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

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Nearly all ferromagnetic transitions have been considered to be continuous or second order, and the most typical examples are the ferromagnetic transitions in Ni, Fe, Co, and $CoFe_2O_4$. However, by precise measurement with electrical resistivity or impedance and differential scanning calorimetry, we show clear evidence for the first-order nature of these "second-order transitions"—a small thermal hysteresis and latent heat. Such first-order signatures are found to be the same as those for the well-recognized first-order transitions in the ferroelectric $BaTiO_3$ and ferroelastic $Ti_{50}Ni_{47}Fe_3$. These results question the existence of genuine second-order transition in ferromagnetic systems. By a phenomenological approach, we further show that the first-order nature of ferromagnetic transition may stem from a coupling of magnetic moment to other order parameter(s) like strain. Such a coupling may provide insight into developing highly magnetoresponsive materials.

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I. INTRODUCTION

Phase transition is the origin of many important phenomena such as ferromagnetism, piezoelectricity, shape memory effect, and superconductivity.[1–4] Thermodynamically phase transitions are classified into continuous (second-order) and discontinuous (first-order) ones, in terms of the continuity of order parameter (a generic physical parameter characterizing the phase transition) at transition temperature.[5] Although almost all structural transitions (e.g., ferroelastic or martensitic transitions and ferroelectric transitions) are known to be of first order, nearly all ferromagnetic transitions have been believed to be of second order;[5–7] typical examples include magnetic elements of Ni, Fe, Co, and magnetic compounds like $CoFe_2O_4$. For a second-order transition there exists no energy barrier between the high-temperature (paramagnetic) phase and low-temperature (ferromagnetic) phase in the free-energy landscape at the transition temperature. This contrasts the discontinuous or first-order transition, which is characterized by the existence of an energy barrier between the high-temperature phase and low-temperature phase at transition temperature.

Previous evidence for ferromagnetic transitions to be second order was mainly from the experimental signature that magnetization (as order parameter) shows a continuous change at the transition temperature T_c^1. However, it becomes aware recently that the continuity of order parameter is not a reliable fingerprint for second-order transition, as weakly first-order transitions also show continuity in order parameter at T_c by pretransitional fluctuation.[8] By contrast, a more reliable and sensitive fingerprint for first-order (or second-order) transition is the existence (or nonexistence) of a thermal hysteresis at transition temperature, which reflects the existence of an energy barrier at first-order transition.[9] Besides, the existence of latent heat upon transition is another important signature of first-order transition.[10] However, little effort was made in the past to determine the order of ferromagnetic transitions using these more sensitive fingerprints.

Recent study with high-resolution synchrotron x-ray diffractometry has revealed that ferromagnetic transition is not a mere magnetic ordering; it is always coupled to the lattice and causes a simultaneous weak structural change.[11] This finding supports earlier theoretical prediction[12] based on magnetoelastic coupling. Such a coupling may in theory modify the nature of ferromagnetic transition, resulting in a first-order transition;[12–16] however, this possibility has remained controversial for decades.[6,7,17,18] Therefore, critical experiment is needed to resolve the dispute.

In the present paper, by precise measurement of thermal hysteresis and latent heat, we show direct evidence for the first-order nature of ferromagnetic transition in a number of typical systems such as Ni, Fe, Co, and $CoFe_2O_4$, which are so far believed to undergo a second-order ferromagnetic transition. By a phenomenological theoretical approach, we further show that such a first-order ferromagnetic transition can be caused by an inevitable coupling between the magnetization and strain. The first-order nature of ferromagnetic transition implies that a pure magnetic ordering does not exist; it simultaneously modifies the residing lattice through the coupling effect. Such a coupling is the origin of multiferroicity (correlation among magnetic, elastic, and ferroelectric properties); it may also provide new insight into how to develop highly magnetoresponsive materials because the responsiveness is determined by the strength of the coupling.

