure, as all available diffraction data suggest that a cubic paramagnet transforms into a cubic ferromagnet,[1] as evidenced by the non-splitting of diffraction peaks in the ferromagnetic phase. So far, structural invariance at the ferromagnetic transition has stood as a foundation stone of the present-day understanding of ferromagnetism.

It should be further noted that the observed structural invariance at the ferromagnetic transition exists in sharp contrast

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to its physically parallel transition — the ferroelectric transition. In the case of ferroelectric transition (an ordering of electric dipoles at T_c),[10,11] the dipole ordering causes a secondary effect, a change in the crystal structure of the host lattice. Such a structural change is caused by a coupling of the lattice strain to the electric dipoles so that the dipole ordering produces an ordering of the strain, i.e., a significant lattice distortion or structural change at T_c. Such a lattice distortion is on the order of 1% for ferroelectrics, and it reveals itself as a splitting of the diffraction peaks.[12] In view of the physical parallelism between ferroelectric transition and ferromagnetic transition, one can consider the phenomenon that ferromagnetic materials do not undergo a structural change at the ferromagnetic transition to be a long-standing puzzle.

The reason for the apparent structural invariance at the ferromagnetic transition can be simply ascribed to a lack of resolution in conventional diffraction studies. This is because the expected structure change is surely commensurate with the magnitude of magnetostriction, which is usually very small, ranging from 2.1×10^{-5} for Fe to 1.6×10^{-3} for the giant magnetostrictive material, Terfenol-D.[6] Such a tiny change in lattice dimension is beyond the resolution limit of conventional laboratory diffractometers (about 5×10^{-3}),[13] thus conventional XRD cannot reveal such a small structure change. Therefore, the way to observe structural changes associated with ferromagnetic transition is to use a powerful synchrotron XRD with high resolution.

With the development of high-resolution synchrotron XRD,[14,15] more and more magnetic transitions have been found to be accompanied by simultaneous structural changes.[16–20] For example, Jauch *et al.* found that the crystallographic symmetry of antiferromagnetic CoO is transformed from cubic (space group $Fm3m$) to monoclinic (space group $C2/m$) at its antiferromagnetic transition ($T_N = 290$ K) by using high-resolution synchrotron XRD.[16] Ishibashi *et al.* observed that the ferromagnetic transition of $NiCr_2O_4$ ($T_c =$ 74 K) is accompanied by a symmetry transition from a tetragonal to an orthorhombic.[17] Very recently, with the superior resolution of a high-resolution synchrotron XRD, we showed clearly that two well-known "cubic" ferromagnets, $CoFe_2O_4$ and Terfenol-D, are actually non-cubic; their crystal symmetry is consistent with their spontaneous magnetization (M_s) direction.[19] Furthermore, based on a structural change concurrent with the ferromagnetic transition, we first developed the magnetic morphotropic phase boundary (MPB) in the ferromagnetic system of $TbCo_2$–$DyCo_2$, providing a way to create large magnetostriction.[20]

In this review, we introduce our recent progress on structural changes that occur simultaneously with ferromagnetic transitions, providing a self-consistent and logical account of crystals' structural variations at the ferromagnetic transition. The substance of this progress is mainly the evidence from the synchrotron XRD for structural change at ferromagnetic transition, a phenomenological theory for crystal structure change upon ferromagnetic transition, and new insight into the magnetic morphotropic phase boundary (MPB). In addition, the implications of such structure changes for the ferromagnetic transition, such as the non-centric symmetry of the ferromagnetic phase and the first-order nature of the ferromagnetic transition, are also discussed.

2. Evidence from the synchrotron XRD for structural change at ferromagnetic transition

We employed the high-resolution synchrotron XRD at the BL15XU beamline in SPring-8. The 2θ resolution is 0.007°, an order of magnitude better than that of a conventional XRD. From the (111) diffraction peak of Si, the strain resolution for synchrotron XRD and conventional XRD was determined to be 5×10^{-4} and 5×10^{-3}, respectively.[13] Ferromagnetic $CoFe_2O_4$, Terfenol-D, and $DyCo_2$ were examined because they are known to have relatively large magnetoelastic coupling,[21] so their structure change is relatively easy to detect. All the samples were ground into powders, and sealed into quartz capillaries with a diameter of 0.3 mm. The powder sample rotation was enabled during measurement. X-ray wavelength was 0.6358 Å (1 Å = 0.1 nm). The temperature of the sample was controlled by a blow-type cryo-cooler with an accuracy of 0.1 K. The cryo-cooler can provide temperatures in the range from 90 K to 400 K.

2.1. Evidence for non-cubic crystal symmetry of cubic ferromagnet in its ferromagnetic state

Contrary to the general belief that these two well-studied compounds of $CoFe_2O_4$ and Terfenol-D are cubic in both paramagnetic and ferromagnetic states,[22,23] our high-resolution synchrotron XRD data shown in Fig. 1 reveal striking results: they are not cubic in the ferromagnetic state.[19] Figure 1(a) shows three high symmetry reflections of $CoFe_2O_4$, {800}, {880}, and {888}, measured at 150 K ($T_c \sim 760$ K). The split {800} and {880} reflections unambiguously prove the ferromagnetic $CoFe_2O_4$ has a lower symmetry than cubic. We further note there is no splitting in the {888} reflection and the intensity ratio of split peaks for the {800} and {880} reflections are 2:1 and 1:2, respectively. These features characterize a tetragonal structure for ferromagnetic $CoFe_2O_4$, and the corresponding lattice parameters are shown on the right side of Fig. 1(a). The direction of spontaneous magnetization M_s is found to be along [001] (to be described below); thus the tetragonal crystal symmetry is consistent with the orientation

of M_s. Compared with the original paramagnetic cubic structure, the lattice distortion is $\varepsilon = (c-a)/a = -1.0 \times 10^{-3}$. Such a small structure change is beyond the resolution limit of conventional XRD, so conventional XRD cannot detect the tiny peak splitting (as shown in the inset of Fig. 1(a)). This explains why ferromagnetic $CoFe_2O_4$ has been regarded as cubic in the past and why there had previously been no evidence for a structure change upon its ferromagnetic transition.

Very similar to the case of $CoFe_2O_4$, figure 1(b) reveals clear evidence for the non-cubic symmetry of Terfenol-D in its ferromagnetic state, because {440} and {222} reflections show clear splitting. The non-splitting of the {800} reflection and the intensity ratio of split peaks in {440} and {222} reflections (about 1:1 and 1:3, respectively) characterize a rhombohedral symmetry for this compound, with the lattice elongated along [111]. The rhombohedral lattice parameters are shown on the right side of Fig. 1(b). The M_s direction is determined to be along [111] (to be described below); thus this rhombohedral crystal symmetry conforms to the orientation of M_s. Compared with its paramagnetic cubic structure, the lattice distortion is calculated as

$$\varepsilon = \frac{d_{222} - d_{\bar{2}22}}{d_{222}} \approx \frac{4}{3}\cos\alpha = 2.1 \times 10^{-3}.$$

Clearly, such a small change in structure is beyond the resolution limit of conventional XRD, and thus no peak splitting is revealed in the conventional XRD measurement (see the inset of Fig. 1(b)). This explains why Terfenol-D in its ferromagnetic state has been regarded as cubic. Obviously this is due to the typically low resolution of the conventional XRD devices that have been used.

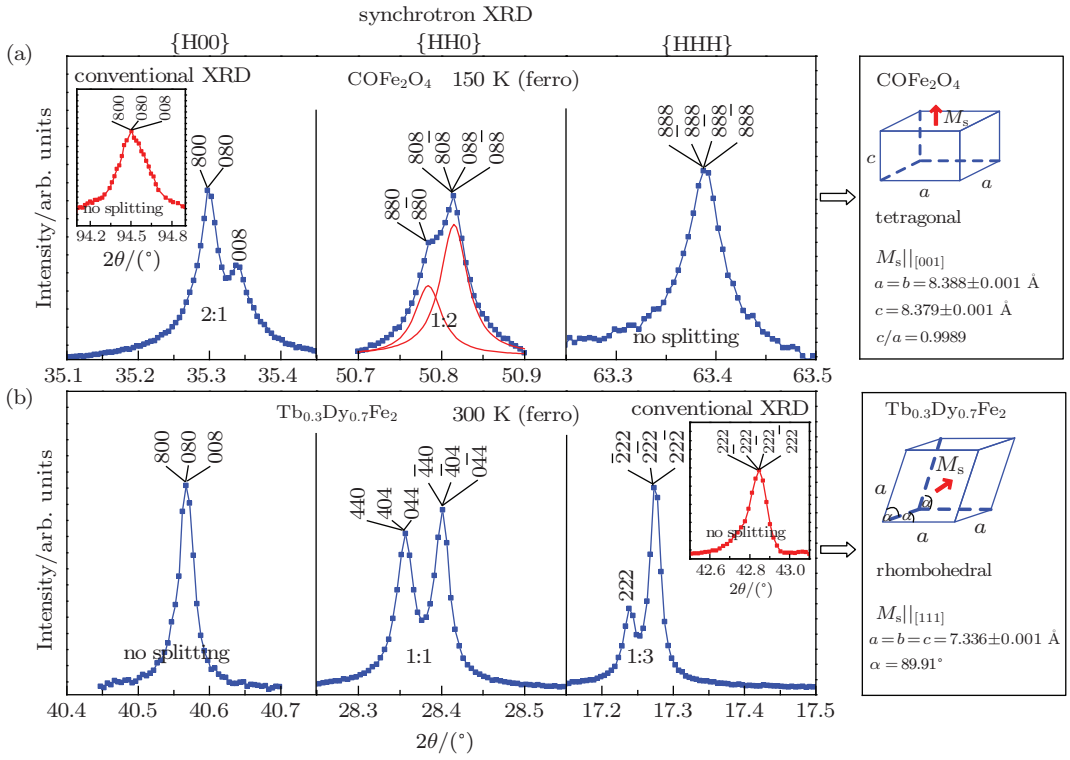


Fig. 1. Sychrontron XRD evidence for the non-cubic symmetry of two typical cubic ferromagnets. (a) {800}, {880}, and {888} reflections in ferromagnetic $CoFe_2O_4$ at 150 K. (b) {800}, {440}, and {222} reflections in ferromagnetic $Tb_{0.3}Dy_{0.7}Fe_2$ at 300 K. For comparison, insets show the peak profiles measured by conventional XRD with Cu K_α radiation.[19]

2.2. Direct evidence for crystal structure change upon ferromagnetic transition in $DyCo_2$

Because the two compounds studied above are known to have cubic symmetry in the paramagnetic state, the lower symmetry in ferromagnetic state suggests that the ferromagnetic transition adjusts the host lattice symmetry into a symmetry that conforms to the M_s direction. We further measured the variation of structure distortion in the ferromagnetic state as a function of temperature. We found that the distortion decreases with increasing temperature and tends to vanish at T_c, as will be later shown in Fig. 4. This indicates that there is a structure change at T_c. Nevertheless, for these two compounds we could not directly observe the structural change at the ferromagnetic transition temperature, because the high T_c (760 K and 665 K for $CoFe_2O_4$ and Terfenol-D, respectively) of these compounds is beyond the temperature range of our cryo-cooler. To directly observe the structural change at T_c, we selected another cubic ferromagnet $DyCo_2$, which has a crystal structure similar to that of Terfenol-D but has a low T_c ($\sim$ 143 K) that is within the reach of our cryo-cooler.

