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^{111}Cd and ^{113}Cd spin-lattice relaxation in $CdMoO_4$ by paramagnetic centers in the absence of spin diffusion

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In an ongoing effort to understand the solid-state spin-lattice relaxation mechanism and its modulation for heavy-nuclei spin-1/2 systems like ^{207}Pb and ^{203}Tl/^{205}Tl, we have serendipitously observed that the recovery of a saturated ^{111}Cd (or ^{113}Cd) nuclear magnetization in $CdMoO_4$ shows the three distinct time regions elucidated by Bodart *et al.* [Phys. Rev. B **54**, 15291 (1996)] when nuclear-spin relaxation is dominated by paramagnetic impurity relaxation in the complete absence of nuclear-spin diffusion.

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^{207}Pb and ^{203}Tl/^{205}Tl solid-state nuclear-spin-lattice relaxation rates in lead nitrate $[Pb(NO_3)_2]$ and in thallium nitrate ($TlNO_3$) convincingly show that the relaxation is caused by a modulation of a local magnetic field by phonons, via a second-order Raman process characterized by a T^2 dependence where T is the temperature.[1,2] In a quest to understand better the origin of the magnetic field that the phonons are modulating, we have investigated ^{111}Cd and ^{113}Cd nuclear-spin-lattice relaxation in cadmium molybdate ($CdMoO_4$). Not only have we confirmed that the Raman second-order phonon process is *not* present, we have observed relaxation by paramagnetic impurities in the complete absence of Cd—Cd spin diffusion, clearly showing the three time regions elucidated by Bodart *et al.*[3] As shown in Fig. 1 for the recovery of the Cd nuclear magnetization in $CdMoO_4$ following saturation, the three regions are: a short-time region where the magnetization is linear in time t; a middle-time region where it is proportional to $\sqrt{t}$; and a long-time exponential recovery as an equilibrium magnetization is reached. Bodart *et al.* saw this behavior using ^{2}H, a quadrupolar nucleus, as the probe nucleus.

^{111}Cd and ^{113}Cd are spin-1/2 nuclei with natural abundances of 12.8% and 12.3%, respectively. There have been very few reports of solid-state ^{111}Cd and/or ^{113}Cd nuclear-magnetic-resonance (NMR) relaxation studies. Spin-lattice relaxation times T_1 have been reported in the pure metal,[4,5] in $Cd_xMo_6Se_8$ ($x=1,2$),[6] and in a variety of doped semiconductor crystals.[7,8]

In the experiments reported here, ^{111}Cd and ^{113}Cd spectra and magnetization recoveries for $CdMoO_4$ were observed using static samples with a Bruker MSL-300 NMR spectrometer at a magnetic field of 7.049 T, where the proton resonance frequency is 300.130 MHz. Both the ^{111}Cd and ^{113}Cd spectra in $CdMoO_4$ are narrow and can be fitted to Lorentzians having a half width at half height of about 250 Hz. The room-temperature ^{111}Cd spectrum peaks at 63.624 MHz and the ^{113}Cd spectrum at 66.555 MHz. Magnetization recovery curves like that shown in Fig. 1 were generated using the saturation-recovery technique. A saturating comb of 20 $\pi/2$ pulses was followed by a waiting time t, with detection of the magnetization with a measuring $\pi/2$ pulse. The $\pi/2$ pulse width was 3.3 μs. Appropriate phase cycling was used to suppress baseline artifacts. To obtain the data in Fig. 1, 1400 scans were accumulated for each of 32 t values between 10 ms and 900 s. The experiment took 51 days of near-continuous operation.

Nuclear-spin relaxation by coupling to paramagnetic centers has been known since the earliest days of NMR and several papers have appeared over the last 55 years.[3,9–16] The paper by Bodart *et al.*[3] is both recent and very thorough. They begin with the exponential relaxation rate T_1^{-1} for a shell of nuclear spins a distance r from a paramagnetic center,

$$\frac{1}{T_1} = \alpha\left(\frac{a}{r}\right)^6, \tag{1}$$

where α is the relaxation rate for a nucleus at a distance a from the paramagnetic center. (We use the same symbols as Bodart *et al.*) From Eq. (3) of Bodart *et al.*,

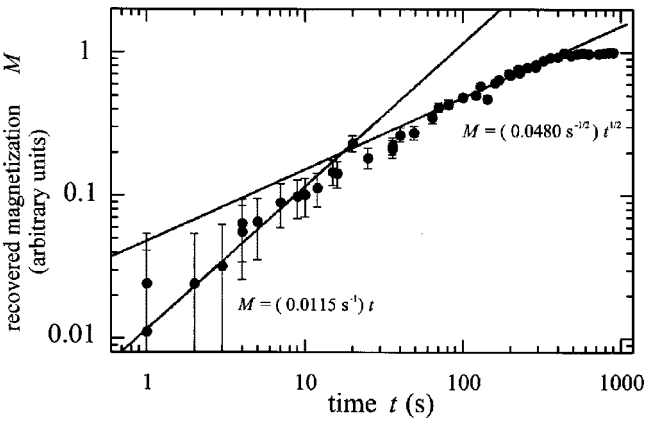

FIG. 1. ^{111}Cd saturation recovery in $CdMoO_4$. One datum, $M=0.00\pm0.03$ at $t=0.01$ s, is not shown.

$$\alpha = \frac{2}{5}\gamma_n{}^2\gamma_s{}^2\hbar^2 S(S+1)\frac{\tau}{1+\omega^2\tau^2}\frac{1}{a^6}. \quad (2)$$

Although the spin-lattice relaxation rate for a shell of nuclei at radius r is independent of the distance scale parameter a, this distance is convenient in analyzing the various time regions. It is roughly the distance to the first shell of nuclear spins. The other relevant parameter is a dimensionless impurity concentration parameter c, which is approximately (about 0.1 to 1 times) c_r, the ratio of the number of impurity sights to the number of nuclear-spin sights. The data in Fig. 1 could be fitted with a single complicated expression found in Bodart *et al.*, but the essence of the physics comes from inspecting the time at which the transition from the linear t region to the $\sqrt{t}$ region occurs, from which it can be shown that for $CdMoO_4$ $\alpha \approx 0.2\ s^{-1}$ and $c \approx 0.06$. A spin-lattice relaxation time of $\alpha^{-1} \approx 5$ s for the cadmium nuclei nearest the paramagnetic center is reasonable and indicates why, in 900 s, an equilibrium magnetization has still not quite been achieved.

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