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A New Mechanism for Spin−Lattice Relaxation of Heavy Nuclei in the Solid State: ^{207}Pb Relaxation in Lead Nitrate

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Abstract: A detailed investigation of the spin−lattice relaxation time, T_1, for ^{207}Pb in solid lead nitrate has been undertaken in an effort to understand the mechanism of relaxation. The results show that the ^{207}Pb T_1 is independent of magnetic field strength and inversely proportional to the square of the temperature. These are signatures of relaxation by a spin-phonon Raman scattering mechanism. Nuclear spin−lattice relaxation in solid lead salts is more efficient for sites with *smaller* magnetic shielding anisotropy. A coupling mechanism is proposed whereby phonons create a local magnetic field by modulating the valence electron shell motion relative to the nuclear/electron core. Literature data suggest that spin-phonon scattering is a common relaxation pathway for other spin-$^1/_2$ heavy nuclei in solids.

Introduction

Lead-containing materials are found in many technological applications: batteries,[1] scintillation detectors for nuclear radiation,[2] optoelectronic memory devices,[3] high-temperature superconductors,[4] and a myriad of electronic applications involving piezoelectricity and ferroelectricity.[5] Compounds containing lead also appear on major environmental hazard lists.[6] Because of the convenient NMR properties of ^{207}Pb ($I = {}^1/_2$, $\gamma_{Pb}/\gamma_C = 0.83$, 22.08% natural abundance[7]) and the high information content of solid-state NMR (δ and span ranges of thousands of ppm), lead NMR is a sensitive structural tool for characterization of solids.[8−11] The linear dependence of the lead chemical shift on

temperature in lead nitrate has found widespread use as a sensitive NMR thermometer.[12,13] An essential, but little appreciated, aspect of these publications is that the relaxation times are surprisingly short for what are, at first sight, magnetically isolated nuclei in diamagnetic rigid solids. In the first detailed study of spin−lattice relaxation in solid lead salts, Fitzgerald, Shore, and co-workers[10] found T_1 relaxation times that ranged from 1.0 s in Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$ to 160 s in the Pb(II) site in Pb$_3$O$_4$. In this paper, a detailed study of spin−lattice relaxation in solid lead nitrate and related compounds is presented. Various nuclear relaxation mechanisms for solids have been treated in Abragam's classic text.[14] Relaxation theory and many examples have also been presented by Spiess.[15] The standard mechanisms include dipole−dipole coupling, scalar coupling, and phonon coupling. Each has its unique signature that specifies its properties. For example, the chemical-shift-anisotropy mechanism, if dominant, results in an observed relaxation time inversely proportional to the square of the magnetic field in the extreme narrowing regime. The observed rate of ^{207}Pb relaxation for solid lead nitrate is independent of field (vide infra) and is too efficient to be explained by processes with motional times in the slow motion regime; see eq 1 below.

We have measured the ^{207}Pb relaxation rate in lead nitrate as a function of temperature and applied magnetic field strength to specify the nature of the interactions producing relaxation. The results suggest that relaxation by a second-order Raman scattering mechanism induced by spin-phonon interactions is dominant in this material.[16] We propose a novel mechanism

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for coupling phonon motion with the nuclear spin in heavy atoms to account for the results for lead nitrate and suggest that it might also explain the literature data for relaxation in many thallium and mercury salts.

Experimental. The temperature dependence of the ^{207}Pb spin−lattice relaxation rate, R, was measured between 146 and 375 K at magnetic field strengths of 4.70 (an NMR Larmor frequency of 41.7 MHz), 7.02 (62.6 MHz), 9.40 (83.7 MHz), and 14.1 T (125.5 MHz) [Figure 1]. Measurements at 62.6 MHz were performed at the University of Delaware on a Bruker MSL 300 spectrometer using a 7-mm MAS probe but without spinning. A $\{\pi-t-\pi/2(\text{add})-T_R-\pi/2(\text{subtract})-T_R\}$ sequence was used to determine T_1, with a relaxation delay, T_R, of at least eight times T_1. 32 to 64 scans were coadded for each of 8 to 12 values of t. In all cases, the time development of the lead magnetization was exponential. Temperature was controlled by a heated air flow and measured both with the lead nitrate thermometer[12,17] and by observing the proton resonance in a small bulb of ethylene glycol in the center of the lead nitrate sample and using the ethylene glycol thermometer.[18] The two methods gave the same sample temperature within ±2 K.

