Proton relaxation in dilute rare-earth ethyl sulfates

I. I. Valeev, V. A. Skrebnev, and F. L. Aukhadeev

Kazan' State University

(Submitted April 4, 1973)
Zh. Eksp. Teor. Fiz. 65, 1198–1204 (September 1973)

Results are presented of an experimental investigation of proton relaxation in lanthanum ethyl sulfate (LaES) with admixtures of the rare-earth ions HO^{3+}, Er^{3+}, Tb^{3+}, or Dy^{3+}. A pulsed spectrometer with an operating frequency of 13.4 MHz was employed in the measurements. At temperatures between 1.5 and 30°K, no heating of the reservoir of impurity dipole-dipole interactions was observed in our samples. Electron-nuclear cross relaxation was observed in the case of Tb^{3+} ions in LaES. The results are interpreted from the viewpoint of spin diffusion theory.

1. INTRODUCTION

Dilute rare-earth sulfates are known to be good materials for achieving considerable proton polarization.[1-3] A significant anisotropy of the spin-lattice relaxation rate is observed if the g factor of the rare-earth ion is anisotropic ($g_{\parallel} \gg g_{\perp} \approx 0$). This allows us to transfer the electron polarization to the nuclear spins by a relatively simple method involving variation of the angle between the magnetic field and the g tensor axis. In this case, the efficiency of the nuclear polarization depends not only on the degree of the electron polarization but also on the rate of the nuclear spin-lattice relaxation. In this connection it is desirable to know the mechanisms of the proton spin-lattice relaxation at helium temperatures. In spite of the fact that the relevant investigations have already been carried out on some rare-earth ions,[2-5] no information is available on the influence of many rare-earth ions on the proton relaxation in ethyl sulfates.

The investigation reported below was intended to provide information on the proton magnetic relaxation in a single crystal of lanthanum ethyl sulfate (LaES) containing Ho^{3+}, Er^{3+}, Tb^{3+}, and Dy^{3+} impurity ions. The investigation was carried out in the 1.5–30°K range.

2. EXPERIMENTAL METHOD AND SAMPLES

We used a pulse NMR spectrometer with a single-coil probe, operating at 13.4 MHz. The detector pass band was 300 kHz wide and the sensitivity was several microvolts. The polarization time of the apparatus was 8 μsec. The measurements were made in the 1.5–30°K range using a glass cryostat and heating a sample. The temperature was measured with a carbon resistance thermometer. The nuclear spin-lattice relaxation time was deduced from the amplitudes of the spin echo signals obtained for various repetition frequencies of a two-pulse sequence (these repetition frequencies were comparable with the proton spin-lattice relaxation rate).

Our single crystals were grown by free evaporation of a saturated aqueous solution of lanthanum ethyl sulfate diluted with rare-earth ethyl sulfates. The evaporation took place at 0°C. When the temperature was raised, the quality of the crystals deteriorated. The solutions were prepared from an oxide of a rare-earth metal, diethyl sulfate, and water in accordance with the prescription kindly supplied by Dr. H. H. Dearman and Dr. D. Baker of the University of North Carolina, USA. The crystals grew in the form of hexagonal prisms about 6 mm thick and their length reached 15 mm. Disk-shaped samples were cut from these crystals in such a way that the symmetry of the crystal field was in the horizontal plane and measurements could be carried out in the two extreme orientations ($g_{\parallel}$ and $g_{\perp}$) by rotating the electromagnet. The presence of impurity ions in the investigated single crystals was confirmed by a study of the ESR spectra recorded at 37 GHz at helium temperature. The concentrations of these ions were deduced from the ESR signals. No other impurities were observed. We prepared the following crystals: LaES + 0.1% Ho^{3+}, LaES + 0.25% Er^{3+}, LaES + 0.2% Tb^{3+}, and LaES + 0.07% Dy^{3+}.

3. RESULTS OF MEASUREMENTS AND DISCUSSIONS

Figures 1–4 give the measured and calculated temperature dependences of the spin-lattice relaxation time. The relaxation time of the rare-earth ions by themselves T_{1e} in ethyl sulfates has been investigated quite thoroughly.[3,6-8] We shall use these results (Table I). Obviously, we may expect other rates of direct processes at low temperatures in our experiments because the resonance field H_0 used by us differed from the fields in which the spin-lattice relaxation has been studied.

