Additional transition induced by magnetoelectric interaction in ferroelectromagnet Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$

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Abstract: Besides the two phase transitions known in ferroelectromagnets, an additional transition was observed experimentally in Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ and the possible mechanism was explored. The magnetic moment shows that anomalous increases when the temperature goes down away from the Néel temperature of 20   30 K. The existence of the hysteresis verifies the weak ferromagnetic property. This additional phase transition is considered to originate from the magnetoelectric coupling between the ferroelectric and antiferromagnetic orders in this compound. From the Mössbauer parameter analysis, it is confirmed that the hybridization of the O 2p, Fe 3d and Nb 4d electron states makes the realization of magnetoelectric coupling possible.

Key words: Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$; ferroelectromagnet; magnetoelectric coupling; magnetoelectric interaction; orbital hybridization

I Introduction

Ferroelectromagnets are relatively new class of compounds with ferroelectric (antiferroelectric) and ferromagnetic (antiferromagnetic) orderings coexisting in a certain temperature range[1, 2]. The existence of the two ordered subsystems can result in the so-called magnetoelectric effect with interesting device potentials, where the dielectric properties of the ferroelectromagnets may be altered by the onset of the magnetic transition or by the application of a magnetic field, and vice versa.

Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ (PFN) has the complex perovskite structure and was discovered and synthesized at the end of the 1950s[3]. Its ferroelectric(FE) Curie temperature (T_C) is around 383 K and the antiferromagnetic(AFM) order begins at a Néel temperature of T_N=143 K[1, 4   14]. In order to avoid the contradicted results caused by the sample inhomogenity, PFN single crystals were grown with high temperature solution growth method and the study of the single crystal samples was concentrated on and powders obtained by grinding them. We have reported a jump in the dielectric constant and loss at the Néel point of PFN, which we assumed to be the result of magnetoelectric interaction[15]. We are interested in the accompanying phenomena and the underlying physics. We noticed in our experiment that besides the assured two phase transitions from paraelectric/ paramagnetic to ferroelectric-paramagnetic and then to ferroelectric-antiferromagnetic, an additional phase transition to a parasitic weak ferromagnetic when the temperature decrease and is away from the Néel point took place. This additional transition was predicted by previous theoretical analysis[1]. The Mössbauer spectra parameters of ^{57}Fe enriched PFN sample explained the results from the interaction of atomic nucleus and orbital electrons.
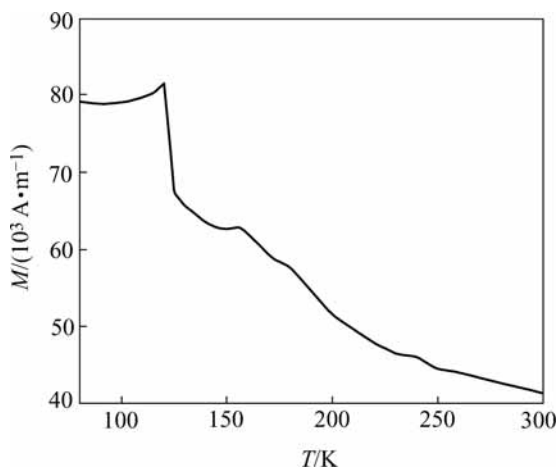
2 Experimental

The investigated samples were single crystals grown from high temperature crystal growth method described in previous papers[15, 16]. The crystals yielded were very dark red in color and showed a high degree of luster 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. The space group and the lattice parameters of the grown crystals are in agreement with the former electronic diffraction and neutron diffraction results. The Mössbauer spectra were measured with a conventional transmission Mössbauer spectrometer operating in the constant acceleration mode. Absorbers were prepared by finely ground 10% ^{57}Fe enriched PFN crystals, in each case weighed to give optimum signal-to-noise and mixed with carbon to randomize the orientations of the microcrystals. A source of up to 25mCi of ^{57}Co in Palladium matrix was used and the spectrometers were calibrated using α-iron at room temperature and all isomer shifts were quoted relative to the calibration. The Mössbauer parameters at 20 K were measured with an oxford flow cryostat.

