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1982 J. Phys. C: Solid State Phys. 15 4835

(http://iopscience.iop.org/0022-3719/15/23/020)

J. Phys. C: Solid State Phys., **15** (1982) 4835–4846. Printed in Great Britain

Spiral magnetic ordering in bismuth ferrite

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Received 18 January 1982

Abstract. New information on the magnetic ordering of the iron ions in bismuth ferrite $BiFeO_3$ was obtained by a study with a high-resolution time-of-flight neutron diffractometer. The observed splitting of magnetic diffraction maxima could be interpreted in terms of a magnetic cycloidal spiral with a long period of 620 ± 20 Å, which is unusual for perovskites.

1. Introduction

The structure and magnetic ordering in bismuth ferrite have been investigated for many years (see e.g. Jacobson and Fender 1975, Fischer *et al* 1980, Freeman and Schmid 1975 and references therein) because this material is known to have two types of long-range order: antiferromagnetic ordering below $T_N = 370\,°C$ (Kiselev *et al* 1963) and ferroelectric ordering (Teague *et al* 1970), with a high Curie temperature about 820–850 °C (Roginskaya *et al* 1966).

$BiFeO_3$ is known to have a rhombohedrally distorted perovskite structure assigned to the space group R3*c*. The atomic positions in the unit cell were determined by x-ray and neutron diffraction (Michel *et al* 1969, Moreau *et al* 1971). The space group R3*c* allows both for the ferroelectric atomic displacement and weak ferromagnetism below T_N (Smolenskii and Yudin 1965, Yudin 1966). From the first neutron diffraction measurements by Kiselev *et al* (1963) an antiferromagnetic G-type spin configuration, where each Fe^{3+} is surrounded by six antiparallel nearest neighbours, could be assigned. The resolution, however, was not sufficient to obtain information on the exact spin orientation. In order to accomplish that with a powder sample, as only such exist for $BiFeO_3$, one needs the intensities of rhombohedrally split lines. Such an experiment was performed in 1964 at the Dubna pulsed reactor and the magnetic moment was reported to be perpendicular to the trigonal axis (Sosnowska *et al* 1966). More work on the magnetic structure was recently performed by Szymański (1980), who did very careful profile analysis on the unresolved magnetic peaks from a triple-axis instrument.

The purpose of the present paper was to investigate the magnetic structure with the high-resolution time-of-flight diffractometer (Steichele and Arnold 1973). This technique offers the optimal resolution at large interplanar distances (Buras *et al* 1965) and is the best tool to analyse the splitting of magnetic diffraction lines.

Preliminary results of the present studies were presented at the XIIth International Congress of Crystallography in Ottawa (Sosnowska *et al* 1982a).

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2. Experimental

2.1. Sample preparation

For these measurements two samples of $BiFeO_3$ of different origin were used. Sample no 1 of about 15 g was prepared in 1964 by a standard ceramic technique and was used in the Dubna TOF experiments (Sosnowska *et al* 1966) and in the double-axis measurements of Fischer *et al* (1980). Sample no 2 of about 50 g was prepared using a modification of the procedure recommended by Achenbach *et al* (1967). The reactants† weighed in a $2Bi_2O_3 \cdot Fe_2O_3$ ratio were mixed and then pressed into pellets which were fired in a streaming argon atmosphere for about 15 h at 750 °C in a quartz tube. The sintered pellets were finely ground, leached several times with concentrated HNO_3 to remove excess Bi_2O_3, washed with distilled water, and finally dried at 150 °C. X-ray Guinier photographs taken with both samples showed sharp $BiFeO_3$ lines with traces of Fe_2O_3 for sample no 2 and small admixtures of Bi_2O_3 and $Bi_2Fe_4O_9$ for sample no 1 (in both cases less than 3%).

The substance was filled in a sample-holder of $10 \times 2.5\ cm^2$ cross section (which corresponds to the dimensions of the neutron beam) and 1 cm thickness. Only the sample material and the two quartz windows (each 0.6 mm thick) of the container could be seen by the neutrons.

