Spin-glass state and long-range magnetic order in Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ seen via neutron scattering and muon spin rotation

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I. INTRODUCTION

Since the discovery of a large magnetoelectric effect in RMn$_2$O$_3$ (Ref. 1) and RMn$_2$O$_5$ (Ref. 2) (R=rare earth), there is a revival of interest in the study of multiferroic materials where the coupling between the electric polarization and the magnetic order is strong. Although coexistence of ferroelectricity and magnetic long-range order is not very common, quite a number of new multiferroics materials have been found recently, such as Ni$_3$V$_2$O$_8$, MnWO$_4$, or LiCuVO$_4$ to cite only a few. Multiferroics that have coupled ferroelectric and magnetic order parameters are also promising materials for applications as it is possible to control the ferroelectric polarization by a magnetic field and vice versa. Therefore, there is an extensive search for materials that show pronounced magnetoelectric effect at ambient conditions. B-site-disordered complex perovskites PbB$_x$B'$_{1-x}$O$_3$ might be attractive candidates as they can adopt various ions which strongly influence the temperature of magnetic and ferroelectric orderings.

Lead iron niobate, Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ (PFN), is one of the well-known complex perovskites that exhibits multiferroic properties. PFN is rhombohedral at room temperature and cubic above the ferroelectric Curie temperature of 383 K. Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ undergoes a diffuse phase transition without pronounced frequency dispersion. In the cubic phase, the symmetry of the chemical cell is $Pm\overline{3}m$. There is a cubic-tetragonal phase transition at $T_c$=383 K followed by a first-order transition at 354 K. The symmetry of the chemical structure of the low-temperature phase of PFN was the subject of some debate. Lampis et al. reported that the structure is monoclinic with space group $Cm$, whereas Ivanov et al. using powder neutron-diffraction data found that the chemical structure of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ has $R3c$ symmetry at $T=10$ K.

The magnetic properties of PFN are also not completely understood. PFN undergoes a paramagnetic to antiferromagnetic phase transition at $T_N$=140–160 K. The magnetic structure was determined by single-crystal neutron diffraction and corresponds to a simple G-type antiferromagnetic arrangement of the magnetic moments at all temperature below $T_N$. Magnetoelectric effect in PFN at low temperatures has been demonstrated long ago and, recently, it was shown that the dc magnetic susceptibility has an anomaly at the paraelectric-ferroelectric phase transition. The dielectric permeability also shows an anomaly at the Néel temperature, which suggests that a biquadratic term in the Landau free energy of the form $P^2M^2$ is responsible for the coupling between the ferroelectric polarization $P$ and the staggered magnetization $M$. Additional magnetic anomalies were reported in the literature for Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ below the magnetic phase transition. Both NMR (Ref. 17) and susceptibility measurements have shown that an additional magnetic phase transition occurs in PFN around $T_g=20$ K that was interpreted as the formation of a spin-glass phase by Kumar et al.

Here we report on muon-spin rotation and neutron scattering results of the magnetic properties of PFN below the Néel temperature. We show that the magnetic ground state of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ is a spin-glass-like state that coexists with long-range antiferromagnetic order below $T_g=20$ K.

II. EXPERIMENTAL

The Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ single crystals used in the muon-spin rotation and neutron-scattering experiments were grown by spontaneous crystallization from the melt following the routine described in Ref. 19. The muon-spin-relaxation measurements were performed using the GPS instrument at the Paul Scherrer Institut (Villigen, Switzerland) on a Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ single crystal between 160 and 5 K. Data were recorded using the zero-field method that allows us to determine both the static and dynamics in disordered spins systems. The neutron-scattering experiments were performed with the cold neutron three-axis spectrometer TASP (Ref. 20) at neutron spallation source SINQ operated in diffraction mode at $K_s=1.97$ Å$^{-1}$. For this experiment a single crystal of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ was oriented with the [1,1,0] and [0,0,1] crystallographic directions in the scattering plane. In that scattering geometry, magnetic Bragg peaks with indices $(h/2,h/2,l/2)$ in the rhombohedral setting can be accessed. The use of a three-axis spectrometer was justified by the
need to improve the intensity-to-background ratio in order to search for possible short-range order at low temperatures.

III. RESULTS

A. \( \mu \)SR

In a \( \mu \)SR experiment, the time evolution of the muon-spin polarization is monitored by recording the asymmetric emission of positrons produced by the weak decay of the muon (muon lifetime \( \sim 2.2 \) \( \mu \)s). The time histogram of the collected positrons is given by

\[
N(t) = N_0 \exp(-t/\tau)[1 + AG_z(t)] + B,
\]

where \( A \) is the initial muon asymmetry parameter, \( N_0 \) is a normalization constant, and \( B \) is a time-independent background. The function \( G_z(t) \) reflects the normalized muon-spin autocorrelation function

\[
G_z(t) = \frac{\langle \bar{S}(t) \cdot S(0) \rangle}{\bar{S}(0)},
\]

where \( \bar{S} \) is the spin of the muon. Hence \( AG_z(t) \), often called the \( \mu \)SR signal, reflects the time evolution of the muon polarization.

