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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 $^{203}\text{Tl}/^{205}\text{Tl}$, 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 $^{203}\text{Tl}/^{205}\text{Tl}$ solid-state nuclear-spin-lattice relaxation rates in lead nitrate [$\text{Pb}(\text{NO}_3)_2$] and in thallium nitrate (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 ^2H , 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 $\text{Cd}_x\text{Mo}_6\text{Se}_8$ ($x=1,2$),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,

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

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.*,

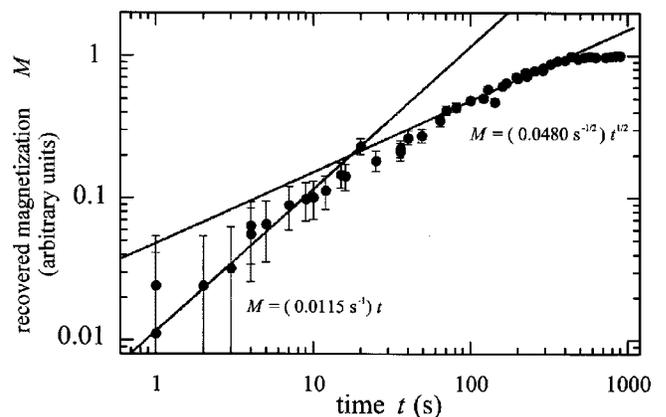


FIG. 1. ^{111}Cd saturation recovery in CdMoO_4 . One datum, $M = 0.00 \pm 0.03$ at $t = 0.01$ s, is not shown.

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

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 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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