Effects of Al substitutions on the magnetic anisotropy of Sm_2Fe_{17} compounds

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Abstract. Compounds in the series Sm$_2$Fe$_{17-x}$Al$_x$ have been investigated. Samples with $x = 0$, 1, 2, 3 and 4 have been shown to be single phased with the Th$_2$Zn$_{17}$ structure. The Curie temperature is found to increase from $T_C = 391$ K for the $x = 0$ sample to $T_C = 471$ K for the $x = 3$ sample. Further substitution of Al for Fe decreased T_C. X-ray diffraction studies of magnetic-field-oriented powders showed that alloys with $x < 2$ exhibit easy plane anisotropy while samples with $x > 2$ exhibit easy axis anisotropy. The $x = 2$ sample showed a mixture of easy plane and easy axis behaviour. This observation represents the first case of clear evidence for room temperature uniaxial anisotropy in the R$_2$Fe$_{17}$ compounds without the addition of interstitial nitrogen or carbon.

1. Introduction

The rare earth–iron compounds of the composition R$_2$Fe$_{17}$ have attracted much attention in recent years as possible high-performance permanent magnetic materials. The large Fe content yields high saturation magnetization while maintaining low cost [1]. In addition these materials can be formed with either the Th$_2$Zn$_{17}$ or Th$_2$Ni$_{17}$ structure across the entire rare earth series [2] and they possess greater thermal stability than other rare earth transition metal binary compounds. However, there are two severe drawbacks to the possible application of these materials as permanent magnet materials: (1) relatively low values of the Curie temperature [3] and (2) the fact that none exhibits an easy axis anisotropy at room temperature. Only Tm$_2$Fe$_{17}$ exhibits an easy axis anisotropy at low temperature with a spin reorientation transition at 72 K [4]. In recent years much progress has been made in understanding the means by which the Curie temperature of these materials may be increased and the methods by which a room temperature easy axis anisotropy may be induced. These studies have centred on changes in the magnetic properties of these materials which result from either substituting other elements into the R$_2$Fe$_{17}$ structure or preparing materials with additional atoms located interstitially.

Extensive studies of the substitution of other elements for Fe in the R$_2$Fe$_{17}$ materials have indicated that, in general, that the addition of Co, Ni, Al and Si, at least up to a certain point, will increase the Curie temperature [5–8]. However, on the basis of these studies there is no evidence that a room temperature uniaxial anisotropy is present [7].

Substantial success has been achieved in improving the hard magnetic properties of the R$_2$Fe$_{17}$ materials by interstitial substitutions. In many cases large increases in the Curie temperature have been observed in materials with interstitial hydrogen, nitrogen or carbon (see, e.g., [3, 7, 9–19]). However, it is only in the case of Sm$_2$Fe$_{17}$C$_y$ ($y > 0.5$) and Sm$_2$Fe$_{17}$N$_y$ ($y > 0.8$) that a uniaxial anisotropy is observed [9, 12].

Although these compounds show considerable promise as possible commercial hard magnetic materials, their utilization requires the development of materials with suitable thermal stability and anisotropic magnets with adequate coercivity.

Recently, we have undertaken extensive studies of the magnetic anisotropy of R_2Fe_{17} compounds with various elemental substitutions for Fe [20]. Here we report the results of our investigations of magnetic anisotropy of $Sm_2Fe_{17-x}Al_x$ compounds. These studies demonstrate that the Curie temperature increases with increasing Al context up to $x = 3$. We have also observed that for $x \geqslant 3$ the material exhibits a room temperature uniaxial anisotropy while maintaining the Th_2Zn_{17} structure up to at least $x = 4$. These results are in contrast to the implications of previous anisotropy studies of this system with smaller values of x and in systems with other rare earths (see, e.g. [3,7]) which have suggested that a room temperature easy axis anisotropy cannot be obtained. The present studies, therefore, suggest the possibility of producing 2:17 type materials with desirable hard magnetic properties as well as reasonable Curie temperatures and good thermal stability.

2. Sample preparation and experimental methods

The compounds $Sm_2Fe_{17-x}Al_x$ ($x = 0, 1, 2, 3, 4$) were prepared by arc melting high-purity Sm (99.98% purity), Fe (99.9% purity) and Al (99.9% purity) in an argon arc furnace. Samples were sealed in quartz tubes under an argon atmosphere and annealed at 1273 K for 72 h followed by quenching into ice–water. Ingots were then ground to yield powder samples.