2.2. Measurements

The measurements were done with the high resolution TOF diffractometer at the FRM research reactor in Garching, which has a thermal flux of $10^{13}\ n\ cm^{-2}\ s^{-1}$. The lay-out and some details of the instrument were reported at the Petten Neutron Diffraction Conference (Steichele and Arnold 1975). The high resolution is based on the use of a 145 m long neutron guide-tube as a flight path and a back-scattering arrangement of two groups of ^3He counters (4 bar) collecting neutrons at scattering angles $174° \leq 2\theta \leq 178°$. The instrumental resolution is $\Delta d/d = 2 \times 10^{-3}$ at $d_{hkl} = 0.6$ Å (measured) (Sosnowska and Steichele 1980) and 7×10^{-4} at $d_{hkl} = 4.5$ Å (calculated) (Peterlin-Neumaier *et al* 1982). The first chopper was running at 8333 rpm or 10000 rpm, giving a pulse width of 129 μs or 100 μs. By the speed of a second chopper one can select the wavelength spread (from 0.1 to 3 Å) of the primary spectrum and by a third chopper one can avoid frame overlap irrespective of the wavelength spread of the neutrons on the flight-path. In the present experiment the speeds of the second and third chopper were reduced by a factor of 2 and 4 compared with the first chopper, thus giving a wavelength spread of about 0.4 Å. By choosing proper phases between the three choppers the mean wavelengths for three different runs were selected to be 9.2, 4.8 and 3.6 Å, where magnetic contributions to the diffraction patterns were expected in the back-scattering configuration.

In experiments where one is not interested in a complete powder pattern, the multi-chopper operation allows a better neutron economy, because with the narrower spectrum the pulse repetition rate can be made higher than in a standard TOF arrangement, where one uses the whole spectrum of the source; in the present experiment the corresponding gain factor was about 7–8.

For the measurement of the primary spectrum the neutrons from two sections of $2.2 \times 1\ cm^2$ at the upper and lower edge of the guide-tube were registered as function of time by two counters identical to those in the back-scattering positions. A typical result

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† Merck product no 1862, 99% Bi_2O_3, 'reinst' and product no 3924, 99% Fe_2O_3 'Zur Analyse'.

of such a monitor spectrum taken simultaneously with the scattered spectrum around 9.2 Å is shown in figure 1.

3. Results and interpretation

The diffraction pattern as measured in the 9.2 Å region is shown in figure 1(*a*) to illustrate the process of data reduction. After subtraction of a wavelength-independent background the data were divided by the primary spectrum (shown in figure 1(*b*)) and by