Measurements at 62.6 (Varian Inova 300), 83.7 (GE-Omega 400 and Varian Infinity 400), and 125.5 MHz (Varian Infinity 600), made at Purdue University, utilized the pulse sequence above with at least 8 t values, an acquisition time of 0.5 s, and relaxation delays of at least 5 times T_1. At 125.5 MHz, relaxation delays of 40−52 s were used for the experiments below room temperature. At 200 K this was 3 times T_1 and so the 125.5 MHz points shown in the figures have small (<5%) systematic errors and the reported rates are presumably larger than the true values. All variable-temperature experiments were done with the temperature controlled by cooled/heated N$_2$ in the probe. At 83.7 MHz, the temperature and T_1 values were determined on samples spinning at 5−6 kHz using the lead nitrate chemical-shift thermometer.[12] The literature calibration was checked against melting point standards.[19] At 62.6 and 125.5 MHz, static samples were used for T_1 measurement and the temperature was measured from the peak maximum of the ^{207}Pb powder pattern.[17] In this nonspinning configuration, the sample and thermocouple temperatures agreed within ±3 K on both instruments.

Measurements at 41.7 MHz (4.7 T) were performed at Dalhousie University with a Varian Infinity spectrometer. All experiments were performed on a static sample of lead nitrate using a 7.5 mm double resonance probe. In each case, the standard inversion−recovery pulse sequence was used with 12 t values and relaxation delays of at least 8 T_1. Temperature control was achieved using N$_2$ gas. Temperatures were obtained by measuring the span of the ^{207}Pb NMR powder pattern.[13]

Possible Mechanisms for ^{207}Pb Relaxation in Solid Pb-(NO$_3$)$_2$. Crystalline lead nitrate has cubic symmetry ($Pa3$) with four molecules in the unit cell.[20] Each lead ion is coordinated to six nitrate oxygens (Pb−O 2.748 Å) with a second oxygen from each nitrate in a second coordination shell (Pb−O 2.869 Å) and local S_6 symmetry. The remaining two nitrates are not
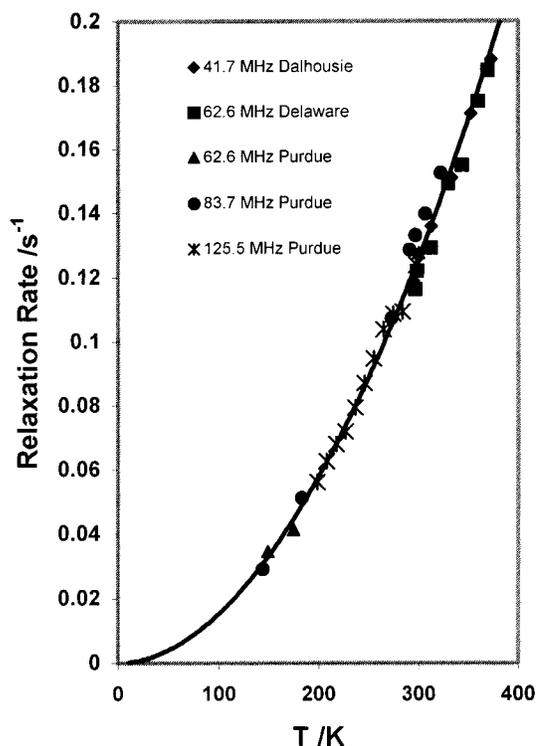
Figure 1. ^{207}Pb spin−lattice relaxation rate (R/s^{-1}) vs temperature (T/K) in solid Pb(NO$_3$)$_2$ at various field strengths. The best fit line is to the function $R = (2.22 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-1.92})T^{1.92}$.
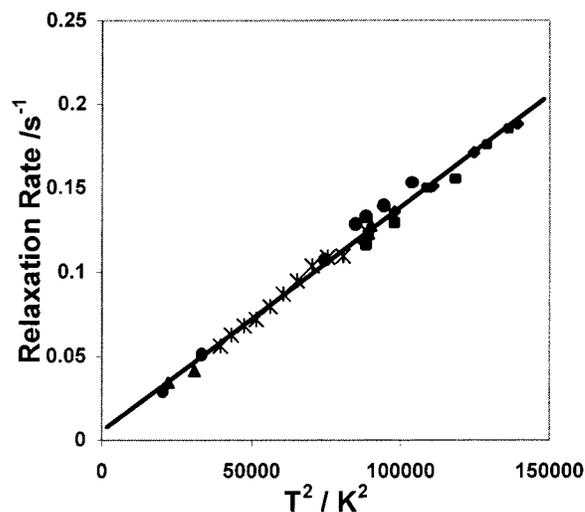
Figure 2. Best fit correlation of ^{207}Pb spin−lattice relaxation rate (s^{-1}) in solid Pb(NO$_3$)$_2$ vs temperature squared (K^2): $R = (1.33 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-2})T^2 + 0.0056 \text{ s}^{-1}$. Symbols are defined in Figure 1.

