

Noncubic crystallographic symmetry of a cubic ferromagnet: Simultaneous structural change at the ferromagnetic transition

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Conventional diffractometry over the past decades has revealed that the ferromagnetic transition, an ordering of the magnetic moment, involves no crystal structure change in general; thus a cubic paramagnet has been considered to transform into a cubic ferromagnet upon a ferromagnetic transition. However, with high-resolution synchrotron x-ray diffractometry (XRD), we show direct evidence for (i) the noncubic symmetry of typical cubic ferromagnets CoFe_2O_4 , $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ (Terfenol-D), and DyCo_2 and (ii) a simultaneous structural change at ferromagnetic transition temperature (T_C) in DyCo_2 . These results suggest that ferromagnetic transition is also a structural transition, yielding a low crystallographic symmetry that conforms to the spontaneous magnetization (M_S) direction. *In situ* XRD observation further revealed that the switching of magnetic domains is also a switching of the noncubic crystallographic domains, in the same way as the ferroelectric domain switching. By a phenomenological approach based on magnetoelastic coupling, we proved theoretically that structure change upon a ferromagnetic transition is a general effect for all cubic ferromagnets. Our work leads to a simple and unified mesoscopic explanation for both magnetostriction in ferromagnets and electrostrain effect in ferroelectrics. It may also provide insight for developing highly magneto-responsive materials.

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I. INTRODUCTION

The ferromagnetic (or ferrimagnetic) transition, an ordering of the magnetic moment, is central for both a fundamental understanding of ferromagnetism and the vast applications of ferromagnetic materials. Over the past decades, a huge wealth of crystal structure data of various ferromagnetic materials, determined mostly by conventional x-ray diffractometry (XRD), have been collected,¹ and they indicate that in general there is no change in the host crystal structure or symmetry upon a ferromagnetic transition.^{2,3} 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 (like Ni_2MnGa , Fe-Pt alloys, etc.) exist, but their large structure change (1%–10%) is known as due to a simultaneous martensitic transition.⁴ Therefore, from available experimental evidence it seems that the ferromagnetic transition involves no structural change as a whole.

However, the existence of a magnetostrictive effect in all known ferromagnetic systems seems to suggest that the magnetic moment is invariably coupled to the crystal lattice;^{5,6} hence there is a possibility that magnetic ordering may cause a change in crystal structure. Such a possibility was suggested by a phenomenological theoretical study 40 years ago.⁷ It can also be inferred from the tables of magnetic symmetry listed in Ref. 8 that a change of crystal symmetry upon magnetic ordering is likely. Nevertheless, it seems that a consensus has not yet been reached even among different theories.⁹ Thus there exists a discrepancy between the available experimental facts and theoretical prediction or inference, and among different theories. Clearly, a careful and high-resolution experiment is needed to resolve these contradictions.

It should be further noted that the observed structure invariance of the ferromagnetic transition sharply contrasts its physically parallel transition–ferroelectric transition (an ordering of electric dipoles at T_C),^{10,11} where the electro-lattice (dipole-elastic) coupling causes a significant lattice distortion or structure change at T_C . Such a lattice distortion is the order of 1% for ferroelectrics and reveals itself as a splitting of diffraction peaks.¹² In view of the physical parallelism between the ferroelectric transition and ferromagnetic transition, there seems no reason why the ferromagnetic transition should not involve a structure change.

In the present paper, we shall show that the apparent structure invariance for the ferromagnetic transition is a result of the smallness of the structure change, which is beyond the strain resolution limit of conventional XRD (about 5×10^{-3}) used in the past. With improved resolution by using high-resolution synchrotron XRD,^{13,14} we show clearly that two well-known cubic ferromagnets CoFe_2O_4 and Terfenol-D are actually noncubic; they possess crystal symmetry consistent with their spontaneous magnetization (M_S) direction. To provide direct evidence that such a symmetry lowering happens at the magnetic ordering temperature T_C , it is desirable to perform an *in situ* monitoring of the structure change around T_C . However, these two compounds have high T_C (760 and 665 K for CoFe_2O_4 and Terfenol-D, respectively), which is beyond the range of our XRD heating device. To directly observe the structure change at T_C , we selected another cubic ferromagnet DyCo_2 , which has a similar crystal structure with Terfenol-D but has a lower T_C (~ 143 K), which is within the temperature range of our heating/cooling device. *In situ* observation of structure change of DyCo_2 upon its ferromagnetic transition showed that a ferromagnetic transition indeed involves a symmetry lowering, or a structure change. Finally we show with a phe-

