Structure and magnetocrystalline anisotropy of $R_2Fe_{17-x}Ga_x$ compounds with higher Ga concentration

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(Received 4 May 1995; accepted for publication 19 July 1995)

The effect of Ga substitution for Fe in R_2Fe_{17} (R=Y, Sm, Gd, Tb, Dy, Ho, Er, and Tm) compounds on the structure and magnetocrystalline anisotropy has been studied by means of x-ray diffraction and magnetization measurements. Both iron sublattice anisotropy and rare earth sublattice anisotropy are found to be modified by the introduction of the gallium atoms. A uniaxial anisotropy is shown in $R_2Fe_{17-x}Ga_x$ (for R=Y, Gd, Tb, Dy, Ho, Er, and Tm) compounds with high Ga concentration, whereas a reversal change in the easy magnetization direction is observed in the samples for R=Sm. The contributions to the uniaxial orientation of the magnetization in these compounds result from not only the rare earth sublattice, but also the iron sublattice. © *1995 American Institute of Physics.*

The fact that none of the R_2Fe_{17} (R=rare earth elements) compounds exhibits a room temperature *c*-axis anisotropy restricts the possible applications of these materials as permanent magnets. In order to improve the room temperature uniaxial anisotropy of these compounds, many investigations have been focused on either substituting other elements into the R_2Fe_{17} structure or preparing materials with additional atoms located interstitially.[1–3] Recently, it was found that an easy *c*-axis anisotropy was induced by the substitution of Ga or Al for Fe in Sm_2Fe_{17} without introducing interstitial carbon or nitrogen atoms.[4,5] These compounds seem to give us a new hope in obtaining stable and high performance permanent magnets. However, it is difficult to distinguish whether the increase in the bulk uniaxial anisotropy results from the enhancement of Sm^{3+} sublattice uniaxial anisotropy or the decrease in the iron sublattice planar anisotropy. In order to obtain more information concerning the effect of Ga substitution on the magnetocrystalline anisotropy for the rare-earth iron 2:17 compounds, we extend this study to the whole lanthanide series, including R=Y, which has no contribution to the magnetocrystalline anisotropy of rare earth sublattices.

Samples with the nominal composition $R_2Fe_{17-x}Ga_x$ (R=Y, Sm, Gd, Tb, Dy, Ho, Er, and Tm; $0 \leqslant x \leqslant 8$) were arc melted in a high purity argon atmosphere. The button alloys were remelted at least four times to ensure homogeneity, then annealed under an argon atmosphere at 1273 K for 24 hours, followed by quenching into water. X-ray diffraction measurements on powder samples were performed using Cu $K\alpha$ radiation to determine the crystallographic structure and phase purity. X-ray diffraction patterns indicate that all samples have a hexagonal Th_2Ni_{17}-type structure or a rhombohedral Th_2Zn_{17}-type structure. The lattice constants *a*,*c* and the unit cell volumes can be obtained from fitting the rotation anode x-ray data. In order to compare the volumes of the hexagonal cells with the rhombohedral cells, we have multiplied the former by 3/2. Figure 1 shows the unit cell volumes of $R_2Fe_{17-x}Ga_x$ compounds as a function of Ga concentration. It can be seen that the substitution of larger Ga atoms for smaller Fe leads to an approximately linear increase in the unit cell volumes at a rate of about 8.7 $Å^3$ per Ga atoms.

The values of Curie temperature were derived from the temperature dependence of magnetization $\sigma(T)$ curves measured by a vibrating sample magnetometer in a low magnetic field of 1 kOe. The Ga-concentration dependence of Curie temperature indicates that the maximum values of Curie temperature occur at about x=3. In general, the Curie temperature in Fe-rich rare-earth–iron compounds is mainly dominated by the exchange interaction of the iron sublattice, which is strongly dependent on the Fe–Fe interatomic distance. The generally low values of Curie temperature in R_2Fe_{17} compounds result from the relatively small Fe-Fe distance in these materials. The initial increase in Curie temperature corresponds to an increase in the positive Fe-Fe exchange coupling as a result of increasing interatomic distance. At higher Ga-concentrations, the magnetic moment

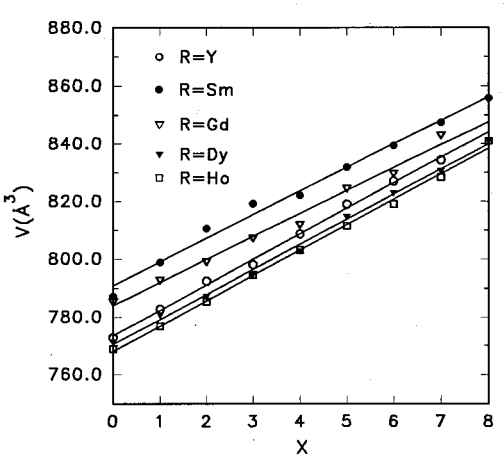

FIG. 1. The unit cell volumes of $R_2Fe_{17-x}Ga_x$ compounds as a function of Ga content.

