Phase Transition with Suppression of Magnetism in BiFeO₃ at High Pressure

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The magnetic behavior of a Bi⁵⁷FeO₃ powdered sample was studied at high pressures by the method of nuclear forward scattering (NFS) of synchrotron radiation. The NFS spectra from ⁵⁷Fe nuclei were recorded at room temperature under high pressures up to 61.4 GPa, which were created in a diamond anvil cell. In the pressure interval 0 < P < 47 GPa, the magnetic hyperfine field $H^{Fe}$ at the ⁵⁷Fe nuclei increased reaching a value of ~52.5 T at 30 GPa, and then it slightly decreased to ~49.6 T at $P = 47$ GPa. As the pressure was increased further, the field $H^{Fe}$ abruptly dropped to zero testifying a transition from the antiferromagnetic to a nonmagnetic state (magnetic collapse). In the pressure interval 47 < P < 61.4 GPa, the value of $H^{Fe}$ remained zero. The field $H^{Fe}$ recovered to the low-pressure values during decompression.

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INTRODUCTION

The bismuth ferrite BiFeO₃ belongs to a class of ferromagnetolectric materials (multiferroics) that have both a spontaneous electrical polarization and a spontaneous magnetization [1, 2]. Due to the record high antiferromagnetic Néel temperature ($T_N = 643$ K) and the ferroelectric’s Curie temperature ($T_C = 1083$ K) between multiferroics [3, 4], the BiFeO₃ crystal is very attractive from both fundamental and applied aspects of science. It has the rhombohedrally distorted perovskite structure with space group $R̅3c$, and the unit cell parameters in the hexagonal representation are $a = 5.58$ and $c = 13.9$ Å (or $a_c = 3.96$ Å and $a_r = 0.69^\circ$ in the rhombohedral setting) [5, 6].

In a local atomic scale, BiFeO₃ has the $G$-type antiferromagnetic structure, in which each iron ion has six iron neighbors with opposite spin directions [7]. However, the antiferromagnetic order is not homogeneous and a complex spatially modulated cycloid spin structure is present with a long wavelength of about 620 Å, which is incommensurate with the crystal lattice [8–11].

As was shown by Zvezdin and Pyatakov [1], the crystal symmetry of BiFeO₃ allows the existence of a linear magneto electric effect, spontaneous magnetization, and toroidal moment. However, due to the spatially modulated spin structure, these effects average to zero over the crystal volume and they can be observed only when the spatially modulated structure is destroyed [1]. Several mechanisms can suppress the modulated structure, and one of them is a strong applied magnetic field. The measurements in pulsed and static magnetic fields revealed an appearance of all three effects at the critical field of about 180–200 kOe when the modulated spin structure is transformed to a uniform state [12–14]. The substitution of rare-earth ions for bismuth ions in BiFeO₃ can also destroy (suppress) the spin modulation, and the magnetoelectric effect appears [15].

In the present study, external high pressures were applied to a BiFeO₃ crystal to modify its magnetic properties. The method of resonant nuclear forward scattering (NFS) of synchrotron radiation at ⁵⁷Fe nuclei was used to investigate the parameters of the magnetic hyperfine interactions.

EXPERIMENT

High-quality BiFeO₃ powder samples in which iron was enriched with ⁵⁷Fe isotope to 98% were prepared. For the high-pressure studies, a plate of BiFeO₃ was made by precompression of the initial powder between diamond anvils. The thickness of the plate was about 5–10 microns. In an optical microscope, the plate had a transparent deep red color. To perform the NFS studies at high pressures, a Bi⁵⁷FeO₃ plate with the dimensions

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~90 × 90 μm² was placed into a high-pressure cell with diamond anvils. The diameter of the working surface of the diamonds in the cell was about 300 μm, and the diameter of the hole in the rhenium gasket where the sample was placed was about 100 μm. To create a quasi-hydrostatic pressure, the working volume of the cell was filled with the polyethyl-siloxane liquid PES-5. The pressure value was determined by the standard ruby fluorescence technique. Several ruby chips with dimensions of about 1 μm were placed into the cell along with the sample. They were placed at different distances from the center of the working volume to evaluate the pressure gradient in the chamber.

The NFS experiments were performed at the 16-ID-D beamline at the Advanced Photon Source at Argonne National Laboratory. The time spectra of the NFS from the $^{57}$Fe nuclei (which may be considered as the time-domain Mössbauer spectra [16]) were recorded at room temperature in the pressure range up to $P = 61.4$ GPa during compression and decompression runs. A high-resolution monochromator with a 2.2 meV bandwidth was tuned to the nuclear resonance energy of 14.4125 keV of the Mössbauer transition in the $^{57}$Fe [17]. The polarization vector of the gamma rays was horizontal and parallel to the sample plane.

Figure 1 presents the scattered radiation intensity versus the time that elapsed after the nuclear excitation by an incident pulse. The measurements for different pressure values were performed in the 24 bunches mode of operation. These bunches were evenly distributed with 154 ns separation between them. The damped decay of the nuclear excitation was modulated in time by quantum and dynamic beats. The quantum beats were caused by the interference of the scattered radiation components with different frequencies as a result of the nuclear level splitting into sublevels due to the hyperfine interaction. The period of the quantum beats is inversely proportional to the hyperfine splitting and, in the case under study, to the magnetic field $H^{\text{Fe}}$ at the iron nuclei. The dynamic beats are caused by multiple scattering processes and are determined by the sample thickness. A detailed description of the method can be found in review [18].

Under pressures below 47 GPa, the main feature of the spectra is pronounced quantum beats. The spectra indicate that, over the whole pressure range from ambient pressure to 47 GPa, the period of beats slightly decreases indicating an increase of the magnetic hyperfine field $H^{\text{Fe}}$ under pressure. When the pressure increases above 47 GPa, the high frequency quantum beats disappear signaling the disappearance of the magnetic field $H^{\text{Fe}}$ at the $^{57}$Fe nuclei (Fig. 1). At decompression from the maximum pressure of 61.4 GPa to below 47 GPa, high frequency quantum beats appeared again indicating the reversibility of the magnetic transition. At ambient pressure, the value of the field $H^{\text{Fe}}$ calculated from the NFS spectra is 49.3 T, which is consistent with that obtained from previous Mössbauer [19, 20] and NMR [21, 10] experiments.

We also recorded the $^{57}$Fe-Mössbauer absorption spectrum of our Bi$^{57}$FeO₃ sample in transmission geometry (Fig. 2). At room temperature, the six-line spectrum has slightly broadened resonance lines with a noticeable asymmetry of the first and sixth lines. As it was suggested by Zalesskii et al. [21] from analysis of the NMR data, such features of the spectrum may appear due to a distribution of values of the magnetic hyperfine fields at iron nuclei. In the spatially modulated cycloid spin structure of the BiFeO₃ crystal, the magnetic moments of Fe ions turn in the plane perpendicular to the hexagonal plane along the propagation

![Fig. 1. Evolution of NFS time spectra in the Bi$^{57}$FeO₃ powder sample with pressure increase (a) and pressure decrease (b) runs. The spectra are recorded at room temperature without applying an external magnetic field.](image1)

![Fig. 2. The $^{57}$Fe-Mössbauer absorption spectrum of the Bi$^{57}$FeO₃ powder sample recorded at room temperature in transmission geometry. The symbols are the experimental points. The resulting fit to two subspectra is shown by a solid line.](image2)