3 Results and discussion

Temperature dependence of magnetic moment (M) of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ was obtained in the vicinity of its Néel temperature and the result is shown in Fig.1. It is noticed that the magnetization first shows an inflexion which corresponds to the reported antiferromagnetic phase transition point at about 143 K and then goes up as temperature(T) continues to decrease at a temperature of 20 30 K below T_N. BOKOV et al[3] found this behavior when they published the result of the magnetic property of PFN in 1962. They did not pay attention to the magnetoelectric coupling. They explained that the magnetic moments of some Fe^{3+} ions in the antiferroelectric regions are not ordered and the system can be considered paramagnetic in the first approximation. In our experiment, we assumed

that the increase of magnetic moment at lower temperature may be related to the ferroelectric ordering, since there exists a prediction that the magnetoelectric coupling induces a new transition in ferroelectromagnets[1].

We proved the assumption by measuring the magnetic moment under the applied magnetic field. A magnetic field from 558 A/m to 558 A/m at the temperature of 80 K was applied to the (100)-oriented single crystal PFN sample. Fig.2 shows the hysteresis under the above-mentioned magnetic field. It confirms the existence of weak magnetic property at this temperature.
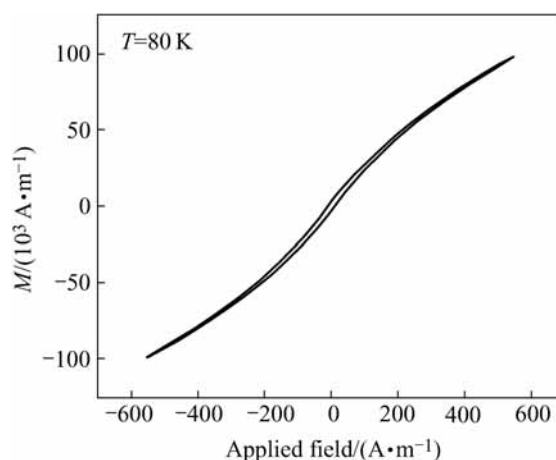
Fig.2 *M-H* hysteresis measured under magnetic field from 558 A/m to 558 A/m

In order to characterize this additional transition, we measured its specific heat from room temperature down to 4 K. The results are given in Fig.3 and it is found that within our measurement precision, no anomalies are found in the specific heat. There is no evidence showing first order phase transition in this temperature range.
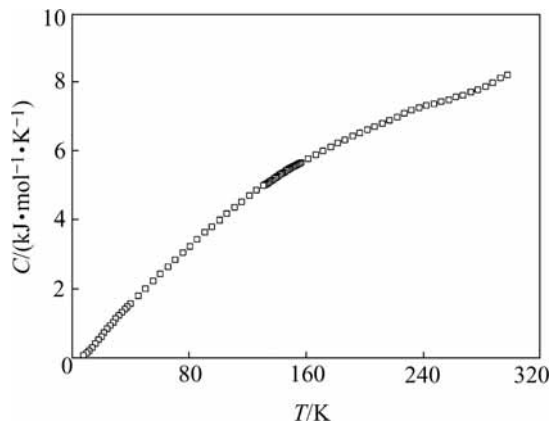

Fig.3 Specific heat of PFN from room temperature to 4 K

Fig.1 Temperature dependence of magnetic moment under field of 80 A/m

As a matter of fact, the perovskite structured materials with transitional metal ions in different

oxidation states at their *B* positions have been found showing several kinds of novel functions in recent years. It was widely investigated both theoretically and experimentally. It has been noticed that the *B* site cations are of great importance to the physical properties of the materials. Firstly, the distribution of the *B* site cations in the lattice strongly affects the physical properties of perovskite compound. One *B* cation interacts with another through oxygen bonds and different neighbors may cause different kinds of interaction with different intensities, which has direct impact on the physical property of the material. The order or disorder of the *B* cations forms three different types of structure, i.e. random, rock salt and layered structures. Secondly, the different sizes of *B* cations produce different structure distortions, which are often the source of different behaviors. Furthermore, the subtle differences of the *B* site ions' electronic and atomic structures bring forth the significant differences in materials physical properties. ANDERSON et al[17] obtained a relationship of *B* site ionic radii difference and their ionic charge difference from both calculation and experiments that if the *B* site ionic radii difference $\Delta R = R_B - R_{B'}$ (R_B and $R_{B'}$ are the *B* cations' radii) is larger than 0.2 Å and their ionic charge difference $\Delta Z = Z_B - Z_{B'}$ (Z_B and $Z_{B'}$ are the charges of the *B* cations) is smaller than 2, the double perovskite *B* site cations are randomly distributed. According to SHANNON radii data[18], Nb^{5+} with six coordinations has the ionic radius of 0.64 Å; the ionic radius of Fe^{3+} high spin with six coordinations is 0.645 Å. In PFN, two *B* site cations are Fe^{3+} and Nb^{5+}, which have the ionic radii difference of 0.005 Å and their ionic charge difference is 2. Both the ionic radii difference and ionic charge difference lie in the ANDERSON's random-distribution range. The *B* site cations in PFN were assumed to be randomly distributed both from Anderson's predication. Another calculation method by LIU et al[19] had a different formula on the ordering of double perovskite *B* site ions distribution also gave the result of random distribution of the *B* site cations. Former experimental data also confirmed the random distribution of the *B* site cations[15]. Random distribution of Fe and Nb cations can lead to local fluctuations in composition. Single crystal consists of large number of domains which might have different T_C value and resulting broad peaks in the temperature dependent dielectric constant at different frequencies. Fig.4 shows the ε—*T* relations of PFN at different frequencies near its Curie point. We do find there exist broad peaks at each frequency.

