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Neutron diffraction structural study of $Ce_2Fe_{17-x}Ga_x$

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Six samples of $Ce_2Fe_{17-x}Ga_x$ with nominal Ga content x equal to 0, 0.3, 0.5, 0.7, 1.0, 2.0 have been studied by powder neutron diffraction at room temperature. Both crystalline and magnetic refinements have been carried out. All six samples adopt the Th_2Zn_{17}-type rhombohedral structure. The only additional phase found is α-iron. Gallium atoms are found to have high affinity for the iron 18h site, and are absent from the 9d and 18f sites. The Ga substitution for Fe leads to an expansion of both the a and c axes. The Curie temperature increases from 238 K for Ce_2Fe_{17} to 406 K for $Ce_2Fe_{15}Ga_2$. Magnetic refinements on the samples with $x=0.3$, 0.5, 0.7, 1.0, and 2.0 reveal that the magnetic moments of the four Fe sites are in the basal plane and that their values increase with increasing Ga content. © *1996 American Institute of Physics.* [S0021-8979(96)34608-0]

I. INTRODUCTION

The studies of high-performance hard magnetic materials consisting of rare-earth (R)-3d transition metals have been reinvigorated after the discovery of the ternary $Nd_2Fe_{14}B$ compound[1,2] and the carbided, hydrided, and nitrided compounds based on the R_2Fe_{17} and RFe_{12} phases.[3,4] It is believed that the lengthened Fe–Fe bonds, with enhanced ferromagnetic exchange, play an important role in the increase of Curie temperature (T_c). It has been found that some iron site substitutional atoms, such as Al, Si, Ti, and Ga, can also enhance the Curie temperature significantly.[8] Thus, it is of interest to look into the influence of the substitutional atom(s) on the crystallographic structure and the intrinsic magnetic properties of these compounds. Recent studies[7,9,10] of $Tb_2Fe_{17-x}Ga_x$, $Nd_2Fe_{17-x}Ga_x$, and $Tb_2Fe_{17-x}Al_x$ reveal that an increase in unit cell volume and Curie temperature can be achieved through the substitution of gallium or aluminum for iron. For the Tb series, the Curie temperature reaches a maximum between $x=3$ and 4 and the easy magnetization direction changes from planar to axial with increasing Ga concentration. In this article, we report a neutron diffraction structural study of $Ce_2Fe_{17-x}Ga_x$ with gallium nominal composition x up to 2.0. Since Ce is expected to be nonmagnetic, the effect of R-Fe exchange may be ignored.

II. EXPERIMENT

$Ce_2Fe_{17-x}Ga_x$ samples with nominal gallium contents of $x=0$, 0.3, 0.5, 0.7, 1.0, and 2.0 were prepared by radio-frequency induction melting of the constituent elements of purity 99.9–99.95%. The samples were wrapped in tantalum foil and annealed in argon atmosphere at 950 °C for one week. They were then crushed and ground for later measurements. Neutron diffraction data were collected at the University of Missouri Research Reactor using the high-resolution linear position-sensitive detector diffractometer at room temperature. The neutron wavelength was 1.4783 Å. Approximately 1 g samples were contained in thin wall (0.1 mm) vanadium holders. The data were accumulated in five settings of the detector in 24 h with 2θ values ranging from 5° to 105° in 0.05° steps. The neutron diffraction powder patterns were analyzed by the Rietveld method[11] using the FULLPROF program[12] for multiphase refinement, including magnetic structure refinement.

III. RESULTS AND DISCUSSION

From the powder neutron diffraction data refinement, all six samples were confirmed to adopt the Th_2Zn_{17}-type rhombohedral structure with the R-3M space group. The refinement results are given in Table I. Both the a and c lattice parameters increase as the gallium content increases, approximately 0.45% per substituted Ga for a and 0.55% for c, as is shown in Fig. 1. The compositional dependence of the unit cell volume is also shown in Fig. 1. The unit cell volume expands from ~775 Å^3 for Ce_2Fe_{17} to ~799 Å^3 for $Ce_2Fe_{15}Ga_2$. The corresponding Curie temperature rises from 238 K for the parent binary phase to 406 K for $Ce_2Fe_{15}Ga_2$. The compositional dependence of the c/a ratio is weak; only a very slight rise is observed. α-Fe was observed in all samples with a maximum of almost 12% in volume.

