Observation of the heating of the dipole-dipole interaction pool of impurity ions in nuclear relaxation

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Results of experimental investigations of nuclear spin-lattice relaxation in lanthanum ethyl sulphate (LaES) containing Tb^{3+} ions are presented. It is shown that at temperatures below 10 °K the nuclear relaxation is determined mainly by the impurity-ion dipole-dipole pool (DDP). At impurity concentrations below 0.15%, a heating of the DDP is observed, because the DDP heat capacity becomes lower than that of the nuclear Zeeman system. Effective nuclear-nuclear cross relaxation is observed for the $c \perp \mathbf{H}_0$ orientation; it can be ascribed to equality of the proton quantum to the nuclear transition between the Tb^{3+}-ion energy levels.

INTRODUCTION

It is known that the dipole-dipole pool (DDP) of the impurity ions frequently plays an important role in nuclear spin-lattice relaxation (NSLR)[1-3]. In this case the impurity correlation time τ_c is due to the spin-spin interactions of the paramagnetic ions. At low impurity concentration and low temperatures, the DDP can become heated and this causes lengthening of the NSLR time[4, 5]. We have previously pointed out[2] the feasibility of observing the heating of the DDP of Tb^{3+} ions in LaES at temperatures 1.5–4°K, and have shown that by studying the NSLR in a wide temperature range it is possible to estimate the rate of the spin lattice relaxation (SLR) of impurity ions.

We present here the results of an experimental study of the mechanisms of NSLR in lanthanum ethyl sulfate single crystals with different concentrations of Tb^{3+} ions. We have observed in studying the heating of the DDP of the impurity ions. We estimate the relaxation times of their SLR. We investigate the cross relaxation between protons and impurity paramagnetic ions.

The experiments were performed on LaES single crystals with Tb^{3+} ion concentrations from 0.3 to 0.01%. No extraneous impurities were observed. The impurity concentration was estimated from EPR signals at 37 GHz and at helium temperature. The details of the pulsed NMR spectrometer and of the low-temperature thermometry, as well as the measurement procedure, were described earlier[2].

1. PROTON RELAXATION AT ORIENTATION $H_0 \parallel c$

The experimental values of the proton SLR are shown by the points of Fig. 1, where the solid lines show the calculated values in the temperature range 1.5–20°K and at different impurity concentrations. The "fast diffusion" condition was satisfied in the entire temperature interval, and the calculation for the lower curve was based on the formula[6]

$$T_I = 0.574 R^3 d^2 b / C, \tag{1}$$

where d is the radius of the diffusion barrier, b is the "pseudo-potential" radius of the ion and R is the radius of the sphere per ion, with

$$C = \frac{6}{5} \gamma_I^2 (\overline{\mu_z^2} - \bar{\mu}_z^2) \frac{\tau_c}{1 + (\omega_I \tau_c)^2}. \tag{2}$$

The expression in the round brackets determines the dependence of C on the polarization of the spins of the magnetic ions, on the temperature, and on the field, and also takes into account the orientation dependence of the magnetic moment of the impurity ion, while τ_c is the correlation time defined by

$$\tau_c^{-1} = T_{1c}^{-1} + T_{2c}^{-1}.$$

In the temperature interval 8–20°K, the correlation time of the impurity is the SLR time of the Tb^{3+} ions, while at temperatures below 8–10°K this role is assumed by the SLR time of the impurity ions. The character of the temperature dependences of the spin-spin and spin-lattice relaxations of the impurity ions is significantly different. This enables us to estimate the SLR time T_{2e}. Figure 1 shows that at temperatures 8–10°K (depending on the concentration), an abrupt change takes place in the slope of the $T_I(T°)$ curves. Thus, at these temperatures we have $T_{2e} \sim T_{1e}$. In our case it is not quite correct to determine T_{2e} from the condition $T_{1e} = T_{2e}$ in the region of the inflection point, inasmuch at this orientation the SLR rates of the Tb^{3+} ion and their concentration dependence are not known accurately enough for direct processes.

