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Signature of weak ferromagnetism by electron paramagnetic resonance in the ferroelectromagnet $Pb(Fe_{1/2}Nb_{1/2})O_3$

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Abstract

An electron paramagnetic resonance (EPR) study on the ferroelectromagnet $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) powder is presented. The EPR spectra show one single broad line in the 300–90 K temperature range. The onset of the para-antiferromagnetic (AF) transition has been determined from the temperature dependence for three main parameters deduced from the EPR spectra: the g-factor, the peak-to-peak linewidth (ΔH_{pp}) and the integrated intensity (I_{EPR}). Below 147 K, a weak ferromagnetic signal (WFS) is observed. This WFS is attributed to canting of Fe^{+3} ion sublattices in the AF matrix, and can be associated with the magnetoelectric effect in this material.

Keywords: Electron paramagnetic resonance; Weak ferromagnetism; Magnetic transitions

1. Introduction

Lead iron niobate $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) was discovered by Smolenskii in 1958 [1]; it is a relaxor ferroelectric with perovskite structure (ABO_3). PFN undergoes a ferroelectric phase transition at about 380 K and an antiferromagnetic (AF) phase transition at about $T_N \sim 145$ K [1–3]. As a result, it becomes a ferroelectromagnet below Néel temperature (T_N).

Evidence of coupling between the ferroelectric and magnetic orders has been reported [2,3]. This coupling can result in the so-called magnetoelectric effect, where the dielectric (magnetic) properties of the ferroelectromagnet may be altered by the onset of the magnetic (electric) transition or by the application of a magnetic (electric) field.

Electron paramagnetic resonance (EPR) is a powerful technique to investigate the nature of magnetic phases in materials at different temperatures [4,5]. To our knowledge, however, studies of the PFN compound with EPR technique are scarce.

In this paper, we study the changes in EPR line shape of PFN powders; these changes in the peak-to-peak linewidth (ΔH_{pp}), the g-factor and the integrated intensity (I_{EPR}) as a function of temperature are investigated to understand the nature of spin-dynamics in the system.

2. Samples preparation and experimental details

The samples used in this study were prepared by the columbite precursor method. In this method, stoichiometric Fe_2O_3 (99% purity) and Nb_2O_5 (99.99% purity) were mixed and calcined in air at 1200 °C for 2 h, obtaining powders of the $FeNbO_4$ precursor. PbO (98% purity) was added and mixed. The calcination temperature was 800 °C for 2 h. Sintering was carried out at 1050 °C for 2 h in a $PbZrO_3$ atmosphere, obtaining powders of PFN. The

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X-ray diffraction powder analysis showed a single PFN phase.

EPR measurements were performed with a JEOL JES-RES 3X spectrometer operating at X-band (8.8–9.8 GHz) with 100 kHz of modulation on the applied DC magnetic field (H_{DC}). H_{DC} could be varied from 0 to 8000 G. The EPR spectra were recorded while cooling the sample in the temperature range 300–90 K. The spectrometer was modified by connecting X and Y input voltmeters that in turn are connected to a PC enabling digital data acquisition [6].

3. Results and discussion

Fig. 1 shows EPR spectra (dP/dH vs. magnetic field) recorded in the temperature range 300–90 K for PFN powders. We observe a single broad symmetric Lorentzian line in the entire temperature range, due to the spin of Fe^{+3} ions. When the temperature is decreased below 147 K a weak absorption line has been clearly observed, see inset of Fig. 1.

Fig. 2(a) shows the temperature dependence of ΔH_{pp} for PFN powders. The linewidth increases when the temperature is lowered from 300 to 147 K, this gradual increase is found to be common to various AF materials [5]. The further increase in ΔH_{pp} can be due to build-up of magnetic correlations preceding the transition to the long-range AF ordering at T_N.

A peak is observed at 147 K, $\Delta H_{pp(max)} = 1876.2$ G, and then decreases approximately 50% in only 10 K; to our knowledge this is quite unusual, and it is most unusually observed in AF materials. A common feature of the EPR signals in AF materials is that approaching the T_N, ΔH_{pp} gradually increases and close to T_N it sharply diverges [7]. But a peak in ΔH_{pp} and a subsequent decrease has been observed by Cheung et al. [8] and Janossy et al. [9] in some antiferromagnets below T_N, though such a decrease in the linewidth remains unexplained to date.

As temperature decreases down to 95 K, ΔH_{pp} increases again, but now with a much smaller rate of growth.

Fig. 2(b) shows that the integrated intensity (I_{EPR}) increases continuously with the decrease in temperature, having a maximum at ~183 K ($I_{EPR(max)}$), followed by a rapid decrease until 137 K; then, for $T < 137$ K a slow decrease is observed.

