Influence of Localized Rare-Earth Moments on ^{45}Sc Nuclear Magnetic Relaxation*

F. Y. Fradin
Argonne National Laboratory, Argonne, Illinois 60439

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Scandium-base alloys of 0.02 and 0.05 at.% of gadolinium and dysprosium have been studied using transient nuclear-magnetic-resonance techniques. The ^{45}Sc nuclear spin-lattice relaxation rate is enhanced in the rare-earth alloys. For $1.6 \leq T \leq 4.2$°K, the relaxation rate is described by $1/T_1 = (1/T_1)_{\mathrm{Sc}}[1+KB_J(x)/H]$, where $(1/T_1)_{\mathrm{Sc}}$ is the pure scandium relaxation rate, K is a constant, and $B_J(x)$ is the Brillouin function for $x \equiv gJ\mu_B H/k_B T$. The T_1 results are explained in terms of enhanced nuclear relaxation due to virtual excitation of the rare-earth magnetic moments.

The effects of dilute localized magnetic moments on the spin-lattice relaxation of the host nuclear spins has recently been the subject of a number of experimental and theoretical investigations. Experiments performed at sufficiently low field on *Cu*Mn[1] and *Cd*Mn[2] yield results in essential agreement with the theory proposed by Benôit, de Gennes, and Silhouette (BGS).[3] This relaxation mechanism involves a simultaneous nuclear spin–electron spin flip, i.e., a *real* excitation of the impurity moment with energy conservation satisfied by the finite response of the electronic Zeeman transition at the nuclear-magnetic-resonance (NMR) frequency. Experiments performed at high fields, where there is not significant overlap of the nuclear resonance and electron resonance response, on *Cu*Mn[4] and *Cd*Mn[2] yield results that have qualitative features in agreement with the theory proposed by Giovannini and Heeger (GH).[5,6] The GH mechanism involves a *virtual* excitation of the magnetic moment which is then de-excited by the scattering of a conduction electron; this second-order process can interfere with the pure-metal Korringa[7] relaxation of the nuclear spins. However, the quantitative comparison[2,6] of the high-field relaxation data indicates an impurity contribution to the spin-lattice relaxation rate three orders of magnitude larger than that predicted by the GH theory.

Both the BGS mechanism and the GH mechanism involve the coupling of the host nuclear spins with the impurity moment via the contact interaction and hence rely on the Ruderman-Kittel-Kasuya-Yosida (RKKY)[8] type of coupling mediated by the conduction electrons. A competing mechanism for relaxation of the host nuclei involves direct dipole-dipole coupling between the host nuclei and the longitudinal fluctuations of the impurity moment.[2,6]

The purpose of this paper is to present high-field data for the relaxation rate of the ^{45}Sc nucleus in dilute scandium rare-earth alloys. The influence of the highly localized $4f$ moments (associated with either gadolinium or dysprosium) on the host nuclear spin-lattice relaxation rate is found to be in good quantitative agreement, over a considerable range of H/T, with the predictions of the model of virtual excitation of the localized magnetic moment. The highly localized $4f$ moments do not suffer from the complication of strong hybridization with the plane waves, as is the case for the virtual d states of manganese in *Cu*Mn and *Cd*Mn. Unfortunately, the rare earths do not have appreciable solubility in the nearly free-electron metals. The rare earths are highly soluble in the strongly exchange-enhanced metal scandium which has a nuclear spin-lattice relaxation time described[9] by $(T_1)_{\mathrm{Sc}}T = 1.14 \pm 0.1$ sec °K.

The results presented in this paper will also indicate the importance of the dynamic bottleneck effect in the coupled conduction-electron–localized-electron system. The bottleneck effect on the local-moment dynamic susceptibility can drastically change the order of magnitude of the nuclear spin-lattice relaxation rate.

Scandium rare-earth alloys were prepared by levitation melting scandium of the highest purity available (<150 ppm rare-earth impurities) with weighed quantities of either gadolinium or dysprosium. A portion of each annealed ingot was filed for the NMR specimen. The measurements were made with a phase-coherent pulsed NMR spectrometer. The ^{45}Sc nuclear-magnetic-resonance profiles (determined by integrating the spin echo following a $\pi/2$-π rf-pulse sequence) in the *Sc*Dy alloys broaden linearly with the magnetization, are symmetric, and have essentially zero average shift relative to pure scandium. This behavior is similar to that reported earlier[10,11] for dilute *Sc*Gd alloys and is consistent with an oscil-

