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# $^{111}\text{Cd}$ and $^{113}\text{Cd}$ spin-lattice relaxation in $\text{CdMoO}_4$ 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  $^{207}\text{Pb}$  and  $^{203}\text{Tl}/^{205}\text{Tl}$ , we have serendipitously observed that the recovery of a saturated  $^{111}\text{Cd}$  (or  $^{113}\text{Cd}$ ) nuclear magnetization in  $\text{CdMoO}_4$  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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$^{207}\text{Pb}$  and  $^{203}\text{Tl}/^{205}\text{Tl}$  solid-state nuclear-spin-lattice relaxation rates in lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] and in thallium nitrate ( $\text{TlNO}_3$ ) 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.<sup>1,2</sup> In a quest to understand better the origin of the magnetic field that the phonons are modulating, we have investigated  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$  nuclear-spin-lattice relaxation in cadmium molybdate ( $\text{CdMoO}_4$ ). 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.*<sup>3</sup> As shown in Fig. 1 for the recovery of the Cd nuclear magnetization in  $\text{CdMoO}_4$  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  $^2\text{H}$ , a quadrupolar nucleus, as the probe nucleus.

$^{111}\text{Cd}$  and  $^{113}\text{Cd}$  are spin-1/2 nuclei with natural abundances of 12.8% and 12.3%, respectively. There have been very few reports of solid-state  $^{111}\text{Cd}$  and/or  $^{113}\text{Cd}$  nuclear-magnetic-resonance (NMR) relaxation studies. Spin-lattice relaxation times  $T_1$  have been reported in the pure metal,<sup>4,5</sup> in  $\text{Cd}_x\text{Mo}_6\text{Se}_8$  ( $x=1,2$ ),<sup>6</sup> and in a variety of doped semiconductor crystals.<sup>7,8</sup>

In the experiments reported here,  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$  spectra and magnetization recoveries for  $\text{CdMoO}_4$  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  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$  spectra in  $\text{CdMoO}_4$  are narrow and can be fitted to Lorentzians having a half width at half height of about 250 Hz. The room-temperature  $^{111}\text{Cd}$  spectrum peaks at 63.624 MHz and the  $^{113}\text{Cd}$  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  $\mu\text{s}$ . 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.<sup>3,9–16</sup> The paper by Bodart *et al.*<sup>3</sup> 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,

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

where  $\alpha$  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.*,

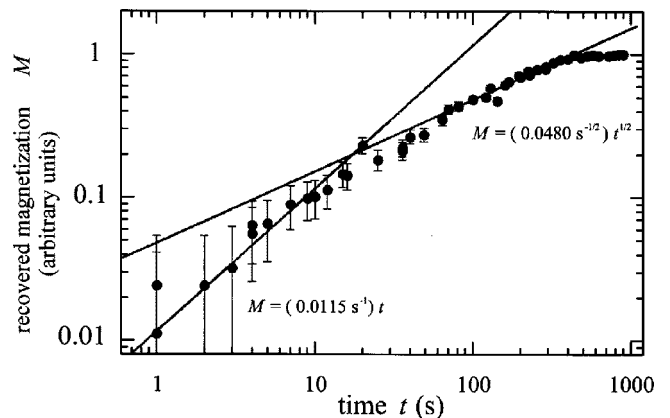


FIG. 1.  $^{111}\text{Cd}$  saturation recovery in  $\text{CdMoO}_4$ . One datum,  $M = 0.00 \pm 0.03$  at  $t = 0.01$  s, is not shown.

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

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  $\text{CdMoO}_4$   $\alpha \approx 0.2 \text{ s}^{-1}$  and  $c \approx 0.06$ . A spin-lattice relaxation time of  $\alpha^{-1} \approx 5 \text{ s}$  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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