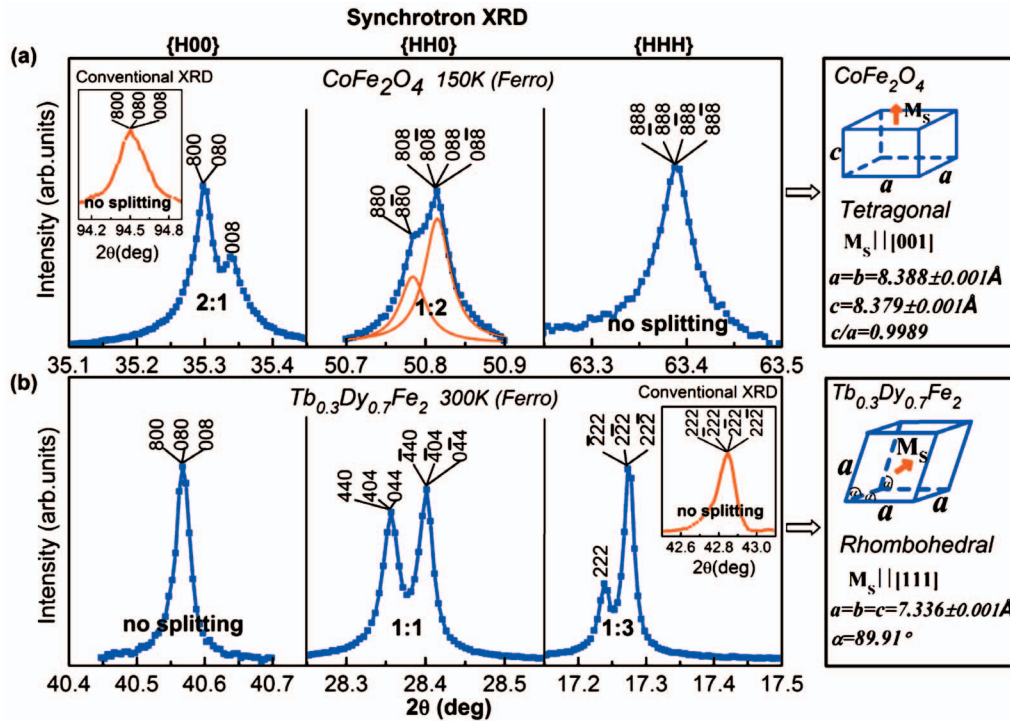


FIG. 1. (Color) Synchrotron XRD evidence for the noncubic symmetry of two typical “cubic” ferromagnets. (a) $\{800\}$, $\{880\}$, and $\{888\}$ reflections in ferromagnetic CoFe_2O_4 at 150 K. (b) $\{800\}$, $\{440\}$, and $\{222\}$ reflections in ferromagnetic $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ at 300 K. For a comparison, the insets show the peak profiles measured by conventional XRD with $K\alpha$ radiation.

nomenological theoretical approach that structure change or symmetry lowering upon ferromagnetic transition is a general effect for all cubic ferromagnets and it stems from the magnetoelastic coupling.

II. EXPERIMENT

We employed 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.¹⁵

Ferromagnetic CoFe_2O_4 and Terfenol-D and DyCo_2 were examined because they are known to have relatively large magnetoelastic coupling¹⁶ so that their structure change may be relatively easy to detect. CoFe_2O_4 was prepared by a traditional solid-state reaction technique using high-purity CoO and Fe_2O_3 ; the Terfenol-D sample was obtained from ETREMA; DyCo_2 alloy was prepared by arc melting of high-purity Dy and Co in an argon atmosphere. 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. The x-ray wavelength was 0.6358 \AA . The temperature of the sample was controlled by a blow-type cryocooler with an accuracy of 0.1 K. The cryocooler can provide a temperature range from 90 to 400 K.

