PHYSICAL REVIEW B **70**, 132101 (2004)

# Magnetoelectric coupling in ferroelectromagnet $Pb(Fe_{1/2}Nb_{1/2})O_3$ single crystals

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(Received 23 December 2003; revised manuscript received 19 April 2004; published 1 October 2004)

The magnetic and dielectric properties of ferroelectromagnet (FEM) $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) single crystals have been investigated. Anomalies in the dielectric constant as a function of temperature have been observed near its Néel temperature of $\sim 143$ K, which are indicative of the so-called magnetoelectric coupling between the ferroelectric and antiferromagnetic orders in this compound. The results coincide with previous theoretical predications. It is demonstrated that a weak magnetic transition appeared at a temperature a little below the Néel temperature, confirming the earlier prediction from the Monte Carlo simulation in a qualitative sense. The magnetic hysteresis measurement proves that there does exist weak magnetic order in PFN crystal below its Néel temperature. The Mössbauer spectra also support the existence of the magnetic order.

DOI: 10.1103/PhysRevB.70.132101 PACS number(s): 77.80.Bh, 75.50.Ee, 75.80.+q

In the complex perovskite compounds $A(BB')O_3$, the angles in the chain $B$ cation-oxygen-$B'$ cation are close to 180°. Therefore, when transition element ions lie in the octahedral $B$ positions, they may become ordered via an indirect exchange interaction through the oxygen ions. Since the ferroelectric ordering in the perovskite lattice arises mainly from the displacements of $A$ and $B$ ions, if magnetic ions are introduced into the octahedral $B$ position, a number of novel effects may appear. The interaction induced a new class of materials, i.e., the so-called ferroelectromagnets FEM's, which are compounds in most cases with ferroelectric (antiferroelectric) and ferromagnetic (antiferromagnetic) orderings coexisting at low temperatures.[1–4] The interaction of the ordered subsystems can result in the so-called magnetoelectric effect with interesting device potentials, where the dielectric properties of the FEM's may be altered by the onset of the magnetic transition or by the application of a magnetic field, and vice versa. Recently there has been a growing interest in a number of FEM's.[5–9]

Lead iron niobate $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) belongs to the series of complex perovskite compounds discovered by Smolenskii *et al.* at the end of the 1950's.[10] It was considered to be ferroelectrically and antiferromagnetically ordered below a certain temperature. Its ferroelectric (FE) Curie temperature ($T_c$) is around 385 K (Ref. 10) or 383 K (Ref. 11) and the antiferromagnetic (AFM) order begins at a Néel temperature $T_N \sim 143$ K.[12] Since it was discovered, there have been intensive studies on both single crystals and ceramics synthesized in different kinds of methods. The majority of these works focus on the fabrication and the structural, magnetic, and ferroelectric property characterizations. Some features of PFN such as the anomaly of dielectric constant and the physical understanding of phase transitions no matter in ceramics and single crystals are quite author dependent. In spite of the generally accepted ferroelectric and antiferromagnetic features, the magnetoelectric (ME) coupling effect associated with the phase transitions below $T_N$ remains the object of continuing debate.[13] For instance, earlier studies on the magnetoelectric coupling gave different results: Astrov *et al.* reported that PFN became a weak ferromagnet only when it was cooled down through AFM transition with both magnetic and electric fields applied simultaneously,[14] while Howes *et al.* presented that they did not find any anomaly in magnetic susceptibility until a temperature as low as 4.2 K.[15] A weak ferromagnetic moment and linear ME effect at approximately 9 K was reported by Watanabe *et al.*[16] Randall *et al.* regarded PFN as a normal ferroelectric with long cooperative interactions between the dipoles though it has a broad phase transition near $T_C$,[17] and Yokosuka proved that PFN undergoes a diffuse phase transition from paraelectric cubic to rhombohedral ferroelectric phase.[18] In addition, Park investigated the low frequency dispersion of PFN and pointed out that the irreversible motion of domain wall of polydomain crystal was the reason of low frequency dispersion.[19] At the same time he pointed that the thermal history influenced the value of dielectric constant significantly and the cooling process got the higher dielectric constant than the heating one.