Fig. 2(c) shows the temperature dependence of the g-factor. Our experiments give a g-value bigger than the one for a free electron (= 2.0023) in the entire temperature range. The g-factor shows a weak decrease in the range 297–183 K and then the g-factor increases when the temperature continues to decrease, reaching a maximum at 147 K ($g_{max} =$ 2.0608). It is remarkable that the g-factor increases significantly from 183 K ($g = 2.0167$) to 147 K. This sharp increase can be due to magnetic fluctuations, i.e., fluctuations in the establishment of the long-range order that precedes the transition to the AF order at T_N. Similarly to the ΔH_{pp} behavior, the g-factor shows a peak at 147 K. For $T \leqslant 137$ K the g-factor increases to $g = 2.0319$ for 95 K.

We turn now to the weak absorption line observed at 137 K, inset of Fig. 1. Only a ferromagnetic impurity in the form of a second phase, with a Curie point close to 137 K, and in a significant concentration could explain this

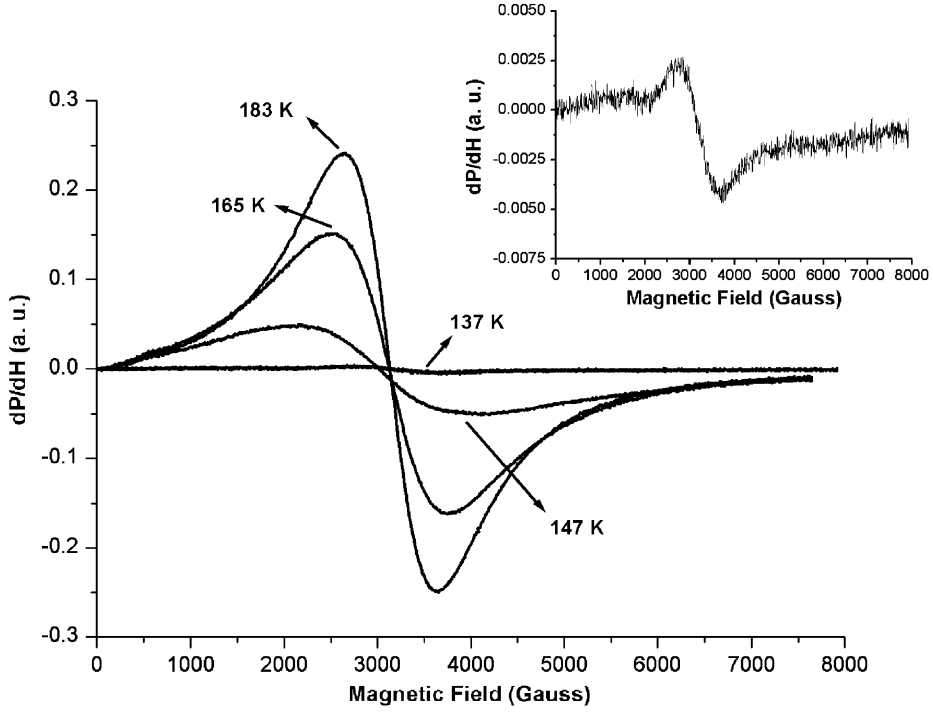

Fig. 1. EPR spectra of $Pb(Fe_{1/2}Nb_{1/2})O_3$ for selected temperatures; the inset shows an extended scale of EPR spectrum at 137 K.

