Suggested search for ^{207}Pb nuclear Schiff moment in $PbTiO_3$ ferroelectric

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We suggest two types of experiments, NMR and macroscopic magnetometry, with solid $PbTiO_3$ to search for the nuclear Schiff moment of ^{207}Pb. Both kinds of experiments promise substantial improvement over the presently achieved sensitivities. Statistical considerations show that the improvement of the current sensitivity can be up to ten orders of magnitude for the magnetometry experiment and up to seven orders of magnitude for the NMR experiment. Such significant enhancement is due to the strong internal electric field of the ferroelectric, as well as due to the possibility to cool the nuclear-spin subsystem in the compound down to nanokelvin temperatures.

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The existence of a permanent electric-dipole moment (EDM) of a quantum particle requires that fundamental parity (P) and time-reversal (T) symmetries are violated. By the CPT theorem, this would also mean the violation of the combined CP (charge-conjugation-parity) symmetry. Studies of T and CP violation in nature provide valuable information for the theories of baryogenesis and for our understanding of fundamental interactions in general. Thus, considerable effort has been put into searches for EDM's of particles, atoms, and molecules.

The current experimental upper limit on the neutron EDM is $d_n \leqslant 6.3\times10^{-26}e$ cm [1]. Experiments with paramagnetic atoms and molecules, the most sensitive of which was performed with Tl atoms [2], provide an upper limit on the electron EDM, $d_e \leqslant 1.6\times10^{-27}e$ cm. The most sensitive experiment with diamagnetic atoms is performed with ^{199}Hg vapor [3]; it gives an upper limit on the EDM of ^{199}Hg atom $d(^{199}\mathrm{Hg}) \leqslant 2.1\times10^{-28}e$ cm. This EDM is mainly induced by the nuclear Schiff moment S, which is usually defined by the P- and T-odd electrostatic potential it generates [4]:

$$\varphi(\boldsymbol{r}) = 4\pi(\boldsymbol{S}\cdot\boldsymbol{\nabla})\,\delta(\boldsymbol{r}). \quad (1)$$

Atomic calculations [5,6] show that the results of the ^{199}Hg EDM experiment [3] lead to the following limit on the Schiff moment of the ^{199}Hg nucleus:

$$S(^{199}\mathrm{Hg}) < 0.75\times10^{-50}\ e\ \mathrm{cm}^3 = 0.5\times10^{-25}\ e\ a_B^3 \quad (2)$$

(a_B is the Bohr radius.) Together with the neutron EDM data [1], this result provides most the significant limits on the models of CP violation in the hadronic sector; see Refs. [3,6,7].

The EDM Collaboration [8] plans to improve the sensitivity of the neutron EDM measurements by two orders of magnitude. Comparable sensitivity is expected in the proposed deuteron EDM experiment [9]. The next generation experiments with the electron EDM are also on the way—these are measurements with metastable levels of PbO molecules [10] and with YbF molecules [11]. The expected improvement of sensitivity compared to the atomic Tl experiment [2] is also about two orders of magnitude. Romalis and Ledbetter suggested to use liquid Xe for EDM measurements [12]. Since Xe atoms are diamagnetic, the measurement is mainly aimed at the ^{129}Xe nuclear Schiff moment. By statistical considerations only, the sensitivity of the experiment is $d(^{129}\mathrm{Xe}) \sim 3\times10^{-37}e$ cm for 10 days of averaging [12]. Taking into account the smaller nuclear charge of Xe, this effectively means improvement by eight orders of magnitude when compared to the present result (2) for ^{199}Hg. The limitations because of the systematic effects are also discussed in Ref. [12]. The solid-state experiment with gadolinium garnet, recently suggested by Lamoreaux [13] to measure the electron EDM, promises a five orders of magnitude improvement over the current Tl result (statistical estimate corresponding to 10 days of averaging.)

In the present paper we suggest using ferroelectric $PbTiO_3$ to measure the Schiff moment of the ^{207}Pb nucleus. The possibility to measure the macroscopic magnetization induced by an electric field, as was suggested by Lamoreaux for gadolinium garnets [13], looks most promising because of the large internal electric field in the ferroelectric. In addition, the nuclear-spin subsystem of the compound can (at least in principle) be cooled down to nanokelvin temperatures. For a 10-day averaging, statistics allows to reach a sensitivity of ten orders of magnitude better than the present result (2). Another possibility would be an NMR experiment (^{207}Pb is a spin-$\frac{1}{2}$ nucleus.) Although the sensitivity improvement is not as large in this case, the NMR experiment does not require nanokelvin temperatures.

