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Mössbauer study of permanent-magnet $R_2Fe_{17-x}M_xC_y$ compounds

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We report Fe^{57} Mössbauer spectroscopy studies of the effect of carbon doping on the magnetic properties of the Fe sites of $R_2Fe_{17-x}M_xC_y$, and of the presence of multiple phases in these systems. In this study two systems, $Sm_2Fe_{14}Al_3C_y$, where $y=0, 1.0, 2.0$, and 3.0 , and $Nd_2Fe_{14.54}Si_{2.46}C_y$, where $y=0, 0.432$, and 2.544 , were measured at room temperature and analyzed. The ternary compounds $R_2Fe_{17-x}M_xC_y$ studied here have the rhombohedral Th_2Zn_{17} structure with c -axis anisotropy. The Al and Si site occupation used in the fitting were taken from previous results. Analysis of the Mössbauer spectra showed that the hyperfine fields for the different sites decreased in the order $6c, 9d, 18f$, and $18h$. The average hyperfine field for $Sm_2Fe_{14}Al_3C_y$ was found to increase with increasing carbon concentration, which is in qualitative agreement with magnetic measurements. For $Nd_2Fe_{14.54}Si_{2.46}C_y$ the average hyperfine field was found to increase for low C concentration and decrease for high C concentration; this behavior is in agreement with our magnetization measurements. The measured average isomer shift relative to α -iron was found to increase with y . In these compounds alloying with C and/or M can improve the magnetic properties such as Curie temperature and magnetization which make them potential candidates for permanent magnet development. © 1996 American Institute of Physics. [S0021-8979(96)36708-0]

I. INTRODUCTION

A large improvement of the hard-magnet properties of Fe-rich intermetallic compounds can be considerably achieved upon introducing nitrogen,¹⁻³ carbon,⁴⁻⁸ or substitutional impurities in the compounds of the type $R_2Fe_{17-x}M_x$ ($R=Ho, Y, Sm, Ce, Pr$, and Nd ; $M=Al, Ga, Si, V, Co$, and Ni).⁹⁻¹⁵ In all these studies the magnetic ordering temperatures were found to increase by substituting other elements for iron or by nitrogenation or carbonation. Wang and Dunlap¹⁶ found that the Curie temperature (T_c) changed from 391 K for Sm_2Fe_{17} to 471 K for $Sm_2Fe_{14}Al_3$. A further increase in T_c can be achieved by adding C or N to these compounds. Shen *et al.*^{17,18} have discovered recently that $Sm_2Fe_{17-x}Ga_xC_y$ can be formed by arc-melting. It is claimed that these materials are more stable at high temperature than those prepared by the gas reaction method. Zheng *et al.*¹⁹ found that T_c goes to 563 K for $Sm_2Fe_{14}Al_3C_3$ which is close to T_c (585 K) for $Nd_2Fe_{14}B$.^{20,21} They found also that the compounds $Sm_2Fe_{14}Al_3C_y$, $0 \leq y \leq 3$, have c -axis anisotropy and the anisotropy field increases from 15 kOe for $y=0$ to more than 100 kOe for $y \geq 2$. Additionally, they found that the magnetization of these compounds increases by a small amount, 96 emu/g for $y=0$ to 100 emu/g for $y=2$, with increasing C concentration.

A neutron diffraction study of $Nd_2Fe_{14.54}Si_{2.46}C_y$, y between 0 and 2.544, by Yelon and Hu²² showed that there are two carbon phases in the sample with $y=2$; one of these phases has low C concentration, $y=0.432$, and the other has high carbon concentration, $y=2.544$; C was found to occupy the $18g$ site for $y=0.432$ and $9e$ site for $y=2.544$. They also found that the fraction of occupancy of Si are 6%, 8%, and

30% for the sites $9d, 18f$, and $18h$, respectively.

In this article we report on Mössbauer experiments for $Sm_2Fe_{14}Al_3C_y$ and $Nd_2Fe_{14.54}Si_{2.46}C_y$ to study the effect of C on the magnetic properties of these compounds. We also use Mössbauer spectroscopy to determine the amount of α -Fe and the presence of multiple phases in these systems.

II. EXPERIMENTAL PROCEDURE

Bulk samples of $Sm_2Fe_{14}Al_3C_y$ with $y=0, 1, 2$, and 3 , were prepared by arc-melting the constituent elements with an Fe-C alloy in a water-cooled copper boat in a flowing argon-gas atmosphere. All the starting elements used were at least of 99.9% purity. The alloys were melted several times to ensure homogeneity. The $Sm_2Fe_{14}Al_3C_y$ samples were wrapped separately in tantalum foil and heat treated in a vacuum at 1100 °C for about 17 h,¹⁹ and subsequently quenched in water.

