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OBSERVATION OF HYPERFINE-ENHANCED NUCLEAR MAGNETIC COOLING

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We point out the suitability of rare-earth ions in singlet ground states for the production of very low temperatures by means of nuclear adiabatic demagnetization. We have observed nuclear cooling in PrBi from an initial temperature of 0.026°K to a final temperature of 0.01°K.

Temperatures of a few millidegrees have so far been produced by three methods: adiabatic demagnetization of electron and nuclear moments, and dilution refrigeration with He^3-He^4 mixtures. We report here on a new method, pointed out theoretically by Al'tshuler,[1] which is an intermediate between the first two: demagnetization of nuclear moments in hyperfine fields generated by external fields through the polarizability of $4f$ electrons in a singlet ground state. A rare-earth ion in a nonmagnetic singlet ground state shows no hyperfine splitting for a nuclear spin $I=\frac{1}{2}$. For larger I there is a small splitting proportional to I_z^2 arising from the mixing of higher lying magnetic states into the ground state by means of the nuclear magnetic moment.[2] In an external magnetic field, however, the singlet ground state can be substantially polarized to exhibit a nonzero $\langle J_z \rangle$ since the field admixes higher excited magnetic states into it. A hyperfine field proportional to the external field results, which gives rise to a hyperfine splitting of the ground state. For this hyperfine field to be large, a highly polarizable singlet ground state (i.e., large Van Vleck susceptibility) is required which means that the energy separation to the next higher magnetic state should be low. Examples of such cases are the rare-earth intermetallic compounds RX with R = Pr or Tm and X = N, P, As, Sb, and Bi. All these compounds have the rocksalt structure. The rare-earth ions are of the non-Kramers type ($J=4, S=1$ for Pr^{3+} and $J=6, S=1$ for Tm^{3+}). Therefore they tend to split into multiplets with a singlet as the lowest state in a crystal field of octahedral symmetry if exchange interactions are not too large.[3,4] The level separations between the lowest singlet and the next higher excited state are of the order of 20°K in the Tm compounds and 70°K in the Pr compounds, and the low-temperature Van Vleck susceptibilities are of the order of 0.5 and 0.1 emu/mole for the Tm and Pr compounds, respectively.[5] The large induced hyperfine fields have been demonstrated by Knight-shift measurements of Jones,[6] who finds Knight shifts of 8900% for Tm^{169} in TmSb and 650% for Pr^{141} in PrAs at 4.2°K. This corresponds to hyperfine splittings of 0.028°K and 0.012°K, respectively, in an external field of 20 kOe, which should be very suitable for nuclear adiabatic demagnetization. In Table I we compare the nuclear cooling efficiency of TmSb and PrBi with metallic Cu, which has been used frequently for nuclear adiabatic demagnetization. Listed are nuclear spin I, nuclear moment μ, effective gyromagnetic ratio γ (kHz/Oe) and effective hyperfine field H_{eff} for

Table I. Nuclear spin I, nuclear moment μ, and effective gyromagnetic ratio γ in the rare-earth nuclei of TmSb, PrBi, and in Cu. The parameter $X = g\mu_N IH_{\text{eff}}/kT$, nuclear heat of magnetization W, and induced hyperfine field H_{eff} are computed for 0.030°K, 20 kOe, and 10^{-2} mole of material.

	I	μ	γ	H_{eff}	X	W
Unit	$\hbar$	μ_N	kHz/Oe	kOe	1	erg
TmSb	$\frac{1}{2}$	−0.227	30[a]	1730	0.48	2880
PrBi	$\frac{5}{2}$	4.28	13[b]	199	1.03	6280
Cu	$\frac{3}{2}$	2.3	~1.2	20	0.0561	23.0

[a]Ref. 6. [b]Ref. 7.

the Tm^{169}, Pr^{141}, and Cu^{63} or Cu^{65} nuclei. Also listed are the ratio $X = Ig\mu_N H_{\text{eff}}/kT$ and the nuclear heat of magnetization

$$W = \int_0^{H_{\text{eff}}} H_{\text{eff}} dM_N \approx \tfrac{1}{2}\chi_N H_{\text{eff}}^2 = N\gamma^2\hbar^2 I(I+1)H_0^2/6kT, \quad (1)$$

for an initial temperature of 0.030°K and an external field H_0 of 20 kOe ($\chi_N = dM_N/dH_{\text{eff}}$ = nuclear susceptibility). Equation (1) overestimates W by about 15% for $X = 1$ since it neglects the curvature of the Brillouin function.

Judging from the large nuclear heat of magnetization, nuclear cooling effects should be easily observable with these starting conditions, if one assumes a typical heat leak of the order of a few ergs per minute. We also expect a short spin-lattice relaxation time due to the strong strain dependence of the induced hyperfine field and also due to the presence of conduction electrons, which should insure good spin-lattice contact even at low temperatures.

We have searched for nuclear cooling in TmSb and PrSb and have seen indications of it. During demagnetization from 16 kG however, sudden irreversible heating was observed at 3 and 6 kOe, respectively, in these materials. In the case of PrSb we have been able to relate this heating effect to the presence of a trace of $PrSb_2$ in our samples, a phase which we found to be metamagnetic and which undergoes a spin-flip transition in 6 kOe. More recently cooling has been observed in PrBi from 0.026°K to 0.010°K using a field of 16 kOe. The experimental setup is sketched in Fig. 1.

