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EFFECT OF Al SUBSTITUION AND INERSTITIAL MODIFICATION BY C IN $SmTbFe_{17}$

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ABSTRACT

Substitution of Al for Fe in $SmTbFe_{17}$ as well as the addition of C results in the increase in the unit cell volume. The saturation magnetization at 80K decreases due to Al substitution. The saturation magnetization of $SmTbFe_{15}Al_2C$ is found to be more than that of $SmTbFe_{15}Al_2$. The Curie temperature is found to increase (from 408 K) by 71 K due to Al substitution (x = 2) and by another 51 K due to subsequent C addition. The planar anisotropy of $SmTbFe_{17}$ is retained by the substitution of Al whereas it is weakened by addition of C.

1. INTRODUCTION

Rare earth - iron intermetallic compounds of the type R_2Fe_{17} (R = rare earth) have attracted considerable attention in recent years as possible candidates for high performance permanent magnet materials [1-3]. R_2Fe_{17} compounds crystallize in either the rhombohedral Th_2Zn_{17} – type or hexagonal Th_2Ni_{17} – type structure. The Curie temperatures (T_C) of R_2Fe_{17} compounds are low and having planar anisotropy at room temperature [4,5]. The enhancement of T_C and uniaxial anisotropy with interstitial modification with N and C in R_2Fe_{17} compounds has attracted considerable attention [6,7]. In addition, non-magnetic elements such as Al, Ga and Si, when substituted for Fe, enhance T_C by a large extent [8, 9]. Suresh and Rama Rao [10] have reported that substitution of Al for Fe in $ErPrFe_{17}$ has increased T_C from 285K to 435K for Al = 3 and with further increase of Al, T_C has decreased. Ingersoll *et al* [11] have reported that substitution of Ga and Si for Fe in $ErPrFe_{17}$ has increased T_C till Ga/Si = 3.5. Venkatesan *et al.* [12] have reported an increase in T_C in $HoErFe_{17-x}Ga_x$ with increasing concentration of Ga up to x=4. Huang and Ching [13, 14] on the basis of band structure calculations explained the enhancement of T_C for Al, Ga, and Si substituted Nd_2Fe_{17} compounds. Sabiryanov and Jaswal [15] showed that there is a good agreement of the experimental and the theoretical results for T_C by considering the Mohn and Wohlfarth model [16]. In this paper, we report the influence on the structural and magnetic properties due to the addition C along with Al substitution.

2. EXPERIMENTAL DETAILS

The compounds $SmTbFe_{17-x}Al_x$ (x = 0, 2) and $SmTbFe_{15}Al_2C$ were prepared by arc melting high pure elements (rare earths of 99.9% purity and Fe of 99.95% purity and Al of 99.99% purity) under Ar atmosphere. The ingots were melted several times and the samples were homogenized in vacuum (10^{-6} torr) at 950°C for seven days and were then quenched in ice water mixture. Structural characterization was carried out on the powders by taking X-ray diffraction patterns using FeK_α radiation. Magnetization measurements were carried out using a vibrating sample magnetometer (Model no. PAR 155) up to a field of 12 kOe and in the temperature range 80 - 600 K. The saturation magnetization (M_s) was found from Honda plots.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns obtained for $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$ are shown in Fig.1. All the compounds have formed in the Rhombohedral (Th_2Zn_{17}) structure with traces of α-Fe. The lattice parameters 'a' and 'c' are found to increase with the Al substitution as shown in Table. 1. This is in accordance with the larger atomic radius of Al compared to that of Fe. The unit cell volume is also found to increase in $SmTbFe_{15}Al_2$ by the interstitial modification by C.

Fig. 2 shows the variation of magnetization of $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$. It is found that the value of magnetization is approaching saturation at 1.2 T. The values of saturation magnetization (M_s) derived from Honda plots of compounds $SmTbFe_{17-x}Al_x$ measured at 80 K decreases from 114 emu/g for $SmTbFe_{17}$ to 102 emu/g for $SmTbFe_{15}Al_2$ and 113 emu/g for $SmTbFe_{15}Al_2C$.