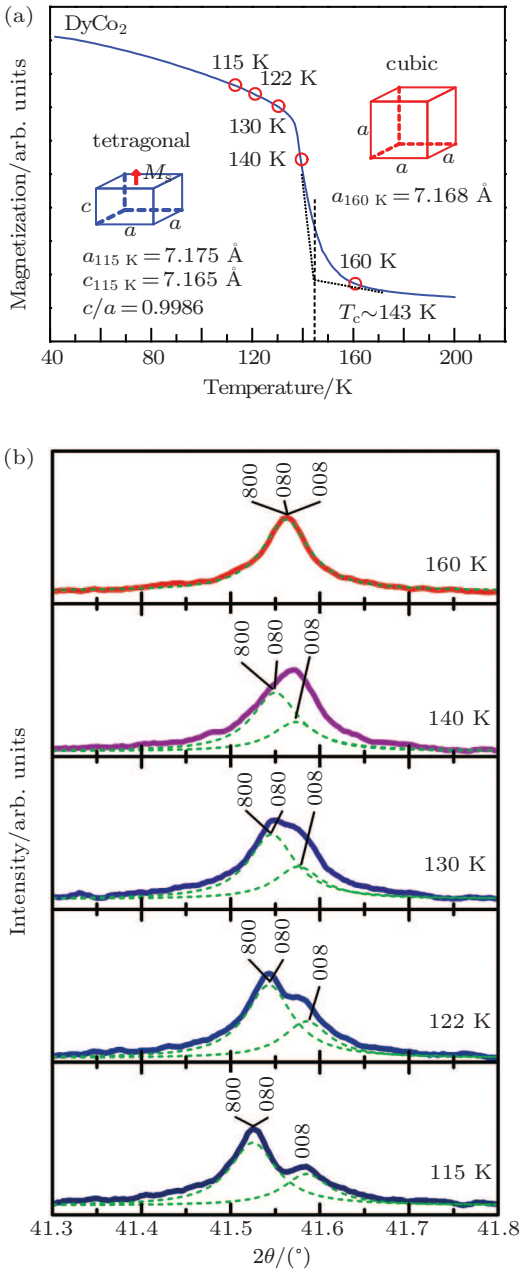


Fig. 2. *In-situ* observation of the structure change of $DyCo_2$ upon its ferromagnetic transition by synchrotron XRD. (a) Temperature dependence of magnetization measured under 2.5 kOe (1 Oe = 79.5775 A/m) magnetic field by vibrating sample magnetometer (VSM); the Curie point (T_c) is 143 K. (b) The splitting of a cubic {800} reflection during ferromagnetic transition; the dashed peaks underneath the experimental peak profile are Lorentzian peaks giving the best fit to the experimental profile. The crystal structures of para- and ferro-phase are shown in Fig. 2(a).[19]

Figure 2 shows clearly the change of crystal structure from cubic to tetragonal accompanying a ferromagnetic transition. As shown in the temperature dependence of magnetization (Fig. 2(a)), $DyCo_2$ has a ferromagnetic transition temperature $T_c \sim 143$ K. At 160 K ($> T_c$), there is no peak splitting in {800} reflection (see Fig. 2(b)); with temperature decreasing to $T < T_c$, the {800} reflection splits into two peaks, and the splitting increases with lowering temperature. This is a direct evidence for a structural change upon ferromagnetic transition. By examining the XRD spectrum and the peak intensities we are able to determine that the structure of the ferromagnetic state is a tetragonal structure consistent with its M_s direction [001]. The lattice parameters of paramagnetic cubic structure and ferromagnetic tetragonal structure are shown in the insets of Fig. 2(a). Therefore, figure 2 provides direct evidence for a structure change at a ferromagnetic transition; this is parallel to the structure change accompanying a ferroelectric transition, like that observed in $BaTiO_3$.[12] The only difference is that the size of the structure change at ferromagnetic transition is one order of magnitude smaller (~0.1%) than that in $BaTiO_3$ (~ 1%). Such a small change is beyond the resolution limit of conventional XRD, and this is why previous structure data determined by conventional XRD concluded that the ferromagnetic state has the same cubic structure as the paramagnetic state.

2.3. *In-situ* XRD observation of the switching of magnetic domains

An important consequence of the non-cubic symmetry of the ferromagnetic phase, as identified in Figs. 1 and 2, is that a magnetic domain will also be a ferroelastic or crystallographic domain, like the case of ferroelectrics.[10] Therefore, a switching of magnetic domains by magnetic field will also be a switching of the host ferroelastic domains, like the switching of ferroelectric domains.[24,25] This can be clearly seen by the change of the synchrotron XRD pattern in response to a magnetic field, as shown in Fig. 3. The experimental setup is shown in Fig. 3(a).

Figures 3(b) and 3(c) show the significant change in diffraction profile by a magnetic field of 4 kOe (1 Oe = 79.5775 A/m) for $CoFe_2O_4$ and Terfenol-D, respectively. For $CoFe_2O_4$, the magnetic field diminishes the 800/080 peak and enhances the 008 peak, but the {888} reflection remains essentially unchanged. Such a change corresponds to a switching of *a*-domain (M_s||[100]) and *b*-domain (M_s||[010]) into *c*-domain (M_s||[001]), without a change of crystal symmetry, which indicates that the M_s direction is along the *c* axis of the tetragonal lattice. For Terfenol-D, the magnetic field diminishes the $\bar{2}22/2\bar{2}2/22\bar{2}$ peak and enhances the 222 peak, but the {800} reflection is almost unaffected. Such a change corresponds to a switching of $[\bar{1}11]$-, $[1\bar{1}1]$-, $[11\bar{1}]$-domains into the [111]-domain, with no change in crystal symmetry. Thus the M_s direction is along the [111] direction of the rhombohedral lattice. The *in-situ* XRD experiment shown in Fig. 3 clearly suggests that magnetic domain switching is also a ferroelastic domain switching process, analogous to the case of ferroelectrics.

Another interesting result in Fig. 3 is that there is no evidence for a magnetic moment rotation up to 4 kOe. From the inset magnetization curves of Figs. 3(b) and 3(c), we can see that 4 kOe field has magnetized both samples nearly to saturation. At such a field strength, it is normally considered that

the magnetic moment may be forced to rotate to a magnetically hard direction (e.g., from [001] to [111] for $CoFe_2O_4$) for certain unfavorably-oriented grains of the sample. As the crystal symmetry always conforms to its M_s direction (as discussed above), the moment rotation would result in a change in the symmetry of the host lattice. However, throughout the whole domain switching process in Figs. 3(b) and 3(c), we find no such symmetry change. This behavior is identical to the domain switching behavior of ferroelectrics: only domain switching occurs, with no rotation of polarity.[10] Thus this result seems to challenge the well-accepted concept of moment rotation in cubic ferromagnets.

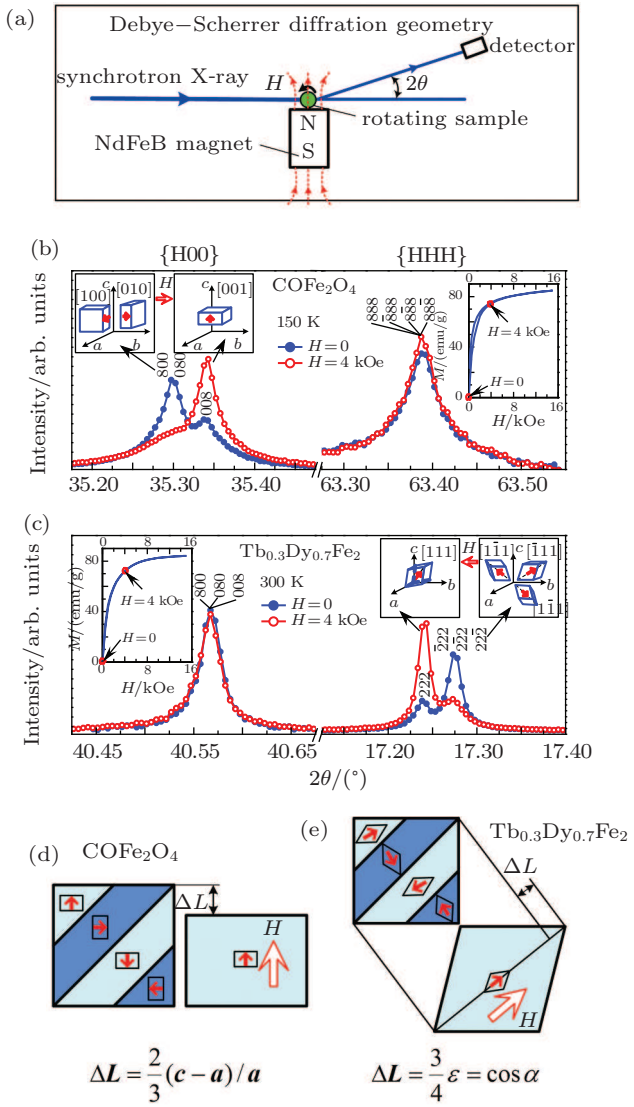


Fig. 3. *In-situ* observation of the changes in XRD patterns affected by a magnetic field $H = 4$ kOe for $CoFe_2O_4$ and $Tb_{0.3}Dy_{0.7}Fe_2$. (a) Experimental setup, in which the magnetic field was introduced by an NdFeB permanent magnet placed under the rotating sample. (b) {800} and {888} peak profiles of ferromagnetic $CoFe_2O_4$ at $H = 0$ kOe and $H = 4$ kOe. (c) {800} and {222} peak profiles of $Tb_{0.3}Dy_{0.7}Fe_2$ at $H = 0$ kOe and $H = 4$ kOe. Panels (d) and (e) show schematically a mesoscopic explanation for anisotropic magnetostriction due to the switching of the non-cubic ferromagnetic (=ferroelastic) domain for the two compounds, respectively. The small rectangles and rhombuses represent the unit cell symmetry being tetragonal and rhombohedral, respectively. ΔL is the anisotropic magnetostriction due to magnetic field H; ε is the spontaneous lattice strain of the low symmetry crystal.[19]