Room temperature x-ray diffraction measurements were made using a Siemens D500 scanning diffractometer with Cu $K\alpha$ radiation. Magnetic anisotropy studies were undertaken using x-ray diffraction methods on samples which had been field oriented. Powders with particles of diameter 125 μm or less were mixed with epoxy resin and aligned at room temperature in an external field of 1 T.

Curie temperatures were obtained from calorimetry measurements carried out on a Fisher Series 300 quantitative differential thermal analyser.

3. Results

Typical x-ray diffraction patterns of the $Sm_2Fe_{17-x}Al_x$ compounds with $x = 0$ and 3 are illustrated in figure 1. Indices of the major peaks for the rhombohedral Th_2Zn_{17} phase are indicated in the figure. No significant diffraction from impurity phases is observed. In particular no precipitated elemental Fe is indicated. Diffraction patterns of the other alloys studied in the present work show that these alloys are also single-phase compounds of the rhombohedral Th_2Zn_{17} structure. The substitution of Al for Fe in these materials results in an expansion of the unit cell. Table 1 summarizes the parameters obtained from the diffraction studies of these materials as a function of Al content. The densities have been calculated on the basis of atomic weights and unit cell volumes. A comparison of x-ray diffraction parameters from this work with previous results on the $Sm_2Fe_{17-x}Al_x$ system as reported in the literature are illustrated in figures 2 and 3.

Room temperature Cu $K\alpha$ x-ray diffraction patterns obtained for the five samples studied in the present work after alignment in an applied magnetic field of 1.0 T are shown in figure 4. Indices of the existent diffraction peaks are shown in the figure. The characteristic magnetic anisotropy present in the sample is determined on the basis of the

Table 1. Parameters obtained from x-ray diffraction studies of single-phase $Sm_2Fe_{17-x}Al_x$ compounds with the Th_2Zn_{17} structure. a and c are the measured lattice parameters, V is the cell volume and ρ is the calculated density.

x	a (Å)	c (Å)	c/a	V (Å^3)	ρ (g cm^{-3})
0	8.558	12.428	1.452	788	7.90
1	8.574	12.530	1.461	798	7.62
2	8.610	12.546	1.457	805	7.38
3	8.629	12.541	1.453	809	7.16
4	8.659	12.598	1.455	818	6.91
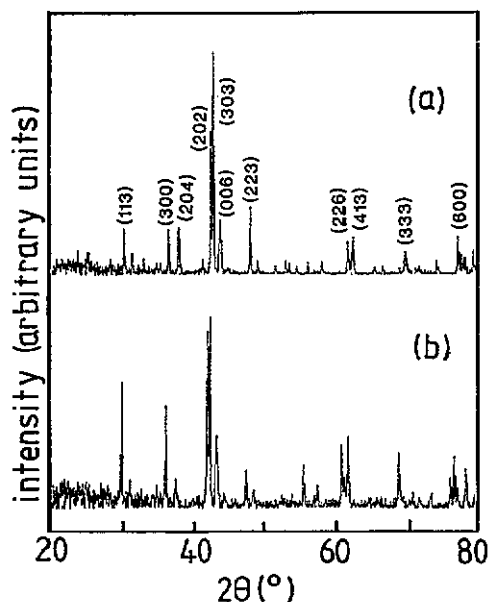
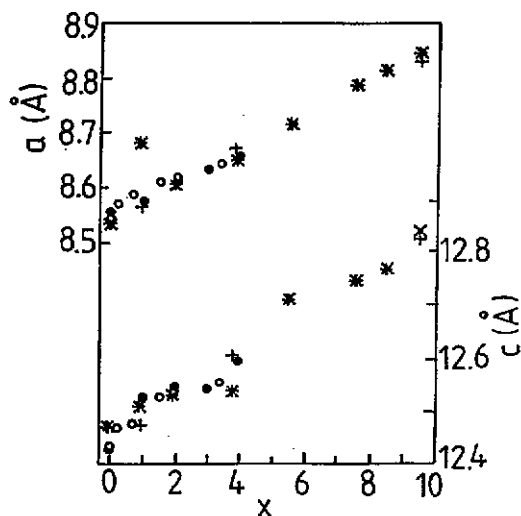**Figure 1.** Room temperature Cu K_α x-ray diffraction patterns for (a) Sm_2Fe_{17} and (b) $Sm_2Fe_{14}Al_3$.

Figure 2. Lattice parameters a and c for the $Sm_2Fe_{17-x}Al_x$ compounds as measured in this work (●), from [7] (○) and from [6] for as-cast (∗) and annealed (+) samples.

