Nuclear polarization of rare-earth ions in insulating Van Vleck paramagnets

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A study has been made of the spin-lattice relaxation of ^{141}Pr nuclei in $Pr_2(SO_4)_3 \cdot 8H_2O$ and ^{169}Tm nuclei in TmES in strong magnetic fields (up to 60 kOe) at ultralow temperatures (70–100 mK). A direct ($T^{-1} \sim H^4$) relaxation of ^{141}Pr nuclei has been detected. The relaxation rate T^{-1} of the ^{169}Tm nuclei does not depend on the strength of the magnetic field or the temperature.

Twenty years ago, Al'tshuler[1] suggested that magnetic cooling could be achieved by making use of a special class of paramagnetic substances known today as "Van Vleck paramagnets." As examples, Al'tshuler[1] studied crystals of compounds of rare-earth elements in which the paramagnetic ions Pr^{3+}, Tb^{3+}, Ho^{3+}, and Tm^{3+} have a nonmagnetic (singlet) ground state. This idea was implemented soon thereafter in extensive experiments by Andres and Bucher (Refs. 2 and 3, for example), who used intermetallic rare-earth compounds. The lowest temperature which has been achieved to date with the help of the compound $PrNi_5$ is[4] 0.2 mK. Fundamental factors appear

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to block any further progress toward ultralow temperatures: In intermetallic compounds of rare earths, the ions are bound by a strong *s-f* exchange interaction, so that such substances have comparatively high magnetic-ordering temperatures. The possible practical use of insulating compounds such as thulium ethyl sulfate (TmES), as proposed by Al'tshuler,[1] remains an open question, since in insulators the spin-lattice relaxation times of the nuclei are extremely long at ultralow temperatures. According to the theory,[5,6] the rate of direct (one-phonon) relaxation of rare-earth nuclei in insulators should increase with increasing field, in proportion to H^4. Estimates of the time T_1 for ^{169}Tm nuclei in TmES yield 9 h at $T = 20$ mK in a field $H = 80$ kOe. No experimental data have been reported on the relaxation of rare-earth nuclei in insulators in strong magnetic fields.

In the present letter we report an experimental study of the spin-lattice relaxation of ^{141}Pr nuclei ($I = 5/2$) in $Pr_2(SO_4)_3 \cdot 8H_2O$ and of ^{169}Tm nuclei ($I = 1/2$) in TmES in fields up to 60 kOe at temperatures in the interval 70–100 mK. The samples are placed directly in the dissolution bath of a ^{3}He–^{4}He refrigerator. The temperature is monitored by calibrated resistance thermometers. The same procedure is used to study the two crystals. We use a *Q*-meter to measure the NMR signal; these measurements are carried out in a comparatively weak magnetic field and at a low frequency: $H_0 = 2000$ Oe and $\nu = 13.4$ MHz for $Pr_2(SO_4)_3 \cdot 8H_2O$ (this was an arbitrarily selected line in the complex magnetic-resonance spectrum of the ^{141}Pr nuclei). For TmES, we used $H_0 = 650$ Oe and $\nu = 17$ MHz; the field $\mathbf{H}_0$ was directed perpendicular to the *c* axis of the crystal. The NMR spectrum was recorded at successive times separated by long intervals $t = 0.5$–10 h, during which the samples were subjected to a strong magnetic field $H = 5$–60 kOe. The value of H_0 was chosen to keep the nuclear relaxation time quite long (1 h for TmES at $T = 70$ mK) and to keep at a negligible level the leakage of nuclear polarization due to the interaction of nuclear spins with impurity paramagnetic centers.

The experimental results can be summarized as follows:

1. The equilibrium magnetization of ^{141}Pr nuclei in the field H at the temperature $T = 80$ mK is established exponentially at a rate $T_1^{-1} = 6.9 \times 10^{-25} H^4$ s^{-1} (Fig. 1). The minimum time T_1, found in experiments with $T = 80$ mK and a field $H = 47$ kOe, is ~ 100 h.

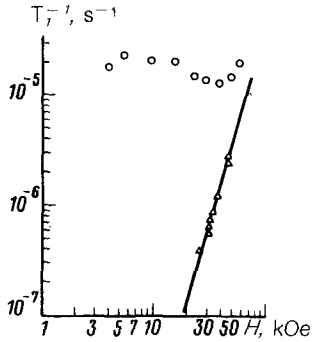

FIG. 1. Relaxation rate of ^{141}Pr nuclei in $Pr_2(SO_4)_3 \cdot 8H_2O$ at $T = 80$ mK (triangles) and of ^{169}Tm nuclei in TmES at $T = 70$ mK (circles) in strong magnetic fields (see the text proper for the details).

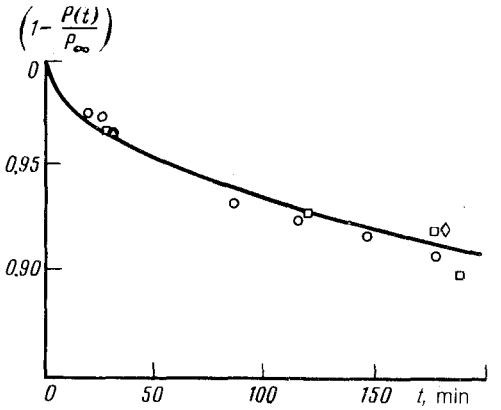

FIG. 2. Time evolution of the nuclear polarization of thulium in a TmES crystal at $T = 70$ mK in strong magnetic fields: Circles—$H = 38.6$ kOe; squares—48.3; triangle—50.2; diamond—57.9. (The sample is a small sphere $R = 2.5$ mm in radius.)

2. The relaxation to an equilibrium magnetization of ^{169}Tm nuclei cannot be described by a single exponential function (Fig. 2). The relaxation rate T_1^{-1}, determined by convention from the initial part of the magnetization evolution curve ($t = 0.5$ h), does not depend on H in the interval from 3 to 58 kOe or on the temperature T in the interval 70–100 mK (Fig. 1).

The field dependence of the rate, $T_1^{-1} \sim H^4$, clearly indicates that the relaxation of the ^{141}Pr nuclei in the praseodymium sulfate crystal occurs through a direct nuclear process.

The fact that the relaxation of ^{169}Tm nuclei in TmES does not depend on the field or the temperature and the fact that this relaxation is not exponential suggest that the exchange of energy of nuclear spins with the lattice and the helium bath occurs by a diffusion process. In ordinary nuclear paramagnets such as CaF_2, the spin-diffusion coefficient is on the order of 3×10^{-12} cm^2/s. Theoretical estimates by various methods described in the literature lead to $D \approx 7.5\times10^{-11}$ cm^2/s. The observed change in the nuclear polarization of the thulium over time can be described as a diffusion process, $\Delta P(t)/\Delta P(0) = (6/\pi^2)\Sigma_{n=1}^{\infty} n^{-2}\cdot\exp[-(\pi n/R)^2 Dt]$, with a diffusion coefficient $D = 4.2\times10^{-9}$ cm^2/s (the solid line in Fig. 2). The reason for this anomalously large value of D is not clear. The reason might possibly be sought in the complex nature of the spin-deformation excitations in magnetically concentrated crystals of rare-earch compounds.[7] At any rate, if a fast diffusion process does occur, it will indicate that there is a real possibility of achieving a high nuclear polarization of powdered insulators by a "brute-force method."

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