Samples of nominal composition $Nd_2Fe_{15}Si_2$ were prepared by arc-melting with constituent elements of at least 99.9% purity under an argon atmosphere. For homogeneity, samples were remelted several times. The resulting ingots were vacuum annealed in quartz crucibles at 1000 to 1100 °C for 4 days. Carbide samples were prepared by heating ground powders, <45 μm diameter, of the original alloy in methane (CH_4) gas. The system was flushed several times with methane gas to ensure minimum oxygen contamination. The carbide samples were prepared by heating at a rate of 10 °C/min to 500 °C and held for 2 h to allow carbon diffusion into the samples. After carbonation the system was evacuated and held at a temperature above 100 °C to ensure that hydrogen was removed from the system.

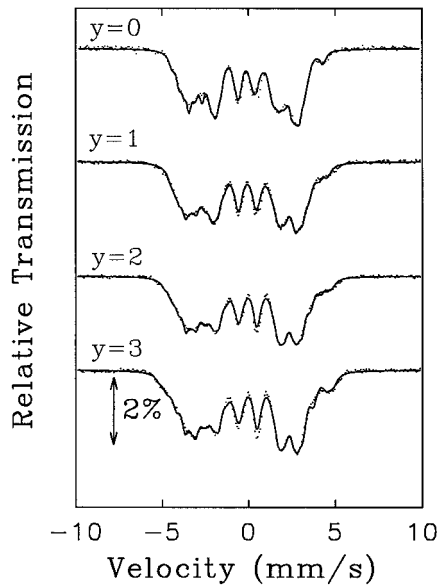


FIG. 1. Room temperature Mössbauer spectra of $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$ compounds. The solid curves represent the fitting.

Room temperature x-ray diffraction measurements on powder samples using a Phillips PWD1710 diffractometer with $\text{Cu } K_\alpha$ radiation showed only the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure with a small amount of α -Fe.

The samples for Mössbauer spectroscopy were prepared by sprinkling a homogeneous thin layer of the powder of the $\text{R}_2\text{Fe}_{17-x}\text{M}_x\text{C}_y$ compounds on a piece of tape. The samples were studied with a Ranger Mössbauer spectrometer, model MS1200. The velocity drive of this spectrometer operates in the constant acceleration mode. A 35 mCi Co^{57} in Rh γ -ray source was used in this experiment. All the isomer shifts were measured relative to α -iron at room temperature and α -iron, with outer lines width of 0.30 mm/s, was also used for calibration. Some of the samples were found to have a small amount of α -iron, less than 5% in $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$, 12% in $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}$, and 20% in $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_2$; this component was subtracted from the raw data before the final fitting.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the room temperature Mössbauer spectra and the fitting (the solid curves) for $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$ with $y=0, 1, 2,$ and 3 and $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_y$ with $y=0$ and 2 . The spectra show that the samples are magnetically ordered for all values of y and all of them have different subspectra with different magnetic hyperfine fields. The spectra were fitted with a set of four subspectra, with linewidth of about 0.40 mm/s, because of the c -axis anisotropy, as mentioned by Long *et al.*,²³ which is similar to the models used by Hu *et al.*,²⁴ Long *et al.*,²⁵ and Yelon *et al.*²⁶ for 2:17 compounds. 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 Al-Omari *et al.*^{14,15} for $\text{Sm}_2\text{Fe}_{17-x}\text{Ga}_x\text{C}_y$ and $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$, Long *et al.*^{23,25,26} for $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, Mössbauer and neutron diffraction by Yelon *et al.*²⁷ for $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$,

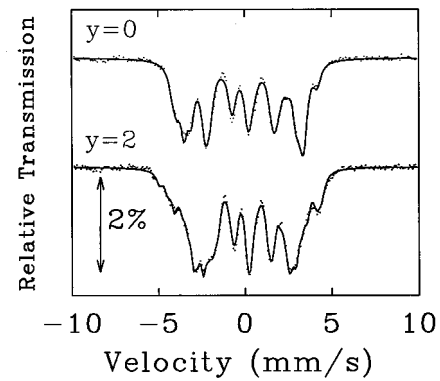


FIG. 2. Room temperature Mössbauer spectra of $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_y$ compounds. The solid curves represent the fitting.

and Mössbauer measurements by Hu *et al.*²⁴ for $\text{R}_2\text{Fe}_{17}\text{N}_{3-\delta}$ showed that the hyperfine fields decrease in the order $6c, 9d, 18f,$ and $18h$. In our fitting and analysis of the data we used the same order.

The relative intensity of various subspectra for different C concentration were the same as of those of $\text{Sm}_2\text{Fe}_{14}\text{Al}_3$ found by Al-Omari *et al.*¹⁵ For $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$ the hyperfine fields for different sites were found to increase with increasing concentration of C as seen in Fig. 3. The average hyperfine field was found to increase from 198 kOe for $y=0$ to 214 kOe for $y=3$ which is in qualitative agreement with the magnetization measurements by Zheng *et al.*¹⁹ The Curie temperature for these compounds increases with y from 483 K for $y=0$ to 563 K for $y=3$.¹⁹ The increase in the average hyperfine field and in the magnetization must be due to the increase in Curie temperature which is due to the increase in the interatomic exchange interactions upon volume expansion.