Figure 1 shows the \( \mu \)SR signal in \( \text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 \) upon passing the Néel temperature. In the paramagnetic phase the signal is consistent with a weak depolarization of the muon signal solely due to nuclear dipole moments. Below the Néel temperature, the muon signal changes rapidly and the initial asymmetry \( A \) is strongly reduced. This indicates that there is a large distribution of internal fields seen by the \( \mu \)s, which is a consequence of the random distribution of the Fe and Nb ions in the chemical lattice. Therefore, the \( \mu \)SR signal is depolarized and the residual asymmetry is close to 1/3 of the value observed in the paramagnetic state. Hence, in the long-range antiferromagnetic phase, the muon signal reflects only muons having their initial polarization along the direction of the internal field at the stopping site.

Below \( T_{N} \), the time evolution of the remaining \( \mu \)SR signal is best fitted assuming the function

\[
G_z(t) = \frac{1}{3} \exp[-(\lambda t)^\beta].
\]

Close to \( T_N \), the power exponent is \( \beta \approx 1 \), reflecting the presence of fluctuating internal magnetic fields with a unique correlation time \( \tau_c \). In this range of temperatures, the depolarization rate \( \lambda \) is proportional to the second moment of the magnetic-field distribution \( \langle B^2 \rangle \) and to the correlation time \( \tau_c \) of the internal field and is given by

\[
\lambda = \gamma_\mu \langle B^2 \rangle \tau_c,
\]

where \( \gamma_\mu \) is the muon gyromagnetic ratio. The temperature dependence of the depolarization rate \( \lambda \) is shown in Fig. 2. It can be observed that there is a critical-like divergence close to \( T_c = 20 \) K. This is a clear evidence that \( \text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 \) undergoes a second magnetic phase transition at the temperature \( T_c \).

Figure 3 depicts the temperature evolution of the \( \beta \) exponent. As already mentioned, at temperatures just below \( T_N \), the muon depolarization is described by an exponential function instead of a stretched exponential, i.e., with the parameter \( \beta \sim 1 \). Upon further cooling below \( T_N \), \( \beta \) continuously decreases and approaches the value of 1/3 at \( T_c \sim 20 \) K. A decrease in the exponent \( \beta \) toward the value of 1/3 has been predicted theoretically and later observed for the dense spin-glass systems \( \text{AgMn} \) and \( \text{AuFe} \) alloys. It is tempting to
attribute this change in $\beta$ to the change in the distribution of the correlation times $\tau$, of the internal magnetic fields at the muon stopping sites as a spin-glass transition is approached from above. However, for a usual paramagnetic to spin-glass transition, one observes that the residual fluctuations lead to a constant value of $\beta$ below $T_g$ while $\lambda$ decreases, reflecting the decrease in the magnitude of the fluctuating field, as the temperature is lowered deeper into the spin-glass phase. However, Fig. 3 also shows that $\beta$ grows as the temperature is lowered below $T_g$ to recover the value $\sim 1$ at $T=2$ K.

The solution to this apparent paradox is that the slow spin fluctuations, arising from the spin-glass state and which persist in a relatively broad temperature range below $T_g$, occur on top of antiferromagnetic fluctuations due to the long-range order. It is then natural to expect that the strong reduction in the critical spin-glass fluctuations in time when the temperature is decreased below $T_g$ leads to the recovery of the weak noncritical antiferromagnetic fluctuations probed by the $\mu$SR signal above $T_g$. We note that as the static component of the $\mu$SR signal is already lost above $T_g$, no indication of a change (i.e., increase) in the damping of this component (as evidenced, for example, in other reentrant spin glasses) could be determined at the spin-glass transition by $\mu$SR.

**B. Neutron scattering**

Figure 4 shows a typical neutron elastic scan along the $(q,q,-2q)$ direction at $T=5.2$ K in Pb(Fe$_{1/2}$Nb$_{1/2}$)$_3$O$_3$. The spectrum consists of a sharp Bragg peak centered around $Q_N=(1/2,1/2,1/2)$ that corresponds to the antiferromagnetic long-range order detected by neutron diffraction previously. A diffuse component is also present in the neutron spectrum that is weaker in intensity and has a width in $q$ that is much broader than the experimental resolution. The magnetic origin of the diffuse component was confirmed using the neutron polarization analysis device MuPAD (Ref. 23) that allows a complete separation of magnetic and nuclear scatterings. Namely, using a neutron-polarized beam for which the polarization is aligned along the scattering vector, magnetic scattering reverses the neutron polarization vector, whereas scattering of nuclear origin leaves the polarization of the neutron beam unchanged. Magnetic scattering therefore appears in the spin-flip channel as shown to be the case for the diffuse component in the inset of Fig. 4.

