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I.A. Al-Omari*

Sitaram Jaswal†

A.S. Fernando‡

David J. Sellmyer**

*University of Nebraska - Lincoln

†University of Nebraska, sjaswal1@unl.edu

‡University of Nebraska - Lincoln

**University of Nebraska-Lincoln, dsellmyer@unl.edu

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Mössbauer study of permanent-magnet materials: $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds

I. A. Al-Omari, S. S. Jaswal, A. S. Fernando, and D. J. Sellmyer

Behlen Laboratory of Physics and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska 68588-0111

The Fe^{57} Mössbauer spectra of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$, where $x=0, 1.0, 2.0, 3.0,$ and 4.0 , have been measured at room temperature and analyzed. The ternary compounds $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ have the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure. Mössbauer measurements showed that all the compounds studied were ferromagnetic. The average hyperfine field was found to decrease with the increasing aluminum concentration, which is in qualitative agreement with magnetic measurements. The decrease in the average hyperfine field was from 224 kOe at $x=0$ to 174 kOe at $x=4$. By fitting the spectra we found that the hyperfine fields for the iron sites decrease in the order $6c, 9d, 18f,$ and $18h$. The measured average isomer shift relative to α -iron was found to increase linearly with x . Analysis of the spectra showed that Al atoms occupy the $6c, 18h,$ and $18f$, but not $9d$, Fe sites and the fraction of occupancy of Al was found to depend on x .

I. INTRODUCTION

It has been discovered recently that the hard-magnet properties of Fe-rich intermetallic compounds improve considerably upon nitrogenation.¹⁻³ Efforts are underway to see if substitutional impurities can accomplish the same goal. Compounds of the type $\text{R}_2\text{Fe}_{17-x}\text{M}_x$, ($\text{R}=\text{Ho}, \text{Y}, \text{Sm}, \text{Ce}, \text{Pr},$ and Nd ; $\text{M}=\text{Al}, \text{Ga}, \text{V}, \text{Co},$ and Ni) have been studied³⁻⁶ and their magnetic ordering temperatures were found to increase by substituting other elements for iron. Weitzer *et al.*⁷ found that the Curie temperature (T_c) changed from 265 K for $\text{Ce}_2\text{Fe}_{17}$ to 385 K for $\text{Ce}_2\text{Fe}_{15}\text{Al}_2$, and from 335 K for $\text{Nd}_2\text{Fe}_{17}$ to 440 K for $\text{Nd}_2\text{Fe}_{15}\text{Al}_2$ and to 520 K for $\text{Nd}_2\text{Fe}_{15}\text{Ga}_2$. Effects of Al substitution on the magnetic anisotropy and Curie temperature of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds have been studied by Wang and Dunlap.⁸ They found that T_c for these compounds depends on the Al concentration (x) and it reaches a maximum of 471 K for $\text{Sm}_2\text{Fe}_{14}\text{Al}_3$, compared to 391 K for the parent compound $\text{Sm}_2\text{Fe}_{17}$. They found also that the anisotropy changed from planar for $x \leq 1$ to uniaxial for $x \geq 3$. These changes in T_c and the anisotropy are promising improvements to the permanent-magnet properties of the parent compounds. Low-temperature measurements for $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ by McNeely and Oesterreicher⁹ showed that the magnetization of these compounds decreases by 83% as x increases from 0 to 9.5. The coercive force (H_c) increases by increasing x and it reaches a value of 15 kOe with $x=9.5$ at $T=4.2$ K. In this article we report on Mössbauer studies for $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ to understand the effect of Al on their magnetic properties and the site occupation of the different Fe sites. Also we use Mössbauer spectroscopy to look for small amounts of α -Fe in these compounds.

II. EXPERIMENTAL PROCEDURE

Bulk samples of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ with $x=0, 1, 2, 3,$ and 4 were prepared by arc melting the elemental constituents in a water-cooled copper boat in a flowing-argon gas atmosphere. All the starting elements used were at least of 99.99% purity.

The alloys were melted several times to insure homogeneity. The samples were wrapped separately in tantalum foils and heat-treated below 3×10^{-6} Torr vacuum at 1000 °C for about 72 h, and subsequently quenched in water.