Most of the contradictions seem to be related to the sample inhomogeneity and different techniques used for characterizations.[13] On the other hand, the evidence of magnetoelectric coupling in PFN has been rarely presented. Moreover, though the two-phase assumption for ferroelectromagnetic PFN is accepted, the physical properties near the two phase-transition temperatures still remain controversial. Facing the variety of earlier reports and the underlying complexity in FEM materials, we grew PFN single crystals using the high-temperature solution growth method and concentrated on the study of the single crystal samples and powders obtained by grinding them. We have measured the temperature dependence of dielectric and magnetic properties to observe if there is any anomaly in the vicinity of AFM phase transition point and to confirm the existence of the magnetically ordered states below $T_N$. We also obtained the Mössbauer spectra of $^{57}Fe$ enriched PFN sample to find out the existence of magnetic order and the hyperfine interaction property.

The investigated samples were single crystals grown from a high-temperature crystal growth method similar to that of Brunskill *et al.*[20,21] PbO was chosen as flux for the high-temperature solution growth of PFN crystals because PbO has proved to be an effective solvent for many oxides as well as for the complex perovskites.[20–22] The use of PbO can also avoid the incorporation of foreign ions into the lattice of the

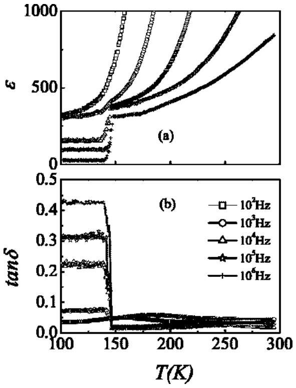

FIG. 1. (a) Temperature dependence of the dielectric constant of PFN crystal at five different frequencies. (b) Temperature dependence of the dielectric loss at five frequencies.

grown crystals, since PbO itself is a starting component of PFN. The pseudobinary PFN-PbO phase diagram given in Brunskill (Ref. 21) was adapted. The eutectic composition is situated at 15 wt.% PbO-85 wt.% PFN with the eutectic temperature of 820±5 °C. The grown crystals were found in the crust at the level of solidified liquid surface. The crystals yielded were very dark red in color and showed a high degree of lustre and pseudo-cube form. The typical size of the crystals was 2–3 mm edge length with the largest ones reaching an edge dimension of 5 mm.

The obtained powders by grinding the grown crystals were characterized by powder x-ray diffraction (XRD) measurement employing a X'TRA Cu $K\alpha$ diffractometer. The Rietveld analysis on the XRD pattern indicated that the samples are single phase of pseudoperovskite PFN within the resolution of the diffraction equipment and can be indexed by rhombohedral structure at room temperature. The lattice parameter $a=b=c=4.015$ Å, the angles between them is $\alpha=\beta=\gamma=89.89°$, in agreement with the x-ray diffraction,[10,12] electronic diffraction,[12] and the neutron diffraction results.[23]

First of all, in order to study the ME coupling effect in PFN, the dielectric properties of PFN crystals were studied at several frequencies by means of an HP4194A Impendence Analyzer from room temperature to 90 K. The single crystal was cut and polished into thin platelets and the electrodes were applied on (001) plane. The dielectric constant and the loss of the $(100)_{\mathrm{cub}}$ platelet at various frequencies from $10^2$ to $10^6$ Hz are shown in Fig. 1. To clarify the phase transition features near $T_N \sim 143$ K, the temperature dependence of $\varepsilon$ in this temperature range was measured with great care on different samples and several repetitions to determine if any coupling exists between the ferroelectric and antiferromagnetic orders. Figure 1(a) shows the temperature dependence of dielectric constant and Fig. 1(b) the dielectric loss (tan $\delta$). The abnormal rapid increase in $\varepsilon$ observed above 470 K can be caused by ionic conductivity of the defected crystal lattice, which is often found in ferroelectric materials. The dielectric loss begins to increase sharply from this temperature, too. We also noticed the pronounced thermal history influence on the value of the dielectric constant such as the result reported by Park,[19] but since we focus this report on the ME coupling, we leave the property near the ferroelectric phase transition to some other place. It is found that in Fig. 1(a) the dielectric constant shows a clear jump near $T_N$ at each frequency from $10^4$ to $10^6$ Hz. The magnitudes of these jumps increase with the frequency. The dielectric constants at low frequencies do not show sharp jumps, but continuous, smooth growth, as at $10^2$ and $10^3$ Hz. The loss exhibits the same tendency. We argue that the resonant frequency of the coupling between ferroelectric and magnetic sublattices may lie between $10^3$ and $10^4$ Hz, which causes the anomaly of the dielectric property below this frequency range. In fact, we are not the first who notice the dielectric permittivity and loss of Pb contained perovskite. Other authors have observed this kind of phenomena. Ye *et al.* found the anomalies of $\varepsilon$ in another Pb-contained perovskite ferroelectromagnet $\mathrm{Pb(Fe_{2/3}W_{1/3})O_3}$ in the vicinity of $T_N$ for their experimental frequencies (from 1 kHz to 1 MHz).[9] They observed that the anomalies did not depend on the applied field. The anomalies could be attributed to a magnetic ordering from the superexchange interaction of $\mathrm{Fe^{3+}}$-O-W-O-$\mathrm{Fe^{3+}}$.

