

Nuclear-spin relaxation of ^{207}Pb in ferroelectric powders

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Motivated by a recent proposal by Sushkov and co-workers [Phys. Rev. A **72**, 034501 (2005); **73**, 022107 (2006)] to search for a P, T -violating Schiff moment of the ^{207}Pb nucleus in a ferroelectric solid, we have carried out a high-field nuclear magnetic resonance study of the longitudinal and transverse spin relaxation of the lead nuclei from room temperature down to 10 K for powder samples of lead titanate (PT), lead zirconium titanate, and a PT monocrystal. For all powder samples and independently of temperature, transverse relaxation times were found to be $T_2 \approx 1.5$ ms, while the longitudinal relaxation times exhibited a temperature dependence, with T_1 of over an hour at the lowest temperatures, decreasing to $T_1 \approx 7$ s at room temperature. At high temperatures, the observed behavior is consistent with a two-phonon Raman process, while in the low-temperature limit, the relaxation appears to be dominated by a single-phonon (direct) process involving magnetic impurities. We discuss the implications of the results for the Schiff-moment search.

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I. INTRODUCTION

The ^{207}Pb nuclear system (nuclear spin $I=1/2$, magnetic moment $\mu \approx 0.58\mu_N$, isotopic abundance $\approx 22\%$) in ferroelectric solids has been proposed for a search for a Schiff moment associated with simultaneous violation of parity (P) and time-reversal invariance (T) in fundamental interactions [1] (see also a discussion of the sensitivity of such a search in Ref. [2]). The idea is that, due to the Schiff moment, a ferroelectric sample would acquire a P, T -odd magnetic polarization along the direction of its electric polarization.

In a compound free of unpaired electrons, at low enough temperatures when lattice vibrations freeze out, we have an isolated system of nuclear spins (in the sense that the spins can freely rotate, but the nuclei cannot move with respect to the lattice) that interact among themselves solely via magnetic dipole-dipole interactions. It was shown in Ref. [1] that lead nuclei in perovskite ferroelectric compounds such as lead titanate (PT) experience a large effective electric field, producing a P, T -odd energy shift. The effect is enhanced in ferroelectric lead compounds due, in part, to the rapid (faster than Z^2) scaling of the effective electric field with the charge of the nucleus, Z , which is also combined with the $\sim Z^{2/3}$ scaling of the Schiff moment [see, e.g., Ref. [3] (Sec. 8.5.1)]. Thus, the ferroelectric compounds proposed for the Schiff-moment search combine the advantage of a large number of particles accessible to a solid-state experiment with an enhancement of the effective electric field similar to that in diatomic molecules (see, for example, the review in [4]).

A crucial requirement for the success of the P, T -violation experiment is a detailed understanding of the behavior of the

isolated nuclear-spin system and, in particular, its relaxation properties. The connection of the relaxation and fundamental limits of sensitivity of condensed-matter P - and T -violation experiments was discussed in Ref. [2], and a related question of magnetic susceptibility was discussed theoretically and modeled numerically in Ref. [5].

In this work, we begin an experimental investigation of the lead nuclear-spin system in the context of this application by studying, using nuclear magnetic resonance (NMR) techniques, longitudinal (T_1) and transverse (T_2) relaxation in ferroelectric powders, and a PT monocrystal as a function of temperature in the range 10–293 K. We find that, at high temperatures, these ferroelectrics undergo a magnetic relaxation due to a two-phonon Raman process. At temperatures much lower than the Debye temperature, the relaxation is dominated by impurities and a single-phonon (direct) process. The results obtained encourage us to further pursue experimental work toward a Schiff-moment search in lead-based solid ferroelectrics.

II. PREVIOUS WORK

A. Studies of lead NMR

The body of work on solid-state NMR of lead prior to 2002 was reviewed in Ref. [6]. Because of the large atomic number of lead, its compounds often display large chemical shifts, up to several thousand ppm. The isotropic and anisotropic parts of the chemical shift tensor, as well as their temperature dependences, have been shown in Ref. [7] to be sensitive probes of the crystalline structure. The ^{207}Pb solid-state NMR study of PT [7] was conducted at sample temperatures between -150 and 60 °C. In Ref. [8], Pb NMR of a single-crystal ferroelectric lead magnesium niobate (PMN) was studied at temperatures down to 15 K. The authors investigated the effect of electric poling on the NMR spectrum. They observed longitudinal relaxation times for lead in the range 1–10 s.

