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# INVESTIGATION OF CRYSTAL AND MAGNETIC STRUCTURE OF $\text{BiFeO}_3$ USING NEUTRON DIFFRACTION

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Polycrystalline material obtained from the ground single crystal of  $\text{BiFeO}_3$  reported as not having the superstructure, shows the superstructure reflections in neutron diffraction pattern. The determined magnetic moment of antiferromagnetically ordered  $\text{Fe}^{3+}$  ions is  $\mu_{\text{Fe}} = (3.70 \pm 0.03)\mu_{\text{B}}$  at 293 K.

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## 1. Introduction

The structure and magnetic ordering in bismuth ferrite have been investigated for many years (see e.g. [1, 2] and references therein) because this material is known to have two types of long range order: G-type antiferromagnetic ordering of  $\text{Fe}^{3+}$  ions below  $T_N = 643$  K [3] and ferroelectric ordering, with a high Curie temperature of about 1103 K (see e.g. [1] and references therein). The magnetic structure of  $\text{BiFeO}_3$  is, in a first approximation, antiferromagnetic with G-type magnetic ordering, but the G-type antiferromagnetic structure has been modified by subjecting it to a long range modulation such as it is manifested in a cycloidal spiral of the length of  $\lambda = 620$  Å, with the  $[110]_H$  spiral direction and  $(\bar{1}10)_H$  spin rotation plane [2] which is unusual for perovskites. The modulation changes with temperature, but it remains visible nearly up the Néel temperature [4]. The higher order satellites of the magnetic reflections were not observed in the diffraction pattern of  $\text{BiFeO}_3$  [2, 4], therefore the spin space modulation is of the harmonic type.

Diffraction patterns obtained by using two different high resolution SR diffractometers, one BNL at Brookhaven and second at the DESY, Hamburg synchrotron sources, proved that the crystal structure of  $\text{BiFeO}_3$  does not show any modulation [5].

Recently very precise ferroelectric and ferroelastic monodomain single crystal X-ray diffraction studies of pure  $\text{BiFeO}_3$  were performed [6]. The structure parameters obtained in Ref. [6] are in agreement with those determined by neutron powder diffraction studies [1]; they confirmed e.g. that in  $\text{BiFeO}_3$  an atomic superstructure appears. It is known that single crystals of  $\text{BiFeO}_3$  exist which do not show superstructure reflections in their diffraction patterns [6, 7]. These crystals are prepared at 1128 K from a  $\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3$  flux containing a small amount of NaCl as additive.

In order to determine the crystal and magnetic structure of these crystals we performed neutron diffraction studies.

## 2. Experimental

The polycrystalline sample of  $\text{BiFeO}_3$ , obtained from a ground single crystal [7], was placed in a thin walled vanadium cylinder of diameter 5 mm and height 50 mm in a helium atmosphere. In order to apply the appropriate absorption correction to the data [8], the transmission of neutrons of the wavelength of  $\lambda = 1.704 \text{ \AA}$  used in the experiment, was measured.

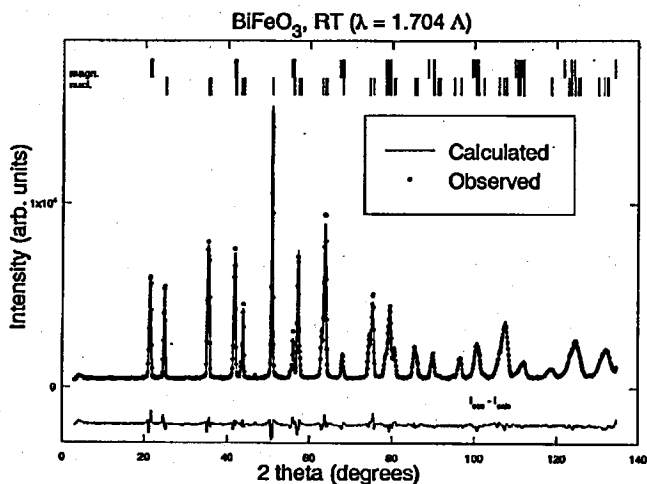


Fig. 1. Observed, calculated and difference neutron diffraction patterns obtained from the ground single crystal of  $\text{BiFeO}_3$  using DMC diffractometer at Saphir reactor with  $\lambda = 1.704 \text{ \AA}$ . Higher bars indicate positions of magnetic reflections, and lower nuclear ones. The small peak at  $2\theta = 46.9^\circ$  is due to the vanadium container (110) reflection.

TABLE  
Results of refinement of crystal and magnetic structure of BiFeO<sub>3</sub> data at RT by using the space group *R3c* and hexagonal unit cell.

Parameter	This work	From Refs. [1, 6]
$a$ [Å]	5.5775(5)	5.57874(16)
$c$ [Å]	13.8616(8)	13.8688(3)
$B$ [Å <sup>2</sup> ]	0.56(3)	0.56(9)
$z_{\text{Bi}}$	0.0	0.0
$z_{\text{Fe}}$	0.2208(2)	0.22077(8)
$x_{\text{O}}$	0.4473(5)	0.4428(11)
$y_{\text{O}}$	0.0198(6)	0.0187(10)
$z_{\text{O}}$	0.9525(3)	0.9520(4)
$\mu_{\text{Fe}}^{\text{r}}$ [ $\mu_{\text{B}}$ ]	3.70(3)	4.00(4)
$R_{\text{p}}$ [%]	11.3	
$R_{\text{wp}}$ [%]	11.8	
$R_{\text{exp}}$ [%]	4.98	
$R_{\text{Bragg}}$ [%]	4.49	
$R_{\text{magnetic}}$ [%]	8.70	

In order to determine the crystal structure of BiFeO<sub>3</sub> we performed a neutron diffraction experiment at RT. The data were collected by using the multidetector powder diffractometer DMC [9] in the high-resolution mode ( $\lambda = 1.7037$  Å), placed at the Saphir reactor in Würenlingen, for scattering angles  $2\theta$  from 3.0° to 134.9° with a step of  $\Delta 2\theta = 0.1^\circ$ .

In Fig. 1 we present experimental data corrected for absorption and the calculated profile obtained using FullProf program [10] and the Kubel and Schmieid [6] model of the crystal structure and magnetic moment ordering from Fischer et al. [1]. In the hexagonal unit cell of BiFeO<sub>3</sub>, corresponding to the space group *R3c*, atoms are located in the following positions: Bi, Fe in 6a:(0,0, $z$ ) and O in 18b:( $x, y, z$ ). In the calculation one overall Debye–Waller factor was assumed. The final results of these calculations are summarized in Table. Figures given in parentheses show the uncertainty of the refined values. One can see that the agreement between experiment and calculated profile is satisfactory ( $R_{\text{wp}} = 11.8\%$ ).

### 3. Summary

One can conclude that neutron diffraction maxima for BiFeO<sub>3</sub> appear as sharp lines. Therefore the polycrystalline material obtained from the ground single crystals of BiFeO<sub>3</sub>, used in these studies, consists of sufficiently large crystalline blocks which do not cause a noticeable line broadening. Our sample is a single phase material. Single crystals obtained by Rakov, Murashov, Bush and Venetsev [7]