Large Magnetostriction from Morphotropic Phase Boundary in Ferromagnets

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For more than half of a century, morphotropic phase boundary (MPB) in ferroelectric materials has drawn constant interest because it can significantly enhance the piezoelectric properties. However, MPB has been studied merely in ferroelectric systems, not in another large class of ferroic systems, the ferromagnets. In this Letter, we report the existence of an MPB in a ferromagnetic system $TbCo_2$-$DyCo_2$. Such a magnetic MPB involves a first-order magnetoelastic transition, at which both magnetization direction and crystal structure change simultaneously. The MPB composition demonstrates a 3–6 times larger ''figure of merit'' of magnetostrictive response compared with that of the off-MPB compositions. The finding of MPB in ferromagnets may help to discover novel high-performance magnetostrictive and even magnetoelectric materials.

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The morphotropic phase boundary (MPB), a phase boundary separating two ferroelectric phases of different crystallographic symmetries in the composition-temperature phase diagram [1–3], is crucially important in ferroelectric materials because MPB can lead to a great enhancement of piezoelectricity (a conversion between mechanical force and electrical voltage [4–6]), the most useful property of this large class of functional materials. The current workhorses of piezoelectric materials, the PZT ($PbZrO_3$-$PbTiO_3$) [5] and PMN-PT ($PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$) [6], are designed to have a composition close to the MPB to achieve maximum piezoelectric effect. Figure 1(a) shows a typical ferroelectric MPB in PZT, which separates a ferroelectric rhombohedral (R) phase (with a spontaneous polarization $\boldsymbol{P}_s \| [111]$) on the $PbZrO_3$ side and a ferroelectric tetragonal (T) phase (with $\boldsymbol{P}_s \| [001]$) on the $PbTiO_3$ side. The rhombohedral and tetragonal ferroelectric phases share a common cubic paraelectric phase at high temperature. Theoretical [7–9] and experimental studies [10–13] have shown that at MPB composition $\boldsymbol{P}_s$ can be easily rotated under small external field, and this causes a high piezoelectric effect.

Ferromagnetic systems are physically parallel to ferroelectric ones [14]; the former involves an ordering of magnetic moment and the latter involves an ordering of polarization below a critical temperature (Curie temperature) T_c. In both systems, the order parameter is coupled to the lattice, leading to magnetoelastic effect and piezoelectric effect, respectively. From the physical parallelism between ferromagnetism and ferroelectricity, it is tempting to ask an interesting question: Can a similar MPB situation exist in ferromagnetic systems [15]? If yes, can such magnetic MPB yield large magnetostriction (magnetic-field-induced distortion [16,17], an effect analogous to the piezoelectricity in ferroelectrics)? Following the definition of MPB in ferroelectrics, a magnetic MPB should be a phase boundary separating two different ferromagnetic states (or different spontaneous magnetization $\boldsymbol{M}_s$ directions) with different crystallographic symmetries.

So far, the major obstacle for the existence of MPB in ferromagnets has been a general observation [by conventional x-ray diffractometry (XRD)] that different $\boldsymbol{M}_s$ directions do not produce a difference in crystal symmetry [14,18], being different from the ferroelectric case. Therefore, for ferromagnetic systems, the condition for MPB seems not satisfied. However, with the great enhancement in the structure resolution by using synchrotron XRD, recent studies have proven that different ferromagnetic states indeed correspond to different crystal symmetries [19], being the same as 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. In the following, we shall see that such a magnetic MPB indeed exists in a binary ferromagnetic system $TbCo_2$-$DyCo_2$, and at MPB composition, there is a significant enhancement of magnetostrictive properties.

The $TbCo_2$-$DyCo_2$ alloys were prepared by arc melting of high-purity (99.9%) Tb, Dy, and Co in argon atmosphere. To observe the tiny lattice distortion and determine the crystal symmetry, we employed high-resolution synchrotron XRD at the BL15XU NIMS beam line of

SPring-8, which can provide a strain resolution of about 5×10^{-4}, an order of magnitude better than that of conventional XRD. All the samples for XRD were ground into powders, and sealed into quartz capillaries with a diameter of 0.3 mm. The capillary was rotated during the measurement to reduce the preferred orientation effect and to average the intensity. X-ray wavelength was 0.65297 Å. The temperature of the sample was controlled by a blow-typed cryo cooler, which can provide a temperature range of 40 to 400 K. Polycrystalline samples were used for physical property measurement. Magnetic properties were measured by SQUID, and the magnetostriction was measured by using strain gauges.