Room-temperature x-ray diffraction measurements on powder samples using $\text{Cu K}\alpha$ radiation showed only the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure with a small amount of α -Fe. The magnetization of the compounds was measured at 5 and 300 K with a superconducting quantum interference device (SQUID) and alternating force gradient magnetometer (AFGM), respectively.

The samples for Mössbauer spectroscopy were prepared by sprinkling a thin layer of the powder of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ on a piece of tape. The samples were studied by using a Ranger Mössbauer spectrometer, model MS1200. The velocity drive of this spectrometer operates in the constant acceleration mode. Co^{57} in Pd was used as the γ -ray source in this experiment. All the isomer shifts were measured relative to α -iron at room temperature and α -iron was also used for calibration.

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature Mössbauer spectra and the fitting (the solid curves) for $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ with $x=0, 1, 2, 3,$ and 4 . The spectra show that all the samples are magnetically ordered for all values of x and all of them have different subspectra with different magnetic hyperfine fields. A standard program was used to fit the spectra, where each spectrum was fitted with a set of seven subspectra, which is similar to the previous models used by Ping *et al.*,¹⁰ Long *et al.*,¹¹ and Yelon *et al.*¹² for 2:17 compounds. The weak features indicated by arrows in Fig. 1 are the first and sixth lines due to α -Fe in samples with $x=1$ and 2. From the relative intensity of the subspectrum the atomic percentage of α -Fe was estimated to be less than 2%. For the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure there are four different iron sites, $6c, 9d, 18f,$ and $18h$, with different environments. Previous Mössbauer measurements by Long *et al.*^{11,13} for $\text{Nd}_2\text{Fe}_{17}$ and

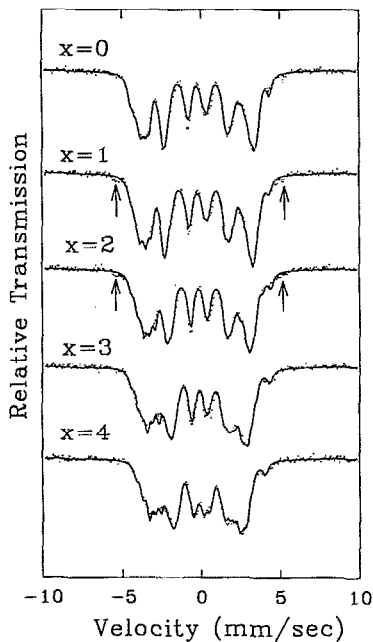


FIG. 1. Room-temperature Mössbauer spectra of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds. The solid curves represent the fitting. Arrows indicate the first and sixth lines due to α -Fe.

$\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, Mössbauer and neutron diffraction by Yelon *et al.*¹² for $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$, and Mössbauer measurements by Hu *et al.*¹⁰ for $\text{R}_2\text{Fe}_{17}\text{N}_{3-\delta}$ showed that the hyperfine fields decrease in the order $6c$, $9d$, $18f$, and $18h$. The $6c$ site has the largest hyperfine field since it has the largest number of iron nearest neighbors. In our fitting and analysis of the data we kept the same order. The seven subspectra used in fitting correspond to one spectrum for $6c$ and two subspectra for each of the other three sites with the relative intensity 2:1. The parent compound $\text{Sm}_2\text{Fe}_{17}$ was studied for comparison with other compounds and other data. The average hyperfine field for different sites and for different Al concentrations was found to decrease with increasing concentration of the nonmagnetic element, Al, as seen in Fig. 2. This decrease is in qualitative agreement with the magnetization measurements by McNeely and Oesterreicher.⁹ The average hyperfine field for the parent compound was 224 kOe which is in good agreement with other values of 221 kOe by Hu *et al.*¹⁰

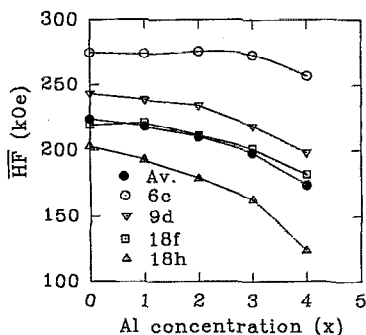


FIG. 2. Dependence of the average hyperfine field for the different Fe sites of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ on the Al concentration x , at $T=295$ K.

