Magnetic relaxation phenomena in Dy-Sc alloys

R. Abbundi
Naval Surface Weapons Center, White Oak, Maryland 20904

and

J. J. Rhyne and D. M. Sweger
Institute of Materials Research, National Bureau of Standards, Washington, D. C. 20234

and

R. Segnan
American University, Washington, D. C. 20014

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Neutron-scattering and magnetization experiments on R_xSc_{1-x} (R = Gd, Tb, Ho, and Er) alloys have given anomalous results for the concentration dependence of the magnetic-ordering temperature. In contrast to conventional theoretical arguments and to data on other rare-earth alloys, these systems require large rare-earth concentrations ($15\% \leq x \leq 39\%$) for the onset of long-range magnetic order to occur. The work which we report here deals with the investigation of the Dy_xSc_{1-x} system in the concentration range $0.02 \leq x \leq 0.75$. The Mössbauer effect was used to examine the magnetic hyperfine interaction at the ^{161}Dy nuclei both as a function of temperature and concentration. Neutron scattering on the samples containing <35-at.% Dy indicated no long-range magnetic order at $T = 4.2$ K. However, each of the alloys investigated, including the 2-at.% Dy alloy which was the lowest concentration measured, exhibits a well-defined magnetic hyperfine splitting at this temperature. The magnitude of this splitting is 45 ± 0.5 cm/sec and corresponds to a field approximately equal to that found in pure Dy metal, and is independent of the Dy concentration contained in the alloy. The observed magnetic hyperfine lines for the alloys in the lower Dy concentration region ($\leq 25\%$) are relaxation broadened with increasing temperature, while the overall splitting remains essentially independent of temperature. These spectra are analyzed in terms of an electronic-spin-relaxation model for an effective spin-$\frac{1}{2}$ system.

INTRODUCTION

The element scandium possesses many similar chemical and electronic properties to the heavy-rare-earth elements and as such is often referred to as a "pseudo rare earth." It forms complete solid solutions with the rare earths Gd through Tm and shows the same general features in its electronic band structure.[1] However, a major difference between Sc and the rare earths is the fact that Sc does not have any $4f$ electrons, which are responsible for the magnetic properties found in the rare earths. Thus Sc (along with Y, La, and Lu) offers an ideal nonmagnetic substitution for investigating the concentration dependence, if any, of the magnetic properties of the rare-earth elements.

Previous work on many heavy-rare-earth–rare-earth alloys has indicated rather conclusively that a linear relationship exists between the ordering temperature and the two-thirds power of the average deGennes factor.[2] The average deGennes factor represents the square of the effective spin for an alloy and is given by

$$\bar{G} = \sum_i C_i G_i \ , \tag{1}$$

$$G_i = (g_i - 1)^2 J_i (J_i + 1) \ , \tag{2}$$

where C_i is the concentration of the magnetic constituent having a deGennes factor G_i, g is the Landé splitting, and J is the total angular momentum. Figure 1 shows a plot of the ordering temperatures versus $\bar{G}^{2/3}$ for many rare-earth–rare-earth alloys.[2] It can also be seen from this figure, that for these alloys, the ordering temperature goes to zero only for zero concentrations of magnetic rare earths. It is noted that this relationship is obeyed both for intra-rare-earth magnetic alloys and alloys with nonmagnetic lutecium.

A slight deviation from the two-thirds power relationship has been found to exist for R-Y alloys (R is a rare earth). Nagasawa and Sugawara[3] have reported that the ordering temperatures for the Tb_xY_{1-x} system depart from the $\bar{G}^{2/3}$ relationship in the very dilute Tb concentration region ($x \leq 0.037$), with $T_N \to 0$ for a 1-at.% Tb sample. Similar results[4] were found for Dy-Y and Gd-Y alloys containing 1-at.% rare earth.

