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

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Motivated by a recent proposal by O. P. Sushkov and co-workers 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 (PZT), 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. This is the first study of temperature-dependent nuclear-spin relaxation in PT and PZT ferroelectrics at such low temperatures. 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 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 large effective electric field, producing P,T-odd energy shift. The effect is enhanced in ferroelectric lead compounds due, in part, to the rapid (faster than $Z^5$) 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] Sect. 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 [1]).

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 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 magnetic relaxation due to a two-phonon Raman process. At temperatures much lower than the Debye temperature, relaxation is dominated by impurities and a single-phonon (direct) process. The obtained results encourage us to further pursue experimental work towards 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 chem-
cal 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. [9] 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.

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 PbZr$_{1-x}$Ti$_x$O$_3$ (PZT, 0 ≤ x ≤ 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 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 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 K to 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 $T \ll T_D$, this process has a $T^2$ 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 $T^5$.) 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 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 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 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 relaxation for nuclei that are far away from an impurity. Dependences of the relaxation rates $\propto T$ and $\propto T^2$ were observed at low temperature. A further investigation of 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 (VNMRS) 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-diameter glass tube and excited using the solenoidal rf coil of a home-built 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 0.1 K; 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 magic-angle spinning at 11 kHz. Pulse widths for a \( \pi/2 \) rotation on this instrument was 3 \( \mu \)s.

Transverse (\( T_2 \)) relaxation times were measured on the 11.7-T system using a \( \pi/2 - \pi/2 - \pi - \pi/2 - \{ \text{acquire} \} \) Hahn echo [Fig. 1 (b)] with echo times (\( \tau \)) at 100 \( \mu \)s, 200 \( \mu \)s, 400 \( \mu \)s, 800 \( \mu \)s, 1.6 ms, 4 ms, and 8 ms. The preparation consisted of a saturation pulse train followed by a 2-min equilibration period for re-polarization 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 \( \text{PbTiO}_3 \) powders were obtained from two different sources: Praxair Specialty Ceramics (chemical purity 99.9\%, particle size 1 \( \mu \)m), and from the group of Prof. M. Jansen at Max Plank Institute for Solid State Research in Stuttgart, Germany (chemical purity unknown). The powder samples from these two sources are denoted as P1 and P2, respectively. Measurements were also made on a \( \text{PbTiO}_3 \) 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 \( \mu \)m).

**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 thirty \( \pi/2 \) pulses separated by 30-ms intervals used to completely depolarize \( ^{207}\text{Pb} \) 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 to 15 recovery times (\( T_R \)) logarithmically spaced between 0 ms and 5 \( \times \) \( T_1 \). The signals were acquired using a spin echo with interpulse delay of 50 \( \mu \)s 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 \( M(t) = M_0[1 - \exp(-\sqrt{t/T_1})] \), 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 \[2\], or paramagnetic-impurity relaxation with fast spin diffusion \[10\]. If, however, the spin-lattice relaxation is due to paramagnetic impurities with slow spin-diffusion, then the magnetization recovers along a stretched exponential curve \[10\]. It should be noted that the chemical shift anisotropy in \( \text{PbTiO}_3 \) 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 \( \approx \) 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 crystal, spin-diffusion can happen, but the spin-flip cannot “hop” between the grains.

Magnetization recovery data for \( \text{PbTiO}_3 \) 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 \( \text{PbTiO}_3 \) 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, 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 of the fact that dipole-dipole interactions may lead to non-exponential relaxation [11], within experimental uncertainties, all our data were consistent with exponential relaxation, so exponential fits were used to extract the relaxation times $T_2$.

Analysis of the transverse-relaxation data at different temperatures results in the value $T_2 = (1.5 \pm 0.2)$ ms, for all the PbTiO$_3$ and the PbZr$_{0.52}$Ti$_{0.48}$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 two of the $\approx 0.7$-ms decay time estimated for PT in Ref. [1] assuming relaxation due to 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, 12, 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, which are the first measurements below room temperature on PT and PZT perovskite ferroelectrics, 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 $T^2$ 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 which 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 samples 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 $\omega_S$. For a Kramers doublet, the relaxation rate of the electronic spin is given by the Kramers relation \[17\]:

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

where $v$ is the velocity of sound in the crystal, $\rho$ is the density and $\xi$ 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 $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{I}$, where $\mathbf{D}$ is a tensor describing the magnetic dipolar coupling between the electron and the nucleus (separated by a distance $r$), while $\mathbf{S} \cdot \mathbf{D}$ 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 and the nucleus due to electron magnetic moment $\mu_e$. 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 PbZr$_{0.52}$Ti$_{0.48}$O$_3$ and the P2 PbTiO$_3$ powders have larger impurity concentrations, and the dominant impurity in PbTiO$_3$ P2 powder has the g-factor of 4.

C. Non-exponential 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 which could lead to the non-exponential behavior include the following. 1) The PZT subunits PbZrO$_3$ and PbTiO$_3$ may exhibit different spin-rotation interactions that modulate the relaxation rate $T_{1e}^{-1}$ of the Raman process \[12\]. 2) 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 temperature is lowered. The presence of paramagnetic impurities leads to 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 ultra-low spin temperature \[2\]. Indeed, with $T_1$ on the order of an hour at 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 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 whether or not the presence of paramagnetic impurities introduces 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 the first experimental study of relaxation properties of $^{207}$Pb in PT and PZT below room temperature. We find that above $T \approx 50$ K, 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 $\approx 1.5$ 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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