coordinated and lie on the principal diagonal of the unit cell above and below the lead (Figure 3a). Each lead ion has 12 equidistant lead ions as next nearest neighbors. A detailed single-crystal NMR analysis of solid Pb(NO$_3$)$_2$ has been reported by Lutz and Nolle.[21] The powder ^{207}Pb NMR spectrum of lead nitrate has been reported by several authors.[8,12,13,17] The powder patterns indicate an axially symmetric CSA pattern whose span diminishes with increasing temperature. Bielecki and Burum[13] report the span of lead nitrate, $\Omega = (\sigma_{33} - \sigma_{11} = \sigma_{\parallel} - \sigma_{\perp})$, to be a linear function of temperature in the range 153−393 K. At 298 K the span is 54 ppm, increasing to ∼90 ppm at 77 K. The linear dependence of the lead chemical shift on temperature

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is consistent with a low-barrier equilibration process that averages two states of lead nitrate ($\Delta E \sim 500$ K) while maintaining the orientation of the tensor axes, i.e., the exchange process does not interchange $\sigma_\parallel$ and $\sigma_\perp$.[22] The equilibration is fast on the NMR time scale, $\tau_{ex} < 10^{-5}$ s. Since $\sigma_\parallel$ has a larger temperature coefficient than $\sigma_\perp$, the high-energy form has a CSA pattern with $\sigma_\parallel$ less shielded than $\sigma_\perp$. At 41.7 MHz, the extrema of the CSA pattern show additional broadening from ^{207}Pb–^{14}N dipole coupling.[23] Since no exchange line broadening processes have been reported, any phonon induced shifts and couplings are averaged on the time scale of the inverse of the ^{207}Pb NMR parameter frequency differences ($\sim 10^{-5}$ s).

The ^{207}Pb relaxation rates increased from 0.03 s^{-1} at 146 K to 0.19 s^{-1} at 370 K. Two functions fit the data well: the power law function shown in Figure 1, $R = AT^{\mathbf{B}}$ with $A = (2.22 \pm 0.1) \times 10^{-6}$ s^{-1} K^{-B} and $B = 1.92 \pm 0.04$, and the linear function $R = AT^2 + B$ with $A = (1.33 \pm 0.03) \times 10^{-6}$ s^{-1} K^{-2} and $B = 0.0056 \pm 0.003$ s^{-1} as shown in Figure 2. We adopted the T^2 function because it was simple and physically sensible, and the intercept was zero within experimental error. There is no discernible dependence of the relaxation rate on field strength.

Nuclear spin relaxation for spin-$^1/_2$ nuclei, such as ^{207}Pb, is induced by a magnetic coupling between the ^{207}Pb nucleus and the lattice. This local magnetic field, B_L, arising from the lattice, fluctuates in time. Relaxation requires the frequencies of the fluctuations in the lattice to match the Larmor frequency of the resonant spins (ω_0) to induce the nuclear spin flips. The general relationship is

$$R = (1/T_1) \, \alpha \, B_L{}^2 \, J(\omega_0) \tag{1}$$

with $J(\omega) = 2\tau_c/(1+\omega^2\tau_c^2)$, where $J(\omega_0)$ is the spectral density function for the lattice fluctuations occurring at the nuclear resonance frequency, ω_0, and τ_c is the correlation time for the lattice fluctuation which frequently involves random rotational and/or vibrational motions. In the following discussion we assume that the motion is in the extreme narrowing region of the relaxation–correlation curve ($\omega_0\tau_c \ll 1$).

The observed ^{207}Pb relaxation in solid Pb(NO$_3$)$_2$ is surprisingly efficient for a relatively dilute spin-$^1/_2$ nucleus in a proton-free solid. To explain this relaxation we explore possible interactions (sources of a local field) that may affect this nucleus: (1) dipole–dipole coupling with ^{14}N, (2) chemical shift anisotropy, (3) Pb–Pb J coupling, (4) coupling to electron spins in paramagnetic impurities, and (5) nuclear spin-rotation coupling. Upon consideration of these mechanisms [vide infra], we identify spin-rotation as the dominant relaxation mechanism by a process of elimination. The source of the frequency match in the spectral density function was initially perplexing, as there is no obvious ion motion to provide the modulation that satisfies the nuclear resonance condition. However, we conclude that a Raman scattering process where two phonon frequencies differ by the lead resonance frequency provides the required energy match to allow energy transfer.