II. EXPERIMENT

Transition thermal hysteresis was measured with high-accuracy four-terminal dc electrical resistivity measurement (for Ni, Fe, and Co) and ac impedance measurement (for $CoFe_2O_4$, because it is dc insulating) using a LRC meter during a heating-cooling cycle. As the thermal hysteresis for ferromagnetic transition is expected to be very small, we take the special care to reduce the measurement error. First, to ensure a high S/N ratio of the measurement, thin wire (0.1 mm in diameter) samples were used. All the samples were of

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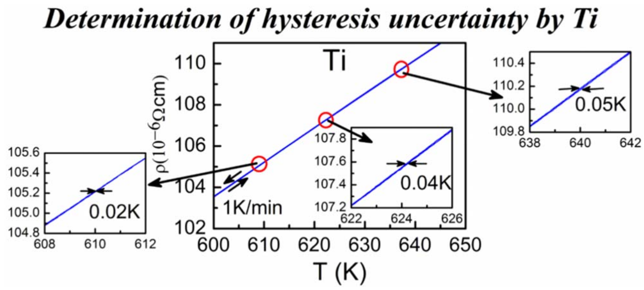


FIG. 1. (Color online) Uncertainty in our hysteresis measurement by electrical resistivity is as small as 0.05 K. Temperature dependence of electrical resistivity during a heating and cooling run is measured for a nontransforming metal Ti. The temperature range is the same as for the measurement of the ferromagnetic transition of Ni.

high purity: Ni (99.9%), Fe (99.5%), and Co (99.99%). $CoFe_2O_4$ was fabricated from 99.9% pure Fe_2O_3 and CoO by a solid-state reaction method. Second, to ensure high-temperature accuracy in the resistivity measurement, the thermocouple was directly welded onto the sample and the cold end of the thermocouple was kept in a water-ice mixture. Third, special care was made to ensure a precise control of temperature ramping and temperature homogeneity throughout the sample. Transition latent heat was measured by differential scanning calorimetry (DSC). To make a comparison with the behavior of a typical first-order transition, we also measured the thermal hysteresis and latent heat for two systems known to undergo a first-order transition: one is $BaTiO_3$ (undergoing a first-order ferroelectric transition);[19] the other is $Ti_{50}Ni_{47}Fe_3$ (undergoing a first-order ferroelastic or martensitic transition).[20]

To show the accuracy and high sensitivity of our hysteresis measurement with electrical resistivity, we tested a nontransforming metal, Ti wire, which should ideally have no hysteresis during a cooling and heating run in the temperature range of our interest. Figure 1 shows the result for a temperature range from 600 to 650 K, the same range as our experiment for Ni. It is clear that the hysteresis uncertainty is as small as 0.05 K. This high accuracy in hysteresis measurement ensures a reliable detection of transition hysteresis down to ~0.1 K. With such a high accuracy, we can reliably determine the small hysteresis associated with ferromagnetic transitions (0.25–1.9 K as will be shown later). Therefore, our resistivity experiment was performed with sufficient accuracy; and it can detect very small transition hysteresis. Such a high accuracy excludes the possibility that the measured hysteresis might be due to experimental error. DSC measurement can detect both transition latent heat and thermal hysteresis, but it has a higher uncertainty in hysteresis (0.2 ~ 0.6 K); thus we mainly use it to show transition latent heat.

We also took into account the possible effect of impurity on the experimental result. We found that the hysteresis associated with ferromagnetic transition is insensitive to impurity level. Transition hysteresis for 99.0%Ni, 99.9%Ni, and 99.98%Ni samples show a very similar hysteresis of 0.25–0.28 K being insensitive to impurity level. This excludes the possibility that the hysteresis may come from certain impurity effect.