It is known[9] that the relaxation of the Zeeman reservoir of nuclei in the homogeneous case, i.e., when the nuclear magnetization is independent of the coordinates, is described by the sum of two exponential functions $\exp(-\lambda_+ t)$ and $\exp(-\lambda_- t)$, where

$$\lambda_{\pm} = \frac{1}{2}\left(\frac{1}{T_I} + \frac{1}{T_{de}} + \frac{C_I}{C_d}\frac{1}{T_{Id}}\right) \pm \frac{1}{2}\left[\left(\frac{1}{T_I} - \frac{1}{T_{de}} - \frac{C_I}{C_d}\frac{1}{T_{Id}}\right)^2 + 4\frac{C_I}{C_d}\frac{1}{T_{Id}}\right]^{1/2}. \quad (1)$$

The ratio of the specific heats of the Zeeman reservoir

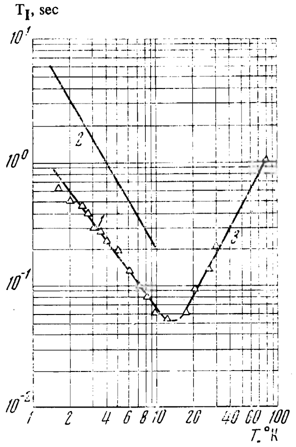

FIG. 1

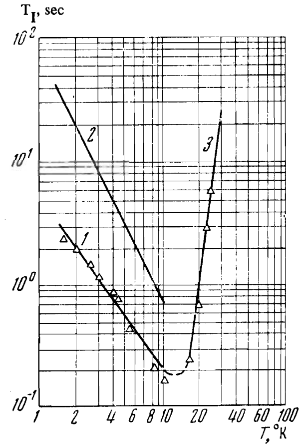

FIG. 2

FIG. 1. Temperature dependences of the proton spin-lattice relaxation time of LaES + Ho^{3+}: Δ) experimental values; 1), 2), 3) calculated curves.

FIG. 2. Temperature dependences of the nuclear spin-lattice relaxation time of LaES + Er^{3+}: Δ) experimental value; 1), 2), 3) calculated curves.

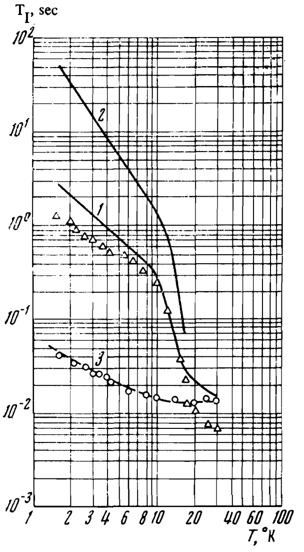

FIG. 3

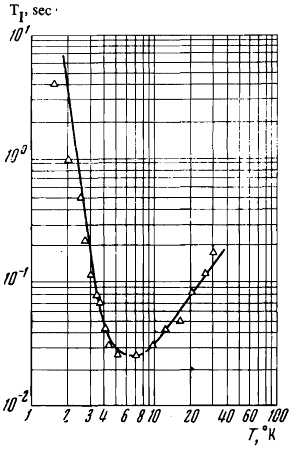

FIG. 4

FIG. 3. Temperature dependences of the experimental (Δ) and theoretical (1, 2) values of the proton spin-lattice relaxation time of LaES + Tb^{3+} for H ∥ C_0. The effect of the electron-nuclear cross relaxation is represented by curve 3, where the experimental values of T_I of the protons are denoted by open circles (in this case, $H_0 \perp C_0$).

FIG. 4. Temperature dependence of the proton spin-lattice relaxation time of LaES + Dy^{3+}: Δ) experimental values of T_I: the continuous curve represents the calculated results.

of nuclei and of the dipole-dipole reservoir is

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

where n and N are the numbers of nuclei and impurity ions per 1 cm^3; I and S are the nuclear and electron spins; ω_n is the resonance frequency; ω_d is the average quantum in the dipole-dipole reservoir, which obeys the relationship

$$\omega_d^2 = \langle \mathscr{H}_d^2 \rangle / \hbar^2 \left\langle \left(\sum_k S_k^z \right)^2 \right\rangle;$$