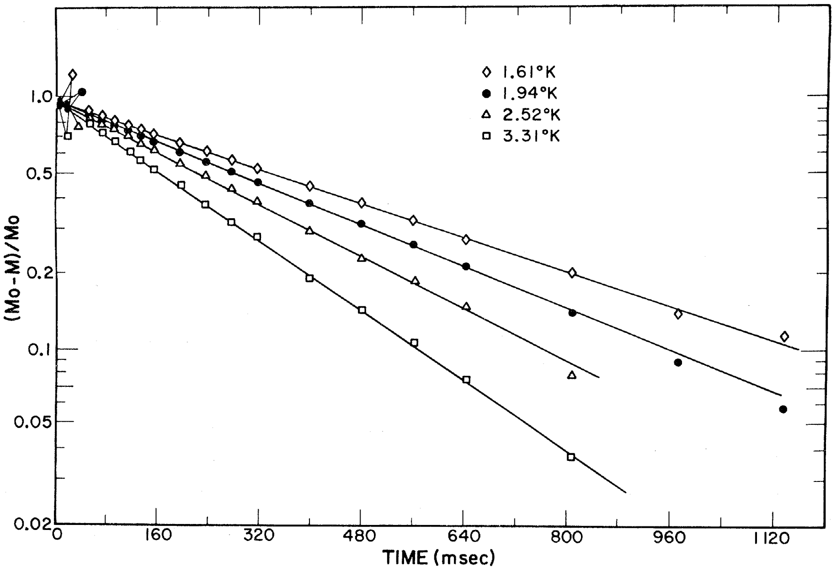

FIG. 1. Recovery curves of the nuclear magnetization of ^{45}Sc in Sc-0.05 at.% Gd at 8 MHz. Data obtained using a saturating pulse train.

latory polarization of the conduction electrons. Comparisons of integrated intensity between pure scandium and the scandium rare-earth alloys indicate that roughly the first-nearest-neighbor shell of scandium to either a Gd or Dy is wiped out of observation.

In Fig. 1 we illustrate typical spin-lattice relaxation curves obtained at 8 MHz for the recovery of the nuclear magnetization in a Sc-0.05 at.% Gd alloy. The data were obtained using a saturating pulse sequence given by $(\pi/2-100\ \mu\mathrm{sec})_{100}$-$\tau$-$\pi/2$, where the rf field was approximately 100 Oe. As can be seen, good saturation was obtained. Single exponential recovery was found in all cases. The spin-lattice relaxation rate $1/T_1$ is considerably enhanced at 4.2°K for the Gd and Dy alloys. The experimental values of $1/T_1$ at 4.2°K and 12 MHz for all the alloys are listed in Table I. The constancy of $(1/T_1)_{\mathrm{imp}}c^{-1}$ indicates that up to 0.05 at.% solute, single-impurity effects dominate the relaxation rate. Here $(1/T_1)_{\mathrm{imp}} = (1/T_1) - (1/T_1)_{\mathrm{Sc}}$, where $(1/T_1)_{\mathrm{Sc}}$ is the pure-metal relaxation rate and c is the atom fraction of solute. Within experimental error, the values of $1/T_1$ are identical for each alloy at 4.2°K for frequencies of 4, 8, and 12 MHz. We have also measured the alloys at 77°K and found the relaxation rate to be identical (within ±2%) to that of pure scandium.

Table I. Spin-lattice relaxation rate at 4.2°K and 12 MHz.

Alloy	$1/T_1$ (sec^{-1})	$(1/T_1)_{\mathrm{imp}}$ (sec^{-1})	$(1/T_1)_{\mathrm{imp}}c^{-1}$ (sec^{-1})
Sc	3.70(2)		
Sc-0.02 at.% Gd	4.10(3)	0.40	2.00×10^3
Sc-0.05 at.% Gd	4.72(3)	1.02	2.04×10^3
Sc-0.02 at.% Dy	4.09(5)	0.39	1.95×10^3
Sc-0.05 at.% Dy	4.67(5)	0.97	1.94×10^3

The noninteracting magnetic-impurity-induced contribution $(1/T_1)_{\mathrm{imp}}$ to the nuclear spin-lattice relaxation rate due to *virtual* excitation of the impurity is[12]

$$(1/T_1)_{\mathrm{imp}} = 4N(E_{\mathrm{F}})J_{s\text{-}f}^2\langle S_z/g\mu_{\mathrm{B}}H\rangle c/T_{1\mathrm{K}}, \qquad (1)$$

where it is assumed that the contact interaction is the dominant electron-nuclear coupling. Here $N(E_{\mathrm{F}})$ is the scandium density of states at the Fermi level for one direction of spin, g is the Landé g factor, $J_{s\text{-}f}$ is the effective s-f exchange interaction constant, $\langle S_z/g\mu_{\mathrm{B}}H\rangle$ is the thermal expectation value of the spin of the localized moment in its local field, μ_{B} is the Bohr magneton, c is the impurity-atom fraction, and $1/T_{1\mathrm{K}}$ is the Korringa[7] relaxation rate (proportional to T). In fact, d-wave polarization of the scandium electrons may be important for the impurity-enhanced nuclear relaxation rate via the core-polarization hyperfine field.[9] We will not attempt to differentiate between s-wave and d-wave contributions, which for scandium can be of similar magnitude. Instead, we will treat the product of $N(E_{\mathrm{F}})$, $J_{s\text{-}f}^2$, and $1/T_{1\mathrm{K}}$ as an appropriate average for the s-electron and d-electron contributions.

