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LETTER TO THE EDITOR

Crystal structure and magnetic properties of $\text{Gd}_3\text{Fe}_{28}\text{Re}$

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Abstract

The structure and magnetic properties of a ternary intermetallic compound $\text{Gd}_3\text{Fe}_{28}\text{Re}$ stabilized by Re in the sixth period has been investigated by means of XRD analysis and magnetic measurement. The compound crystallizes in the monoclinic $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$ -type structure with space group $A2/m$. The lattice parameters are $a = 10.5778(1) \text{ \AA}$, $b = 8.5317(1) \text{ \AA}$, $c = 9.6945(2) \text{ \AA}$, and $\beta = 96.85(1)^\circ$. The preferential occupancy of Re over the $4g$, $4i_3$ and $4i_4$ crystallographic sites were determined successfully by Rietveld refinement of XRD data, which is basically attributed to the effect of size. The compound exhibits planar magnetocrystalline anisotropy perpendicular to the $[204]$ direction. The Curie temperature T_C , the saturation moment M_S and the magnetocrystalline anisotropy field H_A are derived to be 467 K, $35.1 \mu_B \text{ f.u.}^{-1}$ and 69.4 kOe, respectively.

1. Introduction

The discovery of the ternary $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound, which exhibits excellent permanent magnetic performance, lead to a worldwide search for Fe-rich rare-earth-transition metal intermetallics as permanent magnet materials. Initial attention was predominantly focused on the investigation of $\text{R}(\text{Fe},\text{T})_{12}$ compounds of the ThMn_{12} -type structure, where R represents rare-earth, T the stabilizing elements such as Ti, V, Cr, Nb, Mo, W, Ta, Si, Al, etc, on account of the non-existence of binary RFe_{12} compounds [1–4]. The pioneer work by Coey *et al* [5], in which nitrogen atoms were introduced into the interstitial sites of the lattice of $\text{Sm}_2\text{Fe}_{17}$ to form the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ compound that exhibited much better magnetic performance compared to its parent compound, led researchers to investigate $\text{R}_2\text{Fe}_{17}\text{X}$ and $\text{R}(\text{Fe},\text{T})_{12}\text{X}$ ($\text{X} = \text{N}, \text{C}, \text{H}$) compounds [6–9]. Unfortunately, these interstitial compounds are usually unstable at high temperatures, limiting their practical applications.

Essentially, both $\text{R}(\text{Fe},\text{T})_{12}$ and R_2Fe_{17} are derivatives of $\text{R}(\text{Fe},\text{T})_5$ of the CaCu_5 -type structure with appropriate ordered substitution of (Fe,T) – (Fe,T) dumb-bell for R atoms. Further exploitation of the $\text{R}(\text{Fe},\text{T})_5$ derivatives resulted in the discovery of $\text{R}_3(\text{Fe},\text{T})_{29}$ compounds,

which crystallize in a monoclinic structure and can be described more accurately by the space group $A2/m$ than by $P2_1/c$ [10–12]. $R_3(\text{Fe,T})_{29}$ compounds are potential candidates as permanent magnet materials owing to their high performance. In particular, an introduction of N, C as interstitial atoms can lead to a remarkable improvement in intrinsic magnetic properties [13–15]. So far, it has been revealed that many third elements such as Ti, V, Cr, Mn, W, Nb, Mo, etc, can stabilize the 3:29 structure [16–23]. Nevertheless, the role of Re in the sixth period in stabilizing the 3:29 structure is scarcely concerned. It is of both physical and technological significance to explore this effect. We have successfully synthesized a novel ternary compound $\text{Gd}_3\text{Fe}_{28}\text{Re}$. In this letter the crystal structure and magnetic properties of $\text{Gd}_3\text{Fe}_{28}\text{Re}$ are reported. In addition, due to a large difference in atomic scattering factors between Fe and Re, preferential occupancy of Re over different crystallographic positions in the $\text{Gd}_3\text{Fe}_{28}\text{Re}$ structure can be unambiguously determined by Rietveld refinement of x-ray powder diffraction (XRD) data.

2. Experimental procedure

Samples with stoichiometric compositions $\text{Gd}_3\text{Fe}_{29-x}\text{Re}_x$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.1$) were prepared by arc melting the raw materials Gd, Fe and Re with purity better than 99.9% under high purity argon atmosphere. An excess amount of Gd was added to compensate for the weight loss during arc melting and following the annealing processes. As-cast ingots were sealed into an evacuated quartz tube and annealed for one week at 1100° , followed by a water quench. Phases were identified by means of a combination of thermomagnetic and XRD analysis.