(1) The **dipole–dipole coupling** for ^{207}Pb–^{14}N in Pb(NO$_3$)$_2$ was determined to be 55 Hz with a total spread of 330 Hz from the six nearest neighbor nitrates.[23] The maximum contribution to $1/T_1$ (at the temperature at which $\tau_c\omega_0 \approx 1$) is estimated to be 0.0172 s^{-1} at 41 MHz decreasing to 0.006 s^{-1} at 124 MHz. Clearly, these estimates demonstrate that dipole–dipole coupling to the nitrogens cannot account for the observed relaxation rate. Further, the ^{14}N NMR spectrum in lead nitrate in a single crystal

was reported by Harbison and co-workers.[24] It shows four sharp resonances for the four nonequivalent nitrate sites in the cubic unit cell with line widths of <500 Hz. Thus, even though nitrogen may relax via the electric quadrupole mechanism (quadrupole coupling constant of 650 kHz), the observed rate is slower than 10^3 s^{-1} and shows there is little, if any, nitrate tumbling in the solid. The structure obtained by single-crystal neutron diffraction does not show temperature anomalies.[20] We conclude that there is no evidence of nitrate ion tumbling in solid lead nitrate.

(2) Relaxation by **chemical shift anisotropy**, (CSA), is proportional to the square of the applied magnetic field strength and to the magnitude of the chemical shift anisotropy itself.[14,15] CSA relaxation requires ligand reorientation to modulate the chemical shift anisotropy.[25] The single crystal study by Lutz and Nolle[21] showed that the unique component of the shift tensor was oriented along the principal diagonal of the cubic unit cell. There is no evidence of exchange of $\sigma_\parallel$ and $\sigma_\perp$ and T_1 is the same at all points of the powder pattern. We exclude CSA relaxation because the experimental relaxation rate at room temperature is 7.8 ± 0.3 s and is independent of B_0 at least from 4.7 to 14.1 T (42–126 MHz). Finally, if CSA were the source of the field modulation, the rate would follow the span and decrease with increasing temperature, which it does not. Thus, we conclude that chemical shift anisotropy relaxation is not the dominant mechanism in solid lead nitrate.

(3) ^{207}Pb–^{207}Pb ***J* coupling** relaxation is likely to be absent in a solid with little evidence of covalent bonding. Hawk and Sharp[26] give examples of scalar coupling relaxation for lead in covalently bonded PbCl$_4$ and a lack of it in the ionic system Pb(ClO$_4$)$_2$. Their relaxation experiments were performed in the liquid phase. Scalar coupling spin–lattice relaxation requires a match of Larmor frequencies and has a characteristic inverse magnetic field dependence, and a characteristic temperature dependence. Neither of these are observed for solid Pb(NO$_3$)$_2$. Finally, relaxation is unperturbed by dilution of the lead ions with barium ions. In mixed Pb/Ba(NO$_3$)$_2$ crystals, relaxation was constant within a factor of 2 at the 13 independent resonances for ^{207}Pb. The number of nearest neighbors varied from 12 Pb^{2+} to 12 Ba^{2+} with minimal change in relaxation in samples with many different ion ratios.[27,28]

(4) For relaxation by **paramagnetic impurities**, a dependence on field strength and temperature may also be expected, depending on the identity of the impurity and its motional properties.[29] The ^{207}Pb spin–lattice relaxation rate in lead nitrate in each of our laboratories is independent of sample origin and field strength. Our samples included commercial materials, carefully recrystallized samples prepared in different laboratories, and also the mixed Pb/Ba crystals. Consequently, paramagnetic impurities are excluded as a source of relaxation.

(5) **Spin-rotation** remains as the only potential source of relaxation. The phonons in the solid provide the motion leading to the required rotational energy match. Thermal phonon motion is the only motion that has been found in lead nitrate crystals

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and isomorphous alkaline earth metal nitrates by sound absorption, heat capacity, and Brillouin scattering methods.[30]

Relaxation via the Spin-Phonon Interaction. Spin-rotation coupling is an established mechanism for nuclear relaxation in gaseous small molecules and small rapidly rotating groups such as methyl groups.[15,31,32] Spin-rotation is also an important relaxation mechanism for ^{13}C and ^{15}N in orientationally disordered solids where motions in the picosecond regime are present.[33] Relaxation in the rotating molecule occurs by coupling between the nuclear spins and the magnetic field induced by electron currents created as the electron motion lags behind the nuclear rotational motion.[34,35] Spin-phonon relaxation was first treated by van Kranendonk,[16] who used the Debye phonon model to describe the motion in the solid and specified the expression for $J(\omega)$ for phonon induced relaxation. This mechanism has been generalized for spin-$^1/_2$ nuclei by Abragam.[14] A recent paper on relaxation in solid xenon[36] gives results, and a detailed analysis using the formalism over a broad temperature range. Spin diffusion in solids by the spin-phonon interaction process has also been treated by Dolinsek and co-workers.[37] These two-phonon Raman processes involve the absorption and emission of lattice phonons which differ in energy by the nuclear resonance energy, $\hbar\omega_0$. The T^2 dependence comes from the fact that two phonons are involved, each with average energy k_BT in the high-temperature limit. Below the Debye temperature, relaxation is much less efficient and much higher order temperature dependences are found.[14,36,38] The transition matrix element for the second-order Raman process is given by[14]