Kimura *et al.* applied the Ginzburg-Landau theory which was modified by Smolenskii *et al.* in another FEM material $\mathrm{BiMnO_3}$ to explain the origin of the anomaly in $\varepsilon$ due to the magnetic order of FEM's with $T_N \ll T_E$.[7] We assume that the jump in the magnetic (or dielectric) susceptibility of a FEM at the temperature of the ferroelectric (or magnetic) transition can be defined as a second order phase transition[1] by analogy with the jumps in heat capacity and in elastic module in second order phase transitions within the framework of thermodynamic relationships. The underlying physics was supposed to be the magnetoelectric interaction below the temperature of the appearance of AFM phase. We applied Ginzburg-Landau theory to PFN to ascertain if the relation found in $\mathrm{BiMnO_3}$ is valid for PFN. The thermodynamic potential $\Phi$ in a FEM can be written in the form

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2}P^4 - PE + \alpha' M^2 + \frac{\beta'}{2}M^4 - MH + \gamma P^2 M^2, \tag{1}$$

where $P$ and $M$ are the polarization and magnetization, respectively. $\Phi$, $\alpha$, $\beta$, $\alpha'$, $\beta'$, and $\gamma$ are functions of temperature. The ME exchange interaction term takes the form of $\gamma P^2 M^2$. The deviation of dielectric susceptibility is $\chi^E(T) = \partial\Phi^2/\partial P^2$. Below $T_N$ the difference of $\chi^E(T)$ with the values obtained by extrapolation of itself from the paramagnetic phase into the region $T < T_N$ was denoted as $\delta\chi^E$. When $T_N$ and $T_E$ are separated apart enough, such as in PFN, the dependence of the electric parameters on the temperature near $T_N$ can be ignored. Since $\delta\varepsilon = 4\pi\delta\chi^E$, in this case below $T_N$, $\delta\varepsilon$ should be proportional to the square of the magnetic-order parameter

$$\delta\varepsilon \sim \gamma M^2, \tag{2}$$

Fig. 2(a) replots the temperature dependence of dielectric constant at $10^4$ Hz below $T_N$ and the deviation of it from the values obtained by the extrapolation. We also obtained the sample magnetization $(M)$ as a function of temperature $(T)$ under a magnetic field of 80 A/m. The relation of $\delta\varepsilon$ versus $M^2$ is given in Fig. 2(b) and it is found that from 130 to 143 K there exists a roughly linear behavior and $\delta\varepsilon \sim M^2$ in

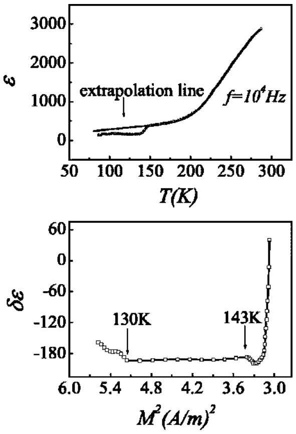

FIG. 2. (a) Dielectric constant at $10^4$ Hz and its extrapolation from the paramagnetic range. (b) The relation between $\delta\varepsilon$ and $M^2$ below $T_N$.

this range is valid. The result implies that the origin of the change in dielectric constant is attributed to the coupling term $\gamma P^2 M^2$ in the thermodynamic potential. In fact, Kimura *et al.* examined that the magnitude of field-induced change of dielectric constant of $BiMnO_3$ as a function of $M^2$ at temperatures in the vicinity of $T_N$ and confirmed that $\delta\varepsilon \propto kM^2$ is valid for the $BiMnO_3$.[7]