$\mathscr{H}_d$ is the operator of the energy in the dipole-dipole reservoir; T_I is the nuclear spin-lattice relaxation time determined ignoring the dipole-dipole reservoir; T_{Id}^{-1} is the probability of energy transfer from the nuclei to the dipole-dipole reservoir. The value of T_{Id}^{-1} can be obtained if the expression for T_I^{-1} is modified by replacing the reciprocal of the electron spin correlation time $\tau_c^{-1} = \tau_S^{-1} + \tau_e^{-1}$ with $(\tau_S^0)^{-1}$. The spin-spin relaxation time of the ions is $\tau_S = \tau_S^0(1 - P_0^2)^{-1/2}$ and the degree of polarization of the electron spins is $P_0 = \tanh(\hbar\nu_e/2kT)$. The quantity τ_e is the spin-lattice relaxation time of the impurity ions.

We can use Eq. (1) in the calculation of the nuclear relaxation time also in the spin diffusion case if the impurity concentration is sufficiently small and the radius of the sphere R enclosing one ion is considerably greater than the radius of the diffusion barrier d. The nuclear spin-lattice relaxation time T_I can be determined using Eq. (10) in[10], which leads to the following well-known expression[9] if b > d (here, b is the "pseudopotential" radius of an ion)

$$T_I = 1.6b^3R^3/C, \tag{2}$$

whereas if d > b, we have

$$T_I = 0.574d^2bR^3/C. \tag{3}$$

The relaxation times determined using Eq. (3) are d/0.574b shorter than the times given by the formula[9]

$$T_I = d^3R^3/C. \tag{4}$$

We shall determine the value of d using the formula

$$d = (3\langle\mu_z\rangle/\mu_I)^{1/4}a_0,$$

where $\langle\mu_z\rangle$ is the average value of the z component of the magnetic moment of an ion; μ_I is the magnetic moment of a proton; a_0 is the internuclear distance. The quantity b occurring in Eqs. (2) and (3) is given by $b = 0.68(C/D)^{1/4}$, where

$$D = \frac{0.15\gamma_I^2\hbar}{a_0}, \quad C = \frac{2}{5}(\gamma_I\gamma_S)^2S(S+1)\frac{\tau_c}{1+(\omega_n\tau_c)^2}(1-P_0^2),$$

where γ_I and γ_S represent the gyromagnetic ratio of a proton and an impurity ion, respectively.

We shall consider first the results of measurements of the nuclear spin-lattice relaxation time of LaES + Ho^{3+} and LaES + Er^{3+}. It is clear from Table I that in the case of the Ho^{3+} ion the values of $g_\parallel$ and $g_\perp$ are of the same order of magnitude. This allows us to make estimates using the formula[11]

$$1/\tau_S^0 = \mathscr{H}\hbar\gamma_S^2 f/b_0^3, \tag{5}$$

where f is the relative concentration of the magnetic impurities and $\mathscr{H}$ is a coefficient which depends on the type of lattice and on the orientation of the external field relative to the axis of the crystal under investigation. For 0.1% Ho^{3+} in LaES we find that $\tau_S^0 = 2.8 \times 10^{-7}$ sec.

In the temperature range 1.5–10° K we find that $1/\tau_S \gg 1/\tau_e$, d > b, and T_I is given by Eq. (3). The ratio C_I/C_d is of the order of 10^3 and at temperatures T > 2° K the inequality $1/T_{de} > C_IT_{Id}/C_d$ is satisfied. In this case, the dipole-dipole reservoir is not heated and Eq. (1) assumes the form

$$\lambda_- = T_I^{-1}.$$

The theoretical temperature dependence of the nuclear spin-lattice relaxation time, calculated using Eq. (3) for the range 1.5–10°K, is represented by curve 1 in Fig. 1. The nuclear spin-lattice relaxation times calculated using Eq. (4) are represented by curve 2. At T > 15°K we have $1/\tau_S \ll 1/\tau_e$ and allowance for the participation of the dipole-dipole reservoir in the relaxation process is of little importance. We calculated the nuclear spin-lattice relaxation times at T > 15°K using Eq. (10) in[10], since, in this case, the values of b and d are of the same order of magnitude. The calculated temperature dependence of the nuclear spin-lattice relaxation time is represented by curve 3 in Fig. 1 and this curve agrees well with the experimental results.