III. RESULTS

A. Evidence for noncubic crystal symmetry of a 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 the paramagnetic state and ferromagnetic state,^{17,18} our high-resolution synchrotron XRD data shown in Fig. 1 reveal striking results: they are not cubic in the ferromagnetic state. Figure 1(a) shows three high-symmetry reflections of CoFe_2O_4 , $\{800\}$, $\{880\}$, and $\{888\}$, measured at 150 K ($T_C \sim 760 \text{ K}$). The split $\{800\}$ and $\{880\}$ reflections unambiguously prove that 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 the 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 manifested in the inset of Fig. 1(a)]. This explains why ferromagnetic CoFe_2O_4 had been regarded as cubic in the past and why there had been no evidence for a structure change upon its ferromagnetic transition so far.

Very similar to the case of CoFe_2O_4 , Fig. 1(b) reveals clear evidence for the noncubic symmetry of Terfenol-D in the ferromagnetic state, because $\{440\}$ and $\{222\}$ reflections show a clear splitting. The nonsplitting of the $\{800\}$ reflection and the intensity ratio of split peaks in the $\{440\}$ and $\{222\}$ reflections (about 1:1 and 1:3, respectively) characterize a rhombohedral symmetry for this compound, with the lattice elongated along $[111]$. These 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 $\epsilon = \frac{d_{222} - d_{\bar{2}22}}{d_{222}} \approx \frac{4}{3} \cos \alpha = 2.1 \times 10^{-3}$. Clearly, such a small structure change 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 low resolution of conventional XRD used.

Because the two compounds studied above are known to have cubic symmetry in the paramagnetic state, the lower symmetry in the ferromagnetic state suggests that the ferromagnetic transition lowers 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(a). This indicates that there seems a structure change at T_C . Nevertheless, for these two compounds we could not directly observe the structure change at the ferromagnetic transition temperature, because the high T_C (760 and 665 K for CoFe_2O_4 and Terfenol-D, respectively) of these compounds is beyond the temperature range of our cryocooler. To directly observe the structure change at T_C , we selected another cubic ferromagnet DyCo_2 , which has a similar crystal structure with Terfenol-D but has a low T_C (~ 143 K) to be within the reach of our cryocooler. In the next section, we shall show direct evidence for the structure change of DyCo_2 upon its ferromagnetic transition.

Here we note that in the literature there have been some experimental clues for the low symmetry of certain ferromagnetic phase that exhibits large structural distortion,¹⁹ but it has not been discussed if such a low-symmetry phase is formed by a ferromagnetic transition.

B. Direct evidence for crystal structure change upon a ferromagnetic transition in DyCo_2

Figure 2 shows clearly the change of crystal structure from cubic to tetragonal accompanying a ferromagnetic transition. As shown in the temperature dependence of the 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 direct evidence for a structure change upon ferromag-

