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Observation of novel disordered rhombohedral R_2Fe_{17} (R =rare earth) based compounds

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A recent study of $(SmGd)Fe_{14}Si_3$ showed an anomalous x-ray diffraction pattern [P. C. Ezekwenna, G. K. Marasinghe, J.-H. Nam, W. J. James, W. B. Yelon, M. Ellouze, and Ph. I'Héritier, *J. Appl. Phys.* **87**, 6716 (2000)]. Although all observed peaks could be indexed to the rhombohedral 2:17 phase ($R-3m$) many lines were strongly reduced in intensity. Subsequently, the same phenomenon was seen in neutron diffraction patterns from $Nd_{2-x}Dy_xFe_{17-y}Si_y$ alloys and conventional refinement using the rhombohedral phase left significant residuals. Fourier mapping revealed additional density along the c -axis chains of Fe dumbbells and rare earth atoms. The perfect a - b - c stacking of the $CaCu_5$ layers with regular 1/3 replacement of the rare earth atoms by Fe dumbbells appears to be broken. Detailed analysis shows that excess Fe dumbbells are incorporated into the structure and some reverse substitution is seen. In addition, the weak intensities are associated with a near equivalence of the $9d$ and $18h$ Fe sites, as in the parent $CaCu_5$ phase. The relationship of this new structure to the other $CaCu_5$ derived phases is described. The high Fe concentration creates the possibility of high T_C and higher remanence than in the ordered 2:17 compounds. © 2002 American Institute of Physics. [DOI: 10.1063/1.1453325]

I. INTRODUCTION

A large number of magnetic compounds are based on the $CaCu_5$ structure. Co based compounds form $SmCo_5(1:5)$, Sm_2Co_{17} , and reportedly a $SmCo_7(1:7)$ structure. The first of these is hexagonal, containing one formula unit, but it is reported that a small percentage of the Sm atoms are replaced by Co dumbbells oriented along the c axis.¹ The second structure is rhombohedral (OR), built from three $SmCo_5$ units in which 1/3 of the Sm atoms are replaced in a regular manner by Co dumbbells. The last is a more highly disordered variant on the $SmCo_5$ cell with up to about 23% random dumbbell replacement.² Although the 1:5 and 1:7 structures do not form with Fe, the OR structure forms with Fe and the light rare earths, and a disordered hexagonal (DH) 2:17 structure forms with the heavy rare earths. This structure is based on a two layer stacking of $CaCu_5$ -type units. In the ideal hexagonal structure Fe dumbbells are found only on 2/3 of the c -axis chains, alternating with a single rare earth. In practice some dumbbells are found on all chains and a full 50% substitution is probably not realized on any chain. In addition, certain substituents for Fe, including Ti, Mn, V, Mo, etc., lead to the formation of the 3:29 phase in which two rare earths out of five (40%) are replaced by dumbbells, and the 1:12 phase in which $\frac{1}{2}$ of the rare earths are replaced. It has been thought that the rhombohedral 2:17 phase can only

form as a line compound without disorder and with fixed 33% dumbbell substitution. Recent x-ray and neutron data on samples containing mixed light and heavy rare earth and Si have produced spectra that clearly showed the rhombohedral cell, but could not be well fitted with the stoichiometric model. We have discovered that a disordered rhombohedral (DR) variant also exists. The details of this structure are described in this article.

II. EXPERIMENT

Samples of nominal $R_2Fe_{17-x}Si_x$ (R =rare earth) were prepared with mixtures of Nd+Dy, Nd+Tb and Sm+Tb, and with $x = 1, 2, 3$. The Nd/Dy mixtures spanned the entire range from pure Nd to pure Dy, while the Sm/Tb mixture was prepared only with 50% or less Sm because higher concentration samples would not be measurable with neutrons. The materials were induction melted under an Ar atmosphere and annealed for a minimum of one week at 1073 K. Neutron diffraction measurements were carried out at room temperature on the high-resolution powder diffractometer at MURR on approximately 1 g samples. The neutron data were refined using the FULLPROF version of the Rietveld code.³