Figure 1(b) 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, there exists a ferro-ferro phase boundary separating two ferromagnetic phases, one with $\boldsymbol{M}_s \| [111]$ on the $TbCo_2$-rich side and the other with $\boldsymbol{M}_s \| [001]$ on the $DyCo_2$-rich side [20]. 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. 1(c). The para-ferro transition and the ferro-ferro transition temperatures correspond to the susceptibility peaks (T_C and T_M), as arrowed in Fig. 1(c). The composition dependence of χ' vs T relation is very similar to the permittivity vs T relation in ferroelectric PMN-PT [6]. It is noted that the ferro-ferro transition is often called "spin-reorientation transition (SRT)" to indicate the rotation of magnetic moment at the transition [21,22].

The key evidence for an MPB is from the structure data [see Fig. 1(d)] obtained from synchrotron XRD. It shows that the paramagnetic phase has a cubic symmetry (no peak splitting), and the $\boldsymbol{M}_s \| [111]$ phase has a rhombohedral (R) symmetry (as revealed with the characteristic splitting in 222 peak but no splitting in 800 peak), and the $\boldsymbol{M}_s \| [001]$ phase has a tetragonal (T) symmetry (as shown with the characteristic splitting in 800 peak but not in 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. 1(a)], 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 triple point [9], 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. 1(b).

The most interesting feature of the MPB composition is the significant enhancement of magneto-responsive properties. Figure 2(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 is seen clearly that magnetic susceptibility shows a peak at the MPB composition; the peak value is almost 3 times that of the off-MPB compositions. Accompanying the enhancement of ac susceptibility, the spontaneous magnetization $\boldsymbol{M}_s$ shows a step at the MPB composition, as shown in Fig. 2(b). Figure 2(c) shows the MPB corresponds to a minimum coercivity H_c, which is as low as 15.6 Oe. This indicates that at MPB, it is very easy to switch magnetic moment. Several typical magnetic hysteresis loops are given in Fig. 2(f).

Similar to the ferroelectric MPB in PZT, the magnetic MPB in $TbCo_2$-$DyCo_2$ system also exhibits significant enhancement in magnetostrictive properties. Figure 2(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. 2(g). It is clear that the magnetostriction at MPB composition shows a maximum ($\varepsilon = 828$ ppm) as compared with the neighboring off-MPB composition. For most magnetostriction applica-

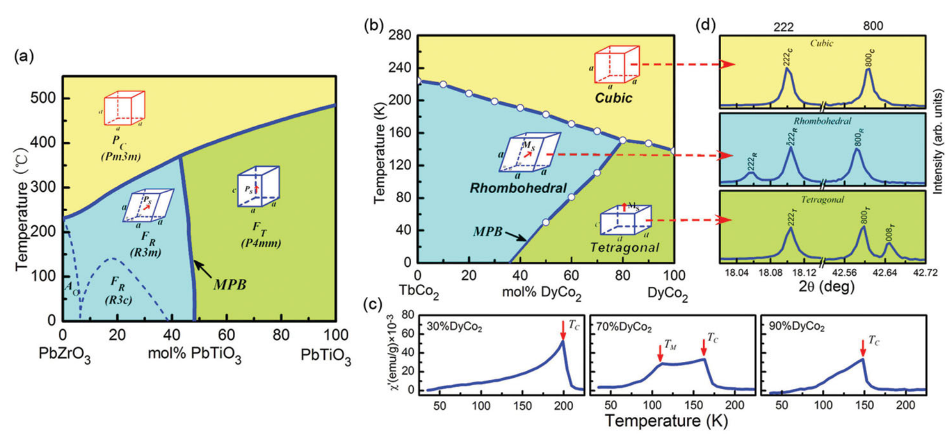

FIG. 1 (color). Morphotropic phase boundary (MPB) in a ferroelectric PZT system ($PbZrO_3$-$PbTiO_3$) and in a ferromagnetic $TbCo_2$-$DyCo_2$ system. (a) Phase diagram of PZT (Ref. [1] p. 136). (b) Phase diagram of $TbCo_2$-$DyCo_2$. (c) Temperature dependent of ac susceptibility χ'. T_c and T_M denote para-ferro and ferro-ferro transition temperature, respectively. (d) Synchrotron XRD profiles of cubic paramagnetic phase, rhombohedral ferromagnetic phase, and tetragonal ferromagnetic phase.