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In some cases, NMR spectroscopy of ^{207}Pb can be done in conjunction with the spectroscopy of other nonzero-spin nuclei in the same compound. For example, Ref. [9] discusses room-temperature magic-angle-spinning (MAS) NMR of oxygen, titanium, and lead in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT, $0 \leq x \leq 1$) and the effect of the composition (x) on NMR spectra. The present authors are unaware of any studies of the longitudinal and transverse relaxation times of ^{207}Pb in PT and PZT below room temperature prior to the present work.

B. Studies of relaxation mechanisms

Of interest to us here is primarily the longitudinal relaxation of nuclear spins in compounds where all electron angular momenta are paired (with a possible exception of paramagnetic impurities). Several mechanisms can lead to such relaxation [10,11]. These processes typically occur as a result of the modulation of the crystal field or ligand field due to lattice vibrations (phonons) and can be, to some degree, experimentally distinguished by the temperature and magnetic-field dependence of relaxation.

There are two types of spin-phonon interaction processes: the “direct process,” in which a spin flip is caused by the interaction with a single lattice phonon, and a “Raman process,” involving an interaction with two phonons. The Raman process has been shown in Ref. [12] to be the dominant relaxation mechanism for ^{207}Pb nuclei in ionic solids such as lead nitrate above their Debye temperature T_D (typically 100–200 K). The nuclear spin-relaxation rate due to this process is proportional to T^2 for $T > T_D$ (each phonon interaction contributes a factor of T in this classical regime). However, for $T \leq T_D$, this process has a T^7 dependence [11]. (This can be derived by integrating the Bose-Einstein energy densities of the two phonons over their frequencies up to the Debye frequency. Since each energy density contains a factor of frequency cubed, the resulting dependence is T^7 .) The relaxation rate for the Raman process is independent of the magnetic field [12]. In Ref. [13], longitudinal spin-lattice relaxation of ^{207}Pb in polycrystalline samples of PbMoO_4 and PbCl_2 was investigated as a function of temperature down to the liquid-nitrogen temperature range. A T^2 dependence of $1/T_1$ was observed and interpreted as a second-order Raman process. A rather complete discussion of the theory is found in Ref. [12], where not only the T^2 scaling with temperature and independence of the NMR frequency are reproduced, but also the magnitude of the relaxation rates is accounted for within an order of magnitude (for lead molybdate, lead chloride, lead nitrate, thallium nitrate, thallium nitrite, and thallium perchlorate). The model explains the relaxation as caused by a Raman process involving the interactions between nuclear spins and lattice vibrations via a fluctuating spin-rotation magnetic field.

Unfortunately, more often than not, impurities are responsible for much of the observed nuclear spin relaxation. Back in the early days of NMR, Bloembergen [14] investigated the nuclear spin relaxation of several (non-Pb) compounds between 300 and 1 K, and found impurities to be the dominant relaxation agent. Spin diffusion is essential in affecting the relaxation for nuclei that are far away from an impurity. De-

pendences of the relaxation rates $\propto T$ and $\propto T^2$ were observed at low temperature. A further investigation of the nuclear spin relaxation caused by paramagnetic impurities was carried out by Blumberg [15]. He conducted saturation-recovery experiments and found that at short times there is a \sqrt{t} dependence of the recovery indicative of diffusion. At longer times, the recovery is exponential, but the exponent is proportional to impurity concentration.