Gallium is found to have high affinity for the iron 18h site, which is filled by 35% Ga for $x=2$. Some Ga is also found in the iron 6c site with less than 10% for the sample with the highest Ga content. However, no gallium is found on either the 9d or the 18f site. The compositional dependence of the gallium site occupancy is shown in Fig. 2. The 6c gallium site occupancy appears to be close to saturation at ~10% for $x>1$. In Ce_2Fe_{17}, the iron 6c site has the largest Wigner–Seitz cell volume[7] followed by the 18h site, while the 9d site is the smallest. Gallium's high affinity for the 18h site is because this site has the most near-neighbor rare-earth atoms in the coordination shell. The effect of Ga having high

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TABLE I. Refinement results for the $Ce_2Fe_{17-x}Ga_x$ solid solutions at room temperature. *Data for Ce_2Fe_{17} are from Ref. 13.

PARAMETER	$x=0$*	$x=0.3$	$x=0.5$	$x=0.7$	$x=1.0$	$x=2.0$
x (refined)	0	0.31	0.52	0.87	1.44	2.39
a (Å)	8.4921(2)	8.5091(2)	8.5136(2)	8.5284(3)	8.5396(3)	8.5742(2)
c (Å)	12.4060(3)	12.4354(4)	12.4394(4)	12.4641(6)	12.4887(6)	12.5425(3)
c/a	1.4608	1.4614	1.4612	1.4615	1.4626	1.4628
V (Å^3)	774.89	779.749	780.843	785.102	788.72	798.549
T_c (K)	238	⋯	⋯	⋯	342	406
Ce, 6c,z	0.3441(5)	0.3427(9)	0.3429(8)	0.3418(6)	0.3422(10)	0.3412(6)
Fe/Ga, 6c,z	0.0970(2)	0.0965(4)	0.0965(3)	0.0956(3)	0.0954(4)	0.0950(3)
Fe, 18f,x	0.2905(1)	0.2906(3)	0.2909(2)	0.2907(2)	0.2915(3)	0.2909(2)
Fe/Ga, 18h,x	0.1678(1)	0.1682(2)	0.1684(2)	0.1681(2)	0.1689(2)	0.1686(2)
Fe/Ga, 18h,z	0.4883(1)	0.4881(2)	0.4877(2)	0.4883(2)	0.4883(2)	0.4885(2)
%Ga, 6c	0	1.8	4.2	7.2	8.1	9.6(5)
%Ga, 18h	0	4.6	7.4	12.8	20.1	35.2(3)
μ, Fe, 6c	⋯	0.2	0.5	0.8	2.2(5)	2.9(4)
μ, Fe, 9d	⋯	0.2	0.5	0.8	1.1(3)	1.6(2)
μ, Fe, 18f	⋯	0.2	0.5	0.8	1.1(3)	1.6(2)
μ, Fe, 18h	⋯	0.2	0.5	0.8	1.8(3)	1.9(3)
χ^2	2.91	2.97	3.62	2.06	4.18	4.27
R factor	5.05	7.03	6.79	5.79	7.33	6.50
Rw factor	7.11	9.49	9.39	7.71	9.69	8.74
Rm factor	⋯	6.13	6.81	4.79	6.06	7.71
ALFA-Fe, % V	5.6	5.1	3.62	0.66	11.9	5.14

affinity for rare-earth atoms surpasses that of the site volume, as is also the case[5,13,14] for Si- and Al-doped samples.

The bond lengths and the site average bond lengths are listed in Table II. Almost all bond lengths increase with increasing Ga concentration, as do the average bond lengths for all four Fe sites. However, two exceptions were observed for $18f-18h$ and $6c-6c$ bond lengths. The $6c-6c$ dumbbell, which is often thought to be responsible for the low Curie temperature of the R_2Fe_{17} compounds, decreases slightly with Ga content despite the increase in the c axis. From this, one would predict a decrease in Curie temperature, which is in contrast with the observations. This phenomenon has also been observed in some other investigations.[13–15] This suggests that it is unlikely that the changes in T_c arise from the changes of the $6c-6c$ bond, but rather, the increase is more likely related to the average bond lengths.

Magnetic refinement has been carried out on samples with $x=0.3$, 0.5, 0.7, 1.0, and 2.0. Ce_2Fe_{17} is not magnetically ordered at room temperature and in all cases cerium is treated as nonmagnetic. The refinement results indicate that the magnetic moments of all four Fe sites lie in the basal plane and the average values of these moments tend to increase with increasing gallium content. The magnetic moments at low gallium contents have been constrained to be equal rather than being refined independently because their moments are too small to give reliable individual values. The refinement results for $x=1$ and 2 samples show that the moments of the $6c$ and $18h$ sites are larger than those of the $9d$ and $18f$ sites, especially that of the $6c$ site. The overall in-