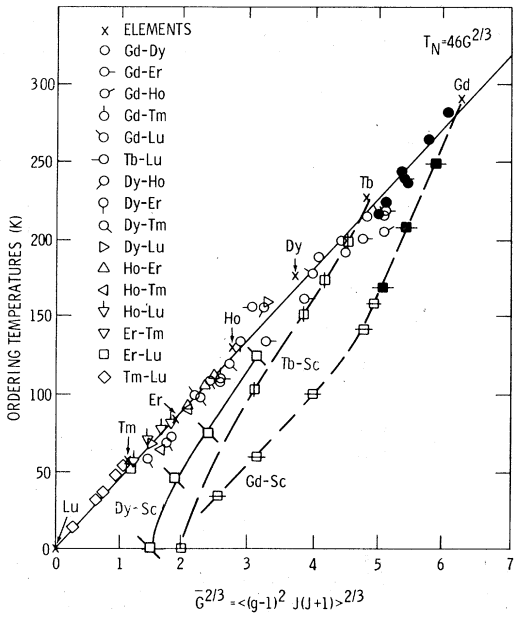

FIG. 1. Ordering temperatures vs $\bar{G}^{2/3}$ for an extensive series of rare-earth–rare-earth alloys, as well as a series of Gd-Sc, Tb-Sc, and Dy-Sc alloys. The open symbols represent Néel temperatures, while the solid symbols are Curie temperatures. The Dy-Sc data are from the present Mössbauer study, and the remainder are from various authors (see Ref. 2).

Thus the ordering temperatures for the *R*-Y alloys go to zero at small but yet finite rare-earth concentrations.

However, results as shown in Fig. 1 on rare-earth–Sc alloys deviate drastically from the $\bar{G}^{2/3}$ relationship. Magnetization data on Gd-Sc alloys have indicated that a sizable departure from the conventional behavior occurs in the lower Gd concentration region, where Nigh *et al.*[5] found that the ordering temperature went to zero at the rather large Gd concentration of 15-at.%.

Child and Koehler have reported neutron-scattering results on the Tb-Sc system[6] which showed that this system exhibited a critical concentration of 25-at.% Tb for the occurrence of long-range order. Likewise, neutron studies on Ho-Sc and Er-Sc alloys[7] reported critical concentrations of 18-at.% Ho and 39-at.% Er for the vanishing of T_N. These results thus indicate that a surprisingly high concentration of magnetic rare earth is necessary to produce magnetic order in *R*-Sc alloys.

Below the critical concentrations for long-range magnetic order, low-field susceptibility data on Gd-Sc and Tb-Sc alloys by Sarkissian[8] and Coles[9] have shown a low-temperature cusp, characteristic of that associated with the cluster freezing temperatures of a spin-glass system. A substantial amount of remanent magnetization and time-dependent magnetization was observed below the spin-freezing temperature.

The work which we report here deals with the investigation of a series of Dy-Sc alloys in an effort to further study the rather anomalous behavior of the *R*-Sc systems and to investigate possible time-dependent or relaxation effects of the spin ordering in the spin-glass concentration regime. We have examined the magnetic hyperfine interaction at the ^{161}Dy nuclei in these alloys as a function of temperature by means of the Mössbauer effect. Neutron-scattering as well as magnetization experiments were also performed on these alloys to confirm the concentration dependence for the onset of long-range magnetic order. Initial experimental results on the observed spectra were published earlier.[10]

EXPERIMENTAL DETAILS

A series of alloys containing 2-, 5-, 10-, 25-, 35-, 50-, and 75-at.% dysprosium were prepared. The constituents were carefully weighed and then arc-melted in an argon atmosphere several times to ensure uniformity. The samples were also weighed after melting to verify that any mass loss was minimal. Following this, Mössbauer absorbers were prepared by filing the samples in a "dry box." The density of ^{161}Dy contained in the absorbers varied from 1.7 to 13.1 mg/cm^2.

The resonance of interest was the 25.6-keV transition in ^{161}Dy. To produce a γ ray of this energy a 131-mg GdF_3 source enriched to 99.99% ^{160}Gd was employed. By means of thermal-neutron irradiation ^{160}Gd produces ^{161}Tb which possesses a 6.9-day half-life and decays by electron emission to ^{161}Dy. Periodic 24-h irradiations at the Natl. Bur. Stand. Reactor resulted in a source strength of approximately 13 mCi. This source yielded an experimentally measured linewidth of 0.53 cm/sec. The γ rays were detected by a high-resolution Si(Li) crystal operated at 115 K and the absorption spectra were stored in a 400 channel multichannel analyzer.