XRD experiments were carried out on a Rigaku D/max 2500 diffractometer with $\text{Cu K}\alpha$ radiation ($40 \text{ kV} \times 200 \text{ mA}$) and a graphite monochromator. A step scan mode was employed with a step width of $2\theta = 0.02^\circ$ and a sampling time of 2 s. Temperature dependence of magnetization was measured by a vibrating sample magnetometer (VSM). Field dependence of magnetization was measured at 5 K by a superconducting quantum interference device (SQUID). XRD pattern of magnetic field aligned sample was used to determine the easy magnetization direction (EMD). The magnetocrystalline anisotropy field was derived from the field dependence of magnetization along the EMD and hard magnetization directions (HMD) at 5 K.

3. Results and discussion

Figure 1 shows part of XRD patterns of $\text{Gd}_3\text{Fe}_{29-x}\text{Re}_x$ for $x = 0.8, 1.0$ and 1.1 to reveal phase purity of the samples. It can be seen that single-phase $\text{Gd}_3\text{Fe}_{28}\text{Re}$ is obtained almost exclusively for $x = 1.0$, while a small amount of Fe or 2:17 phase appears in the samples of $x = 0.8$ and 1.1 as an impurity, as denoted by the downward arrows. Therefore, it seems that the composition region of Re in the Fe-rich 3:29 structure as the stabilizing element is very narrow.

We adopted the monoclinic $\text{Nd}_3(\text{Fe,Ti})_{29}$ structure with space group $A2/m$ [12] as the initial structure to refine the XRD data of $\text{Gd}_3\text{Fe}_{28}\text{Re}$ using the DBW94-11 program [24, 25]. Rietveld refinement results are illustrated in figure 2 and table 1. The pattern factor R_p , the weighted pattern factor R_{wp} and the expected pattern factor R_{exp} , are 6.27%, 8.32% and 5.18%, respectively. The lattice parameters of $\text{Gd}_3\text{Fe}_{28}\text{Re}$ are $a = 10.5778(1) \text{ \AA}$, $b = 8.5317(1) \text{ \AA}$, $c = 9.6945(2) \text{ \AA}$ and $\beta = 96.85(1)^\circ$.

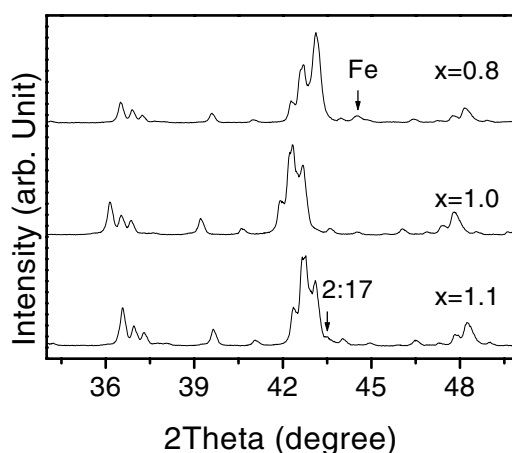


Figure 1. Comparison of the XRD patterns of $\text{Gd}_3\text{Fe}_{29-x}\text{Re}_x$ with $x = 0.8, 1.0$ and 1.1 . Peaks arising from impurity phase are indicated by downward arrows.

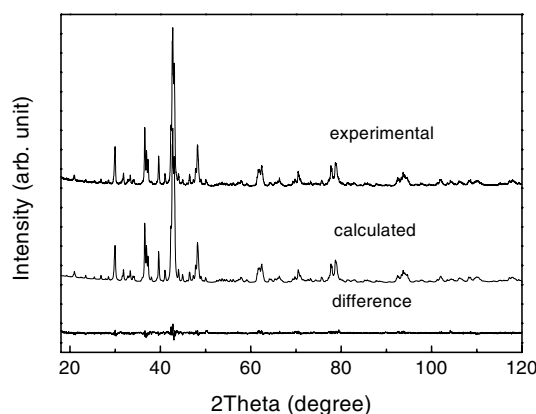


Figure 2. The experimental XRD pattern of $\text{Gd}_3\text{Fe}_{28}\text{Re}$, the calculated profile and the difference between them.