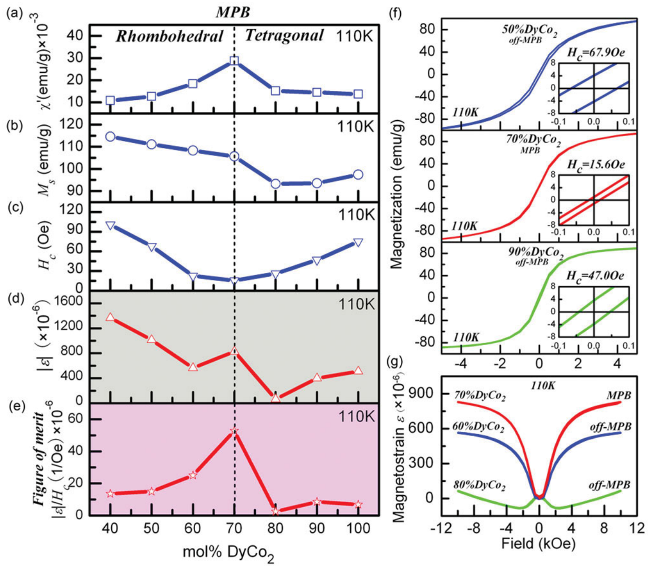

FIG. 2 (color). Composition dependent of physical properties in relation with MPB composition at 110 K. (a) ac susceptibility χ', (b) saturation magnetization $\boldsymbol{M}_s$, (c) coercivity H_c, (d) magnetostriction ε (absolute value) at 10 kOe field, (e) figure of merit ε/H_c, (f) magnetic hysteresis loops, (g) magnetostriction curves.

tions, 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. 2(e), the figure of merit (ε/H_c) at 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 occurring in the ferroelectric MPB of PZT [5]. The above results were obtained from polycrystal samples, which have an averaging effect from different grains; for single crystal samples, we expect much higher enhancement of magneto-responsive properties.

Figure 3 shows direct evidence from *in situ* synchrotron XRD that the magnetic MPB corresponds to a first-order magnetoelastic phase transition between two magnetoelastic phases: R phase with $\boldsymbol{M}_s \| [111]$ and T phase with $\boldsymbol{M}_s \| [001]$. In this experiment, the MPB was approached by varying temperature, rather than by varying composition. Synchrotron XRD was employed to detect the tiny lattice distortion associated with the symmetry change. A 70%$DyCo_2$ sample was tested during cooling from above the MPB (R phase with $\boldsymbol{M}_s \| [111]$) to below the MPB ($T$ phase with $\boldsymbol{M}_s \| [001]$). The characteristic peaks (high-symmetry reflections), 222 and 800, were monitored to determine the crystal symmetry of each phase. As seen in Fig. 3(a), the 70%$DyCo_2$ sample demonstrates a rhombohedral symmetry at 150 K (above MPB), as evidenced by the splitting in the 222 reflection but no splitting in the 800 reflection. Such a rhombohedral symmetry conforms to the magnetization direction $\boldsymbol{M}_s \| [111]$. At 90 K (below MPB), the 222 reflection does not split, but the 800 reflection splits into two peaks. This corresponds to a tetragonal symmetry, conforming to its magnetization direction $\boldsymbol{M}_s \| [001]$.