III. EXPERIMENTAL METHOD

NMR measurements at the ^{207}Pb frequency were done on a 89-mm bore, 11.7 T Oxford magnet using a Varian NMR Systems (VNMR) spectrometer console running VNMRJ 2.1B software. On this instrument, the proton frequency was 500.195 MHz. The rf carrier frequency was set to 104.481 MHz for PbTiO_3 (PT) and 104.495 MHz for PZT. The samples were lightly packed into a 2-cm-long, 0.5-cm-diam glass tube and excited using the solenoidal rf coil of a homebuilt static probe for cryogenic samples. A liquid-helium cryostat surrounded the NMR probe and cooled the NMR tube. The temperature of the sample was monitored using a resistive sensor with a bridge placed in proximity of the glass tube. The temporal stability in the temperature control over the range 10–200 K was better than 0.1K; however, temperature fluctuations inside the sample were not directly monitored and could exhibit higher fluctuations and possibly some internal temperature gradients. To avoid systematic errors in the relaxation measurements arising from possible sample temperature fluctuations, inversion times and echo times were ordered randomly for each experiment and measurements of T_1 and T_2 were compared to those from repeated experiments. We estimate the absolute error in temperature determination to be less than about 1 K. Pulse widths for a $\pi/2$ rotation ranged between 10 and 13 μs over the temperature range, with the dependence mainly due to variations in the coil tuning (Q factor).

Additional control room-temperature measurements with a lead titanate sample were carried out with a 7.1-T magnet (proton frequency 300 MHz) with a Varian CMX Infinityplus spectrometer, under MAS at 11 kHz. The pulse width for a $\pi/2$ rotation on this instrument was 3 μs .

Transverse (T_2) relaxation times were measured on the 11.7-T system using a $\pi/2$ - $\tau/2$ - π - $\tau/2$ -{acquire} Hahn echo [Fig. 1(b)] with echo times (τ) at 100 μs , 200 μs , 400 μs , 800 μs , 1.6 ms, 4 ms, and 8 ms. The preparation consisted of a saturation pulse train followed by a 2-min equilibration period for repolarization of the longitudinal magnetization. At a given temperature, this provided a consistent initial longitudinal magnetization for each point in a T_2 measurement.

IV. SAMPLES

Experiments were performed on four different samples. The PbTiO_3 powders were obtained from two different sources: Praxair Specialty Ceramics (chemical purity 99.9%, particle size 1 μm) and the group of Professor M. Jansen at Max Planck Institute for Solid State Research in Stuttgart, Germany (chemical purity unknown). The powder samples

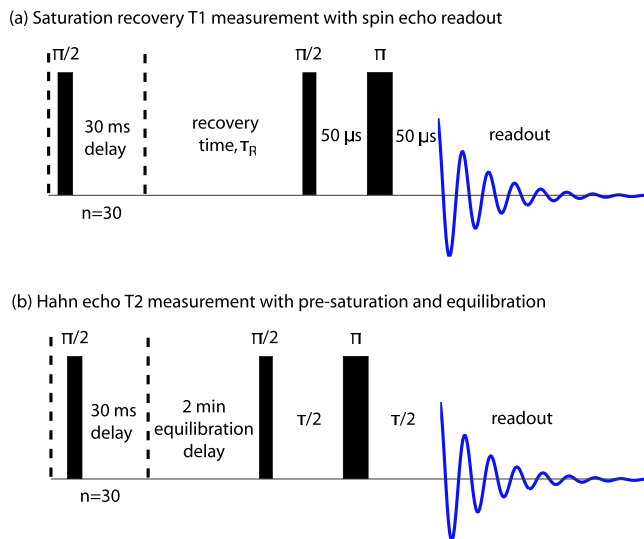


FIG. 1. (Color online) Pulse sequences used for measuring T_1 and T_2 relaxation times. In both cases, a train of $\pi/2$ pulses was used to saturate the magnetization, followed by a recovery period. The T_1 measurement used a spin echo readout to avoid coil ringing artifacts and several values of T_R were used. T_2 measurements used a Hahn echo for several values of τ . The $\pi/2$ pulse widths were in the range of 10–13 μs .

from these two sources are denoted as $P1$ and $P2$, respectively. Measurements were also made on a PbTiO_3 crystal with dimensions 2.3 mm \times 2.8 mm \times 1.3 mm. The fourth sample was $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ powder from Praxair Specialty Ceramics (chemical purity 99.9%, particle size 1 μm).