$$V \sim \hbar F_2 \frac{\omega\omega'}{\nu\nu'}\left[\frac{(n+1)\hbar}{2M\omega}\frac{n'\hbar}{2M\omega'}\right]^{1/2} \qquad (2)$$

where F_2 is the coupling, and ω and ω' are the phonon frequencies which satisfy the relationship $\omega - \omega' = \omega_0$. ω can take all values inside the phonon spectrum between ω_0 and ω_D, the Debye frequency in eq 2. The phonon propagation velocity is ν, M is the atomic mass, and there are n phonons identical to the one emitted and n' identical to the one absorbed. In the high-temperature limit where $k_BT \gg \hbar\omega_D$, the expression for T_1 becomes

$$R = \frac{1}{T_1} \approx \frac{81\pi}{10\omega_D}(F_2)^2\left(\frac{Nk_B}{M\nu^2}\right)^2 T^2 \qquad (3)$$

Abragam estimated F_2 using the dipolar interaction between a pair of protons separated by 2 Å and obtained a relaxation rate given by $R \sim (1.5 \times 10^{-6})(T/\theta_D)^2$, where θ_D is the Debye temperature. This gives a relaxation rate of the order of once per day "which is still much too small to account for any observed relaxation times".[39] However, the key conclusions are

the following: (1) the relaxation rate by spin-phonon interaction is proportional to T^2 above the Debye temperature and (2) relaxation is independent of magnetic field strength. This is just what we have observed for lead nitrate.

Spin-phonon relaxation becomes effective when there is a mechanism for strong coupling between the phonon bath and the nuclear spin. The electric quadrupole and electron–nucleus couplings are sufficiently large to provide this kind of relaxation. Multiple examples of a T^2 dependence for relaxation of quadrupolar nuclei have been reported.[16,40,41] The spin-phonon interaction is also well established as a relaxation mechanism in solid-state EPR.[38,42] In 1976, Villa and Avogadro[43] observed a T^2 dependence for relaxation of both ^{203}Tl and ^{205}Tl in thallium nitrate that they attributed to phonon relaxation; however, they did not establish the coupling mechanism. Fitzgerald and co-workers[36] were able to quantitatively account for the relaxation in solid ^{129}Xe by the spin-phonon mechanism between 20 and 120 K. Their coupling was the effective spin-rotation constant, C_{eff}, which was estimated for xenon from the chemical shift difference between solid and gaseous xenon, $(\sigma_g - \sigma_c)$, using the relationship:

$$\frac{C_{eff}}{h} = \left(\frac{\mu_I}{I\mu_B}\right)\left(\frac{\hbar}{8\pi Mr_0^2}\right)(\sigma_g - \sigma_c) \qquad (4)$$

where $I = {}^1/_2$ is the nuclear spin quantum number with magnetic moment, μ_I, and μ_B is the nuclear Bohr magneton; M is the atomic mass of xenon, and r_0 is the xenon–xenon internuclear distance. Ramsey[44] linked C_{eff}, the spin rotation constant observed in molecular beam resonance, with the paramagnetic contribution to the shielding tensor. The magnetic interaction comes from the quenching of electron orbital angular momentum. Flygare[45] constructed absolute scales for nuclear shielding from the relationship. More recently, Jameson[46] has employed C_{eff}, and the paramagnetic shielding tensor, for establishing absolute shielding scales for many nuclei. Unfortunately, no absolute shielding scale for lead has been established, so we cannot estimate C_{eff} for lead nitrate directly.

A next best, but crude, approximation links C_{eff} with the span of the static shielding pattern in linear systems. Two sets of observations showed that this approach could not be used for lead salts. (1) Shore and Fitzgerald and co-workers[10] showed that the lead site with the *smaller* span had the faster relaxation in all four cases where they measured T_1 for different forms of ^{207}Pb in the same solid (PbO, Pb_3O_4, $PbZrO_3$, and $PbNb_2O_6$). Thus any simplistic use of the span to estimate the required paramagnetic shielding contribution and hence the value of C_{eff} is inappropriate. (2) The span of lead nitrate diminishes with increasing temperature while the isotropic chemical shift (δ_{iso}) increases with temperature.[12] The T^2 dependence of relaxation in lead nitrate shows no evidence of either of these changes. We are forced to conclude that the coupling responsible for relaxation is *not* related to the span of the shielding anisotropy, or the isotropic shift, and is independent of temperature. A new approach to estimating the coupling constant is required.