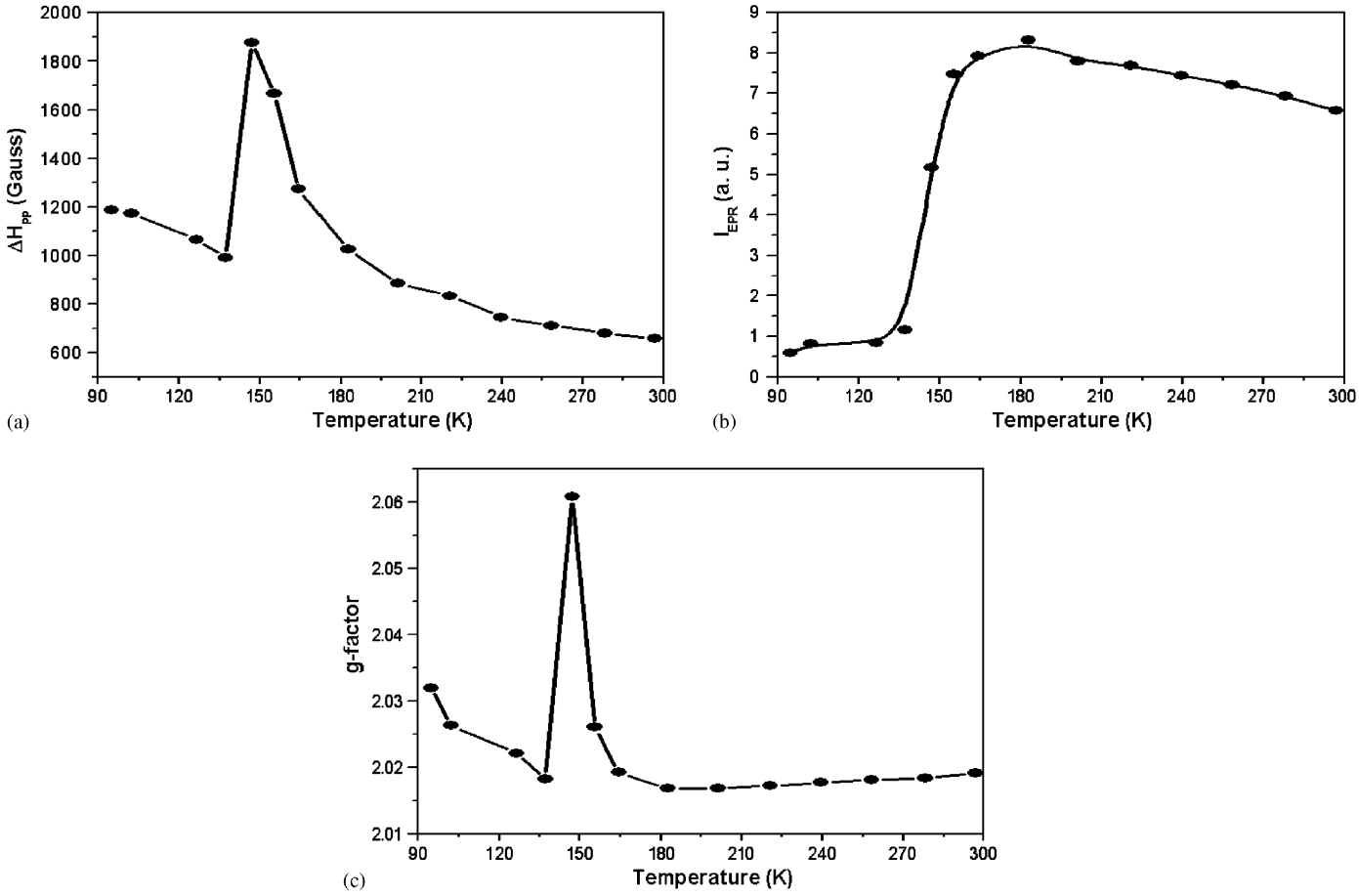

Fig. 2. Temperature dependence of (a) the peak-to-peak linewidth —ΔH_{pp}, (b) the integral intensity —I_{EPR} and (c) the g-factor of PFN. Curves connecting points are only guides for the eye.

absorption line, which is remote. A more sound explanation is as follows: PFN is AF at low temperature; normally AF resonance is observed only at very high frequencies [10], around 100 GHz, or more, far beyond the resonance frequencies used in this experiment, hence no absorption line should be observed at X-band. The presence of a broad absorption line in the AF state can be interpreted in terms of a resulting magnetic moment, i.e., canting between the antiparallel sublattices. Two nondegenerate resonance modes appear, one at very high frequencies (not observed in our experiments at X-band) while the other one occurs at ordinary microwave frequencies, and can be considered similar to a ferromagnetic mode [11].

The increase of both ΔH_{pp} and g-factor in the region 137–95 K are additional indications that a weak ferromagnetic behavior is present in the PFN [12,13].

Recently [14,15] a theoretical study on magnetoelectric coupling in ferroelectromagnetic systems has shown that the coupling has a significant effect on the magnetic variables. The system is assumed as a weak ferromagnet in the direction of ferroelectric polarization. Our EPR measurements are in good agreement with this interpretation.

4. Conclusions

The changes in the parameters ΔH_{pp}, I_{EPR} and g-factor in the EPR spectra for PFN at $T_N \sim 145$ K, are interpreted as a para-antiferromagnetic transition. A residual resonant signal was observed below T_N in the ferroelectromagnet PFN, which is attributed to canting of Fe^{+3} ion sublattices in the AF matrix. The weak ferromagnetic moment, predicted by theoretical models, can also be associated with the magnetoelectric effect.

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