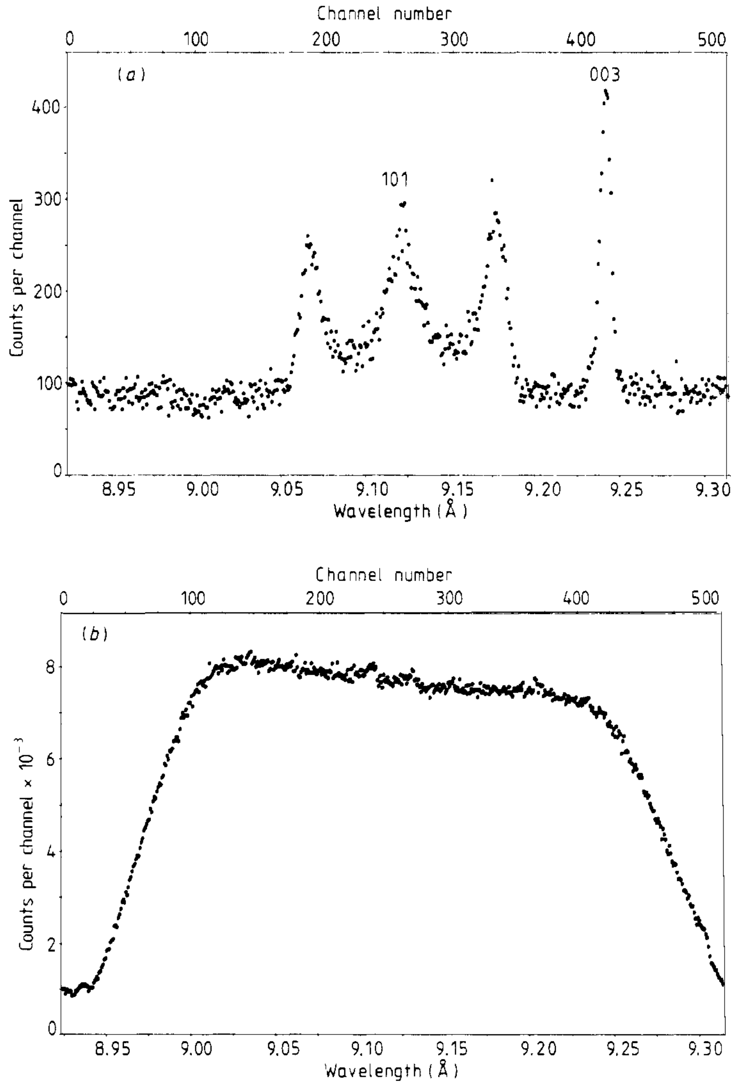

Figure 1. (*a*) TOF spectrum of neutrons scattered from $BiFeO_3$ and measured in backscattering position 1 m away from the sample. Raw data from sample no 2.

(*b*) TOF spectrum of incoming neutrons measured at the sample position. Due to different flight-paths for spectra in (*a*) and (*b*) neutrons of the same wavelength are registered in different channels.

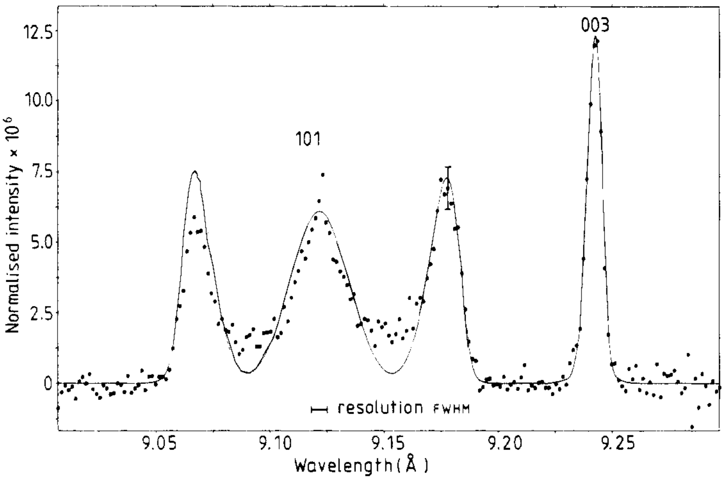

Figure 2. Normalised TOF spectrum from $BiFeO_3$ powder sample no 2 at about 9.2 Å (full circles). The full curve represents the spectrum calculated for the proposed model of spin configuration.

λ^4, the characteristic factor for white radiation diffraction methods (Buras 1963). The result is shown in figure 2. The intensities of the diffraction maxima are then directly proportional to jF_{hkl}^2 where j is the multiplicity factor and F_{hkl} the structure factor of the (hkl) reflection. All other spectra shown in figures 3–5 were also treated in this way.

The spectrum in figure 2 was measured for about 115 h and here one should take into account that the 9 Å region is far beyond the maximum (at about 1.7 Å) of the guide-tube spectrum and that the 9 Å neutrons make about 50 reflections along the entire guide-tube. The λ^4 enhancement of the TOF method yet makes it possible to measure spectra in this wavelength region. A similar run with sample no 1, taken also in about 100 h is shown in figure 3. The linewidth (FWHM) at 9.2 Å to be expected from the spectrometer resolution is drawn in figures 2 and 3. The spectra taken with sample no 2 at about 4.7 Å and 3.6 Å are shown in figures 4 and 5, respectively. The former was