III. RESULTS

Figure 2 shows the temperature dependence of electrical resistivity or impedance in the vicinity of T_c in the ferromagnetic systems of Ni, Fe, Co, and $CoFe_2O_4$ [Figs. 2(a)–2(d)], in the ferroelectric system of $BaTiO_3$ [Fig. 2(e)], and in the ferroelastic system of $Ti_{50}Ni_{47}Fe_3$ [Fig. 2(f)]. 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 second-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, 1.6, 1.9, and 1.5 K, respectively. This behavior is the same as that in the ferroelectric $BaTiO_3$ [Fig. 2(e)] and ferroelastic $Ti_{50}Ni_{47}Fe_3$ [Fig. 2(f)], which are known to undergo a first-order transition. The only difference is that $BaTiO_3$ and $Ti_{50}Ni_{47}Fe_3$ show a larger hysteresis (3.0

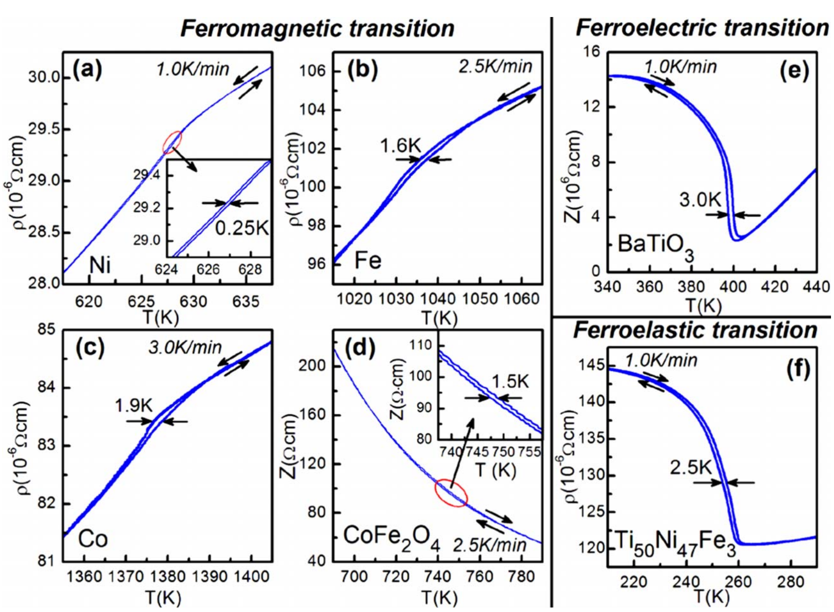


FIG. 2. (Color online) Evidence for transition hysteresis of several typical second-order ferromagnetic transitions. (a) Ni, (b) Fe, (c) Co, and (d) $CoFe_2O_4$. A comparison is made with a typical ferroelectric transition in (e) $BaTiO_3$ and a typical ferroelastic transition in (f) $Ti_{50}Ni_{47}Fe_3$.

