Influence of Tb on easy magnetization direction and magnetostriction of ferromagnetic Laves phase $GdFe_2$ compounds*

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The crystal structure, magnetization, and spontaneous magnetostriction of ferromagnetic Laves phase $GdFe_2$ compound have been investigated. High resolution synchrotron x-ray diffraction (XRD) analysis shows that $GdFe_2$ has a lower cubic symmetry with easy magnetization direction (EMD) along [100] below Curie temperature T_C. The replacement of Gd with a small amount of Tb changes the EMD to [111]. The Curie temperature decreases while the field dependence of the saturation magnetization (M_s) measured in temperature range 5–300 K varies with increasing Tb concentration. Coercivity H_c increases with increasing Tb concentration and decays exponentially as temperature increases. The anisotropy in $GdFe_2$ is so weak that some of the rare-earth substitution plays an important role in determining the easy direction of magnetization in $GdFe_2$. The calculated magnetostrictive constant λ_{100} shows a small value of 37×10^{-6}. This value agrees well with experimental data 30×10^{-6}. Under a relatively small magnetic field, $GdFe_2$ exhibits a V-shaped positive magnetostriction curve. When the field is further increased, the crystal exhibits a negative magnetostriction curve. This phenomenon has been discussed in term of magnetic domain switching. Furthermore, magnetostriction increases with increasing Tb concentration. Our work leads to a simple and unified mesoscopic explanation for magnetostriction in ferromagnets. It may also provide insight for developing novel functional materials.

Keywords: crystal structure, magnetic anisotropy, lattice distortion, magnetostriction

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1. Introduction

The RFe_2 (R = rare earth) Laves phase compounds are known to possess large cubic anisotropy and huge magnetostriction at room temperature as compared to the RCo_2 and RNi_2 compounds.[1,2] The RFe_2 compounds crystallize in a $MgCu_2$ (C15) type structure. These compounds are known to exhibit diverse magnetic properties due to the competition between the exchange interaction and the crystalline electric field effects.[3,4] Among them, $TbFe_2$ and $SmFe_2$ possess the largest known positive and negative magnetostriction at room temperature, respectively. In these compounds, the easy axis of magnetization is parallel to the [111] direction and the magnetostriction coefficient λ_{111} is positive for $TbFe_2$ and negative for $SmFe_2$.[5,6] Barbara *et al.* reported that in the magnetically ordered state, the allegedly cubic $SmFe_2$ and $TmFe_2$ compounds actually show a pronounced rhombohedral distortion at room temperature with easy magnetization direction (EMD) along [111].[7] Cullen and Clark have shown that in the RFe_2 Laves compounds having the spontaneous axis of magnetization parallel to the [111] direction, an internal rhombohedral distortion takes place. This distortion is coupled to the external strain and leads to the giant observed magnetostriction.[8] On the contrary, the $DyFe_2$ and $HoFe_2$ Laves compounds possess EMD parallel to the [100] direction.[9] Cullen and Clark showed that there is no corresponding structural distortion associated with this direction and, therefore, the compounds maintain their cubic symmetry. However, the existence of the magnetostrictive effect in these ferromagnetics systems suggests that the magnetic moment is invariably coupled to the crystal lattice;[10,11] hence magnetic ordering appears to have the potential to cause a change in the crystal structure.

Recently, the Mössbauer effect measurements have been used for the determination of the easy direction of magnetization in polycrystalline magnetic materials containing Fe, including the intermetallic compounds with the cubic Laves structure RFe_2. The first experiment of $GdFe_2$ was done by Bowden e*t al.*[12] The spectrum obtained at 77 K was complicated, suggesting that the easy direction of magnetization lies along neither [100], [110], nor [111]. However, Atzmony and Dariel[13] reported a single six-line pattern, indicating the [100] easy direction, whereas the [110] easy direction has been proposed by Barb *et al.*, who observed a spectrum consisting of two sets of six-lines with equal intensity at 77 K.[14] In order to remove the discrepancies between these results and to find the EMD in $GdFe_2$, we have prepared samples of $GdFe_2$, giving attention to the effect of adding some rare earth in the Gd metal ingots on the EMD. In addition, magnetostriction can be a sensitive tool for the detection of the different mechanisms which constitute the magnetization process.[15] For instance, in a material such as iron, the shape of the magnetostriction-