Equation (1) should be corrected for the nonuniform radial distribution of spin density around the impurity and the wipeout of near-neighbor scandium from the resonance profile. Following Giovannini *et al.*,[6] a factor $F(r_0)$, which takes account of the spatial dependence of the conduction-electron susceptibility, must then be introduced into Eq. (1). Here r_0 is the radius of the nearest shell of nuclei contributing to the resonance signal. Since spin diffusion is found to be unimportant experimentally, the nuclei with $r<r_0$ submitted to high local fields due to spin-density oscillations do not affect the relaxation of the observable nuclei.

In order to treat localized moments with nonzero orbital angular momentum, the total angular momentum of the local moment J is taken to be a good quantum number. We then replace $\langle S_z/g\mu_B H\rangle$ in Eq. (1) by $(g-1)^2 J B_J(x)/g\mu_B H$,[12] where $B_J(x)$ is the Brillouin function and $x \equiv gJ\mu_B H/k_B T$. Here k_B is Boltzmann's constant and T is the absolute temperature. Equation (1) can now be recast into the form

$$\left(\frac{1}{T_1}\right)_{\text{imp}} = 4N(E_F)J_{s\text{-}f}{}^2 \frac{(g-1)^2 J B_J(x)}{g\mu_B H} \times c\frac{1}{T_{1\text{K}}}\left[\frac{1}{3\pi Z}\;\frac{1}{(2k_F r_0)^2}\right], \qquad (2)$$

where the factor in the square bracket is just the average value of the free electron approximation to $F(r_0)$.[6] Here Z is the number of conduction electrons per atom and k_F is the Fermi wave vector. The measured relaxation rate for the 0.05-at.% gadolinium alloy at 8 MHz ($H = 7.72$ kOe) is plotted versus temperature in Fig. 2. The solid line is the best fit of the function $1/T_1 = K_1 T + K_2 T(g-1)^2 J B_J(x)/g\mu_B H$ to the data, where $g = 2.0$ and $J = \frac{7}{2}$. The parameters determined are $K_1 = 0.979$ sec^{-1} °K^{-1} and $K_2 = 0.179\times10^{-16}$ emu. Except for the 1.61°K datum point, the other data points deviate from the curve by less than 2%.

The constant K_1 corresponds to a value of $T_1T = 1.02$ sec °K, which is within experimental error of the measured value of $(T_1)_{\text{Sc}}T$ obtained in pure scandium.[13] In order to make a comparison with the fitted constant K_2, we calculate a value of K_2 from Eq. (2). We estimate $N(E_F) = 2$ states/(eV atom) from the electronic-specific-heat coefficient[14] and $J_{s\text{-}f} = 0.1$ eV from the gadolinium g shift[15] in *Sc*Gd. We also take $T_{1\text{K}}T = 1$ sec °K, $Z = 3$, and $k_F = 1.4\times10^8$ cm^{-1}. Since the experimentally determined wipeout number[16] for Gd in Sc at 4.2°K and 8 MHz is entirely magnetic in origin and given by $N_0 = 10\pm5$, we take r_0 corresponding to the second-nearest-neighbor position to the solute. The value of K_2 determined with these parameters is 0.28×10^{-16} emu. This value is in quite good agreement with the fitted value of 0.18×10^{-16} emu considering the approximations involved.

The ratio of $(1/T_1)_{\text{imp}}$ for Gd to that for Dy at 4.2°K is 1.04, whereas the ratio of the values of $\langle S_z/g\mu_B H\rangle$ is 2.32. Thus, Eq. (2) yields the ratio $(J_{s\text{-}f})_{\text{Gd}}/(J_{s\text{-}f})_{\text{Dy}} = 0.67$. This ratio is consistent