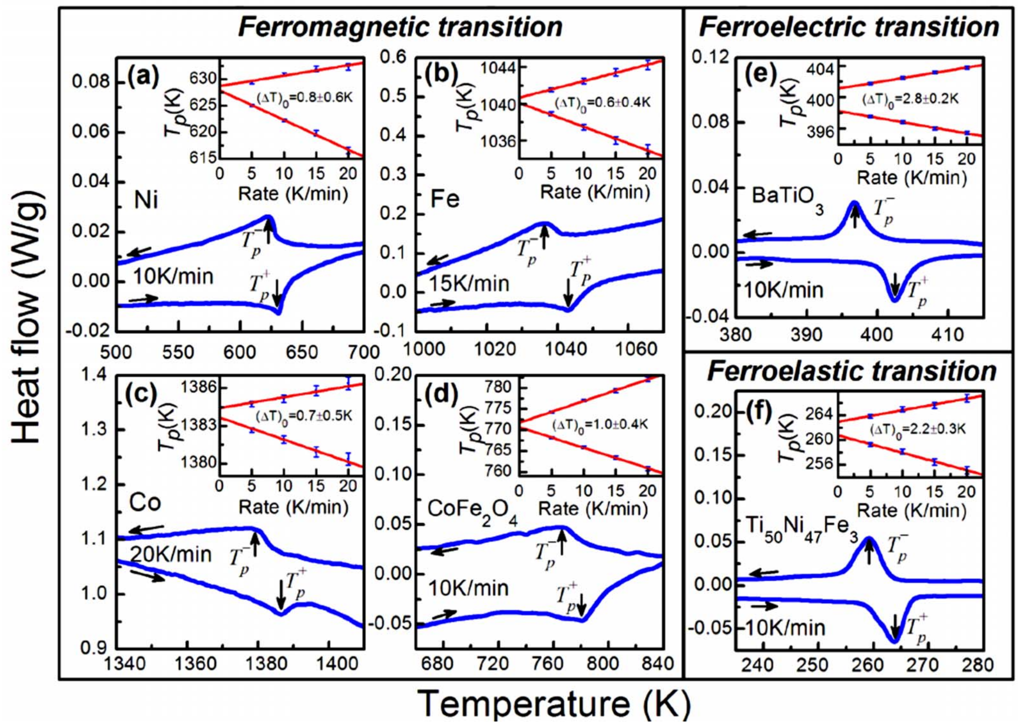


FIG. 3. (Color online) Evidence for the latent heat (DSC peak) of several typical second-order ferromagnetic transitions. (a) Ni, (b) Fe, (c) Co, and (d) $CoFe_2O_4$. A comparison is made with a typical ferroelectric transition in (e) $BaTiO_3$ and a typical ferroelastic transition in (f) $Ti_{50}Ni_{47}Fe_3$. The insets show the change in the thermal hysteresis (difference in the exothermic and endothermic peak temperature) with cooling and heating rate.

and 2.5 K, respectively). As the transition thermal hysteresis is the most prominent character of a first-order transition, the clear hysteresis in Ni, Fe, Co, and $CoFe_2O_4$ can be explained only by assuming these ferromagnetic systems undergo a first-order transition. The small hysteresis (about 0.25–1.9 K) indicates that these ferromagnetic systems undergo a weakly first-order transition.

Another prominent feature of first-order transition is the existence of the latent heat during the phase transition, which can be measured by DSC technique. Figure 3 shows the DSC curves for the typical ferromagnetic systems of Ni, Fe, Co, and $CoFe_2O_4$ [Figs. 3(a)–3(d)] during their ferromagnetic transitions; for a comparison, DSC curves for the ferroelectric $BaTiO_3$ [Fig. 3(e)] and ferroelastic $Ti_{50}Ni_{47}Fe_3$ [Fig. 3(f)] are also shown. It can be seen clearly that all the magnetic samples, Ni, Fe, Co, and $CoFe_2O_4$, show an endothermic and exothermic peak at their ferromagnetic transition temperature, like the case in the $BaTiO_3$ and $Ti_{50}Ni_{47}Fe_3$ at their structural transition temperature. As a second-order transition has no latent heat and a first-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 first-order transition, being qualitatively the same as the first-order nature of ferroelectric transition in $BaTiO_3$ and ferroelastic transition in $Ti_{50}Ni_{47}Fe_3$.

Figure 3 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 [Figs. 3(a)–3(d)]. This hysteretic feature is the same as $BaTiO_3$ [Fig. 3(e)] and $Ti_{50}Ni_{47}Fe_3$ [Fig. 3(f)], which are known to undergo first-order transition. Such a hysteresis does not vanish even when extrapolating the cooling and heating rate to zero, as shown in the insets. The hysteresis at zero cooling and heating rate for Ni, Fe, Co, and $CoFe_2O_4$ are 0.8 ± 0.6, 0.6 ± 0.4, 0.7 ± 0.5, and 1.0 ± 0.4 K, respectively; for $BaTiO_3$ and $Ti_{50}Ni_{47}Fe_3$, they have larger values of 2.8 ± 0.2 and 2.2 ± 0.3 K, respectively. The existence of transition hysteresis by DSC supports more accurate hysteresis measurement by resistivity or impedance, as shown in Fig. 2.

IV. DISCUSSION

Historically there exist a number of well-observed effects, which are not consistent with an ideal second-order ferromagnetic transition. The most familiar effect is the nondivergent susceptibility at T_c,[21] which is common for first-order transitions. However, the linkage of such an effect with possible first-order nature of these ferromagnetic transitions has not been explored. There are also many examples of alleged second-order transitions (e.g., ferroelectric transition in $BaTiO_3$) (Refs. 5 and 19) later turned out to be first order by more precise experiment. Therefore, precise and sensitive experiments are crucial for a correct identification of the order of a transition. In the present work, we used the most sensitive and accurate method—the detection of transition hysteresis and latent heat to examine whether a ferromagnetic transition is second order or first order.