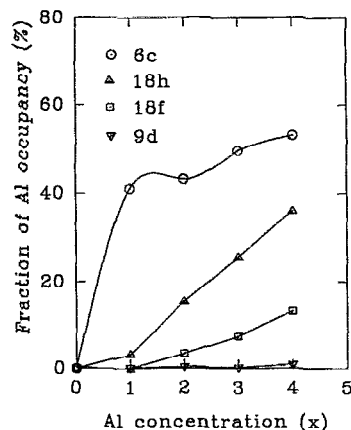


FIG. 3. Dependence of the percentage fraction of aluminum occupancy for different sites on the Al concentration x .

and 216 kOe by Long *et al.*¹¹ for related compounds. The Curie temperature for these compounds increases with x and reaches a maximum at $x=3$: T_c changes from 391 K for $\text{Sm}_2\text{Fe}_{17}$ to 471 K for $\text{Sm}_2\text{Fe}_{14}\text{Al}_3$.⁸ This increase of 20% in T_c in spite of the decrease in the average hyperfine field by 12% must be due to the increase in the interatomic exchange interactions upon volume expansion.

The intensity of each subspectrum is proportional to the Fe-site occupation. Using the fitted intensities we calculated the percentage of iron and aluminum at each site. Figure 3 shows the percentage fraction of Al occupancy of each site for the different sites and for different concentrations. From this figure we see that Al prefers to go to the different sites in the order $6c$, $18h$, and $18f$, but not $9d$, which has the smallest Wigner-Seitz cell volume. This is in agreement with previous observations on $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ by Yelon *et al.*¹²

The average isomer shift (IS) relative to α -iron was found to increase linearly by increasing the Al concentration as shown in Fig. 4, where the circles are the experimental IS and the solid line is the linear fit. The parameters for the linear fitting are given by the equation

$$\overline{\text{IS}}(\text{mm/s}) = -0.12 + 0.03x.$$

Figure 4 shows that $\overline{\text{IS}}$ is negative and the magnitude of $\overline{\text{IS}}$ decreases with increasing Al concentration. This decrease

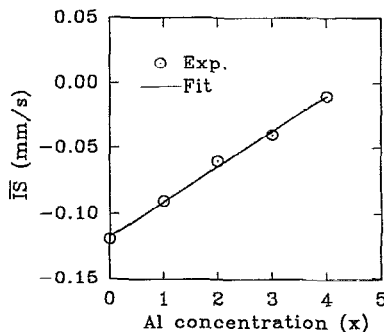


FIG. 4. Dependence of the average isomer shift ($\overline{\text{IS}}$) relative to α -iron for $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds on the Al concentration x .

means a decrease in the probability of finding the s electrons at the nucleus that can be attributed to the expansion of the cell volume. $\overline{\delta IS}/\delta \ln V$ for these compounds was 3.0 mm/s compared to 1.13 mm/s for α -Fe given by Shenon and Wagner¹⁴ and 1.5–2.3 mm/s for R_2Fe_{17} and $R_2Fe_{17}N_{3-\delta}$ at 15 K given by Hu *et al.*¹⁰ The present value is higher than the other values due to the smaller change in the cell volume compared to the others.

IV. CONCLUSIONS

Samples of $Sm_2Fe_{17-x}Al_x$ magnetic compounds have been fabricated and studied by Mössbauer spectroscopy. These compounds have rhombohedral Th_2Zn_{17} single phase with less than 2% α -Fe impurity. All the samples studied are ferromagnetic and the average hyperfine fields, and hence the magnetic moments, are found to decrease as x increases from 0 to 4. Therefore the increase in T_c with x up to $x=3$ must be due to the increase in interatomic exchange interactions between Fe atoms with volume expansion. Adding more Al lowers the exchange interaction due to the decrease in the number of Fe-Fe nearest neighbors, thereby lowering the T_c for $x>3$. Aluminum is found to occupy the three iron sites $6c$, $18h$, and $18f$ with varying degrees of occupancy, but not the $9d$ site. The change in isomer shift with increasing Al concentration corresponds to the decreasing s -electron density at the nucleus caused by the volume expansion.

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