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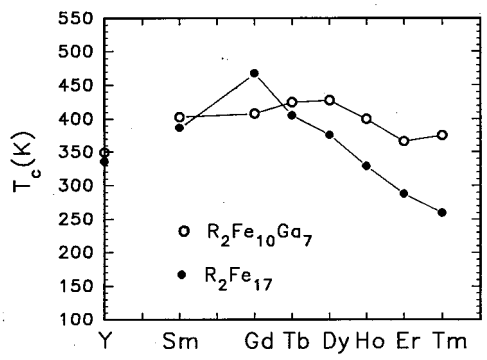

FIG. 2. Curie temperature of R_2Fe_{17} and $R_2Fe_{10}Ga_7$ compounds.

and the number of Fe-Fe pairs decrease drastically, so that eventually T_c decrease too. For example, Fig. 2 shows the Curie temperatures of $R_2Fe_{10}Ga_7$ compounds. For comparison, those of the R_2Fe_{17} compounds are also present. The difference in T_c among the various rare-earth–iron compounds shows the effect of R–Fe interactions on T_c. The Curie temperatures of $R_2Fe_{10}Ga_7$, except R=Gd, are higher than those of R_2Fe_{17} compounds. The competition of the unit cell volume expansion and the magnetic dilution results in a slight enhancement of Curie temperature for $R_2Fe_{10}Ga_7$ compounds. The average increase in the unit cell volumes of $R_2Fe_{10}Ga_7$ compounds is about 7.4% compared with those of the R_2Fe_{17} compounds.

It is possible that the substitution of Ga changes either rare earth sublattice anisotropy or iron sublattice anisotropy or both. In order to distinguish separately the contributions of these two sublattices to the bulk anisotropy, one can either make a full substitution of nonmagnetic Ga atoms for Fe or choose the rare earth elements without contribution to the rare earth sublattice anisotropy, such as Y and Gd. Unfortunately, up to this data, it is impossible to fabricate the single phase 2:17-type samples $R_2Fe_{17-x}Ga_x$ with $x>8$. Thus, we select two series of $Y_2Fe_{17-x}Ga_x$ and $Gd_2Fe_{17-x}Ga_x$ compounds first to investigate the effect of Ga substitution on the magnetocrystalline anisotropy of iron sublattice. The magnetocrystalline anisotropy of these compounds was investigated by means of x-ray diffraction patterns for magnetically aligned powders. The samples were ground to fine powders, mixed with epoxy resin, and then aligned in an applied magnetic field of 10 kOe. Figure 3 shows the room temperature x-ray diffraction patterns of magnetically oriented samples with x=6 and 7. It can be seen that the patterns of $Y_2Fe_{11}Ga_6$ and $Gd_2Fe_{11}Ga_6$ contain the peaks of (220), (300), (330), and (600), while those of $Y_2Fe_{10}Ga_7$ and $Gd_2Fe_{10}Ga_7$ show the diffraction peaks of (006) and (009). The results clearly demonstrate that the easy magnetization direction of iron sublattice changes from basal plane to c axis with increasing Ga concentration.

Figure 4 illustrates the Ga-concentration dependence of easy magnetization direction of $R_2Fe_{17-x}Ga_x$ compounds. For R=Tb, Dy, Ho, Er, and Tm, the change in magnetocrystalline anisotropy is consistent with that for R=Y and Gd. Neutron diffraction studies for $Tb_2Fe_{17-x}Ga_x$ compounds[6]

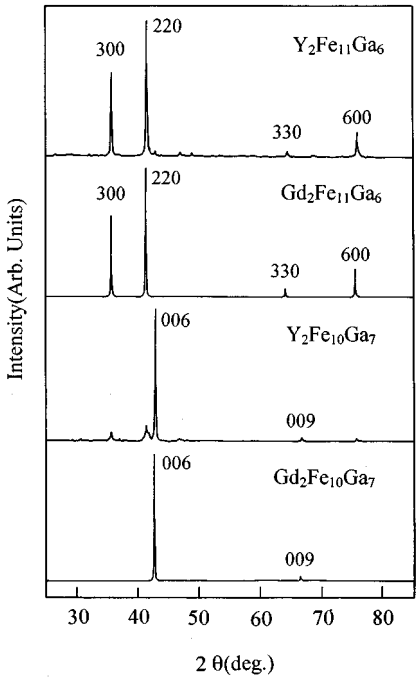

FIG. 3. Cu $K\alpha$ radiation x-ray diffraction patterns of magnetically aligned $Y_2Fe_{17-x}Ga_x$ and $Gd_2Fe_{17-x}Ga_x$ powder samples with x=6 and 7.