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We propose that the spin-phonon coupling occurs via a spin-rotation coupling between the ligands immediately surrounding the lead and the valence-shell electrons which can precess relative to the nuclear core.[47,48] This is based on Overhauser's core/shell model for atoms. In this model, the motion of the lattice phonons perturbs the motion of the valence-shell electrons around the high Z nucleus. Hence, the lattice motion of the neighboring atoms induces electron circulation and creates the magnetic field that couples to the spin. The phonon-dispersion curves for 12 cubic metals including lead have been measured and interpreted by Overhauser using the shell model with a three-parameter fit. "The results for lead showed the presence in this metal, and in other polyvalent metals having a large electron−phonon interaction, of interionic forces of long range and complex nature."[49]

Equations 2 and 3 are still appropriate to model the temperature dependence of the observed relaxation in ^{207}Pb. The phonon dynamics are the same, only the coupling term, F_2, has changed. The challenge is to estimate the magnitude of F_2 responsible for the spin-phonon coupling. The order of magnitude of F_2 can be estimated from eq 3 in combination with the slope of Figure 2, provided the phonon properties of the solid are available.

Phonon Properties. The phonon properties of the alkaline earth metal nitrates and lead nitrate have been studied because of their interesting optical-acoustic coupling properties,[50] and the unusual birefringence observed in cubic lead nitrate.[51] The velocity of sound[52] for lead nitrate was found to be anisotropic in the cubic crystal: $v_{\text{long}}[100] = 8.99 \times 10^5$ cm s^{-1}, $v_{\text{long}}[110] = 10.0 \times 10^5$ cm s^{-1}, $v_{\text{trans}}[100] = 5.44 \times 10^5$ cm s^{-1}, $v_{\text{trans}}[110] = 5.41 \times 10^5$ cm s^{-1}. The pressure and temperature dependences,[53] as well as the temperature dependence of the sound absorption,[54] have been reported. The sound absorption has a maximum at 225 MHz that was attributed to dissipation through the internal nitrate vibrational mode ($v_4 = 735$ cm^{-1}). Similar absorption occurs for strontium and barium nitrates. Michard[50] has also observed an intriguing optoacoustic oscillation in the sound absorption in crystalline lead nitrate. There is no apparent connection between any of these acoustic phonon properties and the NMR observables.[55]

The Debye model, in which $\hbar\omega_D = k_B\theta_D$, can be used to obtain the Debye frequency, $\omega_D = 228$ cm^{-1}, and temperature, $\theta_D = 327$ K, from the mean velocity of sound, v_s

$$\omega_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} v_s \tag{5}$$

where $N = 12$ is the number of oscillators in the unit cell of volume V. A more refined estimate of the Debye temperature for lead nitrate was made from its elastic constants and found to be 198 K.[56] This contrasts with the ^{207}Pb relaxation which

implies an effective Debye temperature below 100 K. (Figure 2) It appears that the large-scale acoustic phonons are not providing the motion to relax the lead nucleus, and so other motions were sought. The Raman/phonon spectrum of lead nitrate in a single crystal has been assigned by Brooker.[57] The external modes have frequencies of 55 (A_g), 100 (F_g), and 130 cm^{-1} (E_g). We conclude that it is these vibrations centered on lead that relax the nuclear spin.

Since the lead relaxation time in lead titanate[10] (8 s) is comparable to that in lead nitrate (7.8 s) at 298 K, and shows a similar temperature dependence,[58] we also considered the phonon properties for this crystal. The lack of connection between the relaxation properties of lead and its isotropic chemical shift or span is emphasized by the similar relaxation times for lead nitrate and titanate. The span of lead in lead nitrate is 54 ppm while that in lead titanate is 2330 ppm; the temperature dependence of the isotropic shift is 0.73 ppm K^{-1} for the nitrate[12] while it is 0.126 ppm K^{-1} for the titanate.[58] We speculate that the bonding electron pairs, which create the paramagnetic shielding, quench the circulation of the shell electrons and diminish their relaxation contribution.

The phonon properties of lead titanate have been extensively studied because of its importance as the prototypical piezoelectric crystal. Grimsditch and co-workers[59] measured the sound velocities in a single crystal of lead titanate to be 4.31×10^5 (longitudinal) and 3.32×10^5 cm s^{-1} (transverse) and found them to be almost independent of temperature below the phase transition. The Debye frequency is estimated to be 324 cm^{-1} from (5) and θ_D is 466 K. This again implies that the Debye phonons responsible for the transmission of sound in the crystal are too high frequency to account for the observed relaxation. Freire and Katiyar[60] analyzed the phonon dispersion curves for lead titanate and showed that there are low-frequency Debye-type acoustic modes present in the crystal with frequencies of 59 (E) and 72 cm^{-1} (A_1). These low-frequency phonon modes are localized at the metal. We again propose that nuclear relaxation occurs by coupling to these modes. Accordingly, we take the effective Debye temperature, θ_D, as 78 K (55 cm^{-1}) for lead nitrate and as 85 K (59 cm^{-1}) for lead titanate for use in eq 3.