Therefore, we admit that the *B* site cations in PFN are randomly distributed and the magnetic Fe^{3+}
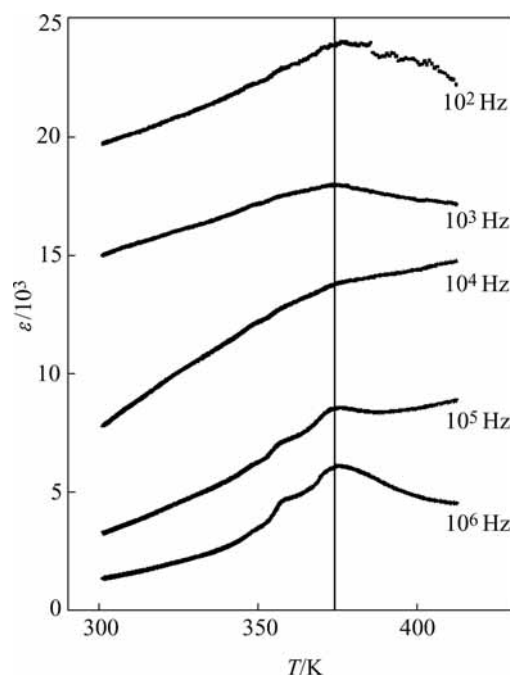
Fig.4 ε—*T* relations of PFN at different frequencies near its Curie point

ions are also randomly distributed. Now that the magnetic iron ions (Fe^{3+}) are also randomly distributed, there will be several kinds of indirect exchange interaction. For one Fe^{3+} ion in a perovskite structure, it lies in the center of an octahedron. The nearest neighbors of any iron ion are six oxygen anions (O^{2-}). The other coordinations connected with the six O^{2-} are possibly either Fe^{3+} or niobium ions (Nb^{5+}). The O^{2-} ions play a role of transferring the information of the next neighbors. Differences caused by the different next neighbors affect the electric field environment at the nucleus of Fe^{3+}. Thus, there will produce interaction between iron nucleus and the electric field environment, which will cause the electric gradient at the iron nucleus to be nonzero even though the octahedra does not have distinct distortion. The nonzero electric gradient at the nucleus of Fe^{3+} will no doubt produce the quadrupole splitting hyperfine interaction, which proved by the existence of the doublet of Mössbauer spectra[15].

The existence of iron ions at the *B* sites provides the opportunity to measure the hyperfine interaction energy by Mössbauer spectroscopy. Similar attempts have been made earlier[10—12]. We have obtained that below the Néel temperature, the Mössbauer sextet appears and both the intensity and the position of the sextet increase when temperature decreases[15], which confirms that the magnetic order appears below the Néel temperature. The obtained Mössbauer parameters

are listed in Table 1.

Table 1 Mössbauer parameters of $Pb(Fe_{1/2}Nb_{1/2})O_3$ at different temperatures

Temperature/ K	Isomer shift/ $(10^{-3} m·s^{-1})$	Magnetic field/T	Quadrupole splitting/ $(10^{-3} m·s^{-1})$	Line width/ $(10^{-3} m·s^{-1})$
300	0.40	0	0.42	0.26
80	0.50	31.8	0.03	0.26
20	0.50	42.7	0.06	0.26

Isomer shift is relative to metallic iron at room temperature; error of isomer shift, quadrupole splitting and line width are all at $0.02/(10^{-3} m·s^{-1})$.