From the thermal hysteresis and latent heat in Figs. 2 and 3, we can clearly see that these typical "second-order ferromagnetic transitions" turned out to be first-order transitions, being the same as the case for a typical ferroelectric transition and a ferroelastic transition. Such a result logically leads to a fundamental question: where is a true second-order ferromagnetic transition? We suggest that the scarcity of true second-order ferromagnetic transition stems from an inevitable coupling between the magnetization and the crystal lattice, as evidence by the existence of magnetostrictive effect in all ferromagnetic systems[22] and by the recent finding that there is a simultaneous structural change accompanying ferromagnetic transition.[11] In the following, by using a simple phenomenological approach, we show the coupling between magnetization $\boldsymbol{m}$ and strain $\boldsymbol{\varepsilon}$ can change an otherwise second-order transition into a first-order transition.

For a ferromagnetic system with two order parameters of $\boldsymbol{m}$ (primary) and $\boldsymbol{\varepsilon}$ (secondary), a generic Landau free energy can be expressed as[11,23]

$$\boldsymbol{F}(\boldsymbol{m},\varepsilon) = \frac{1}{2}\boldsymbol{a}(\boldsymbol{T})\boldsymbol{m}^2 + \frac{1}{4}\boldsymbol{b}\boldsymbol{m}^4 + \frac{1}{6}\boldsymbol{c}\boldsymbol{m}^6 + \frac{1}{2}\boldsymbol{K}\varepsilon^2 + \lambda\varepsilon \cdot \boldsymbol{m}^2. \tag{1}$$

It consists of three contributions: (i) the magnetic energy due to the primary order parameter $\boldsymbol{m}: \frac{1}{2}\boldsymbol{a}(\boldsymbol{T})\boldsymbol{m}^2 + \frac{1}{4}\boldsymbol{b}\boldsymbol{m}^4 + \frac{1}{6}\boldsymbol{c}\boldsymbol{m}^6$, where the coefficient $\boldsymbol{a}(T)$ of the harmonic term is assumed to be temperature dependent; we assume the system intrinsically tends to undergo a second-order transition and thus the coefficient $\boldsymbol{b}$ of the fourth order term is positive ($\boldsymbol{b}>0$); $\boldsymbol{c}$ is the coefficient of sixth order term and $\boldsymbol{c}>0$. (ii) The elastic energy due to the secondary order parameter $\boldsymbol{\varepsilon}: \frac{1}{2}\boldsymbol{K}\varepsilon^2$ ($\boldsymbol{K}$ is the elastic modulus and thus $\boldsymbol{K}>0$). (iii) The magnetoelastic coupling energy: $\lambda\varepsilon \cdot \boldsymbol{m}^2$ (λ is the coupling coefficient).

Minimizing the total energy with respect to the strain (i.e., $\partial F/\partial \boldsymbol{\varepsilon}=0$) yields a relation between $\boldsymbol{m}$ and $\boldsymbol{\varepsilon}$,

$$\varepsilon = -\frac{\lambda}{\boldsymbol{K}}\boldsymbol{m}^2. \tag{2}$$

Substituting Eq. (2) into Eq. (1), we obtain a renormalized 2-4-6 Landau free energy,

$$\boldsymbol{F}(\boldsymbol{m}) = \frac{1}{2}\boldsymbol{a}(\boldsymbol{T})\boldsymbol{m}^2 + \left(\frac{1}{4}\boldsymbol{b} - \frac{\lambda^2}{2\boldsymbol{K}}\right)\boldsymbol{m}^4 + \frac{1}{6}\boldsymbol{c}\boldsymbol{m}^6. \tag{3}$$