The P,T-nonconserving effect due to the electron-nucleus tensor-pseudotensor interaction in ferroelectric $PbTiO_3$ was previously considered by Leggett [14] back in 1978. It was suggested that the sample with the dielectric polarization vector $\boldsymbol{P}$ in a magnetic field $\boldsymbol{H}$ should experience a macroscopic torque of the form $[\boldsymbol{P}\times\boldsymbol{H}]$. Some systematic effects mainly related to the external magnetic field were also considered in Leggett's paper.

$PbTiO_3$ is ionic crystal consisting of Pb^{2+}, Ti^{4+}, and O^{2-} ions. In the ferroelectric state Pb ions are shifted with respect to the central position in the PbO_{12} cluster by $X=0.47$ Å [15,16]; this shift explains the strong ferroelectricity of $PbTiO_3$. Wave functions of oxygen electrons penetrate inside the Pb ion and, because of the displacement, create the electric field gradient at the Pb nucleus. The nuclear Schiff mo-

ment interacts with this gradient which leads to the energy shift.

A similar effect has been considered previously for gadolinium garnets [17] where the ion displacement was induced by an external electric field. In the above paper, the electronic properties relevant to the problem were described in the framework of GdO_8 clusters. In the case of $PbTiO_3$ we have PbO_{12} clusters, but for the first estimate this difference can, arguably, be neglected, and we apply the formula obtained in [17] to our case:

$$\Delta\epsilon/E_0 \sim b\frac{Z^2}{(\nu_s\nu_p)^{3/2}}\left(\frac{1}{3}R_{1/2}+\frac{2}{3}R_{3/2}\right)\frac{(\boldsymbol{X}\cdot\boldsymbol{S})}{a_B e a_B^3},$$

$$b=\frac{16}{\sqrt{3}}(\beta_s\beta_s'+\beta_p\beta_p'). \tag{3}$$

Here $\Delta\epsilon$ is the energy shift caused by the Schiff moment of the ^{207}Pb nucleus, $\boldsymbol{S}$ [18]; $\boldsymbol{X}$ denotes the ion displacement, $E_0=27.2$ eV is the atomic energy unit, $e=|e|$ is the elementary charge, and $Z=82$ is the nuclear charge of Pb; $R_{1/2}$ and $R_{3/2}$ are the usual relativistic enhancement factors. The dimensionless coefficients $\beta_s\sim-0.5$, $\beta_s'\sim0.3$, $\beta_p\sim0.7$, and $\beta_p'\sim-0.2$ are related to the electronic structure of the crystal and allow us to describe the $2p_\sigma$ electrons of the surrounding oxygen ions as the effective s and p electrons of the central lead ion with effective principal quantum numbers $\nu_s\sim1.3$ and $\nu_p\sim1.5$. A straightforward evaluation of Eq. (3) gives the following energy shift:

$$\Delta\epsilon\sim-1.2\times10^6\frac{(\boldsymbol{X}\cdot\boldsymbol{S})}{a_B e a_B^3}\ \text{eV}=-1.1\times10^6\frac{S}{e a_B^3}\ \text{eV}. \tag{4}$$

Comparison of the Eq. (4) with the corresponding estimate in the paper [14] shows that our result is four orders of magnitude smaller. This discrepancy, however, is mainly due to the difference in the experimental limits on the nuclear Schiff moment, on which the estimates are based. This limit has been improved by factor of $\sim4\times10^4$ since 1978 when Ref. [14] was published.

Taking the upper limit on the Schiff moment (2) as a reference point in Eq. (4), we find the energy difference between the spin-up and spin-down nuclear states, essentially, the shift of the ^{207}Pb NMR line:

$$2\Delta\epsilon\simeq1.1\times10^{-19}\ \text{eV},\quad \Delta\nu=\frac{2\Delta\epsilon}{h}\simeq3\times10^{-5}\ \text{Hz}. \tag{5}$$

The width of the NMR line is the central issue for any precise NMR measurement with the principal limitation coming from the dipolar broadening which cannot be removed by the spin-echo technique. Since all the electron spins are compensated in the compound, the broadening is due to the magnetic dipole-dipole interaction of nuclear spins. The second moment of the line shape, $M_2=\int(\omega-\omega_0)^2P(\omega)d\omega$, is given by the following formula [19]:

$$M_2=\frac{36}{5}\sum_j\left(\frac{\mu^2}{r_j^3}\right)^2+\frac{16}{15}\sum_k\frac{I+1}{I}\left(\frac{\mu\mu'}{r_k^3}\right)^2, \tag{6}$$

where r_j and r_k are the distances from a given ^{207}Pb nucleus to all other nuclei with nonzero spin, the first summation is performed over the ^{207}Pb sites (magnetic moment $\mu=0.59\mu_N$ [20]), and the second summation is over the sites ^{47}Ti (spin $I=5/2$, magnetic moment $\mu'=-0.79\mu_N$), ^{49}Ti ($I=7/2$, $\mu'=-1.10\mu_N$), and ^{17}O ($I=5/2$, $\mu'=-1.89\mu_N$). For the natural abundance of isotopes, 22.1% ^{207}Pb, 7.4% ^{47}Ti, 5.4% ^{49}Ti, and 0.038% ^{17}O, Eq. (6) gives $\sqrt{M_2}=4.1\times10^{-13}$ eV. Assuming the Gaussian shape for the NMR line, the half-width is

$$\Gamma=\sqrt{8\ln2M_2}\simeq9.6\times10^{-13}\ \text{eV},\quad \Delta\nu_\Gamma=\frac{\Gamma}{h}=230\ \text{Hz}. \tag{7}$$