V. RESULTS AND DISCUSSION

A. Spin-lattice relaxation

Longitudinal (T_1) relaxation times were measured using a saturation-recovery sequence shown in Fig. 1(a). The saturation preparation is accomplished by applying a train of 30 $\pi/2$ pulses separated by 30-ms intervals used to completely

depolarize ^{207}Pb spins in the sensitive volume despite inhomogeneities in the rf field or inaccuracies in the flip angle. The saturation was checked by confirming that no signal was produced in the limit of zero recovery time. Signals were acquired with 8–15 recovery times (T_R) logarithmically spaced between 0 ms and $5T_1$. The signals were acquired using a spin echo with interspersed delay of 50 μs to avoid signal contamination from probe ringing.

All the magnetization-recovery data were fit with two models: a single exponential $M(t) = M_0[1 - \exp(-t/T_1)]$ and a stretched exponential $M(t) = M_0[1 - \exp(-\sqrt[t]{t/T_1})]$, where M_0 is the equilibrium magnetization and t is the time elapsed after saturation. The use of these models is motivated by the fact that magnetization recovery is well described by a single exponential if the dominant spin-lattice relaxation mechanism is a two-phonon Raman process [12] or paramagnetic-impurity relaxation with fast spin diffusion [16]. If, however, the spin-lattice relaxation is due to paramagnetic impurities with slow spin diffusion, then the magnetization recovers along a stretched exponential curve [16]. It should be noted that the chemical shift anisotropy in PbTiO_3 and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ is on the order of 2000 ppm; thus, in the applied 11.7-T magnetic field, the local magnetic field varies by ≈ 200 G. This is much greater than the local dipole-dipole interaction field, which is on the order of 1 G. This does not mean, however, that spin diffusion is strongly suppressed. The reason for such a broadened line is that we are looking at powder. Each powder grain has a much narrower line, but since there is large NMR-shift anisotropy due to the chemical shift and diamagnetic susceptibility and the grains are randomly oriented, the resultant line is wide. Thus, within each powder crystallite, spin diffusion can happen, but the spin flip cannot “hop” between the grains.

Magnetization-recovery data for PbTiO_3 at $T=10$ K are shown in Fig. 2(a). The data points are well fit with a single exponential; a stretched exponential gives a poor fit. This is the case for all PbTiO_3 data at all temperatures. The situation is different for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. As shown in Fig. 2(b), the stretched exponential gives a much better fit than a single exponential. This is the case for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ at temperatures below 50 K. For the data above 50 K, however, the

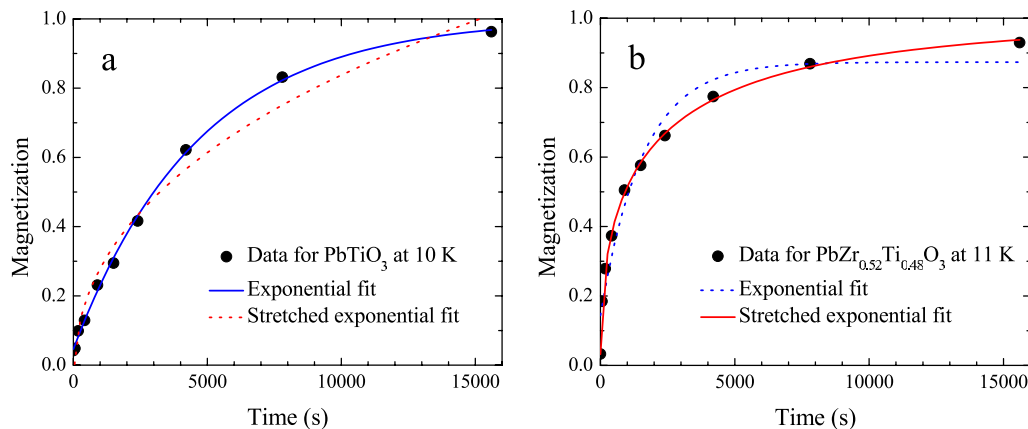


FIG. 2. (Color online) Representative magnetization recovery curves for PbTiO_3 (a) and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (b) powders. Two fits are shown for each data set: a single exponential and a stretched exponential. The PT sample is $P1$ (see text).