At 110 K (i.e., at the MPB temperature), the XRD pattern is consistent with a superposition of R and T profiles [see the middle figure of Fig. 3(a)]. This suggests that the MPB is composed of coexisting R and T phases. Figure 3(b) shows the temperature dependence of lattice parameters as a function of temperature; it is clear that during cooling the system experiences R phase (above MPB), a coexistence of R and T phases (at MPB), and T phase (below MPB). Thermodynamically, the coexistence of R and T phases at MPB indicates that the transition is a first-order transition and the system is bistable with respect to the two magnetization directions and two crystal symmetries ($\boldsymbol{M}_s \| [111]$ for R phase and $\boldsymbol{M}_s \| [001]$ for T

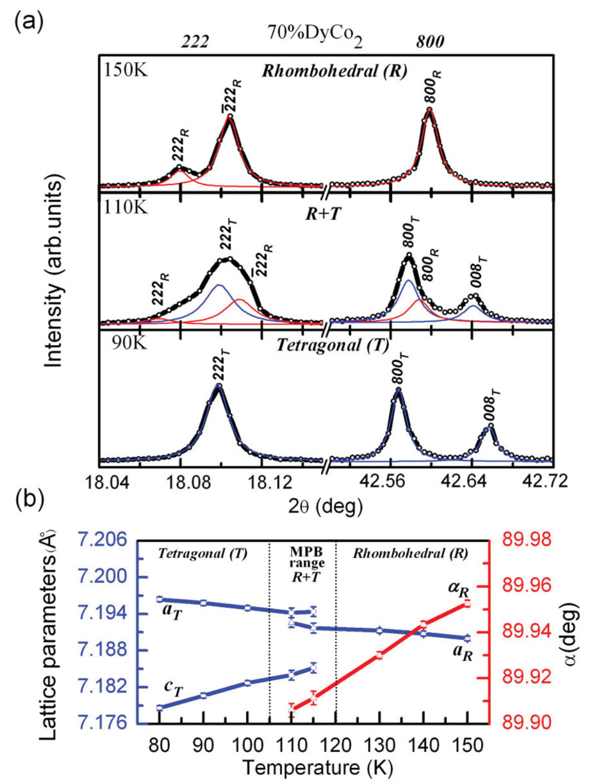

FIG. 3 (color). *In situ* synchrotron XRD evidence for first-order structural transition at MPB. The MPB is approached by changing temperature for a given composition 70%$DyCo_2$. (a) XRD profiles of rhombohedral phase at 150 K (above MPB), a mixture of rhombohedral and tetragonal phase at 110 K (at MPB), and tetragonal phase at 90 K (below MPB). The red and blue peaks underneath the experimental peaks are Lorentzian rhombohedral and tetragonal peaks giving the best fit to the experimental profiles. (b) Temperature dependence of lattice parameters (a_R and α_R stand for the lattice parameters of R-phase with $\boldsymbol{M}_s \| [111]$, and a_T and c_T for that of the T-phase with $\boldsymbol{M}_s \| [001]$); the MPB corresponds to a 2-phase mixture of rhombohedral and tetragonal phases. The error bars are determined by the fitting error in (a).

phase). As a result, the $\boldsymbol{M}_s$ and crystal lattice are unstable and can be changed easily from one configuration to the other by a small external magnetic field. This explains the significant enhancement of magnetic susceptibility, magnetostriction, figure of merit ε/H_c, and minimum H_c observed in Fig. 2.

The finding of magnetic MPB may lead to a number of important consequences. First, it provides a new insight into the nature of a fundamental concept in magnetism: spin-reorientation transition (SRT), which separates two different magnetic states, like the ferro-ferro transition between $\boldsymbol{M}_s \| [111]$ and $\boldsymbol{M}_s \| [001]$ phases shown in Fig. 1(b). So far, it is generally assumed that (i) such a transition is merely a reorientation of magnetization direction and there is no change in crystal symmetry [21,22], and (ii) the transition is continuous (or second order) [23], i.e., a continuous rotation of $\boldsymbol{M}_s$. However, our results, together with a recent finding on the generality of crystal symmetry change upon magnetic ordering [19,24], clearly show that the SRT line is (i) also a border separating different crystal symmetries, and (ii) a first-order transition. Therefore, SRT line is not a pure magnetic phase boundary; rather, it is a magnetoelastic boundary or a magnetic MPB.

