NEUTRON-DIFFRACTION DETECTION OF MAGNETIC ORDERING IN THE FERROELECTRIC BiFeO$_{3}$

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Abstract

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NEUTRON-DIFFRACTION DETECTION OF MAGNETIC ORDERING IN THE FERROELECTRIC $BiFeO_3$

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From the work carried out in our laboratory ($^{1-3}$), it follows that $BiFeO_3$, with a perovskite-type structure, possesses ferroelectric properties. It has been established by X-ray diffraction ($^{1-5}$) that the structure of $BiFeO_3$ is distorted and belongs to the rhombohedral system with an angle α differing little from 90° ($\alpha = 89°24'$).

On the other hand, it has been reliably established by neutron diffraction that a number of compounds of the perovskite type ABO_3, where $B = Fe, Mn$ (see, for example, (^{6})), possess ferro- and antiferromagnetic properties. Suggestions have been made concerning the possible presence in $BiFeO_3$ as well of magnetic ordering of ferro- or antiferromagnetic character (^{1}). In addition, several papers have been published ($^{7-9}$) in which questions of a possible combination of special dielectric and magnetic properties are considered. All this provided the basis for undertaking a neutron-diffraction investigation of $BiFeO_3$, with the aim of establishing the presence of magnetic ordering in this compound and studying it.

The $BiFeO_3$ sample was obtained by sintering stoichiometric amounts of Bi_2O_3 and Fe_2O_3 at a temperature of 800°.* To achieve greater equilibrium, the samples were subjected to repeated grinding and firing at the same temperature. X-ray diffraction analysis showed that, within the sensitivity limits of the method, the $BiFeO_3$ sample contained no impurities of the starting components.

Neutron diffraction patterns of $BiFeO_3$ at room and elevated temperatures were obtained on the neutron-diffraction apparatus of the L. Ya. Karpov Physicochemical Institute (^{10}), at the IRT reactor of the I. V. Kurchatov Institute of Atomic Energy. A pressed cylindrical $BiFeO_3$ specimen 12 mm in diameter was used. For investigations at elevated temperatures, a special attachment was constructed, making it possible to obtain neutron diffraction patterns up to temperatures of 800°. The temperature was monitored by a chromel–alumel thermocouple.

The neutron diffraction pattern of $BiFeO_3$ obtained at room temperature is shown in Fig. 1A. Most of the maxima of coherent scattering were indexed

Fig. 1. Neutronograms of BiFeO3 at room temperature (A) and 600° (B). The indices of reflections h′, k′, l′, referred to the pseudocubic cell with a′ = 2a = 7.926 Å, are given. The theoretically calculated integral intensity of the reflections is represented by diagram lines. Magnetic reflections are marked by the letter M.

Figure 1: Fig. 1. Neutronograms of BiFeO3 at room temperature (A) and 600° (B). The indices of reflections h′, k′, l′, referred to the pseudocubic cell with a′ = 2a = 7.926 Å, are given. The theoretically calculated integral intensity of the reflections is represented by diagram lines. Magnetic reflections are marked by the letter M.

on the basis of a pseudocubic unit cell with $a = 3.963$ Å ($\lambda = 1.050$ Å). The rhombohedral distortion of the unit cell did not manifest itself in any noticeable way in the investigated range of angles θ. However, in addition to the maxima of nuclear coherent scattering, several additional peaks were also present in the neutron diffraction pattern. The magnetic nature of these additional maxima was established by studying the dependence of their intensity on temperature. Thus, in the neutron diffraction pattern of $BiFeO_3$ obtained at a sample temperature > 400°, only maxima of nuclear coherent scattering are present (Fig. 1B).

Magnetic coherent scattering is expressed in the presence of 4 maxima, some of which are superposed on nuclear coherent scattering and for this reason are difficult to evaluate quantitatively. An attempt to index them–

* The synthesis of the samples was carried out by S. A. Fedulov and B. G. Nikolaev. The authors take this opportunity to express their gratitude to them.

···led to the necessity of doubling the period of the pseudocubic elementary cell,

$$a_{\text{magn}} = 2a_{\text{nucl}} = 2 \cdot 3.963 = 7.926 \text{ Å}.$$

In this case the indices of the magnetic reflections will be 111, 311, 331 and $511 + 333$.