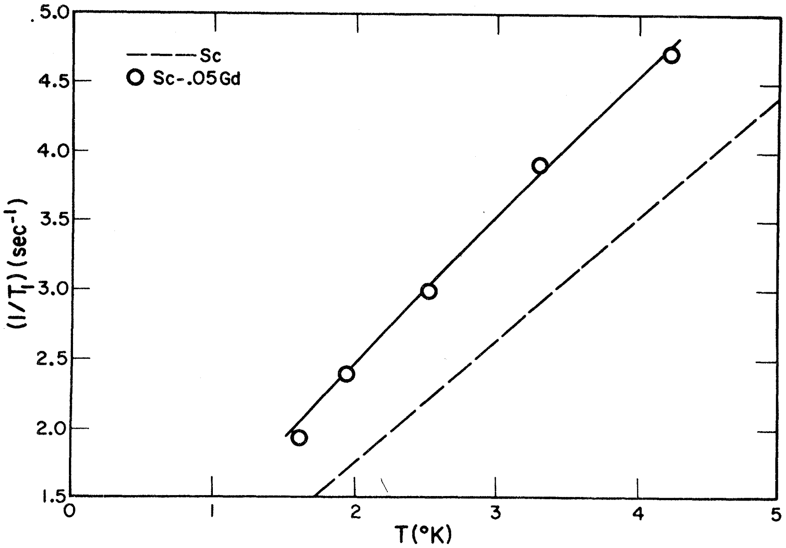

FIG. 2. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in a Sc-0.05 at.% Gd alloy at 8 MHz. Solid curve is a theoretical fit to the data (see text). Dashed line is the experimental spin-lattice relaxation rate in pure scandium.

with the ratio of the enhancements of the paramagnetic moments[10,11] of gadolinium and dysprosium in scandium relative to their respective free-ion moments. In the range of temperature 4.2 to 1.6°K at a field of 7.72 kOe, the quantity $\langle S_z/g\mu_B H\rangle$ is expected to approach saturation. That is, the argument of the Brillouin function $x \equiv gJ\mu_B H/k_B T$ takes on values between 0.86 and 2.25 for Gd and values between 1.23 and 3.22 for Dy. For the relaxation problem we refer to saturation of the local moment in its local field,[12] not in the direction of the applied field. At 1.61°K the field dependence in Eq. (2) predicts the values of $(1/T_1)_{\rm imp}$ at 4, 8, and 12 MHz to be in the ratios 1.59:1.27:1.00 for gadolinium alloys and in the ratios 1.81:1.33:1.00 for dysprosium alloys. By comparison the experimental values of $(1/T_1)_{\rm imp}$ at 4, 8, and 12 MHz are in the ratios 1.55:1.19 :1.00 for the 0.05-at.% gadolinium alloy and in the ratios 1.85:1.32:1.00 for the 0.05-at.% dysprosium alloy. Similarly, at 3.31°K Eq. (2) predicts the values of $(1/T_1)_{\rm imp}$ at 4, 8, and 12 MHz to be in the ratios 1.19:1.11:1.00 for gadolinium alloys and in the ratios 1.30:1.16:1.00 for dysprosium alloys. The experimental values of $(1/T_1)_{\rm imp}$ at 4, 8, and 12 MHz are in the ratios 1.25:1.10 :1.00 for the 0.05-at.% gadolinium alloy and in the ratios 1.39:1.14:1.00 for the 0.05-at.% dysprosium alloy. The estimated uncertainties in $(1/T_1)_{\rm imp}$ are approximately ±2% for the 8- and 12-MHz values and ±11% for the 4-MHz values.

As pointed out by Giovannini *et al.*,[6] neither the BGS mechanism[3] nor the direct dipole mechanism[2,6] predict the correct dependence of $(1/T_1)_{\rm imp}$ on H and T in the high-field regime for either *Cu*Mn or *Cd*Mn. Similarly, neither of these mechanisms are important for *Sc*Gd and *Sc*Dy in the range of H/T used in this experiment. Because of the small dipolar relaxation in scandium,[9] we can safely neglect pseudodipolar relaxation[6] due to the magnetic moment.

In summary, we find that dilute quantities of either Gd or Dy in scandium enhance the nuclear spin-lattice relaxation rate through virtual excitation of the local moment. The reasonable agreement of $(1/T_1)_{\rm imp}$ at high field with the mechanism of virtual excitation of the local moment for *Sc*Gd and *Sc*Dy alloys and the poor quantitative agreement[2,6] in *Cu*Mn and *Cd*Mn alloys could be due to the different dynamics[17] of the coupled conduction-electron–localized-electron systems. It is known that the bottleneck is effective at the electron-spin resonance frequency in *Cu*Mn[6] but not in *Sc*Gd.[15] When the bottleneck is effective, we would expect the molecular field treatments[6,12] of the local-moment enhancement of the nuclear spin-lattice relaxation rate to be incorrect. The relaxation problem should then be solved by a complete many-body analysis similar to the one used in the electron-spin-resonance problem.[17]

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