To determine T_{2e} from the experimental nuclei SLR times at T = 6°K we have used formula (1). The times

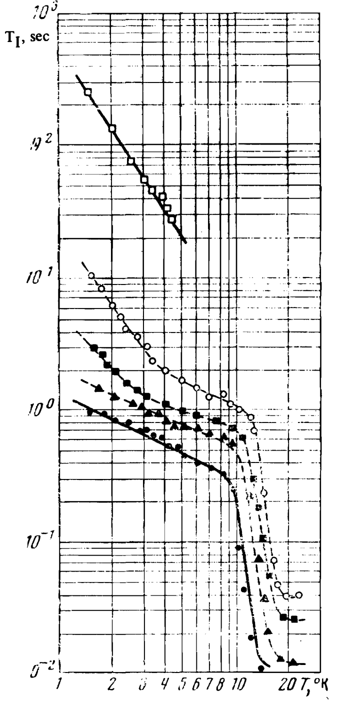

FIG. 1. Nuclear spin-lattice relaxation times as functions of the temperature and concentration in LaES + Tb^{3+}; $H_0 \parallel c$ (●–0.38%, ▲–0.19%, ■–0.15%, ○–0.12%, □–0.01/–experimental values). Solid lines–calculated relations.

obtained in this manner were $T_{2e} = 1.5 \times 10^{-7}/f$. This agrees with the times calculated by the formula[7]

$$T_{2e}=a^3/\varkappa f\hbar\gamma_e^2,$$

where $\gamma_e = 2 \times 10^5$. The large value of T_{2e} is due to the fact that for the Tb^{3+} ion in LaES + T^{3+} we have $g_\perp = 0$ and the possibility of the spin-spin relaxation is determined only by the small initial splitting.

A lengthening of the NSLR was observed at low temperatures and low concentrations of the magnetic impurity ions. Since the relaxation of the nuclei proceed via the DDP in the temperature interval 1.5–80°K, it follows that this lengthening can result from the heating of the DDP of the magnetic ions. It is known from[5] that this requires satisfaction of the conditions

$$T_{dI} \ll T_{Il}, \quad T_{dI} \ll T_{dl}, \quad T_{dI} \ll T_{Id},$$

where T is the relaxation time, while the subscript I, l, and d not respectively the nuclear Zeeman system, the DDP of the magnetic ions, and the lattice.

The relaxation of the nuclei proceeds with a time

$$\lambda_-^{-1}=\left(\frac{C_d}{C_I}T_{dl}^{-1}+T_{Il}^{-1}\right)^{-1}, \tag{3}$$

where

$$\frac{C_d}{C_I}=\frac{NS(S+1)}{nI(I+1)}\left(\frac{\omega_d}{\omega_I}\right)^2$$

is the ratio of the specific heats of the magnetic-ion DDP to the specific heat of the nuclear Zeeman system;

$$\omega_d=\frac{4}{3}\alpha S(S+1)f\left(\frac{\hbar\gamma_e^2}{L^3}\right)^2, \quad \alpha=\frac{3}{20}\xi;$$

ξ ranges from 8.5 to 14.4, depending on the type of lattice[8], while L is the lattice constant. The same reference gives also expressions for T_{Il} and T_{Id} for the case $\omega_I\tau_l \gg 1$, $\omega_I\tau_s \gg 1$ and d > b ("fast diffusion"):

$$T_{Il}=\frac{9d^2bH^2\tau_l}{8\pi(\hbar\gamma_e)^2NS(S+1)}, \quad T_{Id}=\frac{9d^2bH^2\tau_s}{8\pi(\hbar\gamma_e)^2NS(S+1)}$$

where N is the number of magnetic ions per unit volume.

In accord with these conditions, we have quantitatively estimated the NSLR times. For curves with concentrations 0.3 to 0.2% of impurity ions, the condition $T_{dI} \gg T_{dl}$ is satisfied at 2°K (T_{dl} is usually taken equal to $\tau_l/2$). The relaxation is via the DDP, the specific heat of which is large enough, $C_d/C_I = 20$, so that it does not become heated. In this case the nuclear relaxation has a time T_{Id}. On the other hand, for the curve with the concentration 0.01% ($N = 2 \times 10^{17}$ cm^{-3}), we have $C_d/C_I = 1.2 \times 10^{-2}$ even at temperatures 4°K below, and the relaxation probability is $\lambda_- = (C_d/C_I)T_{dl}^{-1}$. In this case the flow of energy from the Zeeman nuclear system to the DDP exceeds the flow of energy from the DDP to the lattice, and the heating of the DDP of the magnetic ions, predicted in[4, 5], will be appreciable. It is seen from Fig. 1 that the calculated NSLR times agree well with the experimental values.