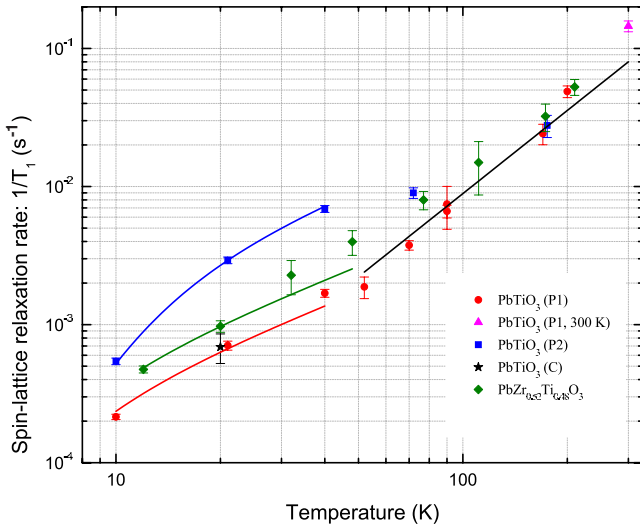


FIG. 3. (Color online) The experimentally determined longitudinal relaxation rates vs temperature. The data were fit to different functions above and below 50 K (see text).

single exponential provides a better fit. This is an indication that spin-lattice relaxation due to paramagnetic impurities, with suppressed spin diffusion, may be the dominant mechanism for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ below 50 K.

Longitudinal relaxation rates $1/T_1$ extracted from the magnetization-recovery fits as in Fig. 2 are plotted in Fig. 3.

B. Spin-spin relaxation

An example of transverse-relaxation data is shown in Fig. 4. Despite the fact that dipole-dipole interactions may lead to nonexponential relaxation [11], within experimental uncertainties, all our data were consistent with exponential relaxation, so exponential fits were used to extract the relaxation times T_2 .

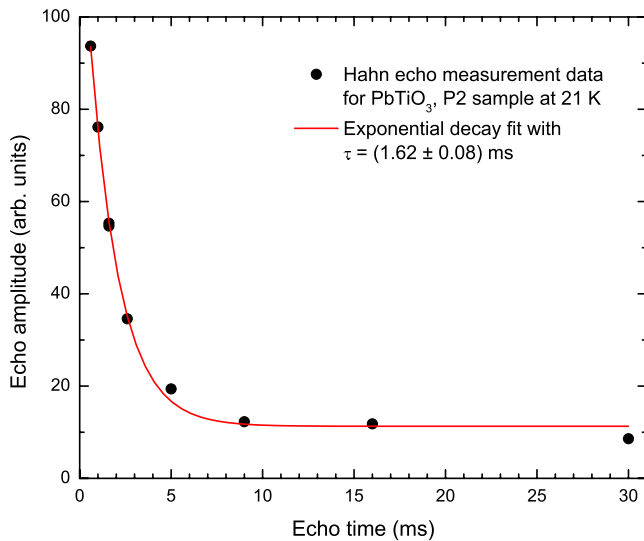


FIG. 4. (Color online) An example of data and exponential-decay fit used to extract the T_2 values.

Analysis of the transverse-relaxation data at different temperatures results in the value $T_2 = (1.5 \pm 0.2)$ ms for all PbTiO_3 and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ powder samples. No temperature variation of T_2 is observed within the experimental uncertainty. (No T_2 data were taken for the crystal.)

The measured T_2 value is within a factor of 2 of the ≈ 0.7 -ms decay time estimated for PT in Ref. [1] assuming relaxation due to a dipole-dipole interaction. The fact that the relaxation rate is independent of temperature is also consistent with relaxation via this mechanism.