The low crystal symmetry of the ferromagnetic phase provides a simple mesoscopic explanation for the commonly observed magnetostrictive effect. As schematically illustrated in Figs. 3(d) and 3(e), the anisotropic magnetostriction in $CoFe_2O_4$ and Terfenol-D can be simply explained by the switching of non-cubic ferroelastic domains. This explanation for magnetostriction is physically the same as the electrostrain effect in ferroelectrics,[24,25] and is also similar to the stress-induced strain effect in ferroelastic materials.[26,27] Figures 3(d) and 3(e) also show that the maximum magnitude of magnetostriction is proportional to the size of lattice distortion. This is why $CoFe_2O_4$ and Terfenol-D have large magnetostriction — because they have large lattice distortion in the ferromagnetic state.

3. Theory and detectability of structural changes concurrent with ferromagnetic transitions

Our results shown above pose a fundamental challenge to the notion that ferromagnetic transition is only a magnetic ordering process, with no change in crystal structure. They suggest that magnetic ordering can change the crystal symmetry of the host lattice to conform with the M_s direction. This crystal symmetry change can be explained by an inevitable coupling between magnetic moment and lattice strain,[8] which changes the host cubic symmetry into one that conforms to the M_s direction. In the following, by using a phenomenological approach, we show theoretically that for a cubic ferromagnetic crystal, the inevitable magnetoelastic coupling can lower the cubic symmetry into one that conforms to its M_s direction, so that crystal symmetry is reduced at Curie temperature T_c. At the same time, we will discuss the detectability of a structure change that accompanies a ferromagnetic transition by XRD technique.

3.1. Theory of structure change upon a ferromagnetic transition

The free energy of a ferromagnetic crystal can be described as follows:[21,28,29]

$$F = F_a + F_e + F_{me}, \tag{1}$$

where F_a is magnetic anisotropic energy, F_e is elastic energy, and F_{me} is magnetoelastic energy.

The magnetic anisotropic energy F_a represents the magnetic energy due to ordering of the magnetic moment, it has the following form for a cubic ferromagnetic crystal in the first-order approximation:[21,28]

$$F_a = K_1(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2), \tag{2}$$

where $\boldsymbol{K}_1$ is a temperature-dependent anisotropic constant and α_x, α_y, α_z are the direction cosines of $\boldsymbol{M}_s$ with respect to the cubic axes.

The elastic energy $\boldsymbol{F}_e$ in a cubic crystal represents the elastic energy of the lattice due to elastic distortion e_{ij}, it is given by[21,28]

$$F_e = \frac{1}{2}c_{11}(e_{xx}^2+e_{yy}^2+e_{zz}^2)+c_{12}(e_{xx}e_{yy}+e_{yy}e_{zz}+e_{zz}e_{xx}) + \frac{1}{2}c_{44}(e_{xy}^2+e_{yz}^2+e_{zx}^2), \quad (3)$$

where c_{ij} is the elastic modulus.

The magnetoelastic energy $\boldsymbol{F}_{me}$ arises from an interaction between magnetic moment and lattice strain. It has a quantum mechanical origin[6,30] and exists in all magnetic systems. For a cubic ferromagnetic crystal, it is usually written as[21]

$$\boldsymbol{F}_{me} = b_1\boldsymbol{M}_s^2\left[e_{xx}\left(\alpha_x^2-\frac{1}{3}\right)+e_{yy}\left(\alpha_y^2-\frac{1}{3}\right)+e_{zz}\left(\alpha_z^2-\frac{1}{3}\right)\right] + b_2\boldsymbol{M}_s^2(e_{xy}\alpha_x\alpha_y+e_{yz}\alpha_y\alpha_z+e_{zx}\alpha_z\alpha_x), \quad (4)$$

where b_1 and b_2 are temperature-dependent magnetoelastic coupling coefficients.

Minimizing the total free energy with respect to all independent strains e_{ij} (i.e., $\partial F/\partial e_{ij}=0$) yields a spontaneous lattice distortion $(e_{ij})_s$ of the initial cubic lattice. The matrix form of this spontaneous strain can be found to be the following for an initially cubic crystal:

$$(e_{ij})_s = \begin{pmatrix} -\frac{b_1}{(c_{11}-c_{12})}\left(\alpha_x^2-\frac{1}{3}\right) & -\frac{b_2}{c_{44}}\alpha_y\alpha_x & -\frac{b_2}{c_{44}}\alpha_z\alpha_x \\ -\frac{b_2}{c_{44}}\alpha_x\alpha_y & -\frac{b_1}{(c_{11}-c_{12})}\left(\alpha_y^2-\frac{1}{3}\right) & -\frac{b_2}{c_{44}}\alpha_z\alpha_y \\ -\frac{b_2}{c_{44}}\alpha_x\alpha_z & -\frac{b_2}{c_{44}}\alpha_y\alpha_z & -\frac{b_1}{(c_{11}-c_{12})}\left(\alpha_z^2-\frac{1}{3}\right) \end{pmatrix}\boldsymbol{M}_s^2. \quad (5)$$

In the following we show that the spontaneous strain expression of Eq. (5) can lead to several important conclusions.

(i) The crystal symmetry is true cubic only in the paramagnetic state, as the spontaneous strain $(e_{ij})_s = 0$ only when $\boldsymbol{M}_s = 0$.

(ii) The crystal symmetry of a cubic ferromagnet is not really cubic, because there exists a spontaneous strain ($(e_{ij})_s \neq 0$) when $\boldsymbol{M}_s \neq 0$. The spontaneous strain lowers the crystal symmetry from cubic, just like the case of ferroelectric crystals.[10–12] Importantly, equation (5) shows that the crystal symmetry always conforms to the $\boldsymbol{M}_s$ direction. For example, if the direction of $\boldsymbol{M}_s$ is along the [001] direction, i.e., $\alpha_x=\alpha_y=0$ and $\alpha_z=1$, the spontaneous strain tensor becomes

$$(e_{ij})_s = \begin{pmatrix} \frac{b_1\boldsymbol{M}_s^2}{3(c_{11}-c_{12})} & 0 & 0 \\ 0 & \frac{b_1\boldsymbol{M}_s^2}{3(c_{11}-c_{12})} & 0 \\ 0 & 0 & -\frac{2b_1\boldsymbol{M}_s^2}{3(c_{11}-c_{12})} \end{pmatrix}. \quad (6)$$

As $e_{xx}=e_{yy}\neq e_{zz}$, and $e_{ij(i\neq j)}=0$, such a lattice distortion produces a tetragonal symmetry, with the c axis of the crystal lying along the $\boldsymbol{M}_s$ direction. Similarly, when $\boldsymbol{M}_s$ is along the [111] direction, i.e., $\alpha_x^2=\alpha_y^2=\alpha_z^2=1/3$, the spontaneous strain tensor becomes

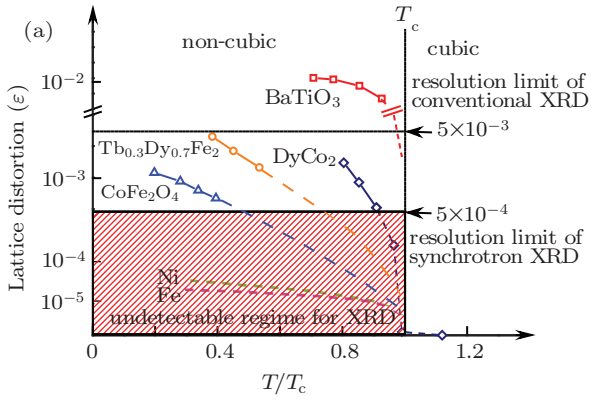
$$(e_{ij})_s = \begin{pmatrix} 0 & -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} & -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} \\ -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} & 0 & -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} \\ -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} & -\frac{b_2\boldsymbol{M}_s^2}{3c_{44}} & 0 \end{pmatrix}. \quad (7)$$

As $e_{xy}=e_{yz}=e_{yz}\neq 0$, and $e_{ii}=0$, such a lattice distortion corresponds to a rhombohedral symmetry, which conforms to the [111] direction of $\boldsymbol{M}_s$. It is noted that Callen and Callen [8] used a group theoretical approach and obtained the same conclusion about the dependence of crystal symmetry on the direction of $\boldsymbol{M}_s$.

(iii) Equation (5) specifies that there is a structure transition associated with the magnetic ordering in all cubic ferromagnets. In the paramagnetic state ($T>T_c$), a cubic crystal is true cubic, as shown above. But when temperature is below T_c, the ordering of magnetic moment produces a non-zero $\boldsymbol{M}_s$ and hence induces a non-zero spontaneous strain in the cubic lattice. This changes the crystal structure from cubic to a lower symmetry that conforms to the $\boldsymbol{M}_s$ direction. Therefore, in addition to the ordering of the magnetic moment, a ferromagnetic transition also involves a structure change. Obviously, this is a general conclusion for all cubic ferromagnets, and the low symmetry structure stems from the magnetoelastic coupling.