Table 2. Magnetic properties of $Sm_2Fe_{17-x}Al_x$ compounds.

x	anisotropy	T_C (K)
0	planar	391
1	planar	417
2	mixed	452
3	uniaxial	471
4	uniaxial	451

x-ray peaks present in each of the patterns. The magnetic anisotropy indicated for each of the compositions studied here is summarized in table 2.

Curie temperatures measured for the present series of alloys are given in table 2. These results are compared with previous Curie temperature measurements for the $Sm_2Fe_{17-x}Al_x$ alloys in figure 5.

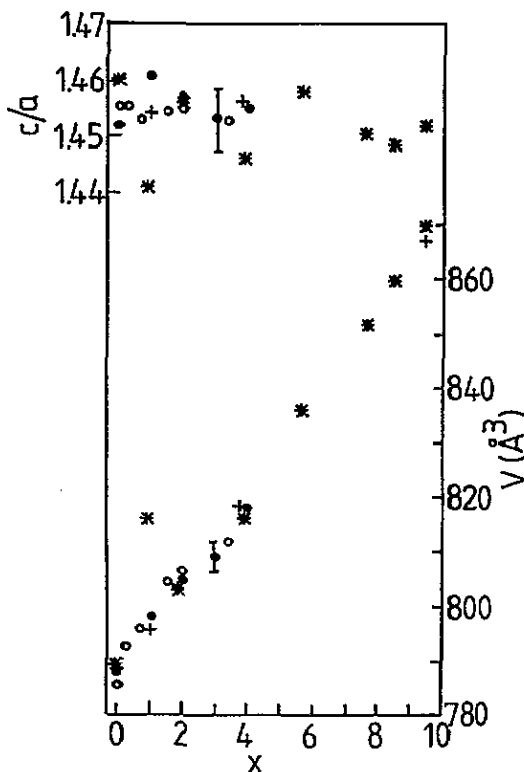**Figure 3.** Ratios c/a and unit cell volumes for the $Sm_2Fe_{17-x}Al_x$ compounds as measured in this work (●), from [7] (○) and from [6] for as-cast (∗) and annealed (+) samples.

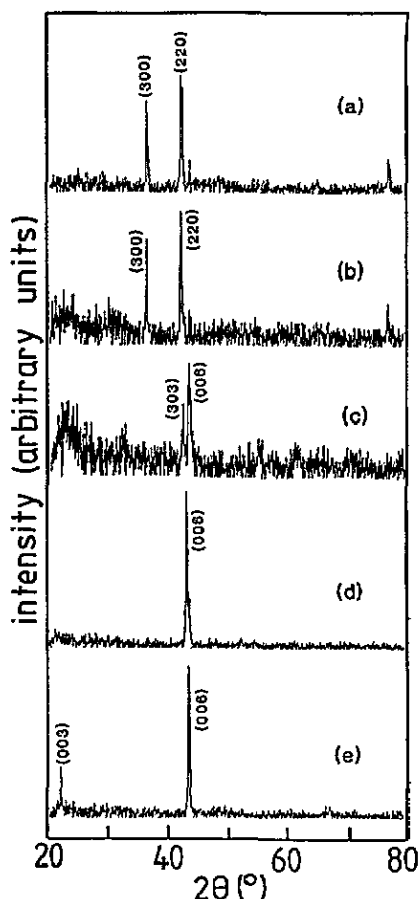**Figure 4.** Room temperature Cu K_α x-ray diffraction patterns of magnetically aligned $Sm_2Fe_{17-x}Al_x$ compounds: (a) $x = 0$, (b) $x = 1$, (c) $x = 2$, (d) $x = 3$ and (e) $x = 4$. The alignment was performed in an applied magnetic field of 1 T as described in the text.