VI. INTERPRETATION OF T_1 RESULTS

A. High-temperature range

In the temperature range of 50–293 K, the observed spin-lattice relaxation rates for all our samples follow the T^2 dependence. This behavior is characteristic of a two-phonon Raman process [11–13,17], a relaxation mechanism investigated and explained in terms of modulations in the spin-rotation interaction by Dybowski and co-workers [12,13]. Our results confirm that this relaxation mechanism is, indeed, the dominant process over the 50–293-K temperature range. We note that Debye temperatures of ionic crystals are in the range 150–350 K, whereas our results exhibit a T^2 dependence down to 50 K.

B. Low-temperature range

At low temperatures (below 50 K) the T^2 dependence is no longer a good fit to the data shown in Fig. 3. Another mechanism dominates spin-lattice relaxation in this regime—this mechanism is most likely the relaxation due to paramagnetic impurities in the samples. The ^{207}Pb nuclear magnetic sublevels are split by an energy corresponding to about 5 mK in the applied field of 11.7 T. Phonons that correspond to that same frequency would normally cause ^{207}Pb nuclear spin flips via the direct process. However, since 5 mK is much smaller than the sample temperature, the energy density of such phonons is greatly suppressed. An impurity with uncompensated electron spin, however, has a much larger magnetic moment. In fact, its magnetic sublevels are split by about 8 K in the applied magnetic field, which is on the order of our sample's temperature (at the lowest temperatures where the data were taken). Therefore such an impurity can interact with the lattice via the direct phonon process—i.e., absorption or emission of a single phonon at the Larmor frequency of the electronic spin ω_S . For a Kramers doublet, the relaxation rate of the electronic spin is given by the Kramers relation [17]

$$\frac{1}{T_{1e}} = \xi \left(\frac{\omega_S}{v} \right)^5 \coth \left(\frac{\hbar \omega_S}{2k_B T} \right) \frac{\hbar}{\rho}, \quad (1)$$

where v is the velocity of sound in the crystal, ρ is the density, and ξ is a dimensionless coefficient that depends on the structure of the impurity. For non-Kramers sites, there is a different expression for the relaxation rate; however, the temperature dependence of T_{1e}^{-1} is the same as in Eq. (1) [10].

Spin-lattice relaxation of nuclei (**I**) in the vicinity of an impurity can be described by a dipolar coupling $\mathbf{S} \cdot \mathcal{D} \cdot \mathbf{I}$,

where \mathcal{D} is a tensor describing the magnetic dipolar coupling between the electron and the nucleus (separated by a distance \mathbf{r}), while $\mathbf{S}\cdot\mathcal{D}$ can be viewed as a random fluctuating local field produced by the electron and seen by the nucleus. At low temperatures where motion is frozen, the fluctuations are mainly due to the spin flipping of the electron, the time scale of which is the relaxation time T_{1e} .

When the power spectrum of these fluctuations contains nonvanishing values at the Larmor frequency ω_l of the nucleus, nuclear relaxation will take place. An argument based on the freezing of relative motions at low temperatures [17] leads to the following estimate for the nuclear spin-lattice relaxation rate of \mathbf{I} due to fluctuations in \mathbf{S} :

$$\frac{1}{T_{1n}}(\mathbf{r}) \sim \left(\frac{B_e}{B_0}\right)^2 \left(\frac{1}{T_{1e}}\right) (1 - P_0^2), \quad (2)$$

where $P_0 = \tanh(\hbar\omega_S/2k_B T)$ is the electronic thermal equilibrium polarization and $B_e = \mu_e S r^{-3}$ gives the order of magnitude of the local magnetic field seen by the nucleus due to electron magnetic moment μ_e . A further level of refinement involves integration of the spatially dependent rates $T_{1n}^{-1}(\mathbf{r})$ in close proximity of the impurities [17]. Finally, mutual spin flip flops of the nuclei cause this relaxation mechanism to spread its effects throughout the lattice. The (temperature-independent) rate of spin diffusion and density of impurities determine whether relaxation is best described by monoexponential or stretched-exponential behavior [16].