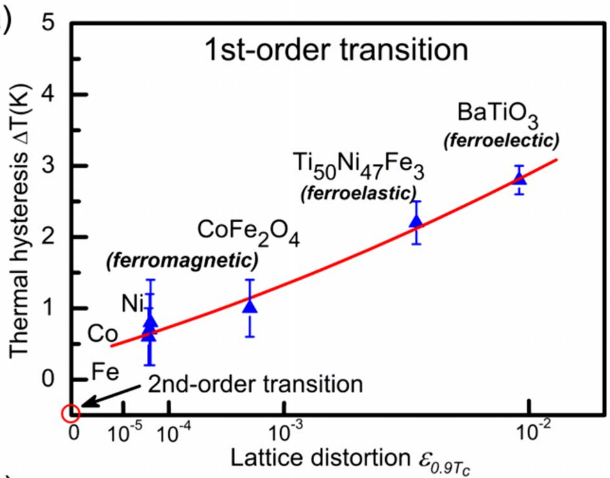
The most interesting consequence of the magnetoelastic coupling is that the fourth order term is renormalized and now it becomes $(\frac{1}{4}\boldsymbol{b} - \frac{\lambda^2}{2\boldsymbol{K}})\boldsymbol{m}^4$. As the coefficient $\boldsymbol{b}(>0)$ is usually a small positive constant[23] and elastic modulus is always positive ($\boldsymbol{K}>0$), a coupling coefficient λ of certain magnitude can make $(\frac{1}{4}\boldsymbol{b} - \frac{\lambda^2}{2\boldsymbol{K}})<0$. Because a negative fourth order term in Landau free energy creates an energy barrier in the free-energy landscape, this leads to a first-order transition and explains why a true second-order ferromagnetic transition is so scarce. It is also noted that a renormalization-group approach[24] also yields a similar conclusion: a second-order transition would change into the first-order transition if a three-component order parameter (e.g., magnetic moment) is coupled to the strain in the fluctuation region near T_c.

Moreover, if the secondary order parameter is volume strain, magnetoelastic coupling can lead to volume magnetostriction, and such a coupling may also result in the first-order ferromagnetic transition, as discussed in MnAs.[25] Furthermore, if the secondary order parameter is an electric dipole, the magnetoelectric coupling may results in a magnetoelectric effect and such a coupling may also create a first-order transition. This interesting prediction needs future verification.

Equation (3) allows for an interesting prediction about the relationship between the strength of the magnetoelastic coupling and the size of the hysteresis of the resultant first-order transition. It is known that the size of hysteresis for a first-order transition is determined by the energy barrier at T_c, which is largely dependent on the magnitude of the negative fourth order term.[26] The more negative is this term, the larger is the transition barrier and the thermal hysteresis. A large magnetoelastic coupling coefficient λ contributes to a large negative fourth order term $(\frac{1}{4}\boldsymbol{b} - \frac{\lambda^2}{2\boldsymbol{K}})\boldsymbol{m}^4$ and thus contributes to a larger transition hysteresis. On the other hand, from Eq. (2) we can see that a larger λ also leads to a larger spontaneous lattice distortion upon the ferromagnetic transition. Therefore, the strength of the magnetoelastic coupling λ can be represented by the magnitude of the spontaneous lattice distortion.[11] As the result, Eq. (3) predicts that the magnitude of transition thermal hysteresis increases with the increase in lattice distortion. Similar conclusion can also be drawn for the ferroelectric transition[20] and ferroelastic transition.[26,27]

Figure 4(a) shows the experimental result about the relationship between the lattice distortion and the thermal hysteresis for the ferromagnetic Ni, Fe, Co, $CoFe_2O_4$, ferroelectric $BaTiO_3$, and ferroelastic $Ti_{50}Ni_{47}Fe_3$ systems we studied. The values of lattice distortion and hysteresis are given in Fig. 4(b). It is of interest to see that the thermal hysteresis in these ferroic transitions indeed increases with increasing lattice distortion, but the relation is not linear. For $BaTiO_3$ and $Ti_{50}Ni_{47}Fe_3$, the lattice distortion is large and can be easily detected by conventional x-ray diffraction (XRD); this corresponds to a relatively large thermal hysteresis (above 2.0 K). For $CoFe_2O_4$, the lattice distortion is smaller and but can be detected by high-resolution synchrotron XRD (Ref. 11); this corresponds to a smaller thermal hysteresis (about 1.0 K). For Ni, Fe, and Co, the lattice distortion is so small that it is out of the detection limit of any available diffraction technique[11] and can be estimated only by indirect magnetostriction measurement; this corresponds to the smallest hysteresis (less than 1.0 K). From Fig. 4, it is noted that a ferromagnetic transition usually has much smaller hysteresis compared with a ferroelectric transition or a ferroelastic transition due to the weaker coupling effect. This explains why ferromagnetic transition in most ferromagnetic systems has been considered as being second order; it is simply because the transition hysteresis is usually too small to detect. Figure 4 also has an important implication: a "true" second-order ferromagnetic transition exists only in a system with zero magnetoelastic distortion or zero magnetostriction [the point at the origin in Fig. 4(a)]. However, such a system does not seem to exist because all known ferromagnetic systems have nonzero magnetostriction. Nevertheless, it should be noted that magnetoelastic coupling may not always be weak. In