Operating in a constant acceleration mode required a spectrometer capable of handling velocities of ±26 cm/sec. This was accomplished by the use of a commercially available velocity transducer. The drive is equipped with a Moiré grating of known spacing which was used to check not only the linearity of the drive but also served as a means for obtaining an absolute velocity calibration.

RESULTS

Neutron-scattering experiments performed on those alloys containing less than 35-at.% Dy showed no evidence for long-range magnetic order at 4 K. Thus no hyperfine splitting from this source would be expected for alloys below this concentration of Dy. However, the entire series of alloys, including the 2-at.% Dy alloy, exhibited a fully split magnetic hyperfine field at

low temperatures. The magnitude of the saturation magnetic hyperfine splitting was found to be 45 ± 0.5 cm/sec, which is approximately equal to the value measured in pure Dy metal[11,12] and is independent of the Dy concentration in the alloy. However, close examination of the data shows that the width of the lines, and in particular the outer peaks, are very much concentration dependent. Figure 2 shows a comparison at $T = 4.2$ K of the 75-, 35-, 10-, 5-, and 2-at.% Dy alloys. As can be seen in the figure, the lines in the spectrum become narrower as the concentration of Dy increases, indicating a broadening of the distribution of hyperfine fields in the more dilute specimens.

As the temperature is raised, the magnetic hyperfine splitting of the 75-, 50-, and 35-at.% Dy alloys closely follows the typical temperature dependence for long-range-ordered rare-earth metals.[12] The Néel temperatures were determined to be 120, 71.5, and 45 K, respectively, for the 75-, 50-, and 35-at.% alloys. The ordering temperatures of these alloys also departed from the $\bar{G}^{2/3}$ relationship (see Fig. 1) and in fact follow a four-thirds power of the average deGennes factor.

The behavior of these three compositions as a function of temperature was in sharp contrast to that exhibited by those alloys containing 25-at.% Dy or less. The observed hyperfine splitting in the $Dy_{0.25}Sc_{0.75}$ alloy, for various absorber temperatures, is shown in Fig. 3. Unlike the samples with higher Dy concentrations, the spectra for this 25-at.% Dy alloy show that the absorption lines remain fixed in position, independent of temperature, reflecting a constant magnitude for the magnetic hyperfine splitting. However, as the temperature is raised the lines are continually broadened and change in relative intensity and thus lose the detail they possessed at $T = 4.2$ K. At 27 K the peaks have become so broad that they have almost disappeared into the baseline, leaving only the central line composed of a quadrupole splitting. A single absorption line was the only satisfactory fit obtained from the least-squares computer fitting routine for this spectrum due to the very short relaxation time. However, it may be argued on close examination of the 27-K spectrum that the full magnetic hyperfine splitting is still evident with extremely broad absorption lines. A spectrum taken at 30 K contains no indication whatsoever of magnetic splitting. Thus the data for this alloy, which exhibits no long-range magnetic order, indicate that the magnetic hyperfine splitting is essentially independent of temperature. The hyperfine lines are relaxation broadened and for $T > 27$ K they can no longer be resolved.

RELAXATION EFFECTS

Relaxation phenomenon denotes the following: The direction of the ionic spin is not invariant but rather changes orientation after some period of time. The