3.2. XRD detectability of a structure change accompanying a ferromagnetic transition

Although structure change upon magnetic ordering occurs in all pseudo-cubic ferromagnetic systems, the lattice distortion involved is often too small to detect, as shown in Fig. 4(a), which shows the magnitude of lattice distortion in the ferromagnetic state for several typical cubic ferromagnets as a function of homologous temperature T/T_c. For a comparison, the lattice distortion for a ferroelectric $BaTiO_3$ [12] is also included. Clearly, $BaTiO_3$ has a large lattice distortion and such distortion can easily be detected by conventional XRD; however, for $CoFe_2O_4$, Terfenol-D, and $DyCo_2$, the lattice distortion can be detected only by synchrotron XRD; for Fe and Ni, lattice distortion is out of the detection regime of any available diffraction technique; thus they will appear to be cubic even when examined by synchrotron XRD. Figure 4(b) shows the relationship between the crystal symmetry of the ferro-phase and the $\boldsymbol{M}_s$ or $\boldsymbol{P}_s$ direction. It can be seen that the former always conforms to the latter. Therefore, a ferromagnetic transition does involve a structural change like a ferroelectric transition, but the change is sometimes too small to detect.



(b) Crystal symmetry versus M_s/P_s direction for several typical pseudocubic ferroic materials

Pseudocubic ferroic materials (ferro-phase)	Crystal symmetry	M_s or P_s direction	$\lvert\varepsilon\rvert_{300\ K}$ $\times10^6$	T_c/K
$BaTiO_3$	T (Ref. [12])	001	10000	402
$Tb_{0.3}Dy_{0.7}Fe_2$	R (this work)	111	2100	665
$CoFe_2O_4$	T (this work)	001	550	760
Ni	R (predicted)	111	32	631
Fe	T (predicted)	001	30	1043
$DyCo_2$	T (this work)	001	0(PM)	143

Fig. 4. Lattice distortion and crystal symmetry for several typical pseudocubic ferromagnetic/ferroelectric materials. (a) Temperature dependence of lattice distortion for several ferromagnetic/ferroelectric materials. The lattice distortion axis is given a cube root scale, so as to reveal the tiny strain determined by synchrotron XRD. The $BaTiO_3$ data are from Ref. [12]; the data points of $CoFe_2O_4$, $Tb_{0.3}Dy_{0.7}Fe_2$, and $DyCo_2$ are from the present work, and the dash lines are estimated from the known magnetostriction coefficients in Ref. [6]. (b) Relation between spontaneous magnetization direction M_s (or polarization direction $\boldsymbol{P}_s$) and crystal symmetry (R: rhombohedral; T: tetragonal). It is noted that $DyCo_2$ is paramagnetic (PM) at room temperature so its room-temperature lattice distortion is zero; at low temperature it has lattice distortion similar to that in Terfenol-D.[19]

From Eq. (5) one can find that the magnitude of lattice distortion is proportional to the magnetoelastic coupling coefficients b_1 and b_2. These coefficients are usually very small, and thus the structure change is often too small to detect by conventional XRD technique. This is why it has been believed that no structure change occurs upon magnetic ordering. If the resolution of XRD is improved, as in the case of our synchrotron XRD, it is possible to detect the structure change for systems with strong magnetoelastic coupling, like $CoFe_2O_4$ and Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_2$).

4. Morphotropic phase boundary in ferromagnets: a way leading to large magnetostriction

4.1. What is the morphotropic phase boundary (MPB)

Usually, morphotropic phase boundary (MPB) refers to a phase boundary separating two ferroelectric phases of different crystallographic symmetries in the composition-temperature phase diagram.[31–33] For more than half a century, MPB in ferroelectric materials has drawn constant interest because it can significantly enhance piezoelectric properties, i.e., a conversion between mechanical force and electrical voltage.[34–36] The current workhorses of piezoelectric materials, PZT ($PbZrO_3$–$PbTiO_3$) [35] and PMN–PT ($PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$),[36] are designed to have a composition close to the MPB to achieve maximum piezoelectric effect. Figure 5 shows a typical ferroelectric MPB in PZT, which separates a ferroelectric rhombohedral (R) phase (with a spontaneous polarization $\boldsymbol{P}_s$||[111]) on $PbZrO_3$ side and a ferroelectric tetragonal (T) phase (with $\boldsymbol{P}_s$||[001]) on $PbTiO_3$ side.[31] The rhombohedral and tetragonal ferroelectric phases share a common cubic paraelectric phase at high temperature. Both theoretical [37–39] and experimental studies [40–43] have shown that with MPB composition $\boldsymbol{P}_s$ can be easily rotated under small external field and this causes a high piezoelectric effect.

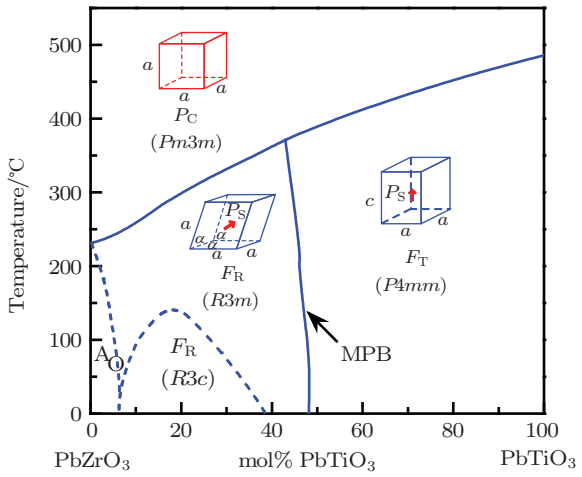


Fig. 5. Typical morphotropic phase boundary (MPB) in a ferroelectric system PZT ($PbZrO_3$-$PbTiO_3$).[31]

Considering the parallelism of the physics of ferroelectricity and ferromagnetism,[3] it is tempting to ask if a similar MPB can exist in another large class of functional materials — ferromagnetic materials [44] — and if it can lead to significant enhancement of the corresponding properties (magnetostrictive effect, or magnetic-field-induced distortion).[6,7] So far, the major obstacle to creating an MPB in ferromagnets has been a general observation (by conventional XRD) that different M_s directions do not produce a difference in crystal symmetry,[1,3] apparently differing from the ferroelectric case. However, with the greatly enhanced structure resolution available in synchrotron XRD, our recent studies have proved that different ferromagnetic states indeed correspond to different crystal symmetries,[19] just as in the ferroelectric case; but lattice distortion due to different crystal symmetries is usually too small to be detected by conventional XRD. Therefore, now we have good reason to expect the existence of a magnetic MPB.

4.2. Morphotropic phase boundary in ferromagnetic systems

In the following we shall see that such a magnetic MPB indeed exists in a binary ferromagnetic system RCo_2–$R'Co_2$ (R, R′: rare earth element), and that with MPB composition there is a significant enhancement of magnetostrictive properties.[20] Figure 6(a) shows the composition-temperature phase diagram of a binary ferromagnetic system $TbCo_2$–$DyCo_2$, which is a solid solution of two terminal compounds, $TbCo_2$ and $DyCo_2$. This system exhibits a common paramagnetic phase at high temperature. In the ferromagnetic state a ferro–ferro phase boundary separates two ferromagnetic phases, one with M_s||[111] on $TbCo_2$-rich side and the other with M_s||[001] on $DyCo_2$-rich side.[45] The whole phase diagram and the ferro–ferro phase boundary are determined from the AC susceptibility χ' versus temperature T relation, as typically shown in Fig. 6(b). The para–ferro transition and the ferro–ferro transition temperatures correspond to the susceptibility peaks (T_c and T_M), as indicated by arrows in Fig. 6(a). The composition dependence of χ' versus T relation is very similar to the permittivity versus T relation in ferroelectric PMN–PT.[36] It is noted that the ferro–ferro transition is often called the spin-reorientation transition (SRT) to indicate the rotation of magnetic moment at the transition.[46,47]

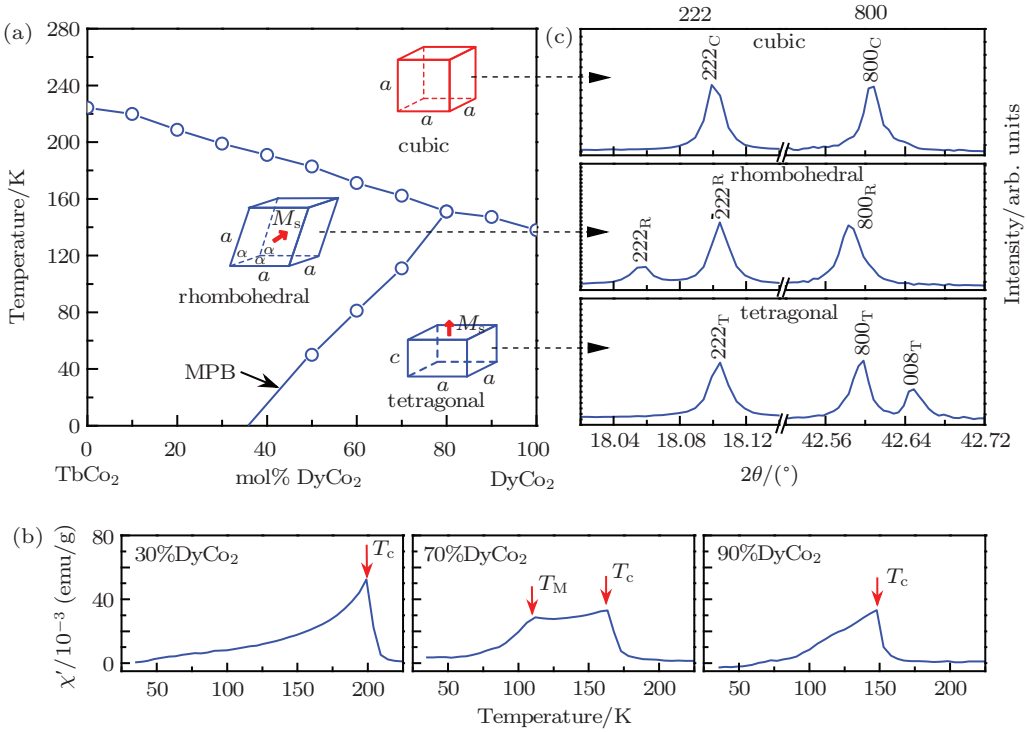


Fig. 6. Magnetic morphotropic phase boundary (MPB) in the ferromagnetic $TbCo_2$–$DyCo_2$ system. (a) Phase diagram of $TbCo_2$–$DyCo_2$. (b) Temperature dependence of AC susceptibility χ'. T_c and T_M denote para–ferro and ferro–ferro transition temperatures, respectively. (c) Synchrotron XRD profiles of cubic paramagnetic phase, rhombohedral ferromagnetic phase, and tetragonal ferromagnetic phase.[20]

The key evidence about an MPB is in the structure data (see Fig. 6(c)) obtained from a synchrotron XRD. It shows that the paramagnetic phase has a cubic symmetry (no peak splitting), and the M_s||[111] phase has a rhombohedral (R) symmetry (as revealed by the characteristic splitting in the 222 peak but no splitting of the 800 peak), and the M_s||[001] phase has a tetragonal (T) symmetry (as shown with the characteristic splitting in the 800 peak but none in the 222 peak). Therefore, the ferro–ferro phase boundary between the ferromagnetic R-phase and T-phase is both a ferromagnetic phase boundary and a crystallographic phase boundary; hence it is a magnetic MPB. This magnetic MPB exhibits considerable similarity with the ferroelectric MPB in PZT (Fig. 5), which is a phase boundary between ferroelectric R-phase and T-phase.