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field curve for a polycrystalline sample changes markedly in the regions associated with domain wall displacements, rotation of the magnetization against anisotropy. This description is much clearer in magnetostriction than in the corresponding magnetization curves. Magnetostriction measurements have been previously reported in the isostructural compounds $R\mathrm{Fe}_2$ (R = Tb, Dy, Ho, Er). [3,4] In these materials, over the temperature range 77–300 K, the magnetostriction was found to be below saturation at the maximum applied field of 2.5 T. However there are rarely studies on ferromagnetic Laves phase GdFe_2. The objective of the present work is to study the structural symmetry and magnetostriction in the ferromagnetic GdFe_2 and the effect of the rare earth (Tb) substitution on the structural and magnetoelastic properties.

2. Experimental details

In order to clarify the influence of rare earth impurities, the samples of pure GdFe_2 alloy and with a small amount of Tb were prepared by the arc melting method with the raw materials of Gd, Tb (99.5%), and Fe (99.9%) in an argon atmosphere. To ensure homogeneity, the samples were melted four times. High-resolution synchrotron XRD experiments were performed to determine the crystal symmetry. For the experiments, small parts of the samples were ground into powder and sealed into quartz capillaries with a diameter of 0.3 mm at beamline 11-BM, Advanced Photon Source (APS), Argonne National Laboratory. The wavelength of the synchrotron x-ray was 0.413677 Å. During the synchrotron XRD measurement, the capillary was rotating in order to average the intensity as well as to reduce the preferred orientation effect. The polycrystalline samples were used for the physical property measurements. The magnetizations (M) versus temperature (T) curve was measured by a vibrating sample magnetometer (VSM). The magnetization (M) versus magnetic field (H) hysteresis loops were measured by using Quantum Design SQUID. The room temperature magnetostriction was measured with the standard strain gauge bridge technique with a gauge factor of 2.11±1% under fields of 10 kOe and 50 kOe.

3. Results and discussion

Figure 1(a) shows the [222], [440], and [800] reflections measured by high resolution synchrotron XRD. It is clearly seen that at high temperature 850 K, the characteristic reflections of 222, 440, and 800 show no splitting. All these characteristic reflections can be fitted by a single peak as shown in Fig. 1(a). These features characterize a cubic structure for ferromagnetic GdFe_2. At 300 K, characteristic 222 and 440 peaks can be fitted by single peaks, indicating that there is no splitting in 222 and 440 reflections, but characteristic splitting in 800 reflections can be fitted by double peaks, indicating the splitting in 800 reflections as shown in the bottom of Fig. 1(a). These features show that GdFe_2 has a lower cubic symmetry and characterizes a tetragonal symmetry. The direction of the spontaneous magnetization M_s is along [100] (Fig. 1(b)). The lattice parameters corresponding to different crystal symmetries are shown in Fig. 1(b). The lattice parameter a is a little bit larger than c, indicating a small tetragonal distortion of GdFe_2.

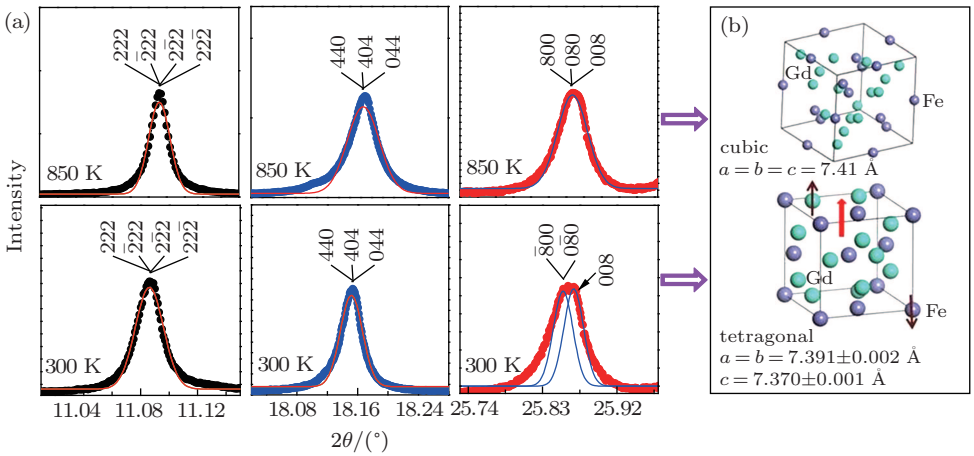


Fig. 1. (color online) (a) The synchrotron x-ray diffraction patterns (typical 222, 440, and 800 peaks, with wavelength of 0.413677 Å) for GdFe_2 at 850 K and 300 K. The resonant black, blue, and red lines are the experimental XRD data and the thinner red and blue lines are the fitted ones. (b) The corresponding cubic and tetragonal structures with lattice parameters. The red arrow shows the easy magnetization direction of the tetragonal phase.