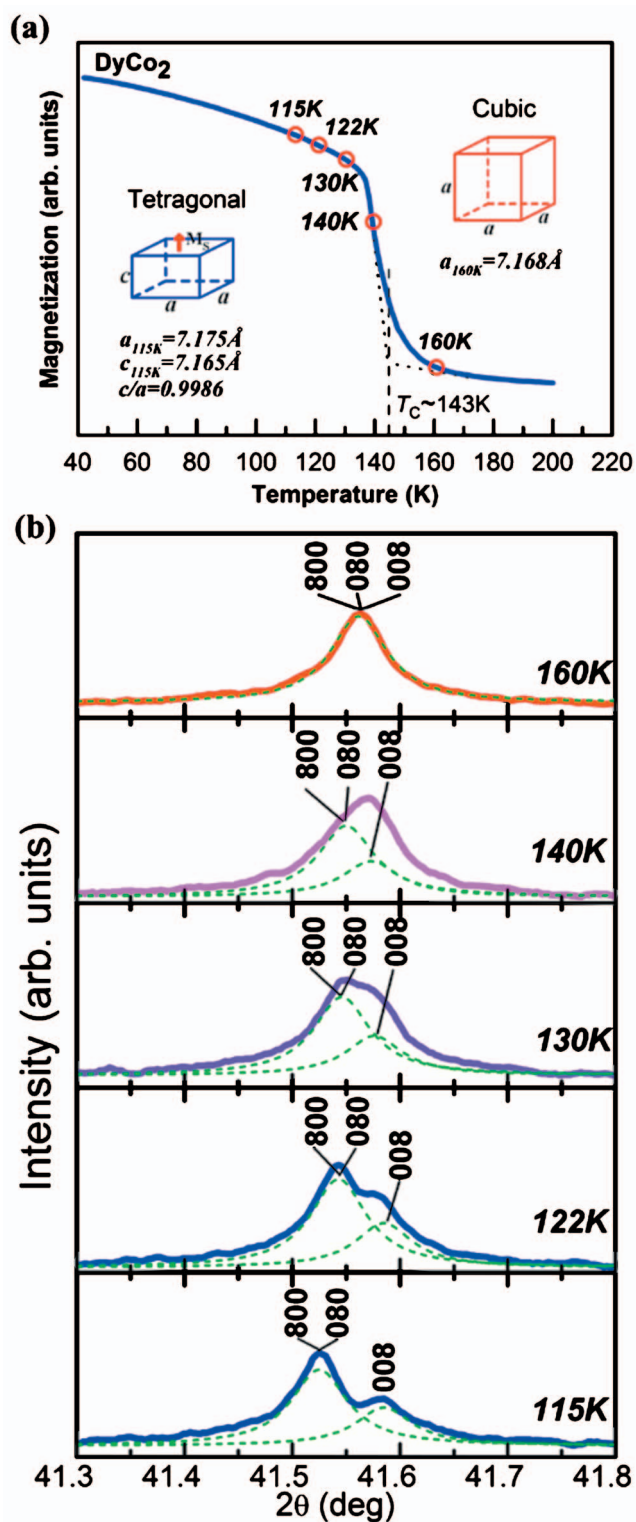


FIG. 2. (Color) *In situ* observation of the structure change of DyCo_2 upon its ferromagnetic transition by synchrotron XRD. (a) Temperature dependence of magnetization measured under 2.5 kOe magnetic field by a vibrating sample magnetometer (VSM); the Curie point (T_C) is 143 K. (b) The splitting of a cubic $\{800\}$ reflection during a ferromagnetic transition; the dashed peaks underneath the experimental peak profiles are Lorentzian peaks giving the best fit to the experimental profiles. The crystal structure of the paraphase and ferrophase is shown in (a).

netic transition. By examining the XRD spectrum and the peak intensities we are able to determine the structure of the ferromagnetic state to be a tetragonal structure, being 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, Fig. 2 provides direct evidence for a structure change at a ferromagnetic transition; this is parallel to the structure change accompanying a ferroelectric transition like in BaTiO_3 .¹² The only difference is that the size of the structure change at the ferromagnetic transition is one order of magnitude smaller ($\sim 0.1\%$) than that in BaTiO_3 ($\sim 1\%$). 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.

C. *In situ* XRD observation of the switching of magnetic domains

An important consequence of the noncubic 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.^{20,21} This can be clearly seen by the change of the synchrotron XRD pattern by 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 for CoFe_2O_4 and Tefernol-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 the a domain ($M_S \parallel [100]$) and b domain ($M_S \parallel [010]$) into the c domain ($M_S \parallel [001]$), without a change of crystal symmetry, which indicates that M_S direction is along the c axis of the tetragonal lattice. For Tefernol-D, the magnetic field diminishes the $\bar{2}22/\bar{2}22/\bar{2}22$ peak and enhances the 222 peak, but the {800} reflection is almost unaffected. Such a change corresponds to a switching of $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ domains into a $[111]$ 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, identical 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 curve of Figs. 3(b) and 3(c), we can see that the 4 kOe field has magnetized both samples to a near-saturation value. 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