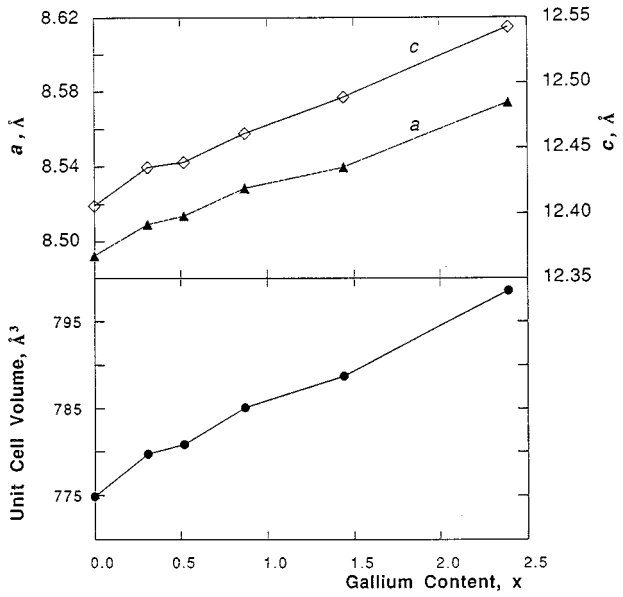

FIG. 1. Compositional dependence of the lattice parameters a, c, and the unit cell volume of $Ce_2Fe_{17-x}Ga_x$ solid solution.

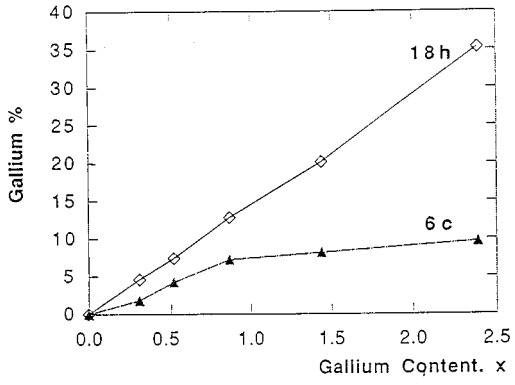

FIG. 2. Compositional dependence of the gallium site occupancy of $Ce_2Fe_{17-x}Ga$ solid solution.

TABLE II. Bond lengths and site averaged average bond lengths for the $Ce_2Fe_{17-x}Ga_x$ solid solutions.

Bond	$x=0$	$x=0.3$	$x=0.5$	$x=0.7$	$x=1.0$	$x=2.0$
Fe(6*c*)–Fe(6*c*)	2.4068(35)	2.3975(70)	2.4008(53)	2.3853(53)	2.3803(71)	2.3806(53)
Fe(6*c*)–Fe(9*d*)	2.5994(8)	2.6072(17)	2.6081(13)	2.6181(13)	2.6213(17)	2.6337(13)
Fe(6*c*)–Fe(18*f*)	2.7448(12)	2.7495(23)	2.7537(18)	2.7525(18)	2.7584(24)	2.7645(18)
Fe(6*c*)–Fe(18*h*)	2.5338(12)	2.6424(27)	2.6415(22)	2.6502(19)	2.6441(28)	2.6600(24)
Fe(9*d*)–Fe(18*f*)	2.4282(4)	2.4340(9)	2.4353(9)	2.4415(9)	2.4447(13)	2.4546(9)
Fe(9*d*)–Fe(18*h*)	2.4475(9)	2.4506(18)	2.4506(18)	2.4565(9)	2.4532(18)	2.4651(18)
Fe(18*f*)–Fe(18*f*)	2.4670(6)	2.4745(12)	2.4783(12)	2.4807(22)	2.4884(18)	2.4951(12)
Fe(18*f*)–Fe(18*h*)	2.3036(11)	2.5619(23)	2.5651(23)	2.5642(22)	2.5665(34)	2.5752(23)
Fe(18*f*)–Fe(18*h*)	2.8394(13)	2.6189(25)	2.6165(25)	2.6321(23)	2.6306(35)	2.6457(25)
Fe(18*h*)–Fe(18*h*)	2.4852(13)	2.4960(21)	2.5009(21)	2.5032(11)	2.5152(22)	2.5204(26)
AVER BL						
Fe, 6*c*	2.6377	2.6648	2.6671	2.6696	2.6713	2.6806
Fe, 9*d*	2.4702	2.4653	2.4761	2.4828	2.4834	2.4946
Fe, 18*f*	2.5566	2.5678	2.5698	2.5742	2.5777	2.5871
Fe, 18*h*	2.5211	2.5441	2.5453	2.5513	2.5527	2.5636

crease in site moments is the result of the increase in Curie temperature and the larger degree of magnetic order at room temperature.

IV. CONCLUSIONS

Both the *a* and *c* lattice parameters show a similar dependence on Ga content in the $Ce_2Fe_{17-x}Ga_x$ solid solutions. The gallium atoms have a high affinity for the iron 18*h* site. The easy magnetization direction is in the basal plane.

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