As the identification of the "acoustic mode" phonons has changed, the Abragam model and eq 3 must be modified to:

$$R = \frac{1}{T_1} \approx \frac{81\pi}{10\omega_D}(F_2)^2\left(\frac{T}{\theta_D}\right)^2 \tag{6}$$

Substitution of the lead nitrate phonon value, $\omega_D = 1.04 \times 10^{13}$ s^{-1}, gives an estimate of the magnitude of the spin-phonon coupling constant, F_2, (60 kHz) from T_1 at 298 K. The slope of the plot of T_1 versus the square of the temperature, Figure 2, is used equivalently to estimate the coupling as 63 kHz as the intercept is near zero. The relaxation time for lead titanate at 298 K combined with its phonon parameters gives a coupling of 67 kHz. While the available temperature data for lead titanate are qualitative at best,[61] the two-point plot gives the coupling

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(61) Harbison[58] uses relaxation delays of 8 s at 333 K and 90 s at 123 K, while Fitzgerald et al.[10] report a T_1 of 7.8 s at 298 K.
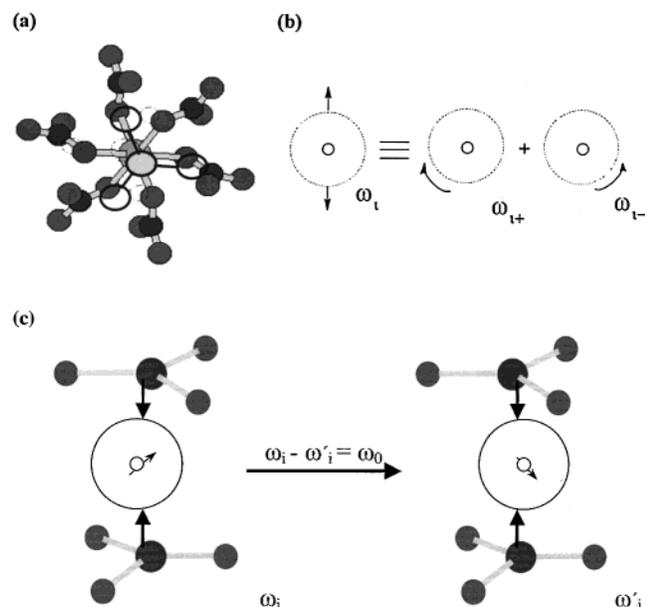
Figure 3. (a) Neutron diffraction structure of lead nitrate[20] viewed along [111] crystal axis. The uncoordinated axial nitrates are shown transparently. (b) The equivalence of a linear oscillator and a pair of counter-rotating oscillators. (c) Two low-frequency A_g phonons of the axial nitrates impacting the electron cloud (dotted) around the lead nucleus resulting in a nuclear spin flip.

as 62 kHz. The similar magnitude of these couplings indicates that there is a common coupling mechanism which we propose to be a fraction of the ^{207}Pb–electron dipole coupling constant. For a 5d electron at the Pb^{2+} radius of 1.32 Å,[62] the dipole coupling is calculated to be 712 kHz. The observed coupling, then, corresponds to a shell-core rotation lag of approximately 0.09 of one 5d electron. Alternatively, a single electron at 2.9 Å would give the observed coupling, which is coincidentally close to the Pb–O bond distance.

The obvious question then is why this relaxation mechanism does not occur for nuclei in solids across the Periodic Table and for all the electrons around the atom, since the dipole coupling is inversely proportional to the cube of the electron–nucleus separation and does not depend on the electron identity. Our answer is that the relevant electrons are those subject to phonon perturbation of their angular momentum. According to Overhauser, the coupling occurs via the r^{2l} factors of the shell charge-density model in which the deformation of the ion during vibration is critically linked to the angular-momentum wave functions: see Table 3 of ref 47b. It is also indicated by the large Faraday effect observed[63] in Pb^{2+} and an intriguing magnetic perturbation of the electrogyration which is also large for lead.[64] Thus we picture relaxation as arising from the phonon perturbation of the motion of the shell of 5d electrons which is then magnetically transmitted to the nucleus by the electron–spin dipole coupling (Figure 3). The quantitative calculation of this fractional perturbation is beyond us at this time and is a state-of-the-art problem for theorists.[65]

Spin-Phonon Relaxation for Other Nuclei. Our proposed spin-phonon relaxation mechanism should contribute to relax-