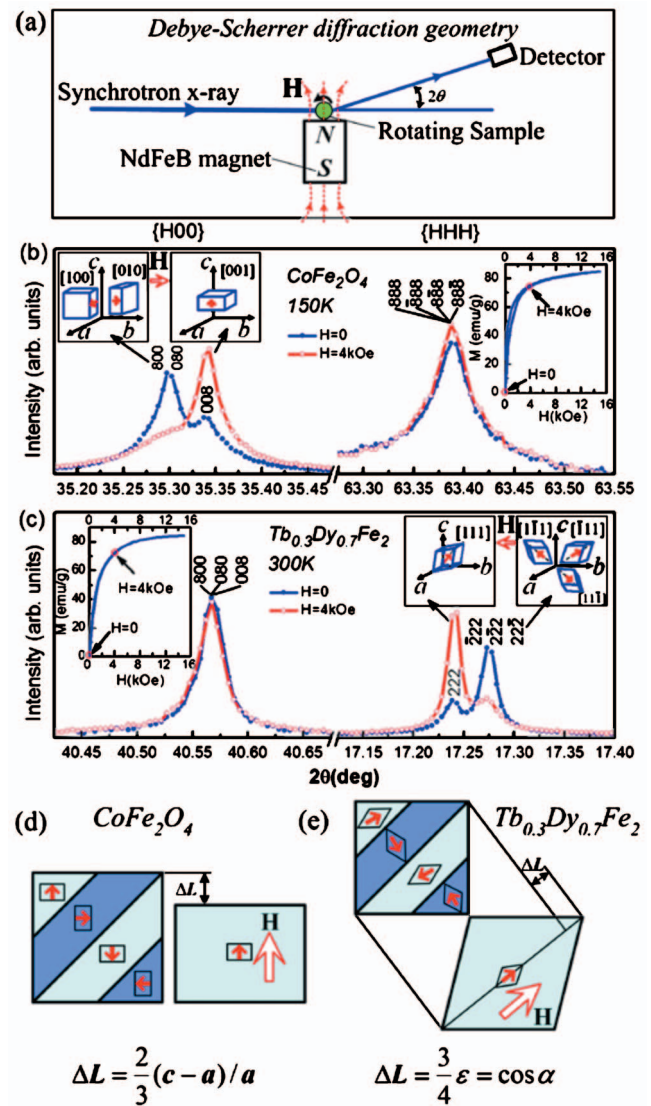


FIG. 3. (Color) *In situ* observation of the change in XRD pattern by a magnetic field $\mathbf{H}=4$ kOe for CoFe_2O_4 and $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$. (a) Experimental setup, in which the magnetic field was introduced by a NdFeB permanent magnet placed under the rotating sample. (b) {800} and {888} peak profiles of ferromagnetic CoFe_2O_4 at $\mathbf{H}=0$ kOe and $\mathbf{H}=4$ kOe. (c) {800} and {222} peak profiles of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ at $\mathbf{H}=0$ kOe and $\mathbf{H}=4$ kOe. (d) and (e) show schematically a mesoscopic explanation for anisotropic magnetostriction due to the switching of the noncubic ferromagnetic (=ferroelastic) domains for the two compounds, respectively. The small rectangles and rhombuses represent the unit cell symmetry to be tetragonal and rhombohedral, respectively. ΔL is the anisotropic magnetostriction due to magnetic field \mathbf{H} ; ε is the spontaneous lattice strain of the low-symmetry crystal.

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 do not find such a symmetry change. This behavior is identical to the domain-switching behavior of ferroelectrics: there exists only domain switching, no polarization rotation.¹⁰ Thus this result seems a challenge to the well-accepted concept of “moment rotation” in cubic ferromagnets.

IV. DISCUSSION

A. Theory for structure change upon a ferromagnetic transition

Our results shown above pose a fundamental question to the notion that the ferromagnetic transition is a pure magnetic-ordering process, without a change in crystal structure. They suggest that magnetic ordering can change the crystal symmetry of the host lattice into one that conforms to the M_S direction. This crystal symmetry change can be explained by an inevitable coupling between magnetic moment and lattice strain,⁷ 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 the true crystal symmetry is no longer cubic. Crystal symmetry lowers at the Curie temperature T_C .