It would be interesting to check whether such a magnetoelectric coupling can activate any magnetic transition or not. Figure 3(a) shows the temperature dependence of $M$ from room temperature to 4.2 K. The $1/\chi$-T curve we deduced has the similar shape with what observed by Watanabe.[16] The inset of Fig. 3(a) shows the details of temperature dependence of $M$ around $T_N$. We notice in the inset that as the temperature goes down the magnetization first shows an inflection which corresponds to the reported antiferromagnetic phase transition point at about 143 K and then goes up as $T$ continues to decrease at a temperature 20–30 K below $T_N$. In fact, Bokov *et al.* have already found this behavior when they published the result of the magnetic property of PFN in 1962. They explained that the magnetic moments of some $Fe^{3+}$ ions in the antiferroelectric regions are not ordered and the system can be considered as paramagnetic in the first approximation. These anomalies agree with our former Monte Carlo simulation results.[24] In the simulation, the magnetic and electric order parameters were introduced into the magnetoelectric coupling system. When imposing a nonzero coupling the response of magnetization is generated. Our experimental result of $M$-$T$ curve is similar with the curve of $g=10$, where there are also two features observed. A magnetization measurement was carried out with a magnetic field of between +558 to −558 A/m at the temperature of 80 K. Figure 3(b) shows the hysteresis. It confirms the existence of weak magnetic property. So we can deduce that there exists weak magnetic order below $T_N$, which originates from the ME coupling. The abnormal $M$-$T$ relation near $T_N$ is possibly caused by the ME interaction.

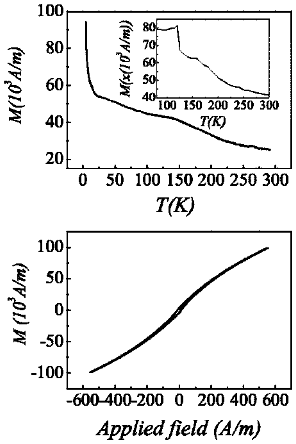

FIG. 3. (a) The temperature dependence of magnetization under the field of 80 A/m, the inset gives the $M$-$T$ curve measured near $T_N$. (b) The $M$-$H$ hysteresis measured under the magnetic field of −558 to +558 A/m.

The coincidence of the experimental and simulation results confirms the existence of magnetoelectric coupling and corresponds to the previous theoretical prediction of the magnetoelectric-interaction induced additional transitions in the magnetic and ferroelectric subsystems.[1] In FEM's, Smolenskii *et al.* introduced the concept of magnetoelectric susceptibility to characterize the change in the polarization under the onset of an external magnetic field and in magnetization under the onset of an electric field. The ME coupling was denoted by the response of the system to the action of an external field and can be described by an electromagnetic susceptibility tensor $X$. Huang *et al.* applied the concept in the attempt to explain the ME coupling in $YMnO_3$ (Ref. 8) and found that below $T_N$ in the absence of an external field it is very likely of a magnetostrictive effect associated with a lattice change accompanying the Néel transition. This produces an S-shaped anomaly in the $\varepsilon$-$T$ curve. We observed the magnetoelectric effect of PFN crystal and found the change is a downward jump. This result is similar to the S-shaped anomaly in $YMnO_3$. We suppose that the jump in $\varepsilon$-$T$ relation in PFN can be explained by the ME coupling accompanying the onset of the Néel transition.

In order to clarify the magnetic order of PFN below $T_N$, we applied Mössbauer spectroscopy to investigate the hyperfine interaction around iron ions in the PFN sample. For Mössbauer spectra, the energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the isomer shift, quadrupole splitting and magnetic splitting. The isomer shift (IS) arises due to the nonzero volume of the nucleus and the electron charge density due to $s$ electrons within it and it produces a shift in the resonance energy of the transition. The quadrupole splitting (QS) comes from the interaction between the electron field gradient at the nucleus and the electric quadrupole moment of the nucleus itself. In the case of $^{57}Fe$, it gives a two line spectrum or "doublet." In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field, which is known as Zeeman splitting. Magnetic splitting gives, in $^{57}Fe$, six possible transitions, which corresponds to a sextet.