The large scattering contrast between Fe and Re allows the preferential occupancy of Re over different crystallographic sites to be accurately determined by Rietveld refinement. Upon performing the refinement, we purposely put Re atoms on all possible crystallographic sites, and then refine occupancies on these sites as free parameters. As a consequence, it was found that Re atoms preferentially occupy exclusively the $4g$, $4i_3$ and $4i_4$ sites, which have only one neighbouring Gd atom, as outlined in table 1. Following the Miedema model [26], the mixing enthalpy for Gd and Re is -4 kJ mol^{-1} , while that for Gd and Fe is -1 kJ mol^{-1} . Thermodynamic consideration would anticipate that Re atoms favour the $4i_2$, $8j_3$ sites etc, which have the largest area of contact with Gd. Obviously, the preferential occupation of Re atoms in the $\text{Gd}_3\text{Fe}_{28}\text{Re}$ structure cannot be reasonably accounted for by the effect of mixing enthalpy. According to the Rietveld refinement results, the average distance of every crystallographic site to the neighbouring Fe can be derived, and those of the $4g$, $4i_3$ and $4i_4$ sites to the neighbouring Fe are 2.675 , 2.682 and 2.683 \AA , respectively. Assuming that Re and Fe atoms behave as hard spheres with metallic radius 1.38 and 1.27 \AA [27], respectively,

Table 1. Rietveld refinement results for the $\text{Gd}_3\text{Fe}_{28}\text{Re}$ compound with $A2/m$, occupancy of Re atom, average distance of sites to neighbouring Fe, and the number of neighbouring atoms.

Atoms	Sites	x	y	z	Average distance of sites to neighbouring Fe	Re (%) occupancy	The number of neighbouring atoms
Gd	2a	0.0	0.0	0.0	3.127		20Fe
Gd	4i	0.4027(1)	0.0	0.8129(1)	3.149		19Fe
Fe	2c	0.5	0.0	0.5	2.492		10Fe+2Gd
Fe	4e	0.0	0.25	0.25	2.500		10Fe+2Gd
Fe/Re	4g	0.0	0.3598(1)	0.0	2.675	21.18	13Fe+1Gd
Fe	4i ₁	0.1126(2)	0.0	0.7201(1)	2.554		10Fe+2Gd
Fe	4i ₂	0.2951(3)	0.0	0.0949(1)	2.565		9Fe+3Gd
Fe/Re	4i ₃	0.2512(1)	0.0	0.5221(2)	2.682	13.05	13Fe+1Gd
Fe/Re	4i ₄	0.1388(1)	0.0	0.2957(4)	2.683	14.78	13Fe+1Gd
Fe	8j ₁	0.6263(2)	0.1447(1)	0.6846(3)	2.578		10Fe+2Gd
Fe	8j ₂	0.8060(1)	0.2171(2)	0.0902(2)	2.578		10Fe+2Gd
Fe	8j ₃	0.4063(2)	0.2513(1)	0.0665(2)	2.553		9Fe+3Gd
Fe	8j ₄	0.1984(1)	0.2529(3)	0.1552(1)	2.491		10Fe+2Gd

$$a = 10.5778(1), b = 8.5317(1), c = 9.6945(2) \text{ \AA}, \beta = 96.85(1)^\circ, V = 867.8(1) \text{ \AA}^3, R_p = 6.27\%, R_{wp} = 8.32\%, R_{exp} = 5.18\%$$

one can conclude that each of the three sites mentioned above can accommodate a Re atom. However, all of the distances for other sites are smaller than 2.580 Å. If Re atoms occupy these sites large strain would arise. Therefore, the effect of size dominates over that of mixing enthalpy.

Given that both binary $\text{Gd}_3\text{Fe}_{29}$ and $\text{Gd}_3\text{Re}_{29}$ compounds are nonexistent, and the composition region of Re in $\text{Gd}_3\text{Fe}_{29-x}\text{Re}_x$ is very narrow as well as Re atoms preferentially occupy the specific crystallographic sites, $\text{Gd}_3\text{Fe}_{28}\text{Re}$ can undoubtedly be considered as a ternary intermetallic compound composed of Gd, Fe and Re. According to the Rietveld refinement results on the Re concentration, a formula of $\text{Gd}_3\text{Fe}_{28.02}\text{Re}_{0.98}$ was deduced. The difference between the refined and starting stoichiometric Re concentration is within the experimental error. So far, not only Ta and W in the sixth period but also Re can stabilize the 3:29 phase, forming ternary compounds $\text{Gd}_3\text{Fe}_{29-x}\text{M}_x$ ($M = \text{Ta}, \text{W}, \text{Re}$) [19, 28]. Moreover, it seems that the amount of M needed to stabilize the 3:29 phase increases with the decrease of atomic radius of M.