In order to clarify the influence of the rare earth impurity, the high resolution synchrotron XRD profiles for $\mathrm{Gd}_{0.9}\mathrm{Tb}_{0.1}\mathrm{Fe}_2$, $\mathrm{Gd}_{0.7}\mathrm{Tb}_{0.3}\mathrm{Fe}_2$, and $\mathrm{Gd}_{0.5}\mathrm{Tb}_{0.5}\mathrm{Fe}_2$ are shown in Fig. 2(a). The results show that the splitting in 222 and 440 reflections can be fitted by double peaks and the characteristic splitting in 800 reflections can be fitted by single peaks. These features show that $\mathrm{Gd}_{0.9}\mathrm{Tb}_{0.1}\mathrm{Fe}_2$, $\mathrm{Gd}_{0.7}\mathrm{Tb}_{0.3}\mathrm{Fe}_2$, and $\mathrm{Gd}_{0.5}\mathrm{Tb}_{0.5}\mathrm{Fe}_2$ have a rhombohedral symmetry with EMD

along [111] as shown in Fig. 2(b). From Fig. 2(a), it is clear that the splitting in 222 and 440 characristics becomes more obvious as the Tb concentration increases. The observed structural evolution of $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$ is consistent with the established relation between the easy axis direction and the crystal symmetry as shown in Figs. 1(b) and 2(b).[16]

The previous study reveals that the easy axis of magnetization which is usually a major crystallographic direction depends on whether the magnetocrystalline anisotropy comes mainly from the interaction of the rare earth (RE) or transition metal (Fe) ions with the crystalline electric field (CEF). With regard to the magnetocrystalline anisotropy of RE, it is believed that the 4f electrons in the RE ions are responsible for the main part of the magnetic anisotropy and that the CEF acting on the 4f electrons dominates this property.[17] In case of the Gd compound, because of the zero orbital magnetic moment ($L = 0$) for Gd,[18] the spin–orbit coupling almost disappears and there is no crystal field anisotropy. High resolution synchrotron XRD results show that a major symmetry axis as a direction of easy magnetization, i.e., [111], can be obtained for $GdFe_2$ by adding a small amount of Tb. From this, it can be concluded that the magnetic anisotropy of $GdFe_2$ is very weak so that some specific rare earth impurities are able to enforce their own anisotropy.

In the past, it was shown that a ferromagnetic transition involves only an ordering of magnetic moment and the crystal structure remains unchanged, i.e, paramagnet cubic changes into ferromagnetic cubic below the Curie temperature evidenced by 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 the crystal structure. Our high resolution synchrotron XRD gives direct evidence for the lower symmetry of the cubic ferromagnets. These results reveal that the ferromagnetic transition is also a structural transition, resulting in a low crystallographic symmetry, which is a general effect for all cubic ferromagnets.

In $GdFe_2$, a tetragonal distortion with EMD along [100] results in the splitting of the (800) reflections as shown in Figs. 1(a) and 1(b). Thus we used characteristic (800) peak splitting to calculate magnetostriction coefficient λ_{100} for $GdFe_2$. The calculated λ_{100} is 37×10^{-6}, which agrees well with the previous reported value 42×10^{-6}.[9]

The temperature dependence of the magnetization (M–T) measured by VSM is shown in Fig. 3. The Curie temperature T_C, which is derived by extrapolating M^2 to zero on the basis of the linear part of the M^2 versus T curve, is found to be 798 K, which agrees with the previous reported value. The Curie temperature decreases with increasing Tb concentration (Fig. 3). In rare-earth–transition-metal (RFe_2) compounds, T_C