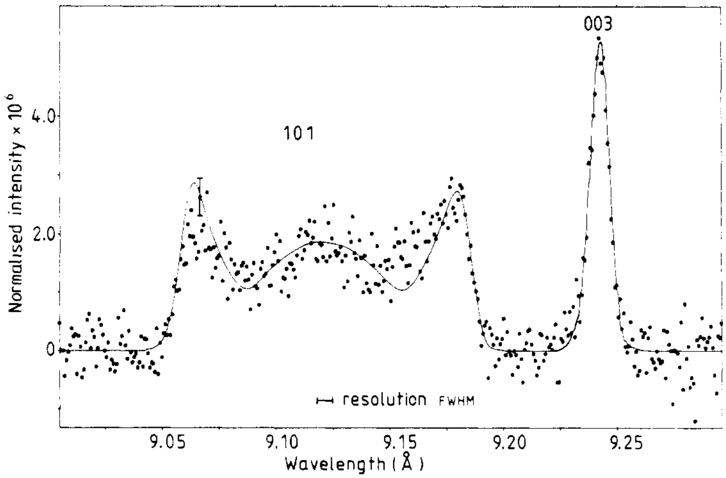

Figure 3. Same as figure 2, but for sample no 1.

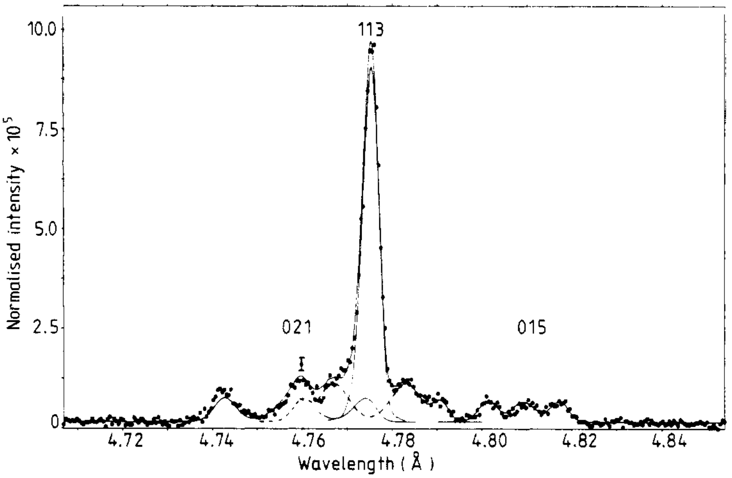

Figure 4. Normalised TOF spectrum from $BiFeO_3$ powder sample no 2 at about 4.76 Å.

measured for 50 h and the latter for 117 h in order to overcome the smaller magnetic form factor of the iron ion at the momentum transfer. All these spectra were collected at room temperature.

In the following we use hexagonal notation for $BiFeO_3$ with $a = 5.779$ Å and $c = 13.867$ Å (Bucci *et al* 1972). In this notation for the antiferromagnetic G-type ordering as hitherto reported for $BiFeO_3$, magnetic reflections can occur only for $-h + k + l = 3n$ with l odd.

At the position of the (003) reflection we observe a sharp peak whose width is about 30% larger than the instrumental resolution. At all other wavelengths, where one expects purely magnetic scattering (101, 105, 107, 205 reflections) we observe no sharp lines, but broadened patterns, the centres of which, however, coincide with the positions calculated from the lattice constants. At the expected (113) and (211) peak positions where nuclear and magnetic scattering are superposed, the magnetic contributions can be seen at the base of the nuclear Bragg reflections.

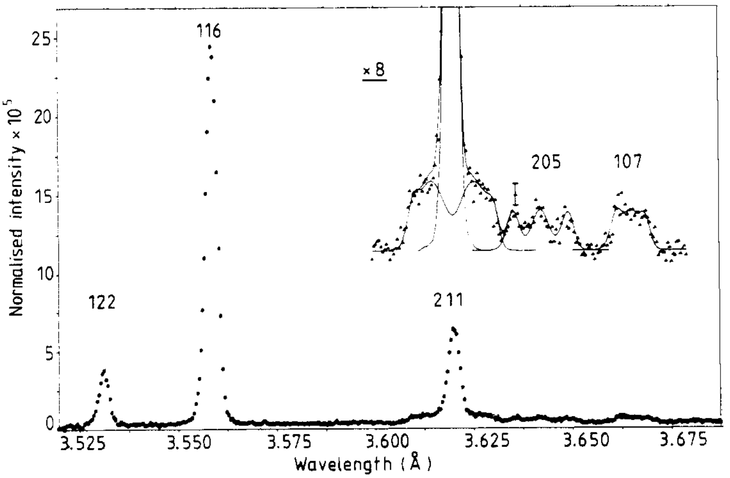

Figure 5. Normalised TOF spectrum from $BiFeO_3$ powder sample no 2 at about 3.6 Å.