Figure 3 shows the temperature dependence of magnetization at a low field. The Curie temperature, $T_C = 467$ K, was derived by extrapolating the M^2-T curve to $M^2 = 0$. To determine the easy magnetization direction (EMD) and the magnetocrystalline anisotropy field (H_A) of $\text{Gd}_3\text{Fe}_{28}\text{Re}$, fine powder was mixed with epoxy resin and filled in cylindrical and disc-shaped containers, respectively. The containers were mounted on a motor that rotated under a magnetic field of 1 T perpendicular to their axes until the mixture solidified. The disc-like and cylindrical aligned samples thus obtained were utilized for the XRD experiment and the measurement of the field dependence of magnetization of the hard magnetization direction (HMD), respectively. The XRD pattern for the disc-like sample is shown in figure 4. It can clearly be seen that the (204) peak is intensified, indicating that $\text{Gd}_3\text{Fe}_{28}\text{Re}$ exhibits an EMD in the basal plane perpendicular to the [204] crystallographic direction. The field dependencies of magnetization for the fine free powder and magnetic aligned sample at 5 K are illustrated in figure 5. According to the law of approach to saturation, by extrapolating $1/H$ to zero on the linear part of the $M-1/H$ curve of the fine powder sample, a saturation

moment, $M_S = 35.1\mu_B \text{ f.u.}^{-1}$, is derived. Within the framework of mean-field theory for two sublattices, and assuming that the moment of Gd sublattice is antiparallel to that of Fe sublattice and $Gd^{3+} = 7.0\mu_B$, the average Fe moment, $\mu_{Fe} = 2.01\mu_B$, is figured out, which is very close to the atomic moment of pure Fe. The magnetocrystalline anisotropy field, H_A , is estimated to be 69.4 kOe by extrapolating ΔM to zero on the $\Delta M-H$ curve ($\Delta M = M_{\parallel} - M_{\perp}$).

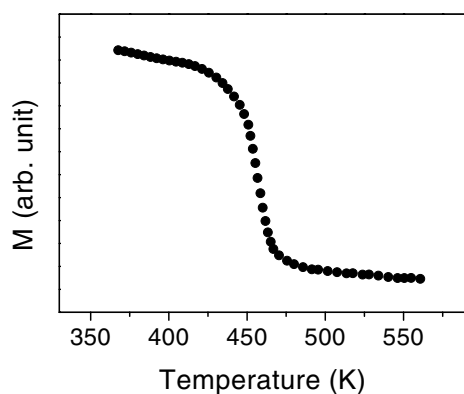


Figure 3. The temperature dependence of magnetization at a low field for $Gd_3Fe_{28}Re$ measured by VSM.

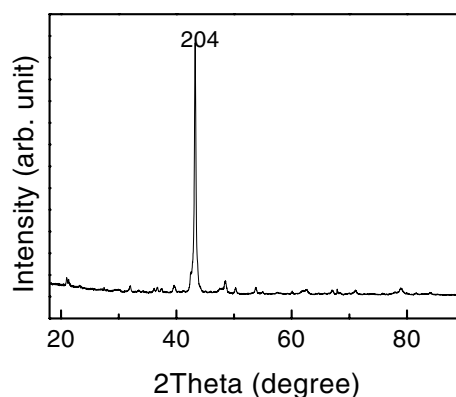


Figure 4. The XRD pattern of the magnetic aligned sample of $Gd_3Fe_{28}Re$.

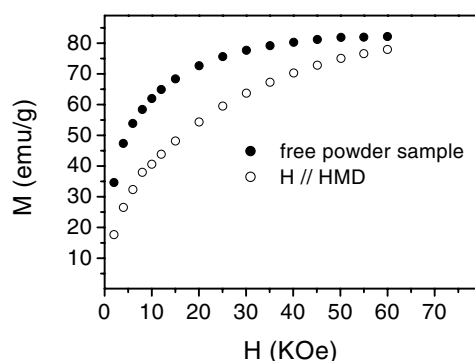


Figure 5. The field dependencies of magnetization of free powder and magnetic aligned samples of $Gd_3Fe_{28}Re$ measured by SQUID.

4. Conclusions

A novel ternary intermetallic compound $Gd_3Fe_{28}Re$ with Re in the sixth period as the stabilizing element has been successfully synthesized. The compound crystallizes in the $Nd_3(Fe,Ti)_{29}$ type structure with the space group $A2/m$. The preferential occupancy of Re over the $4g$, $4i_3$ and $4i_4$ crystallographic sites in the $Gd_3Fe_{28}Re$ structure was determined unambiguously by Rietveld refinement of the XRD data. The preferential occupancy of Re can be basically accounted for by the effect of size instead of that of mixing enthalpy. The compound has an EMD in the plane perpendicular to the $[204]$ crystallographic direction. The Curie temperature, the saturation moment and the magnetocrystalline anisotropy field are derived to be 467 K, $35.1\mu_B \text{ f.u.}^{-1}$ and 69.4 kOe, respectively.

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