The values of $g_\parallel$ and $g_\perp$ are also of the same order for lanthanum ethyl sulfate doped with Er^{3+}. An estimate of τ_S^0 gives 8.1×10^{-8} sec. In the temperature range 1.5–10° K the condition $1/T_{de} > C_IT_{Id}/C_d$ is satisfied

Ion	T_{1e}^{-1}, sec^{-1}	Reference	$g_\parallel$	$g_\perp$	Reference
Ho^{3+}	$T_{1e}^{-1} = 37.6\left(\mathrm{cth}\frac{0.392}{T}\right)^2 + 2.91\cdot T^7 + 1.27\cdot 10^5(e^{8,T} - 1)^{-1}$	[7]	7.7	3.86	[8]
Er^{3+}	$T_{1e}^{-1} = 11.5T + 10^{-2}T^9 + 4{,}1\cdot 10^{10}\cdot e^{-58\ T}$	[6]	1.47	8 85	[8]
Tb^{3+}	$T_{1e}^{-1} = 59T + 0.92\cdot 10^{-2}\cdot T^7$	[6]	17.72	<0.3	[8]
Dy^{3+}	$T_{1e}^{-1} = 1.3\cdot 10^{-5}\cdot T^9 + 0.64\cdot 10^7\cdot e^{-23/T}$	[3]	10.8	<0.6	[8]

Temperature T is measured in °K.

and the nuclear spin-lattice relaxation time can be calculated from Eq. (3). The results of these calculations are represented by curve 1 in Fig. 2, whereas curve 2 in the same figure gives the results of calculations based on Eq. (4).

At temperatures above 17°K we have $\tau_S \gg \tau_E$. A calculation of the values of d and b shows that $d \gg b$. The temperature dependence of the nuclear spin-lattice relaxation time calculated from Eq. (3) is in good agreement with the experimental results. Thus, in the case when the proton magnetic relaxation in ethyl sulfate involves the participation of the Ho^{3+} and Er^{3+} ions at low temperatures, the spin-spin relaxation time of the ions can be regarded as the correlation time of the impurities. Obviously, at high temperatures, the proton relaxation via the Er^{3+} ions is much stronger than via the Ho^{3+} ions.

Figures 3 and 4 give the temperature dependences of the nuclear spin-lattice relaxation times of lanthanum ethyl sulfate containing Tb^{3+} and Dy^{3+}. It is clear from Table I that the g factors of these ions are strongly anisotropic. In view of the very small value of $g_\perp$ of the Tb^{3+} and Dy^{3+} ions, the value of τ_S for ethyl sulfates containing these ions is considerably greater than for the crystals containing the Ho^{3+} and Er^{3+} ions. In the temperature range 1.5–15°K we find that LaES + Tb^{3+} satisfies the condition $d \gg b$ and the rate of the nuclear spin-lattice relaxation is described by Eq. (3). In calculating the quantities occurring in Eq. (3) at temperatures $T < 10°K$ we used τ_S given by

$$\tau_s = 1.1 \cdot 10^{-5}(1 - P_0{}^2)^{-1/2},$$

and at $T > 10°K$ we assumed that the correlation time was equal to the spin-lattice relaxation time of the ions. We found that in the T = 15–20°K range the values of d and b were of the same order of magnitude and we calculated the nuclear spin-lattice relaxation time using Eq. (10) in[10]. At $T > 20°K$ we found that $b > d$ and used Eq. (2).

Curve 1 in Fig. 3 represents the theoretical values of the nuclear spin-lattice relaxation times. We can see that the measured and calculated values of these relaxation times are in good agreement. The slope of curve 1 changes in the region where $\tau_S \approx \tau_e$. Thus, our measurements allow us to estimate τ_S characterized by a factor $g_\perp$ close to zero. In the case of LaES + Tb^{3+}, this relaxation time is approximately three orders of magnitude longer than the relaxation times τ_S of LaES + Ho^{3+} and LaES + Er^{3+}. The possibility of the spin-spin relaxation for $g_\perp \approx 0$ in LaES + Tb^{3+} can be explained by the initial splitting of the lower doublet and imperfection of the crystal lattice. Curve 2 in Fig. 3 represents the temperature dependence of the nuclear spin-lattice relaxation time calculated from Eq. (4).