This kind of pattern was observed with both samples. The similarities and differences are best discerned in the 9.2 Å region because of the very high resolution there. In both cases the positions of the peaks, the span of the triplet, the intensity ratio $I(003)/I(101)$, and the slopes of the steep outer flanks agree within the experimental error. The inner flanks and the central peak are broadened for both samples, however this inner structure is much more smeared out for sample no 1.

Two additional runs were performed on sample no 2 in the 9.2 Å region at 77 K and 463 K. Within the poorer statistics the intensities of the outer lines of the (101) triplet seem to be more equal than at RT, but otherwise no drastic changes in the pattern were observed.

No contribution to these spectra can be expected from other phases found in the samples and higher-order contaminations such as in double-axis spectrometry do not exist by principle in the TOF method. Moreover the purely magnetic origin of these broadened patterns was established by their disappearance at temperatures above the Néel point in runs at 4.7 Å and 9.2 Å with sample no 1.

From the above we conclude that the hitherto accepted G-type antiferromagnetic structure is not a complete and satisfactory description of the spin structure in $BiFeO_3$. However, if the G-structure is modified somewhat by subjecting it to a long-range modulation such as is manifested in a spiral structure one can obtain agreement with the experiment. Analysis of the experimental data was therefore attempted on the basis of a helical spin configuraton.

Such a situation gives rise to satellite peaks associated in general with reciprocal lattice vectors

$$\boldsymbol{\tau}^{\pm}_{hkl} = \boldsymbol{\tau}_{hkl} \pm \boldsymbol{q} \tag{1}$$

where $|\boldsymbol{\tau}_{hkl}| = 1/d_{hkl}$ and $\boldsymbol{q}$ is the spiral propagation vector.

The existence of only one diffraction peak at the (003) position indicates that $\boldsymbol{q}$ must be perpendicular to the c^* axis, i.e. the propagation vector must lie in the hexagonal base plane. In that case $|\boldsymbol{\tau}^{+}_{003}| = |\boldsymbol{\tau}^{-}_{003}| \cong |\boldsymbol{\tau}_{003}|$ for $|\boldsymbol{q}| \ll |\boldsymbol{\tau}_{003}|$ and only one sharp line at the (003) position can be seen in the powder pattern. From the observed (003) linewidth and the period of the spiral determined below we can conclude, that the angle of the spiral propagation vector $\boldsymbol{q}$ out of the (a^*b^*) plane must be smaller than ±2°.

At none of the other purely magnetic peak positions do we observe a sharp central line as could be expected from a well ordered system of collinear spin components as realised for instance in a conical spiral system. Thus we conclude that a simple spiral exists in $BiFeO_3$ and all the magnetic scattering is found in the satellites.

The length and direction of the $\boldsymbol{q}$-vector can be found from analysing the width and the shape of the magnetic scattering patterns. In figure 6 we show a section of the reciprocal lattice around the (101) point. The full circles represent a pair of satellites due to the magnetic helix, the open circles are related to the first two by three-fold symmetry. The six satellites in the powder pattern can arise either from different $\boldsymbol{q}$-vectors or the same $\boldsymbol{q}$-vector in crystallites or domains having another orientation or form a triple-$\boldsymbol{q}$ arrangement. This cannot be decided from a powder pattern.