For $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_2$ the spectrum was fitted with three phases. The first was $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_{0.432}$, the second was $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_{2.544}$, and the third was FeSi. The first two phases were ferromagnetic with four subspectra, with different isomer shifts, quadrupole shifts, and hyperfine fields, and the third phase was paramagnetic with 5% relative intensity.

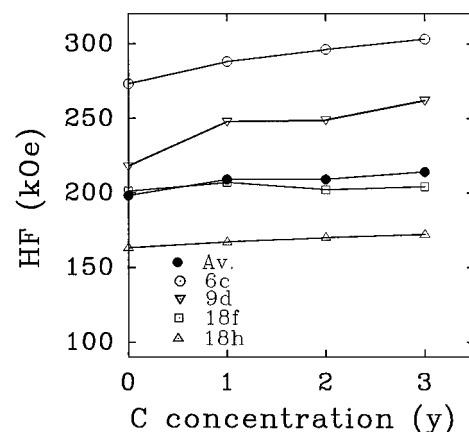


FIG. 3. Dependence of the hyperfine field for the different Fe sites of $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$ on the C concentration y , at $T=295$ K.

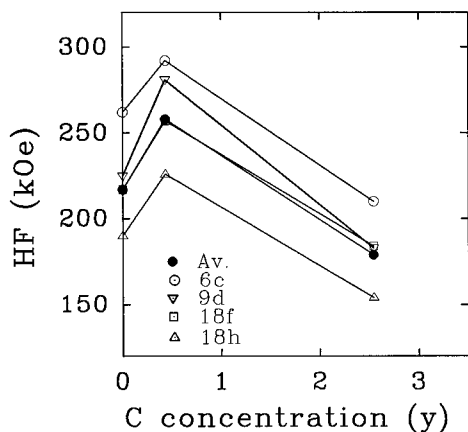


FIG. 4. Dependence of the hyperfine field for the different Fe sites of $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_y$ on the C concentration y , at $T=295$ K.

Guided by the results of Yelon and Hu,²² the intensity of the second phase, high C concentration, was twice the intensity of the first phase, low C concentration. The relative intensities of various subspectra for different C concentrations were the same as of those of $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}$ found by Yelon and Hu,²² since we used the same samples. The hyperfine fields for different Fe sites were found to increase for $y=0.432$ and decrease for $y=2.544$ as shown in Fig. 4. The increase of H_{hf} at lower carbon concentration is due to the enhancement of the Curie temperature which shifts the thermomagnetization curve to higher temperature which is similar to previous observations by Shen *et al.*⁵ for $\text{Tm}_2\text{Fe}_{17}\text{C}_x$. The magnetizations for $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_y$ were measured with our magnetometer and found to decrease from 123.2 emu/g for $y=0$ to 118.4 emu/g for $y=2$; this behavior is in agreement with our Mössbauer measurements for the weighted average hyperfine field which decreases from 217 kOe for $y=0$ to 205 kOe for $y=2$.

The average isomer shift ($\overline{\text{IS}}$) relative to α -iron was found to increase by increasing the carbon concentration for both systems: the increase was from -0.04 mm/s for $y=0$ to -0.01 mm/s for $y=3$ in $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}_y$ and from -0.04 mm/s for $y=0$ to -0.03 mm/s for $y=2.544$ in $\text{Nd}_2\text{Fe}_{14.54}\text{Si}_{2.46}\text{C}_y$. This increase implies a decrease in the s -electron density at the nucleus which can be attributed to the expansion of the cell volume which is similar to the effect of adding nitrogen to the 2:17 compounds as seen by Hu *et al.*²⁴ IS for FeSi was found to be 0.24 mm/s which is in agreement with other values by Shinjo *et al.*²⁸

IV. CONCLUSIONS

Samples of $\text{R}_2\text{Fe}_{17-x}\text{M}_x\text{C}_y$ magnetic compounds have been fabricated and studied by Mössbauer spectroscopy. These compounds have the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure with a small amount of α -Fe impurity. All the samples studied are ferromagnetic and the average hyperfine fields and hence the magnetic moments are found to depend on C concentration in each system. There is a qualitative agreement

between the measured hyperfine fields and the magnetization values. Samples prepared by arc-melting were found to have a single carbon phase, in contrast to those prepared by the gas reaction method, which we and others have found to possess multiple C phases probably due to the different particle sizes. The change in isomer shift with increasing C concentration corresponds to the decreasing s -electron density at the nucleus caused by the volume expansion. The high Curie temperature and uniaxial anisotropy for these compounds with $0 < y < 3$ are promising properties for hard magnets.

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