It is known that in the R_2Fe_{17} compounds the total magnetic moment follows the variation of the magnetic moment of the Fe sublattice, for a given rare earth sublattice. The combined effect of the charge transfer between the valance band of substituent atom and the 3d band of Fe and or magnetic dilution could affect the magnetic moment of the Fe sublattice and T_C. The substitution of a non-magnetic metal or metalloid in the R_2Fe_{17} compounds leads to changes in the density of states (DOS) of the 3d band. Huang and Ching [13, 14] have shown from the electronic structure calculations in Al/Ga/Si substituted Nd_2Fe_{17} that the variation in T_C mainly depends on the density of states (DOS) at E_F. They have obtained partial density of states of Ga (4p) band that has been hybridized with the Fe (3d) band and shown that the Ga (4p) band extends all the way to the Fermi level. Suresh and Rama Rao [10] have observed a decrease in the magnetization of $ErPrFe_{17-x}Al_x$ with increasing Al content. Huang and Ching [13] have reported a similar observation in $Nd_2Fe_{17-x}Al_x$ and have attributed the same to charge transfer from 3d band of Fe to the valence band of Al.

According to band structure calculations, the volume dependence of magnetization '$\partial M/\partial V$' is related to the electronic band structure and guided by the relation where, $N\uparrow(E_F)$ and $N\downarrow(E_F)$ are, respectively, the average spin up and spin down densities of states per Fe atom at the Fermi level and I is the Stoner parameter. Both spin – up sub bands are filled in R_2Fe_{17} compounds. The density of states at the Fermi level even for a weak ferromagnet such as R_2Fe_{17} is quite high. Therefore according to Eq. 1 $\partial M/\partial V$ is large and positive. This implies that for a given increase in the unit cell volume, the increase in the magnetization is larger in $SmTbFe_{15}Al_2C$

$$\frac{V}{M}\left\{\frac{\partial M}{\partial V}\right\} = \left\{\frac{5}{3}\right\}\frac{2I}{\left[\dfrac{1}{2N_{\uparrow}(E_F)} + \dfrac{1}{N_{\downarrow}(E_F)} - I\right]} \qquad (1)$$

compound when compared to that of without carbon.

The variation of the Magnetization with temperature of $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$ compounds are shown in Fig.3. It shows the order disorder transition with respect to the temperature. Curie temperatures (T_C) are found at the point of inflection. T_C is found to increase for both Al substitution and C addition in $SmTbFe_{17}$ compound. The value of T_C for $SmTbFe_{17-x}Al_x$ increases from 408 K for x = 0 and 479 K for x = 2 and by another 51 K due to subsequent C addition In the case of the Nd_2Fe_{17} compound, Si, Ga or Al, partially replacing Fe, preferentially occupies the 18h site and interacts strongly with the nearby Fe atoms leading to a modification in the DOS at the Fermi level [13.14].

Sabiryanov and Jaswal [15] have investigated the effect of Si, Ga or Al substitution on the electronic structure and T_C of Sm_2Fe_{17} by means of self-consistent spin-polarized band. In this model the value of T_C is given as

where, M_0 is the Fe magnetization at 0 K per unit cell and χ_0 is the exchange enhanced ferromagnetic susceptibility, at 0 K, and is given by

They have shown that the magnetization decreases with increasing Si, Ga or Al. Thus T_C

$$T_C \propto \frac{M_0}{\chi_0} \qquad (2)$$

$$\chi_0^{-1} = \left[\frac{1}{2N_{\uparrow}(E_F)} + \frac{1}{N_{\downarrow}(E_F)} - I\right]\frac{1}{2\mu_B^2} \qquad (3)$$

increases with x, as there is a depopulation of the 3d band. T_C increases in spite of a decrease in M_S for both Al substitution and C addition. This can be due to a decrease of $N\uparrow(E_F)$ and $N\downarrow(E_F)$ leading to a large increase of χ_0^{-1} overriding the decrease of M_S. Suresh and Rama Rao [10] have observed an increase in the T_C of $ErPrFe_{17-x}Al_x$ with increasing x, up to x = 3, by about 150 degrees. This has been explained on the basis of a modified Mohn - Wohlfarth model, taking into consideration the spatial variations of spin density leading to an additional exchange [16].

In the compound $SmTbFe_{15}Al_2C$ the enhancement of Fe – Fe exchange interaction due to increase in inter-atomic distances leads to enormous increase in T_C. This occurs as a direct consequence of the volume expansion with carbon insertion. As a result there is band narrowing of 3d band leading to the increase in the magnetization. In the fig. 3 it is seen that the moment value is very close to zero value after transition. This could be due to the decomposition of the compound.