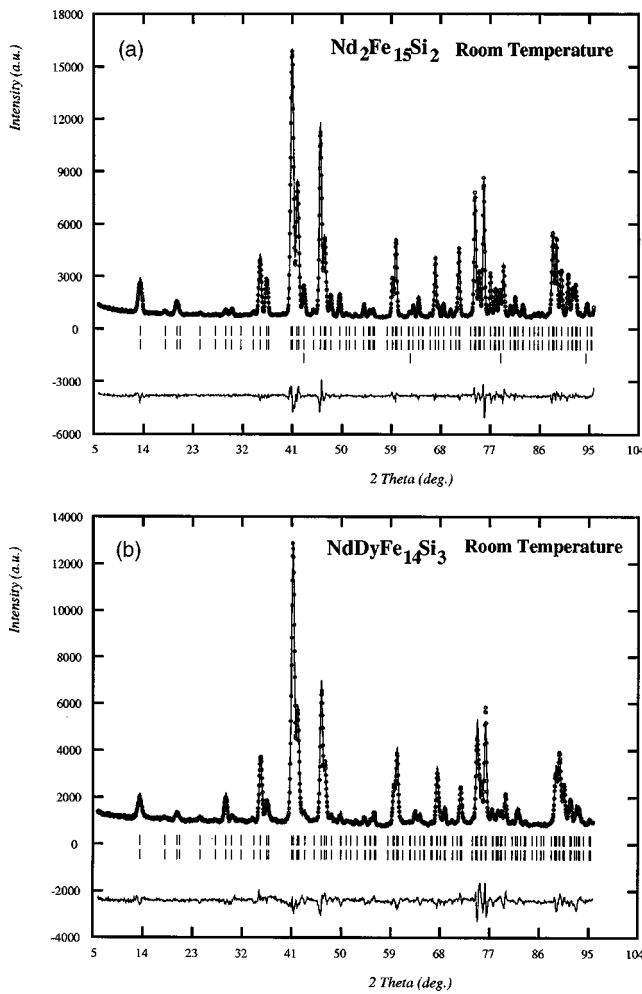


FIG. 1. (a) Neutron diffraction data and fitted diagram for $\text{Nd}_2\text{Fe}_{15}\text{Si}_2$ at room temperature. (b) Neutron diffraction data and fitted diagram for $\text{NdDyFe}_{14}\text{Si}_3$ at room temperature.

III. RESULTS AND DISCUSSION

The neutron diffraction pattern for $\text{Nd}_2\text{Fe}_{15}\text{Si}_2$ (case 1) is shown in Fig. 1(a). It is typical of the ordered rhombohedral phase and about 55 peaks can be clearly distinguished in the diagram. Figure 1(b) shows the neutron diffraction diagram for $\text{NdDyFe}_{14}\text{Si}_3$ (case 2). Although all of the peaks seen in Fig. 1(b) are indexed on the same rhombohedral structure, there are distinct differences between the two diagrams. One notices a broadening of the peaks, probably related to stacking faults, and it is only possible to count about 45 peaks. More significantly, it is clear that the large peaks are hardly changed in intensity while there is a substantial reduction in the intensity of the small peaks. Those small peaks arise from the breaking of the symmetry of the CaCu_5 cell in the tripled rhombohedral cell, with the splitting of the $3g$ site into the $18h$ and $9d$ sites and with the replacement of the rare earth by Fe dumbbells. The decrease in their intensity implies that the $9d$ and $18h$ are now more closely equivalent (which is borne out in their coordinates—Table I), and that the distinction between rare earth and dumbbell positions is being blurred.

Refinement of the data for case 2 using the ordered rhombohedral model is unsatisfactory, and Fourier maps

TABLE I. The coordinates at $9d$ and $18h$ sites of $\text{Nd}_2\text{Fe}_{15}\text{Si}_2$ and $\text{NdDyFe}_{14}\text{Si}_3$.

	x	y	z
$9d$	$1/2$	0	$1/2$
$18h$ of $\text{Nd}_2\text{Fe}_{15}\text{Si}_2$	$0.1684(1)$	$-0.1684(1)$	$0.4914(2)$
$18h$ of $\text{NdDyFe}_{14}\text{Si}_3$	$0.1667(3)$	$-0.1667(3)$	$0.4941(4)$

show additional density along the c -axis chains. In particular, density is seen at $0\ 0\ 0.24$ and $0\ 0\ 0.44$ (and equivalents). The Fe dumbbells that replace the rare earth atom at $0\ 0\ 0$ in the OR structure are found approximately at $0\ 0\ 0.1$ and $0\ 0\ 0.9$, while the rare earth atoms are found at $0\ 0\ 0.34$ and $0\ 0\ 0.66$. The extra density strongly suggests some Fe dumbbells replacing the rare-earth atoms at $0\ 0\ 0.34$ and $0\ 0\ 0.66$. The data were thus modeled assuming some disorder of the Fe dumbbell positions, but with a constraint that the 2:17 stoichiometry be preserved, i.e., reverse substitution of Fe dumbbells by rare earth atoms at $0\ 0\ 0$. Relaxing this constraint leads to only a small improvement for case 2, i.e., the deviation from stoichiometry is small. However, in other samples from the NdDy series T/R ($T = \text{Fe} + \text{Si}$) ratios as high as 9.5 are fitted, especially in the cases with high Dy content that tend to form as two phase samples consisting of mixtures of DH and rhombohedral phases with differing total rare earth in each phase. Since the rare earth content is no longer fixed by stoichiometry, its scattering power cannot be used as the reference for determining the scattering power of the Fe sites as they are substituted by Si. Reasonable results, however, are reached if it is assumed that no Si occupies the $9d$ sites, as is the case in the OR structure. Refinement of the magnetic structure is also problematical unless a constraint is applied between the $9d$ and $18h$ moments. We have assumed them to be equal, but other constraints would also give stable refinements.