2. ANGULAR DEPENDENCE OF NSLR AT AN ORIENTATION CLOSE TO $H_0 \perp c$

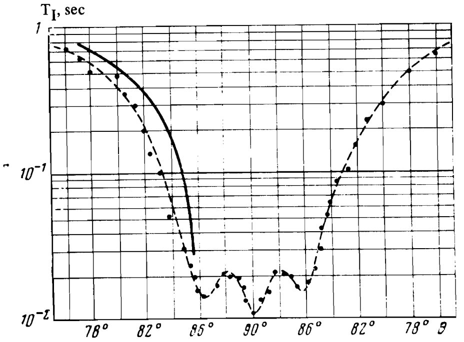

FIG. 2. Angular dependence of the nuclear SLR time in an orientation close to $H_0 \perp c$. Dark points—experimental results. The solid line shows the relative change of the magnetic moment of the ion.

The study of the angular dependence of the proton SLR, shown in Fig. 2, reveals a cross-relaxation effect at the orientations $\theta_1 \approx 90°$ and $\theta_2 \approx 86°$, and a monotonic increase of T_I with decreasing θ. The appearance of cross-relaxation effects is due to the presence of splitting in the energy spectrum of the Tb^{3+} ion, which coincide in magnitude with the proton quanta. Let us examine the structure of the energy levels of the Tb^{3+} ions in the tetragonal field of lanthanum ethyl sulfate with allowance for the initial splitting and the hyperfine interaction. The Hamiltonian of this system is of the form

$$\mathscr{H}=\beta g_\parallel H_z\hat{S}_z+\Delta\hat{S}_x+A\hat{S}_z\hat{I}_z, \tag{4}$$

where g = 17.72 ± 0.02, Δ = 0.387 ± 0.001^{-1}, A = 0.209 ± 0.002 cm^{-1}, and $H_z = H_0 \cos\theta$, with H_0 = 3146 G, S = 1/2, and I = 3/2.

The computer-calculated energies of the levels corresponding to the Hamiltonian (4) are shown in Fig. 3 as functions of θ. It is seen that the cross-relaxation effects turn out to be significant for $\theta \approx 90°$ (the transition $1/2 \leftrightarrow 1/2$) and $\theta = 85.5°$ (transition $-1/2 \leftrightarrow -3/2$). Transitions for the remaining cases when the splittings of the protons and Te^{3+} coincide are forbidden.

Using the value of the proton SLR time at $\theta \approx 90°$, we can estimate the SLR time of the Tb^{159} nuclei from the formula[9]

$$1/T_I(H')=N_S/N_IT_I(\mathrm{Tb}^{159}),$$

which yields $T_I = 5 \times 10^{-4}$ sec. This is close to the Tb^{159} ion SLR time measured by Jeffires[10] at the orientation $H_0 \parallel c$ with allowance for the value of the field.

The shortening of the SLR nuclear relaxation times for $\theta < 85°$ cannot be connected with cross-relaxation effects, since the hyperfine splitting at these angles exceeds the proton quantum by several orders of magnitude. What takes place at these orientations is the usual nuclear SLR via the paramagnetic impurity. Estimates show that the correlation time is the SLR time of the impurity ions. Flip-flop transitions that ensure the SLR of the paramagnetic ions are possible when the projection of the nuclear spin is conserved for each of the ions. The calculation of the average magnetic moment by the formula

$$\bar{\mu}_z=\sum_i\left(\frac{\partial E_i}{\partial H_0}\right)\exp\left(-\frac{E_i}{kT}\right)\Big/\sum\exp\left(-\frac{E_i}{kT}\right)$$

should be carried out with allowance for this circumstance. The relative change of the magnetic moment of the ion effective in the NSLR is shown in Fig. 2 by the solid line. Thus, the radius of the diffusion barrier depends strongly on the angle. At an orientation close to $H_0 \perp c$, the concept of the diffusion-barrier radius has no physical meaning, since it becomes smaller than the distance from the ion to the nearest proton. In this case

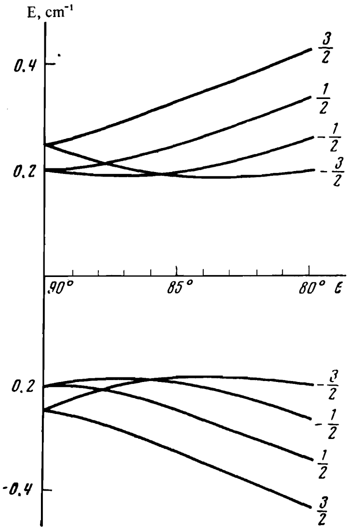

FIG. 3. Energy levels of the Tb^{3+} ion as functions of the angle θ.

the greater part of the protons relaxes directly to the ion, and the correlation time of the impurities due to the spin-spin interactions of the ions. Thus, a study of the temperature dependence of the NSLR time makes it possible to observe experimentally the heating of the DDP of the purity ions when their concentration is decreased.

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