In Table 1, it can be seen that there is a significant difference between above and below the Néel temperature. At 300K that is above the antiferromagnetic phase transition temperature of 143 K, the quadrupole splitting is $0.42/(10^{-3} m·s^{-1})$ and that of 80 K and 20 K are respectively $0.03/(10^{-3} m·s^{-1})$ and $0.06/(10^{-3} m·s^{-1})$. $Pb(Fe_{1/2}Nb_{1/2})O_3$ is confirmed to have the rhombohedral space group in the ferroelectric phase below 383 K. The distortion of structure from cubic is very small that the rhombohedral has the angel of 89.92° [3, 20]. The powder XRD result of crystal at different temperatures indicated that there is no distinct peak shift in the experimental temperature range[14]. Since no distinct structure differences below and above the Néel temperature are observed, the quadrupole splitting which comes from the interaction of nuclear moment with an asymmetric electronic charge distribution will benefit little from the structure change.

Because there is little crystal structure change in $Pb(Fe_{1/2}Nb_{1/2})O_3$ between both above and below its Néel temperature, the significant quadrupole splitting change may come from the influence of magnetic order to the orbital hybridization. At room temperature, PFN is in its paramagnetic phase and so the *B* site cations are all completely magnetic disordered. Therefore, the electrons in the valence band are strongly scattered. The charge transportation ability along Fe-O-Nb bond is restricted. Below the Néel temperature, the onset of the antiferromagnetic ordering brings forth the polarization of the electrons in the valence band. The spins of five 3d electrons of Fe^{3+} have the opposite direction with the spin of four 4d Nb^{5+} ions. Their hybridization through the 2p orbital of O^{2-} is strengthened. In this way, the number of 3d electrons of Fe^{3+} increases and this leads to the isomer shift value as shown in Table 1. Actually, From Table 1, it can be seen that the isomer shift value of $Pb(Fe_{1/2}Nb_{1/2})O_3$ at 80 K and 20 K are 0.50, which is larger than the typical isomer shift value of the trivalence high spin state iron ions. It indicates that the

valence of Fe ion is smaller than trivalence. This change of valence coming from the additional electrons appears on the 3d orbital of Fe ions. In this case, there are $5+\delta$ electrons on the 3d orbital of Fe. The additional δ comes from the hybridization with Nb ions. At the same time, the e_g orbital of iron ions in the octahedral crystal field receives extra electrons from the hybridization, which decrease the quadrupole splitting significantly.

The hybridization of the Nb 4d electron with O 2p has been confirmed in many cases. For example, DUAN et al[21] calculated the total and partial densities of states of $KNbO_3$ and found that the bottom of the conduction band is mostly derived from Nb 4d electron states, while the O 2p electrons dominate the top of the valence band, a mixture of Nb 4d and O 2p electron states in the valence band (-5 eV to 0 eV) is also significant. They considered that the nonlinear optical behavior of $KNbO_3$ comes from the hybridization of the O 2p and Nb 4d electron states. UHM et al[22] also found the strong hybridization between Fe 3d and O 2p orbitals in perovskite $R_{1/3}Sr_{2/3}FeO_3$ (R=Pr, Sm, and Nd), which also have Fe ions on the *B* site of perovskite structure.

From the above discussions and examples, we considered that there exist hybridization among the Fe 3d orbital, O 2p orbital and Nb 4d orbital in $Pb(Fe_{1/2}Nb_{1/2})O_3$. It is the electronic orbital hybridization that creates possibility for the existence of magnetic and ferroelectric coupling and the induced additional transition. If there is no hybridization, the electrons in both Fe^{3+} and Nb^{5+} are localized and the indirect exchange between $Fe^{3+}-O^{2-}-Fe^{3+}$ is also randomly distributed, and the exchange interaction on the conductive band cannot carry through.

4 Conclusions

An additional transition in $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) single crystals grown by high temperature solution method has been found. The *M-T* curve shows a transition to weak magnetic property below the Néel temperature. The *M-H* hysteresis confirms the existence of the weak magnetic property. This additional transition is considered to originate from the magnetoelectric interaction between the ferroelectric and antiferromagnetic orders in this compound. The hybridization of the O 2p, Fe 3d and Nb 4d electron states serves as the platform for the existence of magnetoelectric coupling and the additional transition to weak ferromagnetic property.

References

[1]   SMOLENSKII G A. Ferroelectromagnets[J]. Soviet Physics: Solid State, 1982, 29: 475   493.

[2]   SCHMID H. Introduction to the processing of MEIPIC   2[J]. Ferroelectrics, 1994, 1: 161   164.

[3]   BOKOV B A, MYLNIKOVAL I E, SMOLENSKII G A. Ferroelectric antiferromagnetics[J]. Sov Phys JETP, 1962, 15: 447   450.