We also note that such a magnetic MPB intersects with the ferro–para line to form a kind of triple point,[39] where paramagnetic cubic phase, ferromagnetic R-phase, and ferromagnetic T-phase are in equilibrium. For the $TbCo_2$–$DyCo_2$ system, the triple point is at about 80% $DyCo_2$, as shown in Fig. 6(a).

Figure 7(a) shows another composition-temperature phase diagram of binary ferromagnetic system $Tb_{1-x}Gd_xCo_2$ (abbreviated as xGd hereinafter),[48] which is determined by the Curie temperature T_c detected from magnetization (M) versus temperature (T) curves (Fig. 7(b)) and the crystal structure (Figs. 7(c1)–7(c4)) detected by the synchrotron XRD with an X-ray wavelength of 0.850052 Å. It is noted from the M–T curves (Fig. 7(b)) that, with the increase of Gd concentration, the T_c of $Tb_{1-x}Gd_xCo_2$ increases monotonously. As for the X-ray diffraction profiles, it is revealed that at 120 K, with increasing concentration of Gd, $Tb_{1-x}Gd_xCo_2$ exhibits a composition-induced crystallographic phase transition from rhombohedral (R) symmetry (bottom section of Fig. 7(c1) for 0.5Gd and bottom section of Fig. 2(c2) for 0.8Gd, with the characteristic splitting in the 222 peak but no splitting in the 800 peak) to tetragonal (T) symmetry (bottom figure of Fig. 7(c4) for 1.0Gd with the characteristic splitting in the 800 peak but no splitting in the 222 peak). As for the XRD profile of 0.9Gd, it corresponds to superposition of R symmetry profile and T symmetry profile, similar to the MPB structure in the ferroelectric case.[31] The observed structural evolution at 120 K is consistent with the established relation between the easy axis direction and the crystal structure.[19] And at higher temperatures, such evolution is also observed from the XRD profiles of 0.5Gd, 0.8Gd, 0.9Gd, and 1.0Gd. The structural evolution of $Tb_{1-x}Gd_xCo_2$ revealed by XRD profiles demonstrates the existence of MPB in $Tb_{1-x}Gd_xCo_2$, and among the possible compositions, 0.9Gd is closest to MPB.

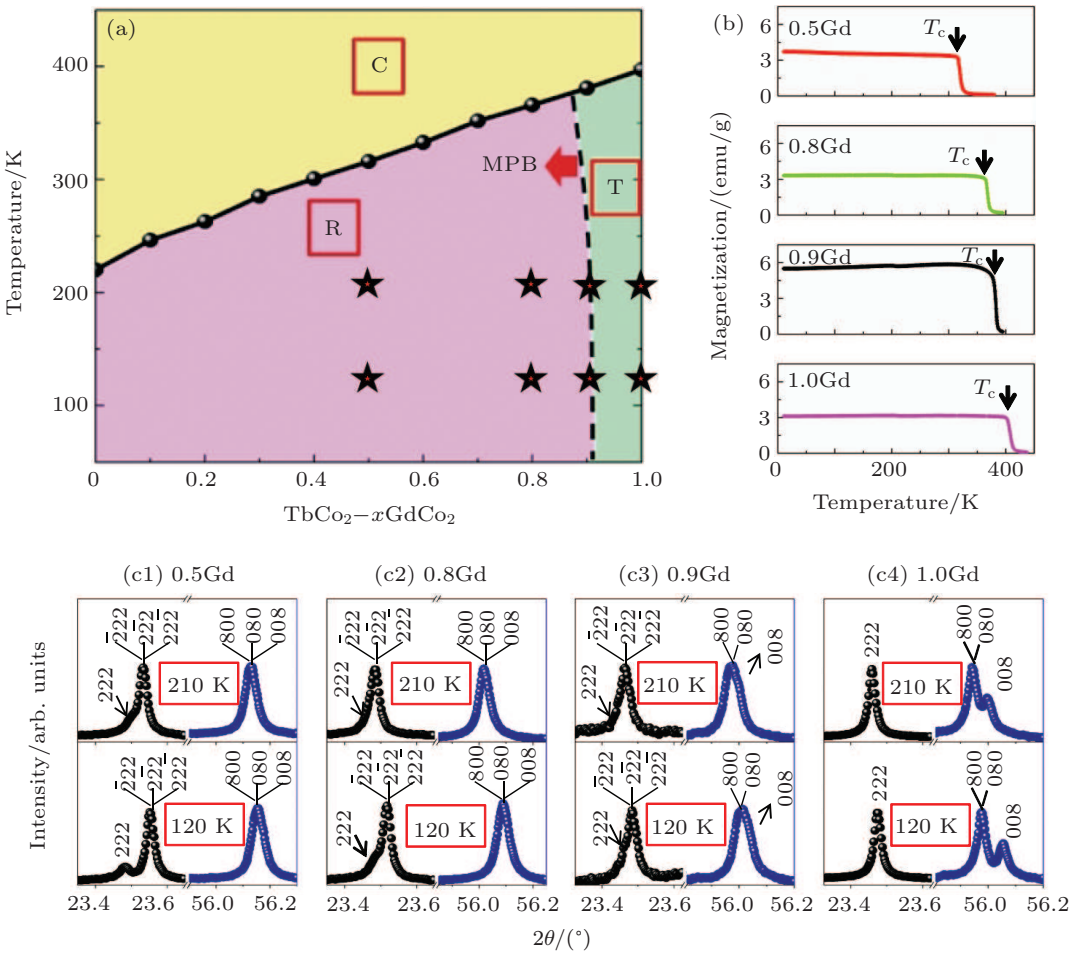


Fig. 7. Magnetic morphotropic phase boundary (MPB) in the ferromagnetic $TbCo_2$–$GdCo_2$ system. (a) Phase diagram of $Tb_{1-x}Gd_xCo_2$ (C, R, and T denote cubic, rhombehedral, and tetragonal symmetries). (b) Magnetization (M) versus temperature (T) curves in 0.5Gd, 0.8Gd, 0.9Gd, and 1.0Gd. (c) Synchrotron XRD profiles of 0.5Gd, 0.8Gd, 0.9Gd, and 1.0Gd. The red star symbols in Fig. 7(a) mark the sites of X-ray diffraction data in the phase diagram.[48]

4.3. Magnetic properties of morphotropic phase boundary

The most interesting feature of the MPB composition is the significant enhancement of magneto-responsive properties. Figure 8(a) shows the composition dependence of AC susceptibility χ' in $TbCo_2$–$DyCo_2$ system at 110 K in relation with the MPB composition (70% $DyCo_2$). It can be seen clearly that magnetic susceptibility peaks at the MPB composition;

the peak value is almost three times that of the off-MPB compositions. Accompanying the enhancement of AC susceptibility, the spontaneous magnetization M_s shows a step at the MPB composition, as shown in Fig. 8(b). Figure 8(c) shows that the MPB corresponds to a minimum coercivity H_c, which is as low as 15.6 Oe. This indicates that at MPB composition it is very easy to switch magnetic moment. Several typical magnetic hysteresis loops are given in Fig. 8(f).