A first conventional adiabatic-demagnetization stage (chromium potassium alum) is used to generate temperatures around 0.015°K. A superconducting switch (tin), operated by the fringe field

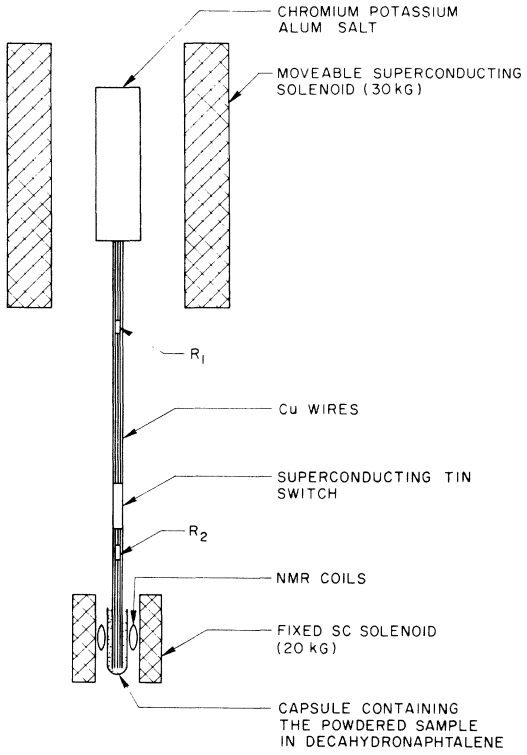

FIG. 1. Experimental arrangement.

of the second stage, is used to make and break thermal contact between the sample and the chrome-alum. Temperatures are measured with As-doped Ge resistors R_1 and R_2, R_1 having been calibrated down to 0.015°K against a cerium-magnesium-nitrate thermometer. Nuclear-magnetic-resonance coils are also located around the sample. A typical run is shown in Fig. 2. The first stage is initially demagnetized to about 1 kG and the movable superconducting coil lowered until the tin switch opens. This precools

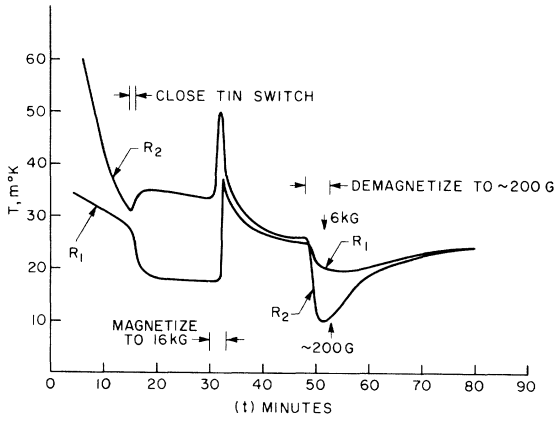

FIG. 2. Nuclear demagnetization run on PrBi (see text).

sample and salt to about 0.030°K. The field is then switched off completely and the coil raised above the salt. This initially heats up the sample somewhat because of the magnetocaloric effect in the tin switch. With the sample at 0.033° and the salt at 0.017°, a field of 16 kG is applied to the sample. Heat of magnetization develops and salt and sample equilibrate at 0.026°K after a while. When the field is switched off, the sample cools. The salt shows some cooling too, which indicates that the superconducting tin switch is leaking. This leaking switch is presumably also responsible for the rather rapid warmup rate of the sample after demagnetization. The lowest temperature has been determined by assuming that R_2 follows the same power law ($T^{-1/8}$) below 0.025°K as it does above that temperature. We searched for the NMR line of Pr^{141} at 10 MHz using a marginal oscillator. Instead of the expected line at 770 Oe,[7] we saw an as yet unidentified broad resonance peak at 150 Oe, the height of which varied as $1/T$ down to 0.1°K and increased at a slower rate below that temperature.[8] From the amplitude of this resonance right after demagnetization we again extrapolate a sample temperature of about 0.010°K.

While the cooling effect is thus obvious, we have not yet reached temperatures as low as expected. A lower limit of the temperature that can be reached is given by the residual hyperfine splitting in zero external field (if $I > \frac{1}{2}$) or eventually by a nuclear-ordering temperature. In the salt $Pr_2(SO_4)\cdot 8H_2O$, where the Pr^{3+} ion is also in a singlet ground state, the residual hyperfine splitting has been measured to be of the order of 10^{-3} °K.[2] Interactions between nuclei via conduction electrons may be enhanced by the high polarizability of the $4f$ electrons. Estimates however indicate that a resulting nuclear-ordering temperature should still be below 10^{-3} °K.

In conclusion, nuclear magnetic cooling using rare-earth intermetallic compounds does seem to be a promising new way to produce very low temperatures. The available cooling entropies are typically two orders of magnitude larger than for metallic copper and the nuclear spin-lattice relaxation time is expected to be at least as short as for Cu. Work is in progress to improve materials and to get a more accurate measurement of the actually attainable lowest temperature.

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