At low temperatures the spin-lattice relaxation of the Dy^{3+} ions in LaES + Dy^{3+} is much more effective than the relaxation of the Tb^{3+} ions. Therefore, in our case, even at T = 2°K the correlation time τ_c is τ_e. In the range 2–5°K we find that $d \gg b$ and we can estimate the nuclear spin-lattice relaxation time from Eq. (3). At $T > 5°K$ the values of d and b are of the same order of magnitude and we must use Eq. (10) given in[10]. It is clear from Fig. 4 that the calculated and experimental values of the nuclear spin-lattice relaxation time are in good agreement throughout the investigated range of temperatures.

In view of the fact that in the orientation close to $\mathbf{H}_0 \perp C_0$, where C_0 is the symmetry axis of the investigated crystal, the Tb^{3+} ions in LaES are characterized by $g_\perp \approx 0$, the resonance frequencies of the protons and Tb^{3+} in LaES + Tb^{3+} are similar and we can expect a strong cross relaxation between the protons and the Tb^{3+} ions. Our measurements indicated that near the $\mathbf{H}_0 \perp C_0$ orientation the proton spin-lattice relaxation time became much shorter. Curve 3 in Fig. 3 represents the temperature dependence of the nuclear relaxation time under the cross relaxation conditions. The temperature dependence of the measured nuclear relaxation time shows that the "bottleneck" of the proton relaxation at $T < 10°K$ is the transfer of energy from the ions to the lattice. At $T > 10°K$ the bottleneck is the transfer of energy from the protons to the impurity ions.

4. CONCLUSIONS

The theory of the nuclear spin-lattice relaxation of impurities presented in[10] gives results which are in good agreement with the experimental data. This means that the diffusion is effective even at distances $r < d$ from an ion, i.e., the Lorentzian shape of the cross relaxation wings agrees better with the experimental results than the Gaussian form. It is shown that at low temperatures the correlation time of LaES + Ho^{3+}, LaES + Er^{3+}, and LaES + Tb^{3+} is the spin-spin relaxation time. If the dipole-dipole reservoir is not heated, the actual value of the spin-lattice relaxation time of the impurity ion is not needed in the calculation of the nuclear spin-lattice relaxation rate. However, if the dipole-dipole reservoir is heated, the rate of nuclear spin-lattice relaxation can be used to estimate τ_e. An investigation of the nuclear spin-lattice relaxation can give information on the rate of the spin-lattice relaxation of ions in that temperature range in which it is difficult to measure τ_e directly and it can also give data on the spin-spin relaxation time of the impurity ions in the $g_\perp \sim 0$ case, i.e., when the calculation of τ_S is impossible.

It is clear from Fig. 3 that, in our case, the cross relaxation shortens the nuclear spin-lattice relaxation time by about one order of magnitude. However, if the correlation time is large, the nuclear relaxation process may be accelerated even more strongly by the cross relaxation.

The authors are deeply grateful to S. A. Al'tshuler for discussing the results of this investigation and to R. Yu. Abdulsabirov for investigating the ESR spectra of our single crystals.

---

[1] C. D. Jeffries, Dynamic Nuclear Orientation, Interscience, New York, 1963 (Russ. Transl., Mir, M., 1965).

[2] K. H. Langley and C. D. Jeffries, Phys. Rev. **152**, 358 (1966).

[3] H. B. Brom and W. J. Huiskamp, Physica (The Hague) **60**, 163 (1972).

[4] A. R. King, J. P. Wolfe, and R. L. Ballard, Phys. Rev. Lett. **28**, 1099 (1972).

[5] F. L. Aukhadeev, I. I. Valeev, and V. A. Skrebnev, Zh. Eksp. Teor. Fiz. **64**, 1699 (1973) [Sov. Phys.-JETP **37**, No. 5 (1973)].

[6] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966).

[7] M. D. Kemple and H. J. Stapleton, Phys. Rev. B5, 1668 (1972).
[8] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans soedineniĭ elementov promezhutochnykh grupp (Electron Paramagnetic Resonance of Compounds of Elements of Intermediate Groups), Nauka, M., 1972.
[9] G. R. Khutsishvili, Usp. Fiz. Nauk 96, 441 (1968) [Sov. Phys.-Uspekhi 11, 802 (1969)].
[10] V. A. Skrebnev, Fiz. Tverd. Tela 15, 527 (1973) [Sov. Phys.-Solid State 15, 365 (1973)].
[11] M. G. Melikiya, Fiz. Tverd. Tela 10, 858 (1968) [Sov. Phys.-Solid State 10, 673 (1968)].

Translated by A. Tybulewicz
120