The structure of the OR 2:17 phase is shown in Fig. 2(a) and the ideal hexagonal structure is shown in Fig. 2(b). With the exception of the c -axis chains of Fe dumbbells and rare earth atoms, the two structures are the same. Figure 3 shows

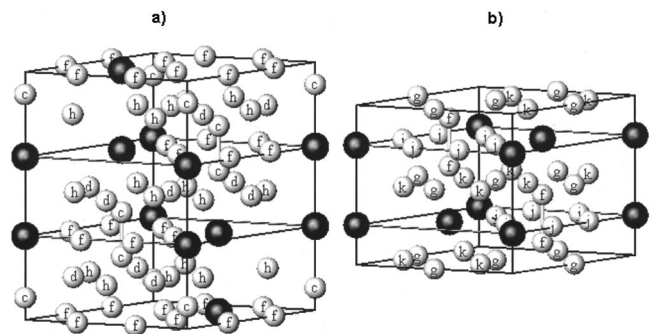


FIG. 2. (a) The unit cell of the ordered rhombohedral 2:17 structure. The large black symbols are rare earth atoms, and Fe atoms are small white symbols. The $6c$ sites are labeled with c , $9d$ sites are labeled with d , $18f$ sites are labeled with f , and $18h$ sites are labeled with h . (b) The unit cell of the (ideal) hexagonal 2:17 structure. The large black symbols are rare earth atoms, Fe atoms are small white symbols. The $12k$ sites are labeled with k , $12j$ sites are labeled with j , $6g$ sites are labeled with g , and $4f$ sites are labeled with f .

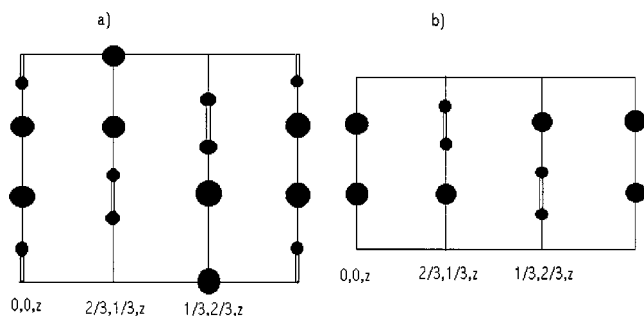


FIG. 3. The stacking side view of the ordered rhombohedral 2:17 structure (a) and the (ideal) hexagonal 2:17 structure (b). The large symbols are rare earth atoms, and the small ones are iron atoms.

a side view of the stacking of those chains for the two ideal structures. The OR structure has the same net dumbbell content on each chain and, thus, the “ideal” c -axis length is the same for every chain. On the other hand the ideal hexagonal structure has no Fe dumbbells on the chain through $0\ 0\ 0$ and 50% dumbbells on the other chains. Since the dumbbells are longer than the rare earth radius, the chains through $0\ 0\ 0$ set one length while the others set a greater length. It is not surprising then that at least some dumbbells are actually found on the $0\ 0\ z$ chain in the real DH systems (with a decreased Fe/R ratio on the other chains). Based on this we expect the c/a ratio for the OR phase to be smaller than for the DH phase. This is observed. Taking, for example, the Dy_2 sample with $x=1$, we generated a two-phase sample of the OR and DH phases. The c/a ratios for these two phases are 1.4616 and 1.472, respectively. If the DR phase contains excess Fe dumbbells, we expect a c/a ratio that is intermediate to the OR and DH phase. This is seen, for example, in the Dy_2 sample with $x=3$ which forms as a pure DR phase with a c/a ratio of 1.4684 and a T/R ratio above 9.5. Apparently, the major role of the Si in these samples is to increase

the c/a ratio with increasing x and thereby allow the different phases to form.

In several samples the fraction of rare earth substituted by Fe dumbbells reaches over 40%, the same as in the 3:29 phase.^{4,5} It is likely that the different c/a ratio (for the underlying $CaCu_5$ -type unit) determines which phase forms. Recent samples produced deliberately away from the 2:17 stoichiometry suggest that still higher dumbbell substitution can be achieved. As the concentration of dumbbells increases, however, all of the weak peaks that distinguish the DR and DH structures are expected to decrease further and it is possible that a different unit cell will be best for describing the distribution of atoms.

The DH phase has been ignored for magnet application since it is based on the heavy rare earths which couple antiferromagnetically. This DR phase, with mixed rare earths and high Fe concentration, has the promise of higher remanence and potentially high T_C . We will be exploring the limits of phase formation with other substituents and pure light rare earth, as well as the limits to T/R ratio to determine if practical magnets can emerge from this interesting new system.

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