The extinction law for nuclear scattering, under the assumption of this large elementary cell, corresponds simultaneously to body- and face-centered cells: the neutronograms contain reflections with $h' = 2n$,

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$k' = 2n$ and $l' = 2n$ (where division in half of h', k', l' gives h, k, l of the ordinary "single" perovskite cell without any extinctions). In connection with the presence

Fig. 2. Dependence of the intensity of magnetic reflection 111 on temperature

Figure 2: Fig. 2. Dependence of the intensity of magnetic reflection 111 on temperature

of antiferromagnetic ordering (a reversal of half of the signs, corresponding to different orientations of the spins, in the expression for determining the structure amplitude), the extinction law for magnetic scattering changes to the inverse one: reflections are present only with

$$h' = 2n + 1, \qquad k' = 2n + 1, \qquad l' = 2n + 1.$$

It follows from this that the magnetic structure of $BiFeO_3$ belongs to type G (according to the nomenclature proposed in ([11]); see also ([16])); this is a simple type of mag-

netic structure, in which each magnetic moment is surrounded by six antiparallel directed moments.

Proceeding from the known magnetic structure and the experimental intensity of the magnetic maximum 111, the effective spin quantum number S was calculated. The conversion of the reflection intensities to an absolute scale was carried out by calculating the intensities of the nuclear-scattering maxima above the Néel point, starting from an ideal undistorted structure, with subsequent correction to room temperature using the nuclear maximum 220. The theoretical intensity values thus obtained were compared with the experimental ones, from which the reduction coefficient was found. The form factor for Fe^{3+} was used ([12]). The value of S determined in this way proved to be 1.98, which is substantially lower than the value $S = 5/2$, characteristic of Fe^{3+}.

The reason for this discrepancy becomes clear when one considers the dependence of the magnetic order on temperature. In Fig. 2 the intensity of the magnetic reflection 111 is shown as a function of temperature. In principle, the usual curve of the Brillouin-curve type should have been obtained, falling to the abscissa at the Néel point. However, the "tail" of the Brillouin curve degenerates in our case into a straight line; the intensity of the magnetic reflection falls to the background value (the Néel point) at a temperature of 380°. It also follows from the curve obtained that at room temperature the magnetic ordering does not reach saturation. This latter circumstance is the reason why the effective spin quantum number ($S = 1.98$) determined from the data obtained is underestimated.

Fig. 2. Dependence of the intensity of magnetic reflection 111 on temperature.

In addition, a certain error was introduced by the fact that, in converting the intensities of the magnetic reflections to an absolute scale by the total intensity of all nuclear reflections, the displacements of atoms from ideal positions in the structure were not taken into account. That these displacements are significant is indicated by the fact that the calculated intensity of all reflections (shown in Fig. 1A in the form of diagram lines, the height of which is proportional to the integrated intensity) does not agree very well with the experimental one. In particular, the experimental value of the 400 reflection (200 in the ordinary perovskite cell), for which $F_n(400) = f_{Fe} + f_{Bi} + 3f_O$, is much smaller than the theoretical value. This is easily explained, since any displacement of O atoms from the (400) planes should lead to a decrease in $F_n(400)$. The O atoms are subject to displacement to a greater extent—this is seen from the fact that the X-ray interference intensities calculated in (^{4}) (which depend primarily on the heavy Bi and Fe atoms) led to a very good value of R, whereas the intensities of the neutron interferences (which depend primarily on the O atoms) differ substantially from the theoretical ones. The character and values of the atomic displacements are being refined.

The investigation carried out is direct, immediate proof of the existence of a new class of chemical compounds combining special magnetic and electrical properties.

In conclusion we would like to note one circumstance concerning the interaction of magnetic and electric fields in crystals. In $BiFeO_3$ we have a case in which the periodicity of the electric field is half the periodicity of the magnetic one. If one assumes that the electric field is pertur-

changes the motion of the electron in the atom, this should entail a certain change in the direction of the magnetic moment. Such an action on neighboring antiparallel magnetic moments should have the opposite direction, as a result of which weak ferromagnetism should appear in such a lattice, due to the noncollinearity of the magnetic moments. It is possible that this phenomenon should occur in all cases where the periods of the magnetic and electric fields are different.

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