Second, magnetic MPB may be a powerful approach for developing high-performance magnetostrictive materials, as evidenced by the significant property enhancement shown in Fig. 2. In this context, it seems that the giant magnetostriction in Terfenol-D ($Tb_{0.27}Dy_{0.73}Fe_2$) [25] may be due to the MPB enhancement effect in the ferromagnetic $TbFe_2$-$DyFe_2$ system, like our $TbCo_2$-$DyCo_2$ system; the details about the MPB in Terfenol-D will be published elsewhere. Finally, the finding of MPB in ferromagnetic system may extend the concept of MPB from ferroelectrics, ferromagnets (present study), to even a broader range of ferroic systems. We anticipate that MPB may also exist in other ferroic systems, such as ferroelastic (martensitic) systems and multiferroic systems, where the MPB is formed between two different strain phases or spin-polarization phases. It is likely to lead to the enhancement of corresponding properties (including elastic or magnetoelectric properties). This interesting prediction awaits future experiment to test.

In conclusion, we found a magnetic MPB in a ferromagnetic $TbCo_2$-$DyCo_2$ system, which separates two magnetic phases with different crystal symmetries. The MPB leads to a significant enhancement of magnetic and magnetostrictive properties. *In situ* observation by synchrotron XRD reveals that the MPB is a coexistence of R and T phases and is a thermodynamically bistable state. Such a bistability can explain the enhancement of properties at MPB. The finding of MPB in ferromagnetic system may provide an effective approach for developing highly magnetostrictive materials (although the present system is limited by its low T_c), and suggests the possibility of MPB in other ferroic systems.

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[1] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).
[2] K. Uchino, *Ferroelectric Devices* (Marcel Dekker, New York, 2000).
[3] M. Ahart, M. Somayazulu, and R. E. Cohen *et al.*, Nature (London) **451**, 545 (2008).
[4] D. Damjanovic, Rep. Prog. Phys. **61**, 1267 (1998).
[5] B. Jaffe, R. S. Roth, and S. Marzullo, J. Appl. Phys. **25**, 809 (1954).
[6] V. E. Colla, N. K. Yushin, and D. Viehland, J. Appl. Phys. **83**, 3298 (1998).
[7] W. Cao and L. E. Cross, Phys. Rev. B **47**, 4825 (1993).
[8] D. Damjanovic, J. Am. Ceram. Soc. **88**, 2663 (2005).
[9] G. A. Rossetti, Jr., A. G. Khachaturyan, and G. Akcay *et al.*, J. Appl. Phys. **103**, 114113 (2008).
[10] B. Noheda *et al.*, Appl. Phys. Lett. **74**, 2059 (1999).
[11] R. Guo and L. E. Cross *et al.*, Phys. Rev. Lett. **84**, 5423 (2000).
[12] K. A. Schönau *et al.*, Phys. Rev. B **75**, 184117 (2007).
[13] W. Liu and X. Ren, Phys. Rev. Lett. **103**, 257602 (2009).
[14] V. K. Wadhawan, *Introduction to Ferroic Materials* (Gordon and Breach, Amsterdam, 2000).
[15] R. E. Newnham, Acta Crystallogr. Sect. A **54**, 729 (1998).
[16] E. du Trémolet de Lacheisserie, *Magnetostriction: Theory and Applications of Magnetoelasticity* (CRC Press, Florida, 1993).
[17] K. B. Hathaway and A. E. Clark, MRS Bulletin **18**, 34 (1993).
[18] JCPDS-International Centre for Diffraction Data: http://www.icdd.com/.
[19] S. Yang and X. B. Ren, Phys. Rev. B **77**, 014407 (2008).
[20] E. W. Lee and F. Pourarian, Phys. Status Solidi (a) **34**, 383 (1976).
[21] S. Hirosawa and Y. Nakamura, J. Phys. Soc. Jpn. **51**, 1162 (1982).
[22] U. Atzmony and M. P. Dariel, Phys. Rev. B **13**, 4006 (1976).
[23] H. Horner and C. M. Varma, Phys. Rev. Lett. **20**, 845 (1968).
[24] S. Yang, X. B. Ren, and X. P. Song, Phys. Rev. B **78**, 174427 (2008).
[25] K. Mori, J. Cullen, and A. Clark, IEEE Trans. Magn. **19**, 1967 (1983).