Magnetically aligned samples for X–ray studies and magnetization measurements were prepared by mixing fine powders of the alloy with epoxy resin and letting the mixture dry in the presence of a magnetic field of 2.5 T [applied perpendicular to the substrate for the X-ray studies and parallel to the substrate for the magnetization studies].

Fig.4 shows the room temperature X-ray diffraction patterns for the oriented samples. In the $SmTbFe_{17-x}Al_x$ compounds, only (300) and (220) peaks are observed revealing a planar anisotropy. However, in the case of $SmTbFe_{15}Al_2C$ in addition to (300) and (220) peaks, the presence of (006) peak indicates that the easy magnetization direction has a tendency to move towards 'c' axis. The magnetization measurements as a function of magnetic field carried out at 300 K along the hard and easy directions for $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$ samples are supporting the findings from the X-ray diffraction studies.

4. SUMMARY

The effects of substitution of Al for Fe in $SmTbFe_{17}$ and interstitial modification by C in $SmTbFe_{15}Al_2$ have been investigated. A unit cell volume expansion is observed for both Al and C additions. Substitution of Al and addition of C leads to decrease in the saturation magnetization. The saturation magnetization then decreases due to a modification in the density of states at the Fermi level. Increase in T_C is observed with Substitution of Al and addition of C. Easy magnetization direction has a tendency to move towards 'c' axis in $SmTbFe_{15}Al_2C$.

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REFERENCES

[1] K. H.J. Buschow, Rep. Prog. Phys. **40** (1977) 1123.
[2] W. E. Wallace, Solid State Chem. **16** (1985) 127.
[3] K. H. J. Buschow and J. S. van Wieringen, Phys. Stat. Solidi **42** (1970) 231
[4] K. H. J. Buschow Rep. Prog. Phys. **54** (1991) 1123 .
[5] M. Valeanu, N. Plugaru and E. Burzo, Solid State Commun. **89** (1994) 519
[6] J. M. D. Coey and H. Sun, J. Magn. Magn. Mater. **87** (1990) L251.
[7] X. –P. Zhong, R. J. Radwanski, F. R. de Boer, T. H. Jacob and K. H. J. Buschow, J. Magn. Magn. Mater. **86** (1990) 76
[8] Z. Wang and R. Dunlap, J. Phys. Condens. Matter **5** (1993) 2047.
[9] Zhao-hua Chang, Bao - gen Shen, and Bing Liang, J. Appl. Phys. **78** (1995) 1385.
[10] K. G. Suresh and K. V. S. Rama Rao, J. Appl. Phys. **79** (1996) 345.
[11] J. C. Ingersoll, G. Markandeyulu, V. S. Murty, K. V. S. Rama Rao, J. Alloys and Compd. **354** (2003) 29
[12] M. Venkatesan, U. V. Varadaraju and K. V. S. Rama Rao, J. Magn. Magn. Mater. **182** (1998) 231.
[13] M. –Z. Huang and W. Y. Ching, J. Appl. Phys. **76** (1994) 7046.
[14] M. –Z. Huang and W. Y. Ching, J. Appl. Phys. **79** (1996) 5545.
[15] R. F. Sabiryanov and S. S. Jaswal, J. Appl. Phys. **76** (1996) 5942.
[16] P. Mohn and E. P. Wohlfarth, J. Phys. F Met. Phys. **17** (1987) 2421.

TABLES

Table-1. Lattice parameters, unit cell volume, saturation magnetization at 80 K and Curie temperature for $SmTbFe_{17-x}Al_x$ (x = 0, 2) and $SmTbFe_{15}Al_2C$

Compounds	**a (Å)**	**c (Å)**	**c/a**	**V ($Å^3$)**	**M_s (80 K) (emu/g)**	**T_C (50 Oe) (K)**
$SmTbFe_{17}$	8.535	12.480	1.462	787	115	408
$SmTbFe_{17}Al_2$	8.581	12.543	1.462	800	102	479
$SmTbFe_{17}Al_2C$	8.679	12.540	1.440	818	113	520