The low-temperature (<50 K) spin-lattice relaxation data were fit with the function

$$\frac{1}{T_{1n}} = A \coth\left(\frac{\hbar\omega_S}{2k_B T}\right) \left[1 - \tanh^2\left(\frac{\hbar\omega_S}{2k_B T}\right)\right], \quad (3)$$

which is just Eqs. (1) and (2) combined. The results are shown with curved lines in Fig. 3. The fit contained one free parameter A . The value $\hbar\omega_S/2k_B = 8$ K was calculated from the applied magnetic field of 11.7 T (assuming an impurity g factor of 2) and fixed for the fits to PbTiO_3 $P1$ powder data and the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ data. It was found, however, that the PbTiO_3 $P2$ powder data were fit much better with the value $\hbar\omega_S/2k_B = 16$ K; i.e., the paramagnetic impurities in this sample have the magnetic moment of 4-bohr magnetons. We can conclude that the model described above gives a satisfactory description of the data below 50 K. The $P1$ PbTiO_3 powder seems to have the smallest concentration of paramagnetic impurities, while the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $P2$ PbTiO_3 powders have larger impurity concentrations, and the dominant impurity in PbTiO_3 $P2$ powder has a g factor of 4.

C. Nonexponential relaxation

We note that although we fit the relaxation data for PZT to a stretched exponential for the reasons discussed above, equally good fits can be obtained by using a biexponential, where the rapid component is roughly half the amplitude of the slower component. Possible additional mechanisms that could lead to the nonexponential behavior include the following. (i) The PZT subunits PbZrO_3 and PbTiO_3 may exhibit different spin-rotation interactions that modulate the re-

laxation rate T_1^{-1} of the Raman process [12]. (ii) The stretched exponential may arise from a distribution of relaxation times, due to some degree of anisotropy in the relaxation rate; however, note that such relaxation behavior is not seen in PT. Unfortunately, the relaxation data alone are insufficient to determine the source of the deviation from a single exponential.

VII. IMPLICATIONS FOR THE SCHIFF-MOMENT EXPERIMENT

The results shown in Fig. 3 are encouraging for the ongoing development of the experiment to search for the P - and T -violating Schiff moment of ^{207}Pb in ferroelectrics. As expected, the spin-lattice relaxation time increases dramatically as the temperature is lowered. The presence of paramagnetic impurities leads to an approximately linear temperature dependence of the relaxation rate below 50 K: $1/T_1 \propto T$, which is much slower than the T^7 dependence, expected if the Raman phonon relaxation mechanism were to dominate. This may prove advantageous for the design of the Schiff-moment experimental search, which relies on achieving a high degree of nuclear spin polarization in high magnetic field and at low temperature, prior to nuclear demagnetization to reach an ultralow spin temperature [2]. Indeed, with T_1 on the order of an hour at a lattice temperature of 10 K, such polarization can be established on this time scale, which is not prohibitively long. After demagnetization, the spin temperature stays low for a time also on the order of $T_1 \sim$ hour, which is when, for example, the Schiff-moment-induced magnetization can be measured by precision magnetometry methods.

Two main questions remain to be answered in future investigations: what is the spin-lattice relaxation time in low magnetic fields and low spin temperatures and does the presence of paramagnetic impurities introduce serious systematics into the Schiff-moment-induced magnetization search? We are currently developing experiments to address both of these questions.

VIII. CONCLUSION

In conclusion, we have presented an experimental study of the relaxation properties of ^{207}Pb in PT and PZT below room temperature. We find that above $T \approx 50$ K, the longitudinal relaxation rate follows the T^2 dependence characteristic of the two-phonon Raman process. On the other hand, as the temperature is decreased below $T \approx 50$ K, the longitudinal relaxation rates drop slower than $\propto T^2$ (as opposed to $\propto T^7$ expected for the Raman process), and the relaxation is probably due to a direct process associated with paramagnetic impurities and nuclear-spin diffusion. While the longitudinal relaxation times T_1 vary between several seconds and over an hour in the temperature range between 290 and 10 K, the transverse relaxation time T_2 is found to be ≈ 1.5 ms for all temperatures and all powder samples studied. The obtained results provide an important input in the design of the experiments to search for P, T -violating effects in solid ferroelectrics.

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