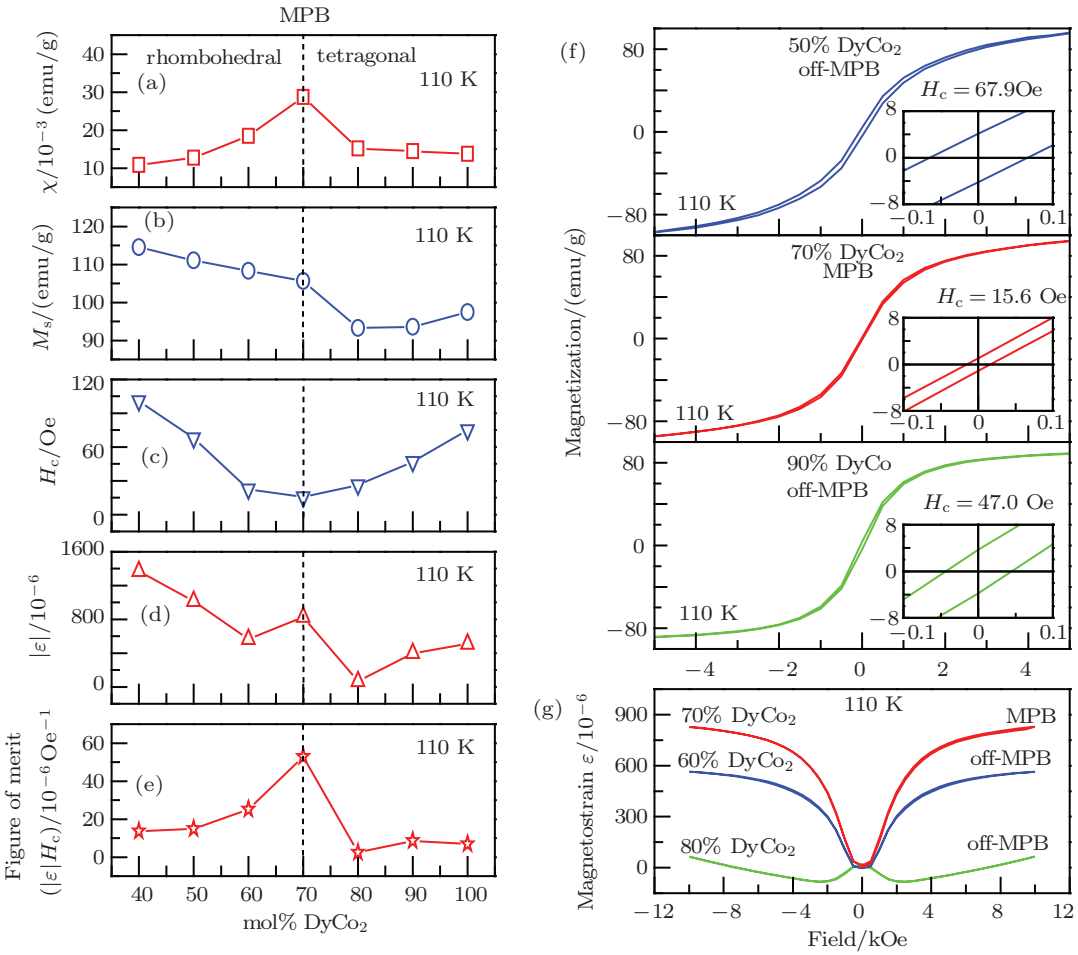


Fig. 8. Composition dependence of physical properties in relation with MPB composition at 110 K. (a) AC susceptibility χ', (b) saturation magnetization M_s, (c) coercivity H_c, (d) magnetostriction ε (absolute value) at 10-kOe field, (e) figure of merit ε/H_c, (f) magnetic hysteresis loops, (g) magnetostriction curves.[20]

Similar to the ferroelectric MPB in PZT, the magnetic MPB in the $TbCo_2$–$DyCo_2$ system exhibits significant enhancement in magnetostrictive properties. Figure 8(d) shows the magnetostriction ε (absolute value) in relation with MPB (70% $DyCo_2$) at 110 K. Several typical magnetostriction curves are shown in Fig. 8(g). It is clear that the magnetostriction in MPB composition shows a maximum ($\varepsilon = 828$ ppm) as compared with the neighboring off-MPB composition. For most magnetostriction applications, the "figure of merit," defined by ε/H_c, is the most important property of magnetostrictive materials, as it reflects the capability of generating a large magnetostriction by a small magnetic field. As shown in Fig. 8(e), the figure of merit (ε/H_c) of MPB composition is about 3 to 6 times higher than that of off-MPB compositions. Therefore, magnetic MPB yields a significant enhancement of magnetoelastic properties, which is very similar to the high piezoelectric effect that occurs in the ferroelectric MPB of PZT.[35] The above results were obtained from polycrystalline samples, in which the grains have an averaging effect; in single crystal samples we expect much greater enhancements of magneto-responsive properties.

5. Implications of the structure change upon ferromagnetic transition

The finding that ferromagnetic transitions involve a structure change may have two important implications. First, the structural change at a ferromagnetic transition implies non-centric crystal symmetry in ferromagnets. This is because crystal symmetry is generally considered to conform to its physical properties; thus the polar physical properties cannot be compatible with centric crystal symmetry (Neumann's principle).[49] Such non-centric symmetry will produce a weak spontaneous polarization P in a ferromagnetic insulator. Sec-

ond, the concomitant strain-magnetic ordering indicates the interesting possibility that a ferromagnetic transition may be a 1st order transition rather than a 2nd order one. This is because a two-order-parameter system usually undergoes a 1st-order transition due to the existence of coupling, as can be seen in the case of ferroelectric transitions (polarization and strain coupling) [10] and ferroelastic transitions (strain and strain coupling).[50] In the next section, we introduce our recent experimental work to verify these two implications.

5.1. A hint of non-centric crystal symmetry in $CoCr_2O_4$ with collinear ferrimagnetic ordering

$CoCr_2O_4$ with a spinel structure is unique among multiferroics.[51–53] The multiferroicity in $CoCr_2O_4$ is usually regarded to stem from the spiral magnetic transition, where the noncollinear spins at the neighboring sites break the inverse symmetry to produce ferroelectricity due to an inverse Dzyaloshinskii–Moriya interaction.[54] It is emphasized that such a multiferroicity in $CoCr_2O_4$ emerges from the onset of a noncollinear spiral magnetic transition ($T_s \approx 28$ K), far below the onset of a collinear ferrimagnetic transition ($T_c \approx 96$ K). However, it is noted that the temperature dependence of dielectric permittivity ε' (ε'–T curve) shows a tiny anomaly at T_c in $CoCr_2O_4$, as reported by Yamasaki *et al.*;[51] this hints at the possible existence of a weak spontaneous polarization $\boldsymbol{P}$ in the collinear ferromagnetic ordering, resulting in non-centric crystal symmetry.

Figure 9 demonstrates the magnetostriction in $CoCr_2O_4$, measured under a magnetic field up to 1 Tesla.[55] It can be seen that the magnetostriction in $CoCr_2O_4$ changes abruptly at the onset of ferrimagnetic transition, at T_c, due to a reduction in crystal symmetry, as shown in Fig. 9(a). Such a reduction in crystal symmetry in $CoCr_2O_4$ during a ferrimagnetic transition has also been confirmed by an experiment with infrared spectroscopy.[56] Since the $\boldsymbol{M}$ of $CoCr_2O_4$ below T_c aligns along the [001] direction,[51] the crystal structure of $CoCr_2O_4$ in a collinear ferrimagnetic ordering corresponds to tetragonal structure due to the principle of the crystal structure conforming to its spontaneous magnetization $\boldsymbol{M}$.[19] Also, such a tetragonal structure of $CoCr_2O_4$ can be revealed by the field dependence of magnetostriction in the collinear ferrimagnetic phase (e.g. $T = 45$ K, as shown in Fig. 9(b)). The reduction of crystal symmetry in $CoCr_2O_4$ below T_c provides us a hint of non-centric crystal symmetry in the collinear ferrimagnetic ordering. Indeed, the observation of non-centric crystal symmetry has been reported for a number of spinels,[57,58] and at the same time Singh *et al.* have reported a weak spontaneous polarization $\boldsymbol{P}$ existing in $CoCr_2O_4$ below T_c due to the non-centric crystal symmetry. [59]

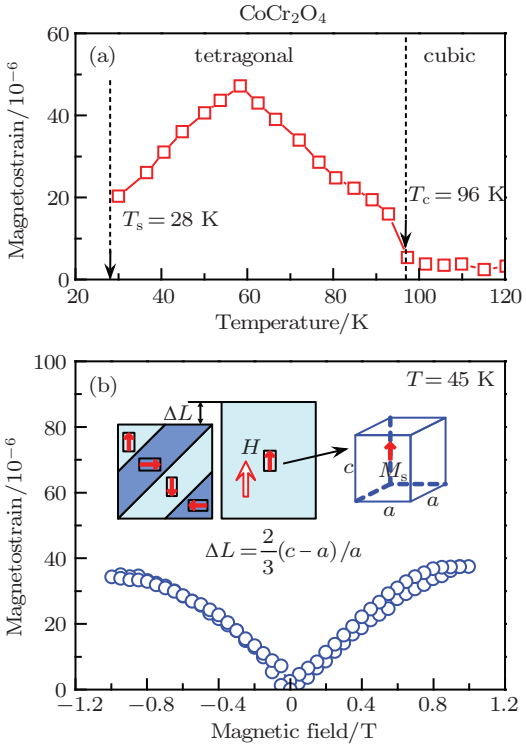


Fig. 9. Magnetostriction in $CoCr_2O_4$ measured by strain gauges. (a) Temperature dependence of magnetostriction under a magnetic field of 1 Tesla near the ferrimagnetic transition temperature ($T_c = 96$ K). (b) Magnetic field dependence of magnetostriction at $T = 45$ K. Inset schematically shows the mesoscopic process of magnetostriction-caused domain switching.[55]

It should be mentioned that the direct measurement of polarization $\boldsymbol{P}$ caused by magnetic field becomes difficult when ferroelectricity is weak. In such a situation, the measurement of change of dielectric permittivity ($\varepsilon' = \mathrm{d}\boldsymbol{P}/\mathrm{d}\boldsymbol{E}$) with magnetic field (i.e., MD effect) is a much more sensitive tool to detect the existence of coupling between $\boldsymbol{P}$ and $\boldsymbol{M}$.[60] Thus, the MD effect can be described by $\mathrm{MD} = \varepsilon'(\boldsymbol{H})/\varepsilon'(0) - 1$, where $\varepsilon'(\boldsymbol{H})$ is the dielectric permittivity under field $\boldsymbol{H}$ and $\varepsilon'(0)$ is the dielectric permittivity under zero field. Figure 10 illustrates the variation of the MD effect in relation with magnetic field in the vicinity of the ferrimagnetic transition temperature ($T_c = 96$ K) in $CoCr_2O_4$.[55,61] We measured two MD effects according to the relationship between the directions of the magnetic field $\boldsymbol{H}$ and the AC electrical field $\mathrm{d}\boldsymbol{E}$: one is a perpendicular MD effect ($\boldsymbol{H} \perp \mathrm{d}\boldsymbol{E}$) and the other is a parallel MD effect ($\boldsymbol{H} \parallel \mathrm{d}\boldsymbol{E}$), as shown in Figs. 10(a) and 10(b), respectively. When $T > T_c$ (e.g. $T = 114$ K), the permittivity of the MD effect (either perpendicular or parallel) does not respond to magnetic field $\boldsymbol{H}$ and the corresponding MD value becomes zero. With temperature decreasing, the permittivity starts to respond to the magnetic field at T_c; but these two MD effects behave in opposite ways. In the case of $\boldsymbol{H} \perp \mathrm{d}\boldsymbol{E}$ below T_c (e.g. $T = 84$ K), the MD value gradually increases with the increase of the magnetic field and finally saturates to a positive value. In contrast, the MD value in the case of $\boldsymbol{H} \parallel \mathrm{d}\boldsymbol{E}$ gradually decreases with increasing magnetic field and finally

saturates to a negative value at $T = 84$ K. With temperature decreasing further, the variation of MD effect with magnetic field at $T = 30$ K is similar to that in the case of $T = 84$ K; but the corresponding saturation values of both MD effects are greatly improved. Evidence of similar behavior has also been observed in another magnetic compound, Mn_3O_4.[62]