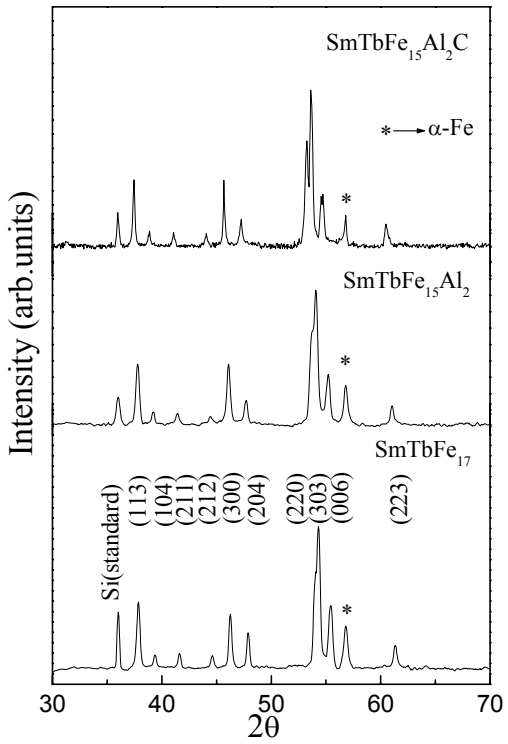

Fig.1 X-ray diffraction patterns of $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$

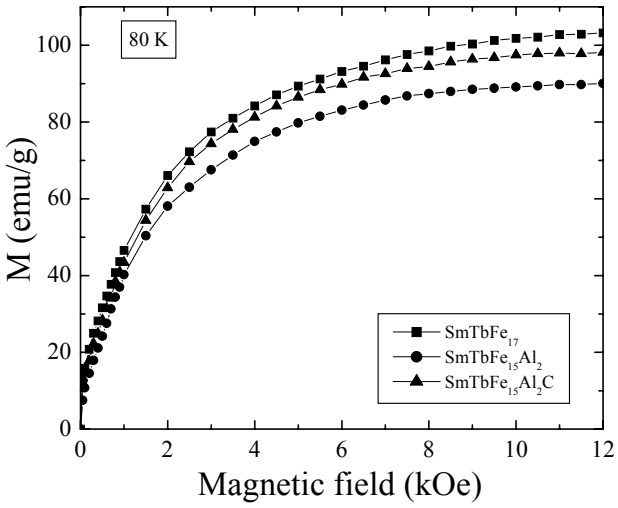

Fig. 2. Variation of M with x in $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$.

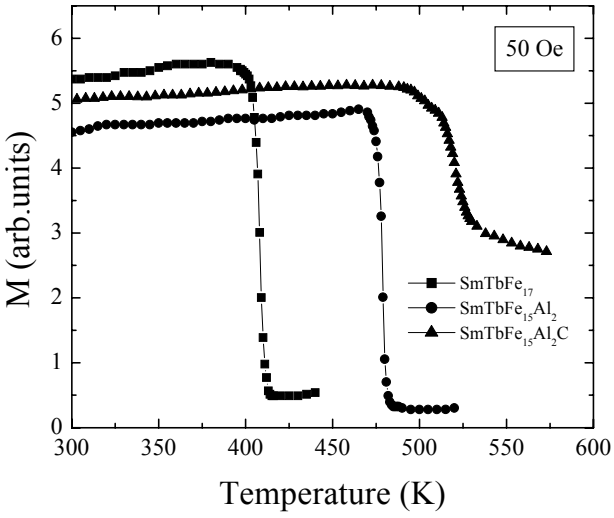

Fig. 3. Variation of T_C with x in $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$.

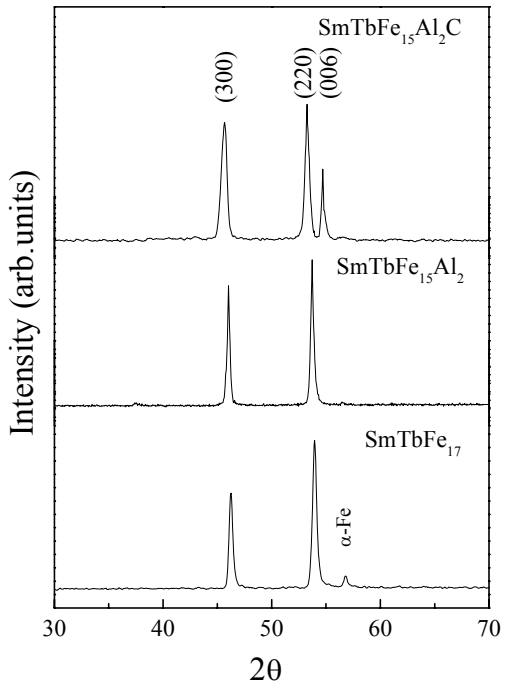

Fig. 4. X-ray diffraction patterns of oriented powders $SmTbFe_{17-x}Al_x$ and $SmTbFe_{15}Al_2C$