also indicated that the magnetic moments are oriented along [001] when $x>5$. However, for R=Sm, the easy magnetization direction changes from basal plane to c axis as x increases from 0 to 2, whereas the easy magnetization direction changes from easy c axis to plane again when $x\geqslant 6$. The modification of magnetocrystalline anisotropy was also found in pseudobinary alloys $R_2(Fe,Co)_{17}$ and $R_2(Fe,Ni)_{17}$ compounds.[7]

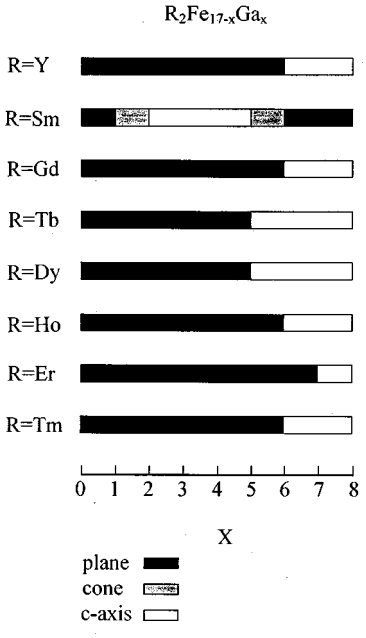

FIG. 4. Easy magnetization direction of $R_2Fe_{17-x}Ga_x$ compounds at room temperature.

From the similar change in easy magnetization direction between R=Tb, Dy, Ho, Er, Tm, and R=Y and Gd, it seems that the iron sublattice anisotropy plays a predominant role in the total anisotropy. If this situation is true, a similar change in magnetocrystalline anisotropy will be predicated in the samples with R=Sm. However, the easy magnetization direction changes from easy c axis to basal plane again when $x>6$. This suggests that the substitution of Ga also influences the rare earth sublattice anisotropy. The anisotropy of rare-earth–iron compounds is determined from the sum of the Fe sublattice anisotropy and the rare earth sublattice anisotropy. It is well known that the anisotropy of Fe sublattice is easy planar for R_2Fe_{17}. The contribution of rare earth sublattice to magnetocrystalline anisotropy arises from the coupling between rare earth ion orbit magnetic moment and the crystal electric field. If the second-order field term is predominant, the anisotropy of rare earth sublattice can be described by the product of the second-order crystal parameter A_{20} and the second-order Stevens coefficient α_J on the basis of single ion model.[8] A negative $\alpha_J A_{20}$ exhibits a uniaxial anisotropy. It has been shown previously that A_{20} is negative in the R_2Fe_{17} compounds. All rare earths except for the Sm, Er, and Tm have a negative α_J: accordingly, their compounds of R_2Fe_{17} have an easy planar anisotropy. For R=Sm, Er, and Tm with a positive α_J, the R sublattices in the R_2Fe_{17} compounds have a uniaxial anisotropy; however, the planar anisotropy of Fe sublattice overcomes the axial anisotropy of R sublattice. Only Tm_2Fe_{17} exhibits a uniaxial anisotropy at low temperature with a spin reorientation temperature of 72 K.[9]

The bulk anisotropy of $Sm_2Fe_{17-x}Ga_x$ with $x \geqslant 6$ is planar, while the iron sublattice exhibits an easy c axis anisotropy when $x>6$. This result demonstrates that the magnetocrystalline anisotropy of Sm^{3+} sublattice changes from easy axis to easy plane with increasing Ga concentration up to $x=6$. This change can be suggested to result from a possible change of the second-order crystal field parameter A_{20} from negative to positive with increasing Ga concentration. For the samples with R=Er and Tm, which exhibit an easy c axis anisotropy at higher Ga concentration, this is because the strong uniaxial anisotropy of iron sublattice suppresses the weak planar anisotropy of rare earth sublattice. A more detailed investigation is in progress.

This work was supported by National Natural Science Foundation of China. The authors wish to express their gratitude to T. S. Ning and M. Hu for their assistance in the x-ray diffraction experimental, to K. C. Jia and S. Y. Fan for his assistance in the magnetic parameter measurements.

[1] F. Weitzer, K. Hiebl, and P. Rogl, J. Appl. Phys. **65**, 4963 (1989).
[2] P. C. M. Gubbens and A. M. van der Kraan, J. Less-Common Metals **159**, 173 (1990).
[3] J. M. D. Coey and H. Sun, J. Magn. Magn. Mater. **87**, L251 (1990).
[4] B. G. Shen, F. W. Wang, L. S. Kong, and L. Cao, J. Phys. Condens. Matter. **5**, L685 (1993).
[5] Z. Wang and R. A. Dunlap, J. Phys. Condens. Matter. **5**, 2407 (1993).
[6] Z. Hu, W. B. Yelon, S. Mishra, G. J. Long, O. A. Pringle, D. P. Middleton, and K. H. J. Buschow, J. Appl. Phys. **76**, 443 (1994).
[7] H. R. Kirchmayr and C. A. Poldy, J. Magn. Magn. Mater. **8**, 1 (1978).
[8] K. H. J. Buschow, Rep. Prog. Phys. **54**, 1123 (1991).
[9] K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1977).