The Pb NMR data for ceramic $PbTiO_3$ are available [21]; the authors of this paper claim that their data are in agreement with the estimate according to formula (6).

It is interesting to compare our estimates (5) and (7) with the parameters of the ^{199}Hg experiment [3]. The effect (5) is a factor of $\sim0.5\times10^5$ larger than that for atomic Hg, but the linewidth (7) is also larger by factor of $\sim2\times10^5$. The number density of ^{207}Pb in the compound at the natural abundance is $n\approx0.33\times10^{22}$ cm^{-3}, while the number density of ^{199}Hg in the experiment [3] was about $n\sim10^{14}$ cm^{-3}. Assuming equal volumes, full polarization of ^{207}Pb nuclei, and assuming the sensitivity scales as $\propto\Delta\nu\sqrt{n/\Gamma}$, we find that sensitivity to the Schiff moment can be improved by six orders of magnitude, compared to the atomic Hg experiment [3]. It is possible to improve the sensitivity of the NMR experiment even further with the magic-angle spinning NMR technique (e.g., see the review in [22],) which allows the narrowing of the solid-state NMR line down towards the liquid NMR limit. According to [22], it should be possible to reduce the dipolar broadening (7) by at least two orders of magnitude, which leads to further improvement of the statistical sensitivity by one order of magnitude.

It is also possible to reduce the dipolar broadening by using samples grown to have reduced concentration of magnetic isotopes. Removal of ^{47}Ti and ^{49}Ti should reduce the width (7) by 30%. Further reduction is possible in the sample with depleted concentrations of ^{207}Pb: the second moment M_2 scales linearly with the number density of ^{207}Pb. In the sufficiently depleted sample the shape of the line is not Gaussian and while $\sqrt{M_2}\propto\sqrt{n}$, the linewidth, should actually scale as $\Gamma\propto n$. The reason for this difference in scaling is as follows: the value of M_2 is determined by the rare events of two ^{207}Pb nuclei occupying neighboring sites; the value of Γ, however, is mainly determined by the typical events of ^{207}Pb nuclei separated by the average distance $r\sim n^{-1/3}$. Therefore, for example, at $n\sim10^{19}$ cm^{-3} the linewidth is $\Delta\nu_\Gamma\sim1$ Hz. The width reduction at the expense of the number density does not improve the statistical sensitivity, but it can be helpful for analysis of systematics.

Broadening due to spin-lattice relaxation is probably not a serious issue. For the sample with a natural abundance of

isotopes the corresponding lifetime is about 1 sec [23] at room temperature. We attribute this relaxation to the combined action of the magnetic interaction between ^{207}Pb and ^{47,49}Ti nuclei and the electric quadrupole interaction of ^{47,49}Ti nuclei with the lattice. If this is correct, the spin-lattice relaxation time in the sample with no ^{47,49}Ti nuclei must be much larger than 1 sec. Since the spin-lattice relaxation rate due to the nuclear quadrupole moment drops dramatically with temperature, another possibility to lower the T_1 in the sample with a natural abundance of isotopes would be to cool the sample down to lower temperature.

A high degree of nuclear spin polarization is extremely important for the sensitivity of the NMR measurement, and the only sensible option we can think of is to use the optical pumping (OP) method. Although the effectiveness of OP NMR has been demonstrated for several classes of samples, including inorganic semiconductors (see, e.g., [24,25]), the applicability of the OP method to this particular compound should be a subject of separate research.

Another experimental approach that looks even more promising than the NMR-type experiment is to measure the magnetization induced by the external electric field. A similar method was suggested by Lamoreaux [13] to measure the electron EDM in gadolinium garnets. Compared to the electron EDM case, we immediately lose three orders of magnitude on the nuclear magneton versus the Bohr magneton ratio only. However, the effective electric field in ferroelectric is four orders of magnitude larger than the external electric field in the gadolinium garnet experiment. Additionally, it should be possible to cool the nuclear spins in $PbTiO_3$ down to 10 nK (e.g., see review [26]), whereas the lowest experimental temperature in gadolinium garnet is probably limited to about 1 K (in both cases, the lowest temperature is determined by the spin freezing); the last argument wins about eight orders of magnitude in sensitivity.