The $^{57}Fe$ Mössbauer absorption spectra were measured between 20 and 300 K using a 25mCi $^{57}Co$ source in Palladium matrix and a standard constant acceleration Mössbauer spectrometer using metallic iron for calibration. In the result-

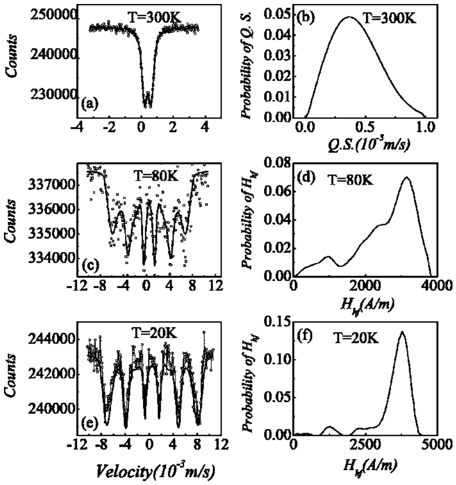

FIG. 4. Mössbauer spectra of $^{57}$Fe in PFN at different temperatures at 300 K (a), 80 K (c), 20 K (e). Distribution of the quadrupole splitting at 300 K (b). Relation between hyperfine field and its probability at 80 K (d) and 20 (K) (f).

ing Mössbauer spectra, $\gamma$-ray intensity is plotted as a function of the velocity. In Fig. 4(a), the room temperature spectrum is fitted by a single quadrupole doublet and the isomer shift value at this temperature equals to 0.413 mm/s. The mean of QS is about 0.420 mm/s. The results imply that $Fe^{3+}$ ion has six ligands in PFN, which agrees to the earlier result of $Fe^{3+}$ locating in the octahedral $B$ position of the pseudoperovskite structure.[12] Figure 4(b) is corresponding to the distribution of the quadrupole splitting at 300 K. The Gauss-like curve indicates that the ligand arrangement of $Fe^{3+}$ ions is randomly distributed. Figure 4(c) is the spectrum at 80 K. The appearance of sextet from the magnetic splitting in the Mössbauer spectra of PFN implies that there exist magnetic orders at this temperature. From Fig. 3(a) we have noticed that below $T_N$ the $M$-$T$ relation is not the usual antiferromagnetic tendency where the magnetization shows a maximum at $T_N$ and then goes down as the temperature decreases. The magnetization in this figure and the ones observed by Bokov[12] and Watanabe[16] all continuously go up from a little below $T_N$ to the lower temperature the experiments reached. In addition, in Fig. 3(b), we do find a hysteresis at the temperature below the reported $T_N$. Therefore, combine the results of Figs. 3(a), 3(b), and 4(c), we suggest the existence of weak ferromagnetic order at low temperature. Figure 4(d) shows the relation between hyperfine field and its probability. It is found that there are three magnetic field peak areas on both curves. The hyperfine field distribution indicates that the magnetic trivalent iron ions have several environment of coordination which causes different magnetic orderings through superexchange interaction of $Fe^{3+}$, O, and $Nb^{5+}$. Figure 4(e) gives the absorption spectra at 20 K. We can find from this figure that the magnitudes of the sextet are stronger than that at 80 K. This confirms that the superexchange interaction becomes larger at the lower temperature. In Fig. 4(f), it is indicated that the hyperfine fields at 20 K are all stronger than that at 80 K and the middle peak area transfers mostly to the right hand side peak area. The hyperfine field distribution at the lower temperature tends to be uniform. Further verifying of the property of the magnetic component is undergoing. The Mössbauer spectra confirm the magnetic order of PFN below $T_N$, but there is still more information that can be investigated through Mössbauer spectroscopy, such as the change in spin state, electronic density, and space structure.

In summary, we have grown $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) single crystals using the high temperature solution method. The dielectric constant shows a jump near its Néel temperature of ~143 K, which are indicative of coupling between the ferroelectric and magnetic orders in PFN. The $M$-$T$ curve shows an upward anomaly as the temperature continues to go down to $T_N$. This result agrees well with our former the Monte Carlo simulation results. The $M$-$H$ hysteresis confirms the existence of a weak magnetic order below $T_N$. The Mössbauer spectra at the temperature below $T_N$ support the existence of weak magnetic ordering. The coincidence of the experimental and simulation results confirms the existence of magnetoelectric coupling and corresponds to the previous theoretical prediction of the magnetoelectric-interaction induced additional transition in the magnetic and ferroelectric subsystems.

The authors thank the Natural Science Foundation of China (Grant Nos. 50332020, 10021001, 10374048) and National Key Projects for Basic Research of China (Grant No. 2002CB613303).

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