Based on the non-centric tetragonal symmetry in $CoCr_2O_4$ below T_c, the above MD effect could be fully explained. Figure 11 illustrates schematically an explanation for MD effects emerging from the onset of the ferrimagnetic transition in $CoCr_2O_4$.[55] When $T > T_c$, the paramagnetic $CoCr_2O_4$ phase has a centric cubic structure and hence it has neither spontaneous magnetization $\boldsymbol{M}$ nor spontaneous polarization $\boldsymbol{P}$, as shown in Fig. 11(a). Thus, there is no contribution from $\boldsymbol{M}$ or $\boldsymbol{P}$ to the permittivity and thus $\varepsilon'(\boldsymbol{H})_\perp = \varepsilon'(0) = \varepsilon'(\boldsymbol{H})_\parallel =$ constant; this can explain the absence of the MD effect above T_c. When $T < T_c$, $CoCr_2O_4$ transforms from its paramagnetic state into its ferrimagnetic state. Such a ferrimagnetic $CoCr_2O_4$ phase is assumed to have a non-centric tetragonal structure to produce polarization $\boldsymbol{P}$ parallel to its $\boldsymbol{M}$ along the [001] direction, as shown in Figs. 11(b), 11(c), and 11(d). As the magnetization $\boldsymbol{M}$ couples to the polarization $\boldsymbol{P}$, both $\boldsymbol{M}$ and $\boldsymbol{P}$ can be switched to the $\boldsymbol{H}$ direction by applying a magnetic field. Thus, the rotation of $\boldsymbol{P}$ driven by the magnetic field enables the dielectric permittivity ($\varepsilon' = \mathrm{d}\boldsymbol{P}/\mathrm{d}\boldsymbol{E}$) to change and therefore produces the MD effect.

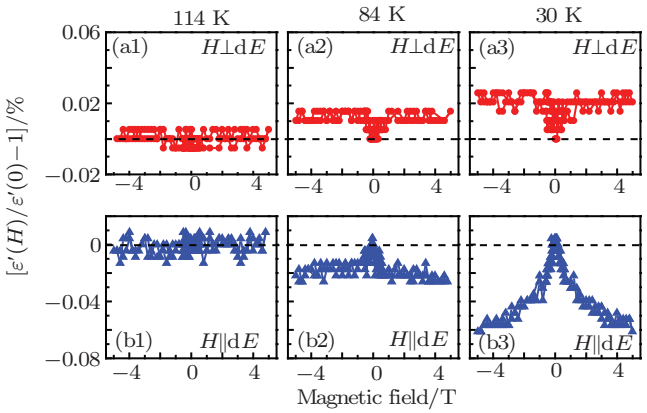


Fig. 10. Magnetic field dependence of magnetodielectric (MD) effect near the ferrimagnetic transition temperature ($T_c = 96$ K) of $CoCr_2O_4$. (a1), (a2), and (a3) show perpendicular MD effect at 114 K, 84 K, and 30 K, respectively; (b1), (b2), and (b3) show parallel MD effect at 114 K, 84 K, and 30 K, respectively. [55]

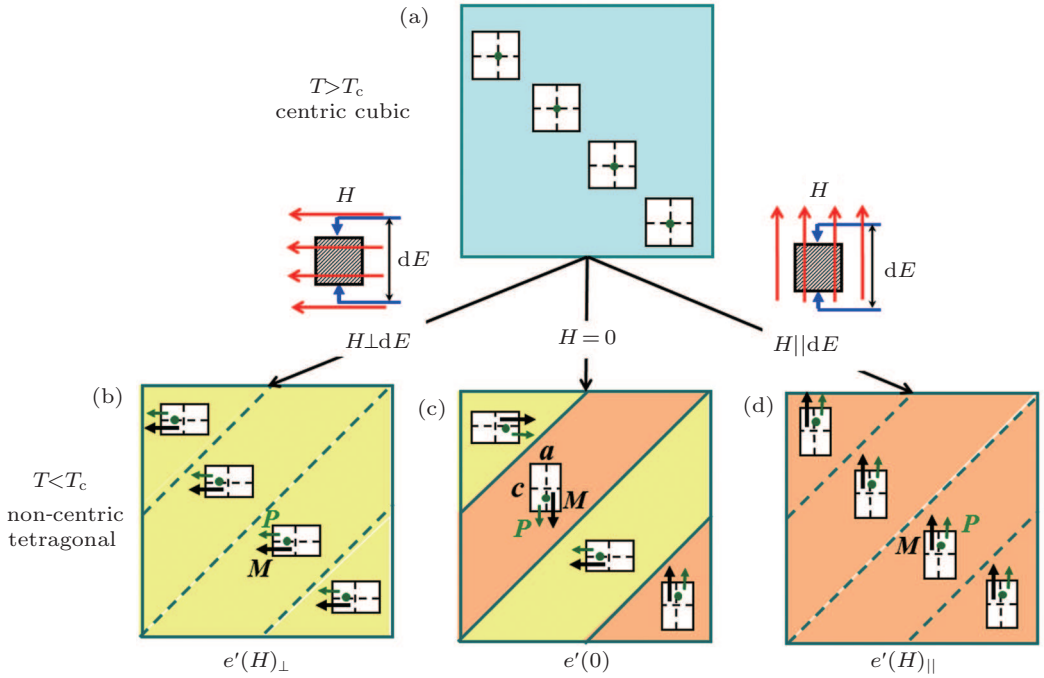


Fig. 11. Schematic explanation for MD effect in both paramagnetic phase ($T > T_c$) and ferrimagnetic phase ($T < T_c$). (a) Equilibrium paramagnetic states with different magnetic field: $\boldsymbol{H} \perp \mathrm{d}\boldsymbol{E}$, $\boldsymbol{H} = 0$, and $\boldsymbol{H} \parallel \mathrm{d}\boldsymbol{E}$. (b) Single domain ferrimagnetic state at $\boldsymbol{H} \perp \mathrm{d}\boldsymbol{E}$. (c) Equilibrium ferrimagnetic (multi-domain tetragonal ($c/a > 1$)) state at $\boldsymbol{H} = 0$. (d) Single domain ferrimagnetic state at $\boldsymbol{H} \parallel \mathrm{d}\boldsymbol{E}$. Small squares and rectangles represent the cubic and tetragonal crystal symmetries respectively. The black and olive arrows in (b), (c), and (d) represent $\boldsymbol{M}$ and $\boldsymbol{P}$ in ferromagnetic state, respectively. [55]

5.2. Evidence for first-order nature of ferromagnetic transition in Ni, Fe, Co, and $CoFe_2O_4$

Thermodynamically phase transitions are classified into continuous (2nd-order) and discontinuous (1st-order) ones, in terms of the continuity of order parameter (a generic physical parameter characterizing the phase transition) at transition temperature.[63] Although almost all structural transitions (e.g., ferroelastic/martensitic transitions and ferroelectric transitions) are known to be of 1st-order, nearly all ferromagnetic transitions have been believed to be of 2nd-

order; [63–65] typical examples include magnetic elements of Ni, Fe, Co, and magnetic compounds like $CoFe_2O_4$. A recent study with high-resolution synchrotron X-ray diffractometry revealed that ferromagnetic transition is not merely a magnetic ordering; rather, it is always coupled to the lattice and causes a simultaneous weak structural change.[19] This finding supports an earlier theoretical prediction [8] based on magnetoelastic coupling. Such a coupling may in theory modify the nature of the ferromagnetic transition, resulting in a 1st-order transition;[8,66–69] however, this proposition has remained controversial for decades.[64,65,70,71] Therefore, a critical experiment is needed to resolve the dispute.

Previous evidence that ferromagnetic transitions are 2nd-order was mainly from the experimental signature that magnetization (as order parameter) shows a continuous change at the transition temperature T_c.[3] However, specialists have recently become aware that the continuity of the order parameter is not a reliable fingerprint for 2nd-order transition, as weakly 1st-order transitions also show continuity in the order parameter at T_c by pretransitional fluctuation.[72] Instead, a more reliable and sensitive fingerprint for a 1st-order (or 2nd-order) transition is the existence (or non-existence) of a thermal hysteresis at the transition temperature, which reflects the existence of an energy barrier at a 1st-order transition.[73] In addition, the existence of latent heat upon transition is another important signature of a 1st-order transition.[74]