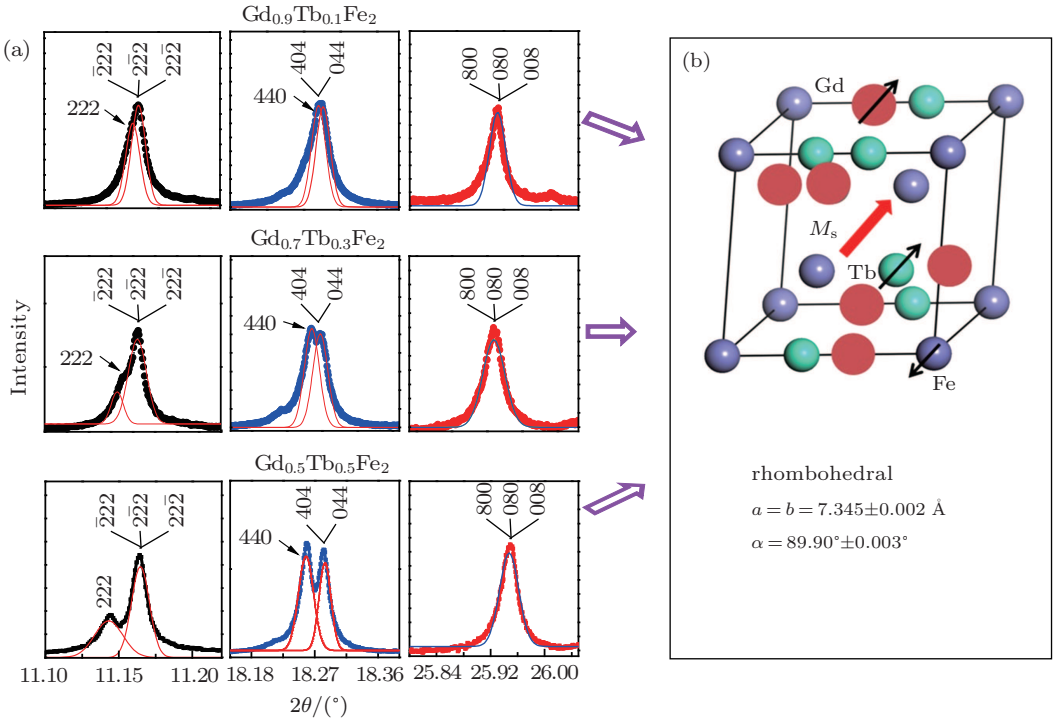


Fig. 2. (color online) (a) The synchrotron x-ray diffraction patterns (typical 222, 440, and 800 peaks, with wavelength of 0.413677 Å) for $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, $Gd_{0.5}Tb_{0.5}Fe_2$ at room temperature. The resonant black, blue, and red lines are the experimental XRD data and the thinner red and blue lines are the fitted ones. (b) Rhombohedral symmetry with corresponding lattice parameters. The red arrow shows the easy magnetization direction of the rhombohedral phase.

is determined by the 3d–3d, 3d–4f, and 4f–4f exchange interactions because of the localized 4f electrons of the rare earth.[19] Generally, for rare-earth transition metal intermetallic compounds, the 3d–4f spin–spin coupling is antiferromagnetic, leading to a parallel alignment of 3d and 4f moments in the light lanthanide compounds ($J = L - S$) and to an antiparallel alignment in the heavy lanthanide compounds ($J = L + S$).[20,21] Here L is the total orbital moment resulting from the momenta of the 4f electrons and S is the total spin moment from the individual spin of electrons. As the 4f orbital of Gd is half filled, the 5d orbital is less than half-filled, and the 3d states of Fe are filled more than half, the ferromagnetic exchange interaction between the 4f and 5d spins and the interatomic exchange interactions between the 3d and 5d electrons lead to an antiparallel 3d–4f coupling.[22,23] This 3d–4f hybridization is strong in $GdFe_2$.[24] Therefore, it is coherent that $GdFe_2$ has high T_C as compared to other RFe_2 compounds such as $TbFe_2$, $SmFe_2$, $TmFe_2$ $DyFe_2$, $NdFe_2$, and $PrFe_2$.