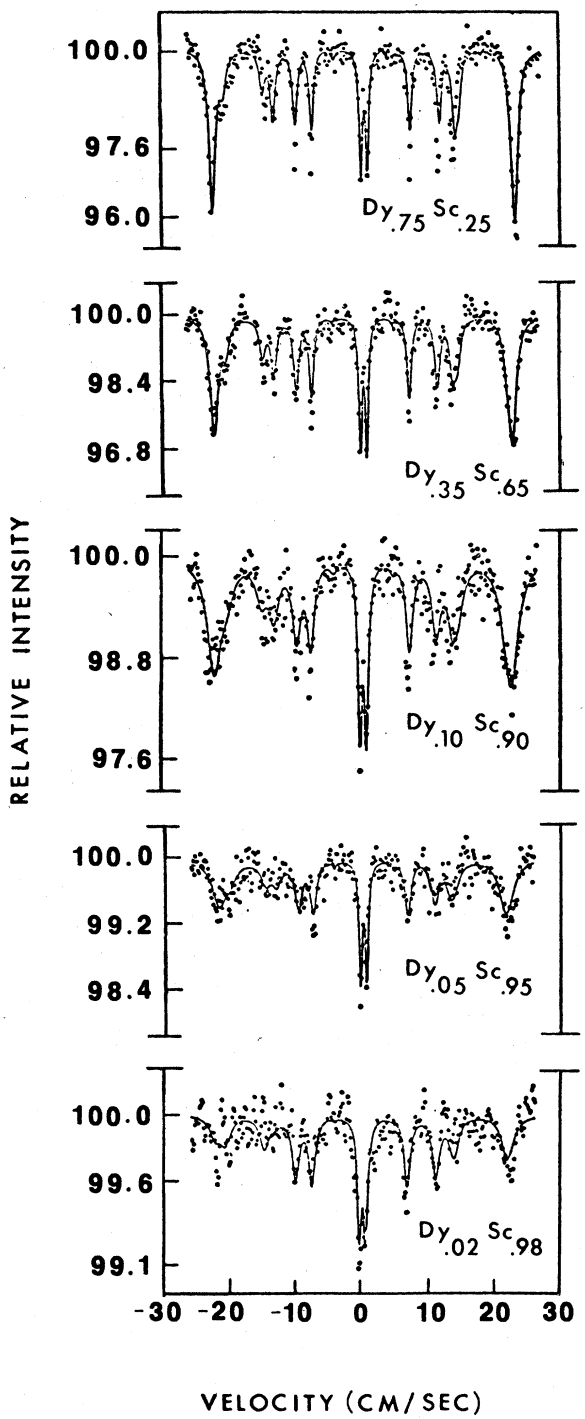

FIG. 2. ^{161}Dy Mössbauer spectra at $T = 4.2$ K for the $Dy_{0.75}Sc_{0.25}$ alloy, $Dy_{0.35}Sc_{0.65}$ alloy, $Dy_{0.10}Sc_{0.90}$ alloy, $Dy_{0.05}Sc_{0.95}$ alloy and the $Dy_{0.02}Sc_{0.98}$ alloy. The solid line represents the least-squares fit of the data.