We investigated the distribution of the diffuse scattering around the $Q_N$ antiferromagnetic Bragg peak and found that it is essentially isotropically distributed in the $[1,1,0]/[0,0,1]$ scattering plane accessible in the present measurements (see Fig. 5). We performed an energy scan through the diffuse component and found that it is resolution limited within the energy window ($\Delta E=0.3$ meV) of the spectrometer. Therefore, the spin fluctuations associated with the diffuse scattering are static in the time window of our experiment.

Within the quasistatic approximation, the energy-integrated neutron cross section is proportional to the generalized static susceptibility $\chi(Q)$. Therefore, the intensity recorded in the neutron spin-flip channel for incident polarization along the scattering vector is

$$I(q) \propto \chi(Q) = \sum_{\text{muon sites}} \delta(Q(Q_{\mu})),$$

reflecting the magnetic scatterings. The inset shows the intensity recorded in the neutron spin-flip channel for incident polarization along the scattering vector.

![FIG. 4.](image_url) (Color online) Transverse scans through the $Q_N=(0.5,0.5,0.5)$ magnetic Bragg peak. The broad component in the spectrum was fitted by a Lorentzian and is emphasized by a bold line. The Bragg peak is a fit to a Gaussian. Inset shows the intensity recorded in the neutron spin-flip channel for incident polarization along the scattering vector.

![FIG. 5.](image_url) (Color online) Distribution of the elastic diffuse scattering measured in Pb(Fe$_{1/2}$Nb$_{1/2}$)$_3$O$_3$ at $T=2$ K. For clarity the intense Bragg peak at $Q_N=(0.5,0.5,0.5)$ was removed and the background subtracted from the data.
The temperature dependence of the magnetic order is homogeneous and does not recover when passing the spin-glass transition. This indicates that the magnetic order is homogeneous and does not recover when passing the spin-glass transition.

There are numerous examples of coexistence between the ferromagnetic and spin-glass states of matter. For example, ferromagnetic and spin-glass orders are known to coexist in AuFe alloys at sufficiently low temperatures. Antiferromagnetic and spin-glass orders are also known to coexist at sufficiently low temperatures, e.g., in Fe0.5Mg0.45Cl2. The coexistence of collinear magnetic long-range order, e.g., ferromagnetic or antiferromagnetic, and spin-glass order is well understood theoretically at the level of the Sherrington-Kirkpatrick (SK) model. In the SK model, this coexistence is the rule below some critical temperatures and down to the lowest temperatures as soon as the magnitude $\bar{J}$ of the mean value of the random exchange coupling $J$ between any two spins is on the order of or larger than the standard deviation $\Delta J$ of its Gaussian distribution.

Classical spin models with short range but random two-body spin interactions [the Edwards-Anderson (EA) model of spin glasses] are not as well understood as the SK model. Monte Carlo simulations suggest that the lower-critical dimension for the onset of spin-glass order when the disorder is dominant, $\bar{J}/\Delta J < 1$, is strictly below three dimensions for Ising spins, a prerequisite for the coexistence of collinear and spin-glass order when $\bar{J}/\Delta J \geq 1$. Fluctuation effects are stronger for Heisenberg spins than they are for Ising spins, as fluctuations in the directions transverse to the direction taken by the collinear order parameter in spin space become available in the former case. Correspondingly, state-of-the-art Monte Carlo simulations give “only” the upper bound of three dimensions for the spin-glass lower-critical dimension when the disorder is dominant, $\bar{J}/\Delta J < 1$. In other words, it cannot be ruled out within the accuracy of available Monte Carlo simulations that the spin-glass phase is quasi-long-range ordered instead of long-range ordered when the classical spins are Heisenberg type in the three-dimensional EA model.

Given the uncertainty of the spin-glass lower-critical dimension for Heisenberg EA spin-glass models, the mere observation that antiferromagnetic and spin-glass orders coexist in Pb(Fe1/2Nb1/2)O3 is not sufficient to establish whether the relevant magnetic degrees of freedom are Ising or Heisenberg type. Although exchange interactions remain to be determined in Pb(Fe1/2Nb1/2)O3, the relatively high Néel temperature of Pb(Fe1/2Nb1/2)O3 suggests that exchange interactions dominate dipolar and single-ion anisotropies in this compound. If this is the case, then Pb(Fe1/2Nb1/2)O3 is a good candidate to study the coexistence of long-range antiferromagnetic and spin-glass orders for the Heisenberg spins of a three-dimensional antiferromagnetic EA model.

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