(a)



(b) **Thermal hysteresis, crystal symmetry and lattice distortion for above ferroic transition**

Ferroic materials (cubic para-phase)	T_C(K)	Non-cubic ferro-phase	$\|\varepsilon\|_{0.9T_c}$ $\times10^{-3}$	Thermal hysteresis (K)
$BaTiO_3$	402	T	8	2.8±0.2
$Ti_{50}Ni_{47}Fe_3$	263	R	3.5	2.2±0.3
$CoFe_2O_4$	760	T	0.4	1.0±0.4
Ni	631	R	0.020	0.8±0.6
Fe	1043	T	0.018	0.6±0.4
Co	1423	R	0.020	0.7±0.5

FIG. 4. (Color online) The relationship between the thermal hysteresis and lattice distortion for several typical ferromagnetic, ferroelectric, and ferroelastic transitions. (a) Lattice distortion (at $0.9T_c$) dependence of the thermal hysteresis. The horizontal axis takes a cube root scale, so as to reveal the tiny strain over a proper scale. (b) Data of the thermal hysteresis, crystal symmetry (*R*: rhombohedral; *T*: tetragonal), and the lattice distortion at $0.9T_c$ for several typical ferroic systems. The distortion data of $Ti_{50}Ni_{47}Fe_3$ and Co are from Refs. 20 and 22, respectively; the data of Ni, Fe, $BaTiO_3$, and $CoFe_2O_4$ are from our recent work (Ref. 11).

ferromagnetic martensite such as Ni_2MnGa, Fe-Pt,[28] the coupling may be quite large, leading to a large structure change at T_c.

The finding of the first-order nature of ferromagnetic transitions may lead to important consequences. First, it indicates that a "pure" magnetic transition does not exist: the magnetic moment is always coupled to other ferroic order parameters like strain and polarization. Such a multiferroic coupling can explain many important multiferroic phenomena such as magnetostriction[22] and magnetoelectricity.[29,30] Second, it may lead to new insight into how to develop highly magnetoresponsive materials. To obtain a high magnetoresponsive effect (such as magnetostrictive effect[22] and magnetocaloric effect[31,32]), a strong-coupling effect is required. By referring to Fig. 4, such materials may be found in the systems with large lattice distortion or large transition hysteresis. Finally, as magnetic elements Ni, Fe, and Co are shown to undergo a weakly first-order ferromagnetic transition, we can predict that another magnetic element Gd, which has been studied recently,[33] may also undergo first-order ferromagnetic transition. This interesting prediction awaits future experiment to confirm.

V. CONCLUSION

In summary, by thermal hysteresis and latent heat measurement we showed that the most typical "second-order" ferromagnetic transitions in Ni, Fe, Co, and $CoFe_2O_4$ turned out to be first-order transitions. We suggest that the first-order nature of ferromagnetic transitions is attributed to an inevitable magnetoelastic coupling in all ferromagnetic systems. The finding of the first-order nature of ferromagnetic transition indicates that a ferromagnetic transition is always accompanied by a coupling effect. Such a coupling leads to the multiferroic effect and may provide an insight into developing highly magnetoresponsive materials. It also suggests a need to reconfirm other alleged second-order transitions so far reported.

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