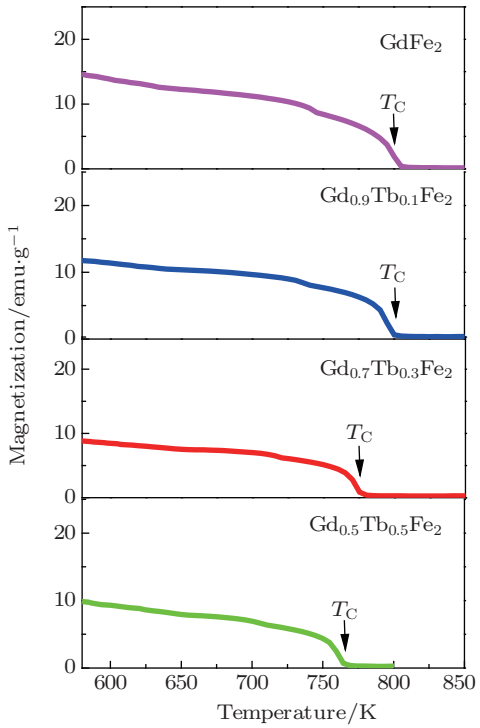


Fig. 3. (color online) Temperature dependence of magnetization (M–T) for $GdFe_2$,$Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$.

The magnetic hysteresis loops for $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$ have been measured at different temperatures as shown in Fig. 4(a). For $GdFe_2$, the magnetization curves show saturation even in fields lower than 12 kOe as shown in Fig. 4(a). It indicates that $GdFe_2$ has a low anisotropy and the magnetic domains easily rotate, yielding saturation magnetization. Figure 4(a) shows that the magnetization varies with the Tb concentration.

Following the general rule of the magnetic coupling, Fe couples antiparallel to the rare earth Gd as shown in Figs. 1(b) and 2(b). The total moment μ for $GdFe_2$ can be written as

$$\mu = \mu_{Gd} - 2\mu_{Fe}. \quad (1)$$

By assuming Gd as a free ion, its magnetic moment is 7 μ_B. Moreover, at 5 K, the M_s for $GdFe_2$ is 81.54 emu/g, which is equivalent to 3.926 μ_B. Then one can calculate that the magnetic moment per ion is 1.53 μ_B in $GdFe_2$. The previous work shows that the magnetic moment per ion is 1.60 μ_B in $GdFe_2$.[25] Our calculated value agrees with the previously reported value. $GdFe_2$ is free of crystal field effects since Gd^{3+} is in an S state. Hence assuming ferromagnetic coupling, the Fe moment in $GdFe_2$ is 1.60 μ_B as contrasted with 1.45 μ_B in $LuFe_2$ or $ZrFe_2$. Thus, the iron moment is variable in the $LnFe_2$ series. The magnetization of $GdFe_2$ is dominated at all temperatures by the Gd sublattice moment, thus the material does not exhibit a spin compensation temperature at which the atomic moments cancel and the overall moment is zero. The decrease in the magnetization with temperature (Fig. 4(a)) is almost entirely due to the temperature change of the magnetic moment of the rare earth atoms. The iron moment μ_{Fe} is nearly temperature independent.

The magnetization measurements show that coercive field H_c increases with Tb concentration as shown in the inset of Fig. 4(a) and decreases in an exponential way as the temperature increases as shown in Fig. 4(b). It must be noted that coercivity is not an intrinsic magnetic property; it depends not only on the temperature but also on the magnetic anisotropy. The temperature dependence of H_c is shown in Fig. 4(b). The temperature dependence of H_c for this compound is related to the saturation magnetization M_s and magnetic anisotropy K. The M_s decreases with increasing temperature for this compound. Thus, the decrease of H_c with temperature should be associated with the decrease of K with temperature.

Figure 5 demonstrates the room temperature magnetostriction curves of $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$ under fields of 10 kOe and 50 kOe, respectively. For $GdFe_2$ under the low field of 10 kOe, the magnetostriction curve shows a V-like shape, as shown in Fig. 5(a). However under the large field of 50 kOe, the magnetostriction curve goes in a downwards direction with further increasing magnetic field and reaches a negative value at $H = 50$ kOe. For $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$, the magnetostriction curves show a V-like shape at both fields of 10 kOe and 50 kOe (Fig. 5(a)).

The previous literature shows that a structure change takes place at the ferromagnetic transition, so the magnetostrictive behavior of the $GdFe_2$ system can be taken into account by the switching of the noncubic ferroelastic domains, and the magnitude of magnetostriction is proportional to the size of the lattice distortion.[18] The state of T-phase (Fig. 1) indicates the domain configuration of the tetragonal

nanodomains. Figures 5(b) and 5(c) schematically explain the mechanism of magnetostriction of $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$. With an applied external magnetic field, the crystal with T-symmetry elongates along the *c*-direction because of the first step of 180° domain switching, exhibiting a V-shaped positive magnetostriction curve ($\Delta L_{T1} > 0$). When the field is further increased, the crystal contracts along the field because of the second step of 180° domain switching, as a result, magnetostriction shows a shrinking behavior ($\Delta L_{T2} < 0$) with a negative magnetostriction curve as shown in Fig. 5(b). For $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$, the crystal with R-symmetry elongates along the field direction and exhibits a positive magnetostriction (V-shaped curve) as shown in Fig. 5(c).