4. Discussion

4.1. Structural properties

The results of the x-ray investigation of the $Sm_2Fe_{17-x}Al_x$ compounds are generally consistent with previous results reported in the literature. Some anomalous behaviour has been seen for small Al concentrations by McNeely and Oesterreicher [6]. It is likely that this behaviour is the result of the fact that the alloys which they investigated show the presence of a substantial quantity of impurity. The unit cell volume as illustrated in figure 3 *shows a linear dependence on Al concentration as we would expect on the basis of a simple* model involving atomic volumes. To a good approximation, therefore, the substitution of larger Al atoms for Fe merely produces an expansion of the lattice. For a linear change in unit cell volume as a function of Al concentration we would expect the corresponding a and c lattice parameters to change more slowly than a linear function. The results as illustrated in figure 2 do not provide sufficient resolution to observe these effects. The
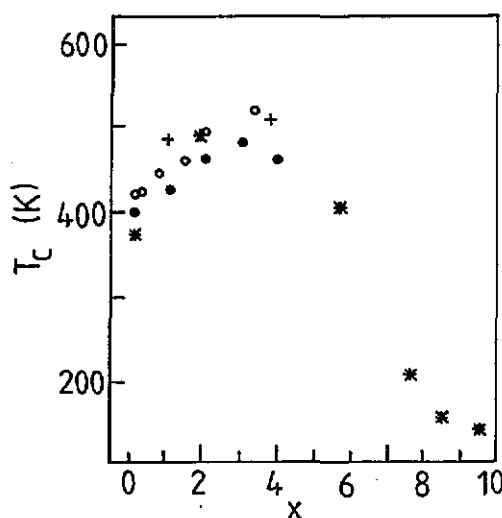
Figure 5. Composition dependence of the measured Curie temperature of $Sm_2Fe_{17-x}Al_x$ compounds. Data are from this work ($\bullet$), [7] (O) and [6] for as-cast (*) and annealed (+) samples.

possibility of any irregularity in the composition dependence of the lattice parameters as a result of preferential Fe site occupancy by the Al cannot be determined on the basis of the measurements to date. Although it has been suggested on the basis of x-ray diffraction peak intensities [6, 21] that Al and Fe are statistically distributed on the available sites, definitive conclusions are difficult to draw. The intensities of the peaks in the present x-ray diffraction patterns are not inconsistent with previous studies. It is relevant, that the present study, as well as previous studies, shows that the ratio c/a is, within experimental uncertainty, independent of the Al content of the $Sm_2Fe_{17-x}Al_x$ compounds. This indicates that the expansion of the lattice caused by the substitution of larger Al atoms for smaller Fe atoms is essentially an isotropic process.

4.2. Magnetic interactions

It is commonly assumed that the magnetic ordering temperature in rare earth–transition metal compounds is dominated by the interactions of the transition metal sublattice (see, e.g., [7]). The generally low values of the Curie temperature result from the relatively small Fe–Fe distance in these materials. This is evidenced by the fact that the Curie temperature typically increases from R_2Fe_{17} to RFe_3 and RFe_2 compounds [22, 23]. The increase in Curie temperature corresponds to an increase in the positive Fe–Fe exchange coupling as a result of the increasing interatomic distance. This is clearly evidenced in studies of the magnetic properties of rare earth–Fe compounds where the lattice constants have been increased by interstitial or substitutional additions. In the case of Al substitutions for Fe the magnetic properties of $R_2Fe_{17-x}Al_x$ with R = Ho and Y have been discussed in some detail by Jacobs *et al* [8]. The value of the Curie temperature is primarily dependent on the magnitude of the exchange coupling between transition metal atoms, J_{TT}. As Jacob *et al* [8] have shown this coupling increases with increasing Al content up to about $x = 3$ in $Y_2Fe_{17-x}Al_x$ and $Ho_2Fe_{17-x}Al_x$ compounds. Beyond this the coupling and hence the value of the Curie temperature decreases with increasing x as a result of either the further dilution of the magnetic species or the further increase in Fe–Fe neighbour distances or both. Jacobs *et al* [8] have also shown that the rare earth–transition metal exchange coupling, J_{RT}, is substantially smaller than the dominant transition metal–transition metal coupling, and that in these compounds it is virtually independent of the Al content. This feature is

suggested by recent band structure calculations (see, e.g., [24–26]) which have predicted that the 3d–4f coupling in rare earth–transition metal compounds will be proportional to the ratio of the 3d and 5d spins. It is probable that the addition of Al will have similar effects on the structure of both the 3d and 5d bands and leave this ratio more or less unchanged. Finally the rare earth–rare earth interaction is expected to be comparatively weak and to be of the long-ranged Rudderman–Kittel–Kasuya–Yosida (RKKY) type.

In the present series of alloys the similarities of the measured Curie temperature trends to those observed in other 2:17 compounds with Al substitutions indicate that the effects of Al on the exchange coupling are similar as well. In all cases a maximum in Curie temperature is seen for alloys with $x \simeq 3$. As the magnetic ordering temperature is dominated by the coupling J_{TT}, it is the effect of the Al additions on the structure of the 3d bands which is of principal consideration. These effects, unlike those responsible for the 3d–4f coupling, do not cancel out.

Early studies of the magnetic hysteresis in Al substituted Sm_2Fe_{17} compounds [6] have shown that the dilution of Fe by non-magnetic Al decreases the saturation magnetization while increasing the coercivity. The present investigations concerning magnetic anisotropy as outlined below suggest that a reconsideration of the hysteretic properties of these alloys may be worth while.