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Table 1. Temperature Dependence of Relaxation Rates for High Z Spin-$^1/_2$ Nuclei

compd	T/K	T_1/s	c^a	y^a
Xe[36]	30–110	50000–2800	3.0×10^{-8}	−0.00002
Tl NO$_2$	120–170	22–10	4.7×10^{-6}	−0.03
Tl NO$_3$[43]	280–470	8.2–1.7	1.2×10^{-6}	0.024
Tl ClO$_4$	310–430	14–8	5.7×10^{-7}	0.016
Tl ClO$_4$	160–500	50–7	5.62×10^{-7}	0.008
Pb (NO$_3$)$_2$	150–370	29–5	1.33×10^{-6}	0.0056
Pb TiO$_3$[58]	120–330	90–8	1.2×10^{-6}	

$^a R = 1/T_1 = cT^2 + y.$

ation of ^{207}Pb in all lead compounds. It should also contribute to relaxation in other heavy spin-$^1/_2$ nuclei such as ^{203}Tl, ^{205}Tl, and ^{199}Hg. Its signatures are the T^2 proportionality and the presence of low-frequency acoustic phonon modes. Most importantly, it provides a rationale for the observation that T_1 for all these nuclei in "rigid" diamagnetic solids are of the order of seconds rather than days or longer. For example, the ^{199}Hg relaxation time in a single crystal of mercurous nitrate is about 5 s, although cross polarization by the protons in static water molecules is not possible.[66] An inverse correlation of relaxation rate with span was also found in mercury salts: mercury acetate (span = 1826 ppm, T_1 = 290 s) and $HgCN_4^{2-}$ (span = 0 ppm, T_1 = 8 s).[67] A relaxation time of 8 s for tetrahedrally coordinated Hg^{2+} in a fully cubic environment would be mystifying without the spin-phonon relaxation mechanism proposed here. This again indicates that the 5d valence shell electrons are the major contributors to relaxation as the Hg^{2+} nucleus lacks 6s electrons. A summary of reported T_1 data for heavy nuclei in solids is shown in Table 1 where the temperature dependence is available. The observed lack of field dependence and correlation with T^2 is noted. These observations together with the narrow range of slopes of the correlation curves and the near zero intercepts support a common spin-phonon mechanism as the source of relaxation. A correlation with the inverse third power of the appropriate Debye temperature remains to be established. This is non-trivial because the relevant modes involve the ligand–heavy metal phonons, not the acoustic modes observed by Brillouin scattering and sound velocity measurements.

Spin–rotation coupling, γN (γ is the spin–rotation tensor,[68] and N is the rotational angular momentum), is important for the enhancement of spin polarization of the noble gases by optically pumped alkali metals. Walker[69] has summarized the available values. The value for xenon–metal pairs is about 70 MHz. To a zeroth order approximation, $\gamma \approx f_{es}(\mu_e/\mu_I)\alpha_{eI}$, where μ_e and μ_I are the electron and nucleus magnetic moments, α_{eI} is the electron–nucleus dipole coupling, and f_{es} is the fractional electron shell orbital angular momentum contribution relative to a free electron. Several points are of interest: (1) the γN coupling is larger than the nucleus–electron dipole coupling for noble gases heavier than neon and (2) the magnitude of γN increases with atomic number for the noble gases, but is largely independent of the identity of the alkali metal. Our proposed coupling model predicts that γN should be proportional to the electron–electron dipole coupling constant between the alkali metal valence electron and the noble gas shell electrons. The magnitudes of γN are consistent with this view. It seems that coupling between alkali metals and the heavy rare gas nuclei

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in the gas phase occurs by the same interaction as the coupling between the outer shell electrons on lead and the lead spin.

Conclusions

The spin−lattice relaxation time for solid lead nitrate has been measured as a function of temperature and applied magnetic field. The relaxation time is of the order of seconds, and independent of magnetic field strength. The rate is proportional to the square of the absolute temperature. These properties are characteristic of spin−rotation relaxation by coupling between the phonon bath and the nuclear spin, as described in eqs 2 and 6. The T^2 dependence implies that the active phonons have a Debye temperature below the temperature minimum of our measurements, 150 K. The acoustic phonons, responsible for sound transmission through crystal dimensions, have Debye temperatures above room temperature, so these are irrelevant for relaxation. We identify the low-frequency Raman active phonon modes centered at lead as the relaxation modes. A new spin-phonon coupling mechanism is proposed in which the phonon motion about the nuclear/electron core of the heavy ion perturbs the valence shell electron orbital angular momentum. The observed coupling of 60 kHz is about 10% of the [207]Pb-5d electron dipole coupling. An estimate of the absolute magnitude of the coupling would require multielectron calculations incorporating relativistic effects which are not yet available. Literature data for relaxation of other spin-$\frac{1}{2}$ nuclei in row 6 of the Periodic Table indicate that this is the major relaxation mechanism for such nuclei in solids.

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