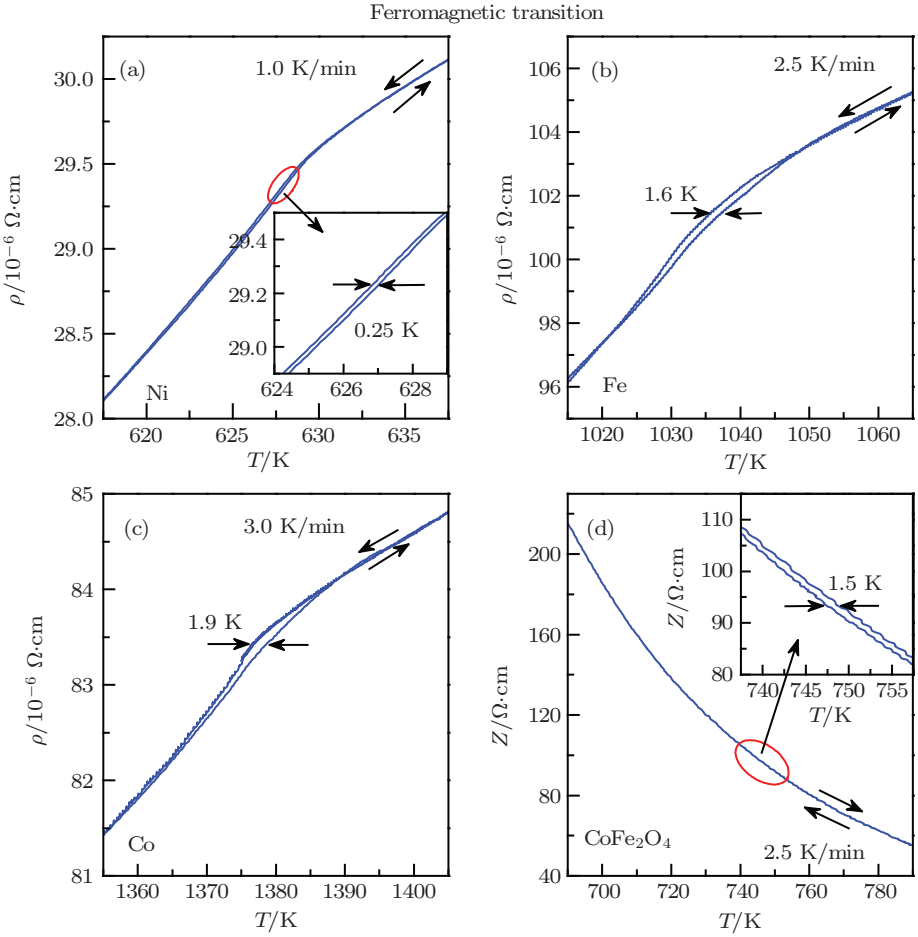


Fig. 12. Evidence for transition hysteresis of several typical 2nd-order ferromagnetic transitions. (a) Ni, (b) Fe, (c) Co, and (d) $CoFe_2O_4$.[75]

Figure 12 shows the temperature dependence of electrical resistivity/impedance in the vicinity of T_c in the ferromagnetic systems of Ni, Fe, Co, and $CoFe_2O_4$ (Fig. 12(a)–12(d)).[75] A cooling–heating cycle was measured to identify whether or not there is a thermal hysteresis around T_c. It is clear that all these typical 2nd-order ferromagnetic systems exhibit a small hysteresis in the vicinity of T_c. The hysteresis for Ni, Fe, Co, and $CoFe_2O_4$ are 0.25 K, 1.6 K, 1.9 K, and 1.5 K, respectively. As the transition thermal hysteresis is the most prominent characteristic of a 1st-order transition, the clear hysteresis in Ni, Fe, Co, and $CoFe_2O_4$ can be explained only by assuming these ferromagnetic systems undergo a 1st-order transition. The small hysteresis (about 0.25 K–1.9 K) indicates that these ferromagnetic systems undergo a weakly 1st-order transition.

Figure 13 shows the DSC curves for the typical ferromagnetic systems of Ni, Fe, Co, and $CoFe_2O_4$ (Figs. 13(a)–13(d)) during their ferromagnetic transitions.[75] It can be seen clearly that all the magnetic samples, Ni, Fe, Co, and

$CoFe_2O_4$, show an endothermic/exothermic peak at their ferromagnetic transition temperature. As a 2nd-order transition has no latent heat and a 1st-order transition has latent heat, the latent heat (i.e., the DCS peak) observed in Ni, Fe, Co, and $CoFe_2O_4$ further suggests that these ferromagnetic systems undergo a 1st-order transition. Figure 13 also shows the existence of a thermal hysteresis during the ferromagnetic transition, as can be seen from the temperature difference between the exothermic peak T_p^- (during cooling) and endothermic peak T_p^+ (during heating) for all these ferromagnetic systems. Such a hysteresis does not vanish even when extrapolating the cooling/heating rate to zero, as shown in the insets. The hysteresis at zero cooling/heating rate for Ni, Fe, Co, and $CoFe_2O_4$ are 0.8±0.6 K, 0.6±0.4 K, 0.7±0.5 K, and 1.0±0.4 K, respectively. The existence of transition hysteresis by DSC supports more accurate hysteresis measurement by resistivity/impedance, as shown in Fig. 12.

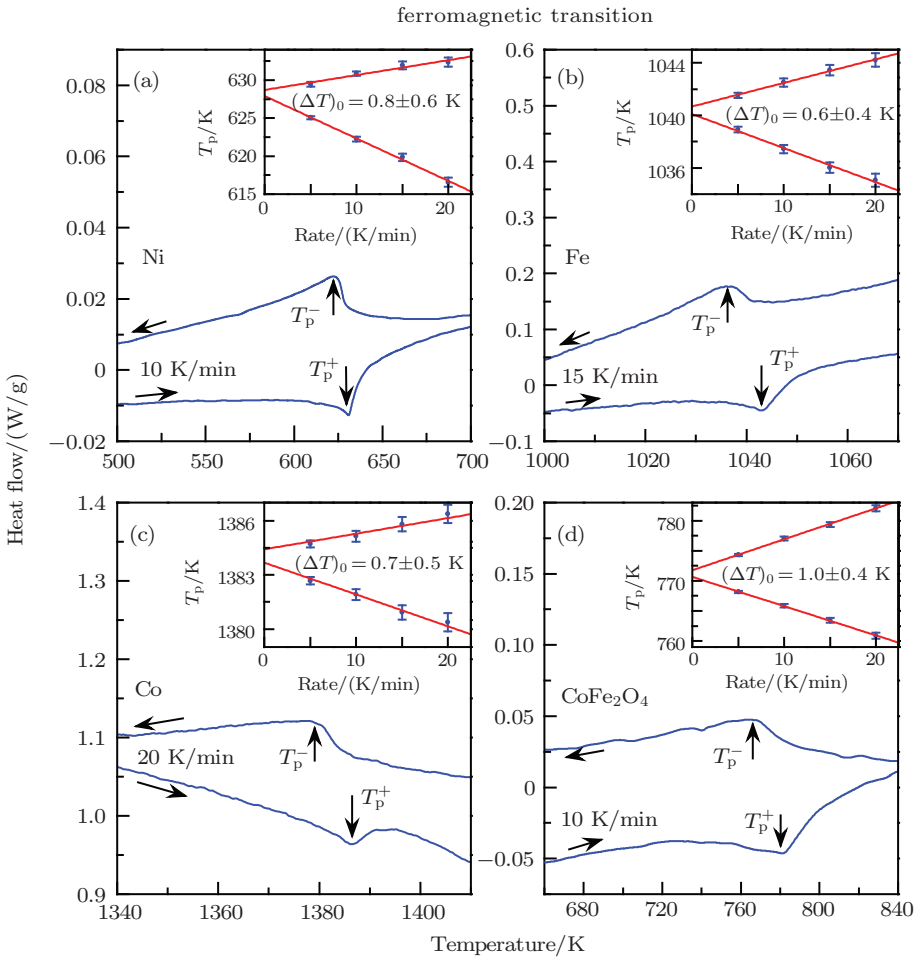


Fig. 13. Evidence for the latent heat (DSC peak) of several typical "2nd-order" ferromagnetic transitions. (a) Ni, (b) Fe, (c) Co, and (d) $CoFe_2O_4$. Insets show the change of thermal hysteresis (difference in the exothermic and endothermic peak temperatures) with cooling/heating rate.[75]

6. Conclusions

(i) A ferromagnetic transition is not just an ordering of magnetic moment alone; it also involves a structure change, although very small in most cases. By phenomenological reasoning, we theoretically proved that a reduction of crystal symmetry is a general effect during a magnetic transition. The reason for the apparent crystal structure invariance with ferromagnetic transition is simply the relatively low resolution of conventional XRD. By employing powerful synchrotron XRD with high resolution, more and more magnetic transitions will be found to be accompanied by simultaneous structural change.

(ii) The low crystal symmetry of the ferromagnetic phase provides a simple mesoscopic explanation for the commonly observed magnetostrictive effect. The maximum magnitude of magnetostriction is proportional to the extent of lattice distortion. As schematically illustrated in Figs. 3(d) and 3(e), the anisotropic magnetostriction in $CoFe_2O_4$ and Terfenol-D can be simply explained by the switching of non-cubic ferroelastic domains. This explanation for magnetostriction is physically the same as that for the electrostrain effect in ferroelectrics,

and is also similar to the stress-induced strain effect in ferroelastic materials.

(iii) Simultaneous structural changes at ferromagnetic transitions may provide new clues for developing highly magneto-responsive materials. This is because ferromagnetic transition is no longer to be understood as just a magnetic ordering process; it also involves a secondary ferroelastic ordering process. The secondary ordering process can even be a ferroelectric ordering, which causes a magnetoelectric effect. The secondary ordering may enhance the change in many physical properties and thus make the system appear more magneto-responsive and multi-ferroic. One can expect large magneto-responsiveness in systems with large lattice strain or strong magnetoelastic coupling.

(iv) Motivated by evidence of a structure change at a ferromagnetic transition, we first developed a magnetic MPB in a ferromagnetic system, which separates two magnetic phases with different crystal symmetries. The MPB significantly enhances magnetic and magnetostrictive properties. Finding an MPB in a ferromagnetic system points to a potentially effective approach for developing highly magnetostrictive materials and suggests the possibility of MPBs in other ferroic systems.

(v) Based on the postulation of non-centric crystal symmetry in ferromagnetic phase, we found a magnetodielectric effect emerging from the onset of the collinear ferrimagnetic transition in $CoCr_2O_4$. Such an MD effect was caused by the coexistence of electric and magnetic ordering that is due to the magnetoelectric coupling below T_c. Our results suggest that $CoCr_2O_4$ may be naturally multiferroic (albeit weak) in the collinear ferrimagnetic ordering and thus would have non-centric crystal symmetry.

(vi) By thermal hysteresis and latent heat measurement we showed that the most typical 2nd-order ferromagnetic transitions in Ni, Fe, Co, and $CoFe_2O_4$ turn out to be 1st-order transitions. We suggest that the 1st-order nature of ferromagnetic transitions is attributable to an inevitable magnetoelastic coupling in all ferromagnetic systems. The finding of the 1st-order nature of ferromagnetic transition indicates that a ferromagnetic transition is always accompanied by a coupling effect. It also suggests a need to reconfirm other alleged 2nd-order transitions previously reported.

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