Let us perform more accurate estimates. ^{207}Pb nuclear magnetization induced by the Schiff moment is

$$M = n\mu\frac{\Delta\epsilon}{k_BT} = -1.1\times10^{6}\, n\mu\,\frac{S}{ea_B^3}\frac{1\ \mathrm{eV}}{k_BT}. \tag{8}$$

Here n is the number density of ^{207}Pb nuclei and μ is their magnetic moment; $\Delta\epsilon$ is given by Eq. (4). The freezing temperature for nuclear spins, T_f, in $PbTiO_3$ is determined by the spin-spin interaction; therefore,

$$T_f \sim \frac{\Gamma}{k_B} \sim 10^{-8}\ \mathrm{K}, \tag{9}$$

where Γ is given in Eq. (7). We take this temperature as the lowest possible for the experiment and substitute $T=T_f$ $=10$ nK in Eq. (8). The expected magnetic induction is then

$$B = 4\pi M = \frac{S_N}{ea_B^3}\times1.8\times10^{17}\ \mathrm{G}. \tag{10}$$

According to Ref. [13], one can achieve the sensitivity of 3×10^{-16} G for 10 days of averaging with a superconducting quantum interference device (SQUID) magnetometer, and it is even possible to do two orders of magnitude better with magnetometry based on the nonlinear Faraday effect [13,27]. The corresponding sensitivity to the nuclear Schiff moment is

$$S \sim 1.7\times10^{-35} ea_B^3 = 2.5\times10^{-60}\ e\ \mathrm{cm}^3, \tag{11}$$

which is ten orders of magnitude better than the present result (2) for ^{199}Hg. The sensitivity (11) is four orders of magnitude better than the value of the nuclear Schiff moment predicted by the standard model, $S\sim10^{-56}e$ cm^3; see Refs. [4,5,7,28].

Because of the substantial hysteresis in the ferroelectric, the energy dissipation from the external electric field reversals can be a serious issue. This problem can be avoided by switching off the external electric field altogether and then rotating the electrically polarized sample in order to effectively reverse the internal electric field. This is possible because the nuclear spins, unlike electron spins, are only weakly coupled to the lattice. With this kind of "rotational reversal," paramagnetic impurities (electronic paramagnetism) constitute a source of potentially dangerous systematics, so the sample should be prepared free of such impurities.

This requirement not to have paramagnetic centers in the system poses a serious problem for nuclear spin cooling. The current cooling technology incorporates the stage that makes use of the so-called "solid-state effect" (see, e.g., [29]), for which paramagnetic impurities are necessary. The spin-lattice coupling through phonon creation or phonon scattering drops dramatically with temperature, and at some point the nuclear spin subsystem becomes effectively decoupled from the lattice—the spin-lattice relaxation time becomes extremely large, and although the lattice temperature can still be lowered by conventional techniques, the nuclear spins cannot thermalize with the lattice. We estimate the temperature at which the nuclear spin system effectively decouples from the lattice—i.e., at which the spin-lattice relaxation time becomes of the order of a day—to be about 10 K for our compound (see [30], also [29]). The "solid-state effect" then allows us to lower the nuclear spin temperature through the hyperfine coupling by saturating one of the ESR lines of the paramagnetic impurity ions with the corresponding rf or microwave field. And after that further cooling is achieved through adiabatic demagnetization. We see two ways to circumvent this problem. First, there is a way to create temporary paramagnetic centers in the compound by illuminating the sample with UV light [16]—optical illumination leads to the trapping of holes on the lead ions, creating Pb^{3+} paramagnetic sites. These sites can be used in nuclear spin cooling and then die out in the process of recombination. Second, we propose to skip the cooling stage, which requires paramagnetic centers altogether, and use "laser cooling" of nuclear spins—polarization of the nuclear spins with the help of the optical pumping technique. In this case, the small value of the spin-lattice coupling is very helpful—it allows us to maintain the low nuclear temperature for longer periods of time.

To summarize, we have suggested two types of experiments, NMR and macroscopic magnetometry, in solid $PbTiO_3$ to search for the nuclear Schiff moment of ^{207}Pb. Both kinds of experiments promise substantial improvement over the presently achieved sensitivities. Statistical consider-

ations show that the magnetometry experiment can offer up to ten orders of magnitude improvement over the present sensitivity to the nuclear Schiff moment (^{199}Hg experiment [3]). With this improvement, the sensitivity is four orders of magnitude better than the value of the nuclear Schiff moment expected from the standard model [4,5,7,28]. Such significant enhancement is due to the strong internal electric field of the ferroelectric, as well as due to the possibility to cool the nuclear-spin subsystem in the compound down to nanokelvin temperatures. The NMR-type experiment does not require such low temperatures, but offers smaller improvement in sensitivity—about seven orders of magnitude when compared to the ^{199}Hg experiment [3].

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