The free energy of a ferromagnetic crystal can be described as follows:^{16,22,23}

$$F = F_a + F_e + F_{me}, \quad (1)$$

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

The magnetic anisotropic energy F_a represents the magnetic energy due to ordering of magnetic moment; it has the following form for a cubic ferromagnetic crystal in the first-order approximation:^{16,22}

$$F_a = K_1(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2), \quad (2)$$

where K_1 is a temperature-dependent anisotropic constant and α_x , α_y , and α_z are the direction cosines of M_S with respect to the cubic axes.

The elastic energy F_e in a cubic crystal represents the elastic energy of the lattice due to elastic distortion e_{ij} ; it is given by^{16,22}

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

where the c_{ij} is the elastic modulus.

The magnetoelastic energy F_{me} arises from an interaction between magnetic moment and lattice strain. It has a quantum mechanical origin^{5,24} and exists in all magnetic systems. For a cubic ferromagnetic crystal, it is usually written as:¹⁶

$$F_{me} = b_1M_s^2 \left[e_{xx} \left(\alpha_x^2 - \frac{1}{3} \right) + e_{yy} \left(\alpha_y^2 - \frac{1}{3} \right) + e_{zz} \left(\alpha_z^2 - \frac{1}{3} \right) \right] + b_2M_s^2(e_{xy}\alpha_x\alpha_y + e_{yz}\alpha_y\alpha_z + e_{zx}\alpha_z\alpha_x), \quad (4)$$

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 $(e_{ij})_s$ to the initial cubic lattice. The matrix form of this spontaneous strain can be found to be the following for an initially cubic crystal:

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

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 paramagnetic state, as the spontaneous strain $(e_{ij})_s = 0$ only when $M_S = 0$.

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

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

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 M_S direction. Similarly, when M_S is along the

[111] direction—i.e., $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \frac{1}{3}$ —the spontaneous strain tensor becomes

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

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 M_S . It is noted that Callen and Callen used a group-theoretical approach⁷ and obtained the same conclusion about the dependence of crystal symmetry on the M_S direction.

(iii) Equation (5) predicts that there will be a structure transition associated with the magnetic ordering in all cubic ferromagnets. In the paramagnetic state ($T > T_C$), a cubic crystal will be true cubic, as shown above. But when temperature is below T_C , the ordering of the magnetic moment produces a nonzero M_S and hence induces a nonzero spontaneous strain to the initial cubic lattice. Such a spontaneous strain changes the crystal structure from cubic to a lower symmetry that conforms to the 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.

B. Detectability of structure change accompanying a ferromagnetic transition by the XRD technique

Although structure change upon magnetic ordering exists in all pseudocubic 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 BaTiO₃ is also included. Clearly, BaTiO₃ has a large lattice distortion and such distortion can be easily detected by conventional XRD; however, for CoFe₂O₄, Terfenol-D and DyCo₂, 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 look “cubic” even when examined by synchrotron XRD. Figure 4(b) shows the relationship between the crystal symmetry of the ferrophase and the M_S or 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.

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; thus the structure change is often too small to detect