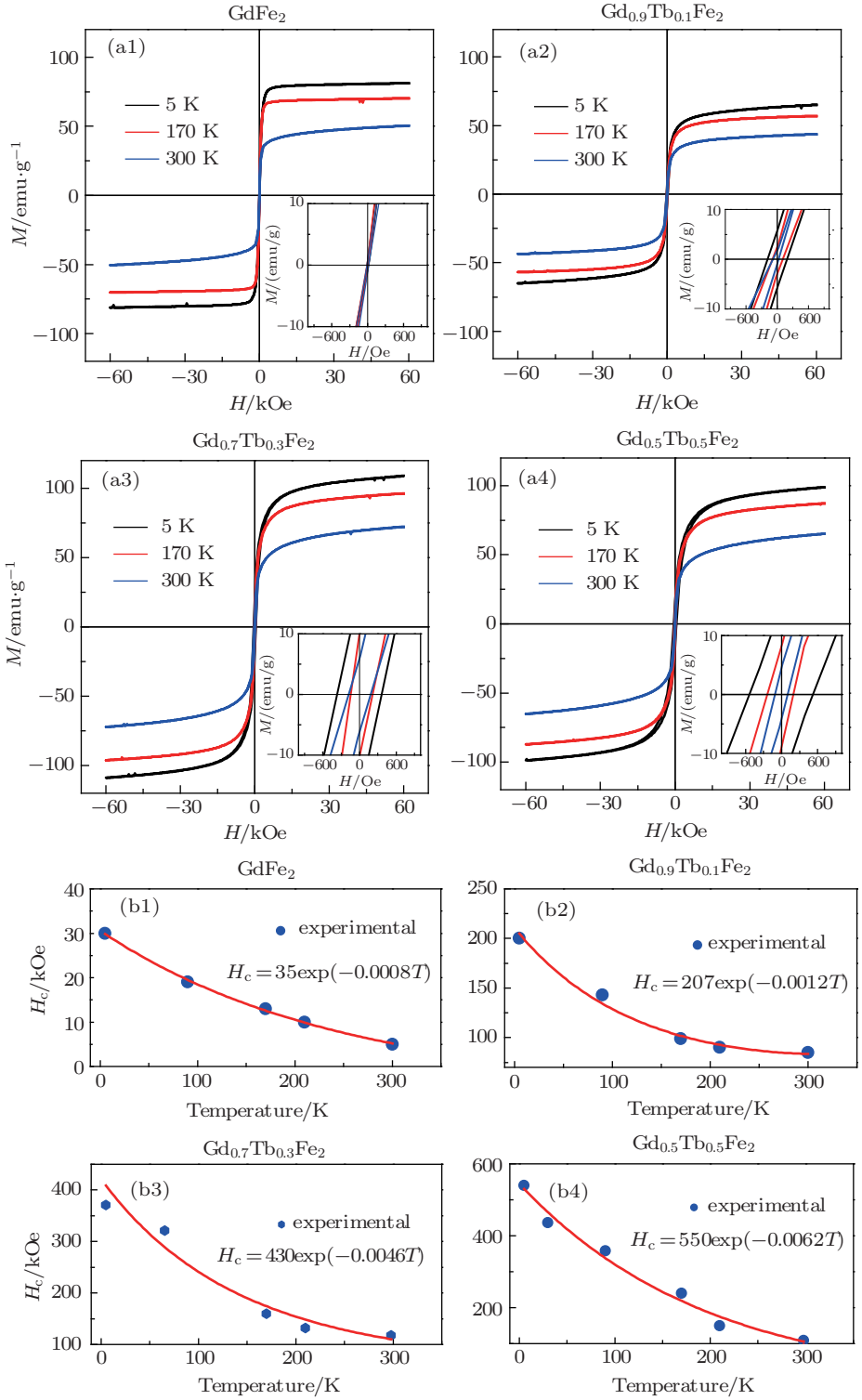


Fig. 4. (color online) (a) Magnetic hysteresis loops at different temperatures. (b) Exponential fitting of coercive field for $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$.