[4]   ASTROV D N, AL'SHIN B I, ZORIN R V. Spontaneous magnetoelectric effect[J]. Sov Phys JETP, 1969, 28: 1123   116.

[5]   HOWES B, PELLIZZONE M, FISHER P. Characterization on some magnetic and magnetoelectric properties of ferroelectric $Pb(Fe_{1/2}Nb_{1/2})O_3$[J]. Ferroelectrics, 1984, 54: 217   320.

[6]   WATANABLE T, KOHN K. Magnetoelectric effect and low temperature transition of Pb(Fe0.5Nb0.5)O3 single crystals[J]. Phase Transitions, 1989, 15: 57   68.

[7]   RANDALL C A, BAHALLA A S. Nanostructural-property relations in complex lead perovskites[J]. Jpn J Appl Phys Part   , 1990, 29: 327   330.

[8]   YOKOSUKA M. Electrical and electromechanical properties of hot-pressed Pb(Fe1/2Nb1/2)O3 ferroelectric ceramics[J]. Jpn J Appl Phys Part   , 1993, 32: 1142   1145.

[9]   BONNY V, BONIN M, SCIAU P, SCHENK K J, CHAPUIS G. Phase transitions in disordered lead iron niobate: X-ray and synchrotron radiation diffraction experiments[J]. Solid State Commun, 1997, 102: 347   352.

[10] ANANTA S, THOMAS N W. A modified two-stage mixed oxide synthetic route to lead magnesium niobate and lead iron niobate[J]. J Euro Ceramic Soc, 1999, 19: 155   163.

[11] ANANTA S, THOMAS N W. Relationships between sintering conditions, microstructure and dielectric properties of lead iron niobate[J]. J Euro Ceramic Soc, 1999, 19: 1873   1881.

[12] ANANTA S, THOMAS N W. Fabrication of PMN and PFN ceramics by a two-stage sintering technique[J]. J Euro Ceramic Soc, 1999, 19: 2917   2930.

[13] BRUNSKILL I H, BOUTELLIER R, DEPMEIRER W, SCHMID H. High-temperature solution growth of Pb(Fe0.5Nb0.5)O3 and Pb(Mn0.5Nb0.5)O3 crystals[J]. J Cryst Growth, 1982, 56: 541   546.

[14] BRUNSKILL I H, TISSOT P, SCHMID H. Determination of the phase diagrams, PbO-Pb($Fe_{1/2}Nb_{1/2}$)O3 and Pb-Pb($Mn_{1/2}Nb_{1/2}$)O3 [J]. Thermochimica Acta, 1981, 49: 351   355.

[15] YANG Y, LIU J M, HUANG H B, ZOU W Q, BAO P, LIU Z G. Magnetoelectric coupling in ferroelectromagnet $Pb(Fe_{1/2}Nb_{1/2})O_3$ single crystals[J]. Phys Rev B, 2004, 70: 132101.

[16] YANG Y, HUANG H B, LIU J M, LIU Z G. Mossbauer studies on high temperature solution grown $Pb(Fe_{1/2}Nb_{1/2})O_3$ single crystals[J]. Ferroelectrics, 2002, 280: 75   82.

[17] ANDERSON M T, GREENWOOD K B, TAYLOR G A. B-cation arrangements in double perovskites[J]. Prog Solid State Chem, 1993, 22: 197   223.

[18] SHANNON R D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides[J]. Acta Crystallographica, 1976, A32: 751   767.

[19] LIU R, XUAN Y, JIA Y Q. A simple method for judging order to disorder in A(BIBI')O3 perovskite compounds[J]. J Solid State Chem, 1997, 134: 420   422.

[20] IVANOV S A, TELLGREN R, RUNDLOF H, THOMAS N W, ANANTA S. Investigation of the structure of the relaxor ferroelectric $Pb(Fe_{1/2}Nb_{1/2})O_3$ by neutron powder diffraction[J]. J Phys: Condens Matter, 2000, 12: 2393   2397.

[21] DUAN C G, MEI W N, LIU J J, HARDY J R. First-principle study on the optical properties of KNBO3[J]. J Phys: Condens Matter, 2001, 13: 8189   8192.

[22] UHM Y R, LEE S W, PARK K T, TOMIOKA Y, TOKURA Y, KIM C S. Charge ordering and mossbauer studies of single crystal R1/3Sr2/3FeO3(R=Pr, Sm, and Nb)[J]. J Appl Phys, 2000, 87: 4873   4876.

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