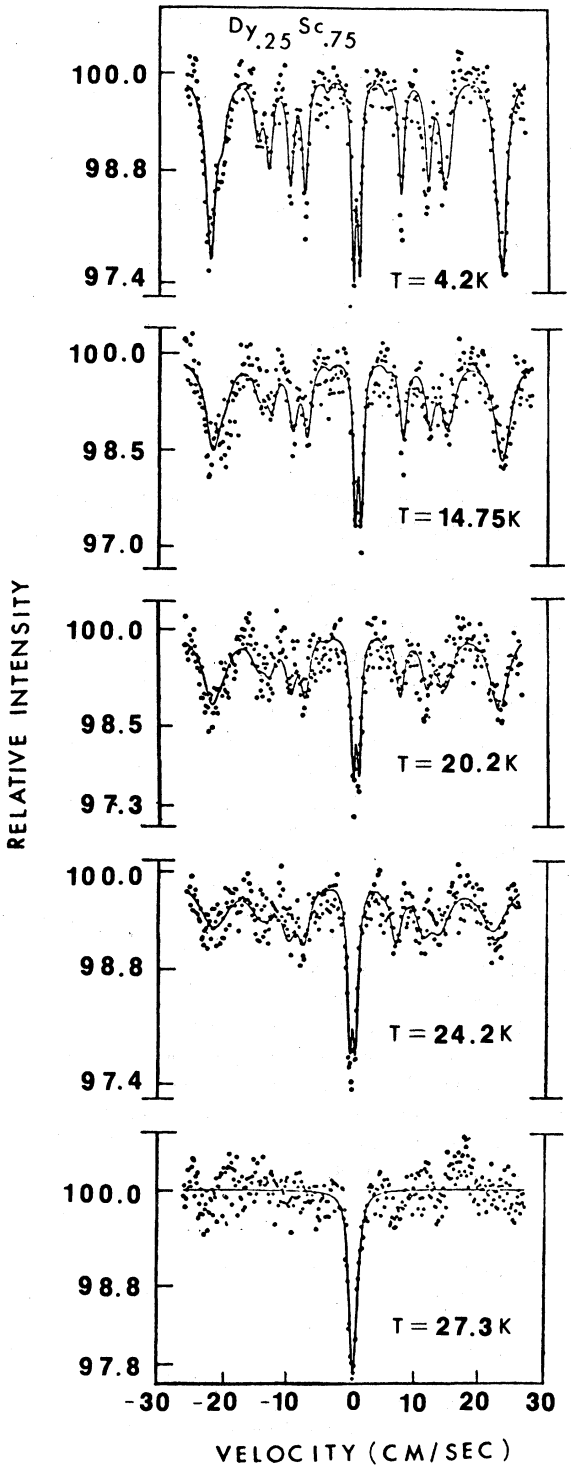

FIG. 3. ^{161}Dy Mössbauer spectra of the $Dy_{0.25}Sc_{0.75}$ alloy as a function of temperature. The solid line represents the least-squares fit of the data.

fluctuation of the ionic spin thus produces a fluctuation of the field at the nucleus. Usually these fluctuations are so rapid that the average field at the nucleus is zero and the Mössbauer effect measures an unsplit absorption line. When the electronic relaxation time is long with respect to the reciprocal of the nuclear Larmor precession frequency ($\tau_R > 1/\omega_L$), fully resolved magnetic hyperfine patterns are observed. In the intermediate range $\tau_R \approx 1/\omega_L$ fluctuations of the hyperfine field manifest themselves in a broadening of the absorption lines in the Mössbauer pattern. The relative amplitudes and sharpness of the individual absorption lines are a very sensitive function of the relaxation time τ_R.

The spectra for the Dy-Sc alloys in the lower Dy concentration region ($\leq$25%) exhibit relaxation behavior and have been analyzed in terms of an electronic-spin-relaxation model known as the "Wickman relaxation model."[13,14] For the particular case of the Dy^{3+} ion, the ground state is a $J_z = \pm\frac{15}{2}$ degenerate Kramers doublet, which constitutes an effective spin-$\frac{1}{2}$ system. In this analysis, rate equations[15] representing the dynamics of the random reversal of the polarity of the magnetic hyperfine field between the two allowed values are used to derive relaxation spectra. Solutions to the rate equations yield the amplitude and half-width of each of the individual absorption lines in the Mössbauer pattern as a function of a particular relaxation time τ_R. This basic model was used in a constrained nonlinear least-squares-curve-fitting routine which fits all 16 lines in the ^{161}Dy spectrum at once, by simultaneous solution of a series of rate equations. The relaxation time is a parameter in the fitting routine which is continuously adjusted by an iterative process until the "best fit" to the data is established.

The relaxation process in this system exhibits a strong concentration dependence. Figure 4 contains a plot of the relaxation frequency ($\omega_R = 1/\tau_R$) at $T = 4.2$ K as a function of the Dy concentration in the alloy. In the dilute Dy region this frequency increases rapidly reflecting the decrease in the strength of the exchange correlations between Dy spins, as one approaches the condition of ordinary paramagnetism. Conversely, near 30-at.% Dy the relaxation frequency has begun to reach its limiting value, as cluster correlations increase to the point where long-range order begins to set in.