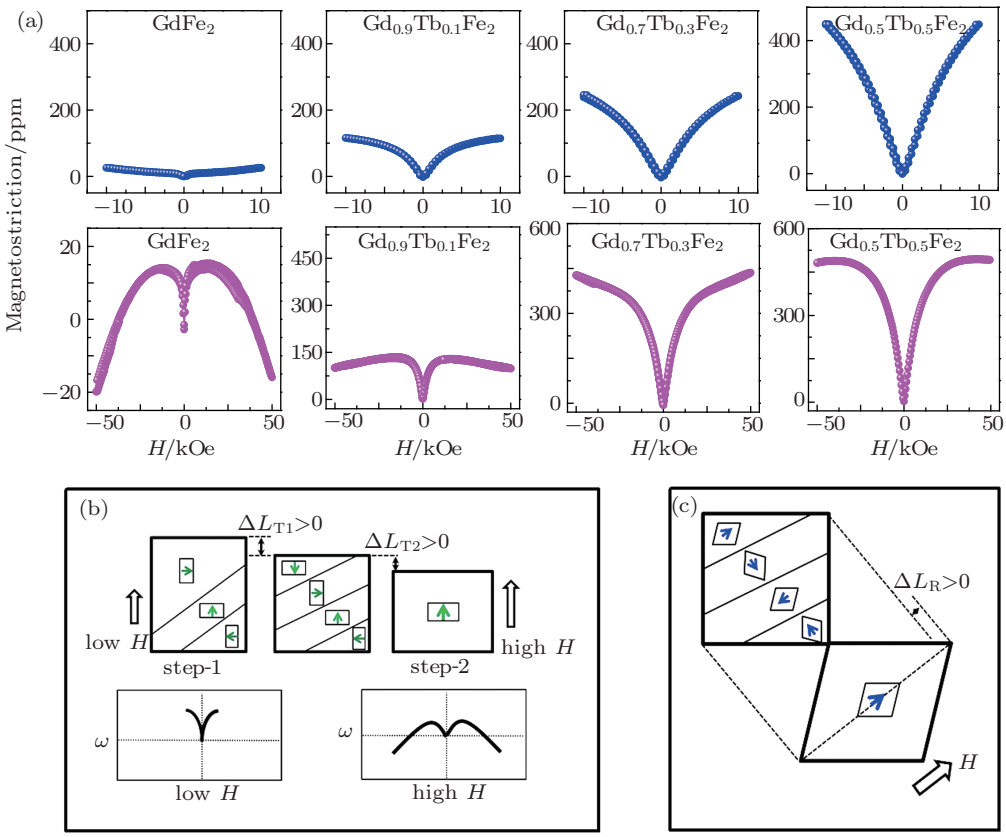


Fig. 5. (color online) (a) Room temperature magnetostriction curves for $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_2$ under applied fields of 10 kOe and 50 kOe. The schematically mesoscopic explanations for anisotropic magnetostriction due to the switching of the noncubic ferromagnetic (ferroelastic) domains with different crystal symmetries, respectively: (b) for $GdFe_2$ with tetragonal phase; (c) for $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, $Gd_{0.5}Tb_{0.5}Fe_2$ with rhombohedral phase. 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 H.

4. Conclusion

The structural and magnetostrictive properties of ferromagnetic $GdFe_2$ have been studied. The $GdFe_2$ crystal has a lower cubic symmetry. The low crystal symmetry of the ferromagnetic phase provides a simple mesoscopic explanation for the commonly observed magnetostrictive effect. The anisotropy of $GdFe_2$ can be changed by adding a small content of Tb. Due to strong 3d–4f coupling, $GdFe_2$ has a high Curie temperature among RFe_2 compounds. A ferromagnetic transition is not just an ordering of the magnetic moment, it also involves a structure change. Simultaneous structural changes at the ferromagnetic transitions may provide a new idea to develop novel materials with high magneto-response. The anisotropic magnetostriction in $GdFe_2$, $Gd_{0.9}Tb_{0.1}Fe_2$, $Gd_{0.7}Tb_{0.3}Fe_2$, and $Gd_{0.5}Tb_{0.5}Fe_5$ can be simply explained by the switching of the non-cubic ferroelastic domains. This explanation for magnetostriction is physically the same as that for the electrostrain effect in ferroelectrics.

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