4.3. Magnetic anisotropy

The in-field x-ray diffraction studies provide information concerning the magnetic anisotropy. These patterns, as illustrated in figure 4, indicate the anisotropies given in table 2 for the samples studied here. In contrast to earlier reports, e.g. [7], that the substitution of Al for Fe in the $Sm_2Fe_{17-x}Al_x$ compounds does not alter the planar anisotropy, the present results clearly show that in alloys with $x > 2$, a uniaxial anisotropy is observed. In a number of previous studies only samples with Al content up to $x = 2$ have been investigated (see, e.g., [3, 27]) and this is, most likely, the reason for the failure of previous studies to observe the effects found in the present work. In addition, a number of previous investigations have dealt with 2:17 compounds involving rare earths other than Sm. As described below, it is the magnetic behaviour of the rare earth sublattice which, in the 2:17 phase, is responsible for the formation of a uniaxial anisotropy under certain circumstances. Studies on 2:17 nitrides indicate that the compound with Sm shows a much greater tendency towards uniaxial anisotropy than compounds with other rare earth [3].

In the R_2Fe_{17} compounds, the magnetization of the Fe sublattice exhibits a planar anisotropy. The net anisotropy is determined from the sum of the Fe sublattice anisotropy and the rare earth sublattice anisotropy. It is the difference in the temperature dependence of these two quantities which is responsible for the presence of the spin reorientation transition in many of these materials. This behaviour has been described successfully on the basis of exchange and crystal field models by Coey and co-workers [3, 10, 11, 28]. The rare earth sublattice anisotropy is determined by the product of the second-order Stevens coefficient, α_j, which reflects the form of the 4f charge distribution of the rare earth ions, and the second-order crystal field parameter, A_2^0. As A_2^0 is typically negative in rare earth transition metal 2:17 compounds [3, 10], and a negative product $\alpha_j A_2^0$ gives a uniaxial contribution from the rare earth sublattice to the total anisotropy, it is in cases where the second-order Stevens coefficient is positive that easy axis anisotropy and hence hard magnetic properties are favoured. This explains the tendency for Sm (which has positive α_j) compounds to exhibit uniaxial anisotropy when similar compounds of many other rare earths (which have α_j negative) retain planar anisotropy.

The present studies of $Sm_2Fe_{17-x}Al_x$ compounds suggest that increasing the Al content of the compounds increases the uniaxial contribution to the anisotropy which results from the Sm sublattice. This would suggest an increase in the magnitude of the negative A_2^0 as Al is substituted for Fe.

It has been suggested that Sm_2Fe_{17} may undergo a magnetic transition at low temperature [29]. There is, however, no clear evidence to associate this with a spin reorientation transition [30]. In the present series of alloys it is apparent that those alloys with $x > 2$ show a room temperature uniaxial anisotropy while those with $x < 2$ do not. It is likely that the substitution of Al for Fe increases the spin reorientation transition temperature in the $Sm_2Fe_{17-x}Al_x$ series. The present investigations indicate that the alloy with composition $Sm_2Fe_{15}Al_2$ has a spin reorientation transition near room temperature. The sample of this composition shows components of both uniaxial and planar anisotropies. This mixed behaviour may be an intrinsic property of the broad spin reorientation transition or it may result from a mixture of anisotropies in the sample characteristic of (say) compositional inhomogeneities. Systematic AC susceptibility of Mössbauer effect studies of these alloys as a function of temperature will be necessary to clarify the details of the effects of Al substitutions on the spin reorientation transition.

5. Conclusions

The present studies have clarified the effects of Al substitutions for Fe in $Sm_2Fe_{17-x}Al_x$ compounds. Compounds with x up to 4 have been studied here and are shown to be single-phased materials with the Th_2Zn_{17} structure. These studies have shown that a room temperature uniaxial anisotropy is developed in alloys with $x > 2$. This represents the first observation of an easy axis anisotropy at room temperature in a rare earth–transition metal 2:17 compound without interstitial substitutions. This indicates the possibility of producing permanent magnetic materials in rare earth–transition metal compounds without the need for interstitial nitrogen or carbon additions and the subsequent reduction in thermal stability. The present investigations also show an increase in the Curie temperature of about 80 K in those compositions which exhibit a clearly defined easy axis anisotropy. Previous investigations on the magnetic properties of unoriented powders of this series [6] have indicated a decrease in saturation magnetization and an increase in coercivity as a function of Al content. In view of the present studies it important to extend these studies to include the magnetic properties of field-oriented samples in order to fully appreciate the possible role of these materials in permanent magnet applications.

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