Relaxation frequencies obtained for the $Dy_{0.25}Sc_{0.75}$ alloy as a function of temperature are shown in Fig. 5. The relaxation frequency increases linearly with temperature between 8 and 23 K. This type of behavior is typical of Korringa relaxation[16] which is found in metallic systems. This relaxation process involves the exchange interaction between the localized moments and the conduction electrons. The relaxation frequency varies linearly with temperature and also with

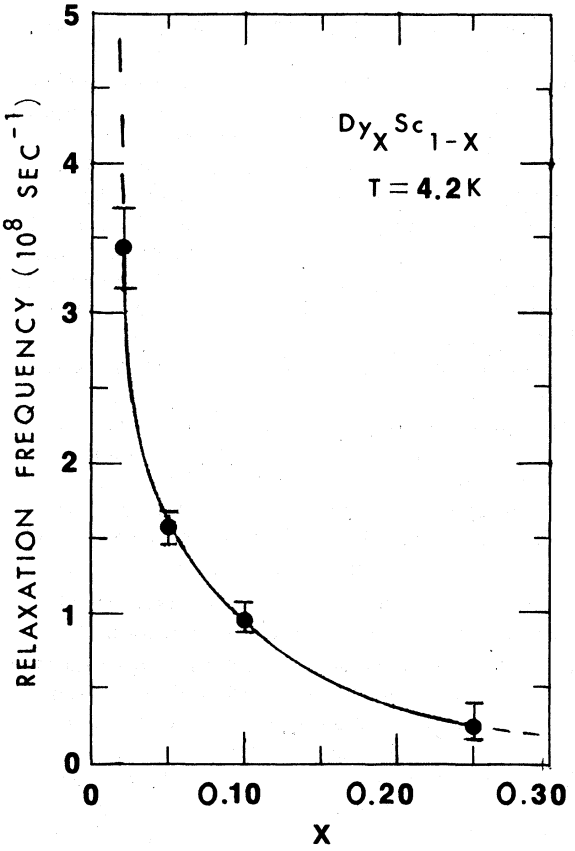

FIG. 4. Relaxation frequency at $T = 4.2$ K as a function of the Dy concentration.

$[J_{sf} n(E_F)]^2$, the square of the exchange constant and the square of the density of states at the Fermi surface. The departure from linearity of the relaxation frequency for $T \approx 4$ K suggests a contribution from a temperature-independent spin-spin relaxation mechanism.

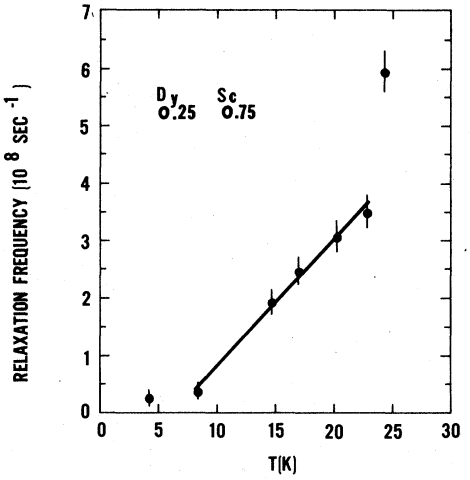

FIG. 5. Relaxation frequency for the $Dy_{0.25}Sc_{0.75}$ alloy as a function of temperature.

CONCLUSIONS

The results of this study rather conclusively demonstrate that there are two distinct regimes of spin ordering in the Dy-Sc system. The alloys with concentrations $\leq$25-at.% Dy exhibit no static long-range magnetic order. This result, coupled with the fact that the magnetic hyperfine splitting remains equal to the saturation value independent of temperature until it can no longer be resolved and the substantial broadening of the absorption lines, indicates that a slow electronic-spin-relaxation mechanism is present in these alloys. The full magnetic hyperfine splitting is observed for temperatures low enough such that the relaxation frequency is slower than the nuclear Larmor precession frequency.

For those alloys with concentrations $\geq$35-at.% Dy the magnetic hyperfine splitting as a function of temperature follows the typical behavior exhibited by rare-earth alloys possessing long-range magnetic order. Thus these concentrations possess a time independent static field at the nucleus.

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