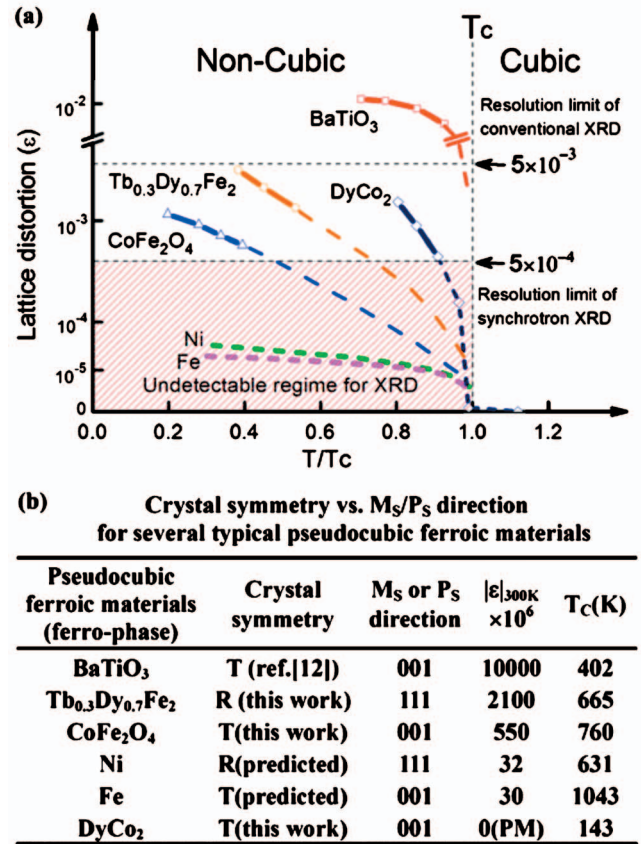


FIG. 4. (Color) Lattice distortion and crystal symmetry for several typical pseudocubic ferromagnetic and ferroelectric materials. (a) Temperature dependence of lattice distortion for several ferromagnetic and ferroelectric materials. The lattice distortion axis takes a cube root scale, so as to reveal the tiny strain determined by synchrotron XRD. The BaTiO₃ data are from Ref. 12; the data points of CoFe₂O₄, Tb_{0.3}Dy_{0.7}Fe₂, and DyCo₂ are from the present work, and the dashed lines are estimated from the known magnetostriction coefficients in Ref. 5. (b) Relation between the spontaneous magnetization direction M_S (or polarization direction P_S) and crystal symmetry (R , rhombohedral; T , tetragonal). It is noted that DyCo₂ is paramagnetic (PM) at room temperature, so its room-temperature lattice distortion is zero; at low temperature it has a similar lattice distortion as Terfenol-D.

by the conventional XRD technique. This is why it has been believed that there is no structure change 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 CoFe₂O₄ and Terfenol-D (Tb_{0.3}Dy_{0.7}Fe₂).

C. Implications of structure change upon the ferromagnetic transition

The finding that the ferromagnetic transition involves a structure change may lead to important consequences. First, 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

CoFe₂O₄ and Terfenol-D can be simply explained by the switching of noncubic ferroelastic domains. This explanation for magnetostriction is physically the same as the electrostrain effect in ferroelectrics^{20,21} and is also similar to the stress-induced strain effect in ferroelastic materials.^{25,26} 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 CoFe₂O₄ and Terfenol-D have large magnetostriction, because they have large lattice distortion in the ferromagnetic state.

Second, the structure change upon a ferromagnetic transition may provide new clues for developing highly magneto-responsive materials, including the recently reported giant magnetocaloric and magnetoresistive materials.^{27,28} This is because the ferromagnetic transition is no longer a pure magnetic ordering process; it also involves a secondary, ferroelastic ordering process. The secondary ordering process can be even 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 multiferroic. One can expect that large magneto-responsiveness will appear in systems with large lattice strain or strong magnetoelastic coupling.

Third, the concomitant strain-magnetic ordering indicates an interesting possibility that a ferromagnetic transition may be a first-order transition rather than a second-order one. This is because a two-order-parameter system (like the present case) usually undergoes a first-order transition due to the existence of coupling, as can be seen in the case of the ferroelectric transition (polarization and strain coupling) (Ref. 10) and ferroelastic transition (strain and strain coupling) (Ref. 29). This seems to support the theoretical result by Bergman

and Halperin.³⁰ This interesting point awaits a future experiment to be verified.

V. CONCLUSION

We show that the ferromagnetic transition is not just an ordering of the magnetic moment alone; it also involves a structure change, although very small in most cases. As a consequence, magnetic domain switching by the magnetic field is also a switching of the noncubic crystallographic domains. This picture is the same as the case of ferroelectrics and ferroelastics. The moment rotation process is not found in the two systems studied. Our finding unifies the mesoscopic explanation for both magnetostrictive effect in ferromagnetic materials and electrostrain effect in ferroelectric materials. It may also provide insight into how to seek materials with giant magneto-responsive properties. Finally we have proved theoretically that crystal-symmetry lowering is a general effect during a magnetic transition.

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