The $\boldsymbol{q}$-vector which is described by its length and its orientation ψ relative to the a^* axis, can be expressed with the help of satellite indices δ' and δ'' as

$$\boldsymbol{q} = \delta'\boldsymbol{a}^* + \delta''\boldsymbol{b}^* \tag{2}$$

where $\delta'|\boldsymbol{a}^*|$ and $\delta''|\boldsymbol{b}^*|$ are the components of $\boldsymbol{q}$ along $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$.

Depending on the angle ψ between $\boldsymbol{q}$ and $\boldsymbol{a}^*$ one obtains for a powder geometrical

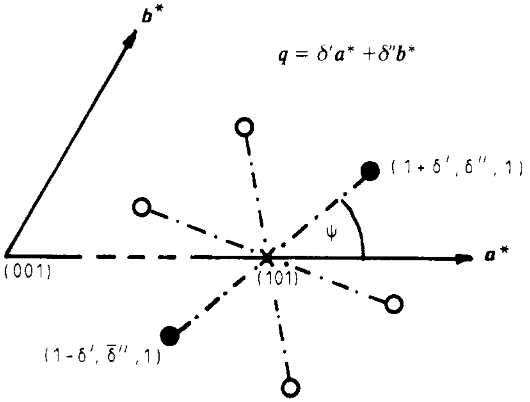

Figure 6. Possible configuration of satellites around the (101) reciprocal lattice point in $BiFeO_3$.

loci of $|\tau^{\pm}|$ = const having 3, 4 or 6 different values. For all ($h0l$) reflections we observe only three peaks, therefore we conclude that ψ must be 30°, i.e. $\delta' = \delta'' = \delta$. This implies that for (hhl) reflections we should observe four and for (hkl) reflections six peaks which is consistent with experiment. The magnetic reflections can then be indexed as shown in table 1 and good agreement between measured and calculated peak positions is obtained with $\delta = 0.0045$.

As has already been pointed out, all of the observed magnetic satellite peaks are broadened. A slight rotation of the whole satellite system out of the [110] direction would obviously broaden the satellite lines as seen at the (101) peak position, but not as much as observed. In addition no angle ψ would yield the asymmetric shape of the (101) peak.

An explanation of this pattern can however be found, when we extend our model in the following way.

We assume, that the satellites are not discrete points, but have some finite dimension in the a^*b^* plane due to imperfections of the sample. One can think of imperfections of the following types.

(*a*) A non-homogenous spiral period would appear as a smearing of the satellite points along the q-direction. Such an effect, however, cannot reproduce the broad central line and the steep outer flanks in the (101) pattern. Even an asymmetric distribution of the period lengths would not explain the whole pattern.

(*b*) When we give up the assumption of a perfect phase relation between neighbouring spirals over large regions of crystallites we obtain a smearing of the satellite points perpendicular to q. A finite coherence length perpendicular to the spiral direction would reproduce the broad central line but not the asymmetric side peaks in the (101) pattern.

(*c*) The best agreement with the spectra can be achieved if the spiral axis directon is allowed to vary in the basal plane. Then the satellite point is smeared out to an arc around the (hkl) points. This circular smearing of satellites gives rise in the (101) triplet to steep outer and 'flat' inner flanks of the side peaks and a central peak wider than the side peaks. The width of this distribution determines the overall broadening. In this model the major difference between sample no 1 and sample no 2 would be a wider distribution of spiral directions in sample no 1.

We finally can derive information on the type of spiral from the intensities of the

Table 1. Magnetic satellites of $BiFeO_3$ and calculated and observed line position (Å).

$(hkl)_0$	hkl	λ_{obs}	λ_{calc}	$(hkl)_0$	hkl	λ_{obs}	λ_{calc}
003	$2\delta, -\delta, 3$	9.242	9.245	107	$1-2\delta, \delta, 7$	3.669	3.669
	$\delta, \delta, 3$				$1-\delta, -\delta, 7$		
	$-\delta, 2\delta, 3$				$1-\delta, 2\delta, 7$	3.666	3.666
	$-2\delta, \delta, 3$				$1+\delta, -2\delta, 7$		
	$-\delta, -\delta, 3$				$1+2\delta, -\delta, 7$	3.662	3.662
	$\delta, -2\delta, 3$				$1+\delta, \delta, 7$		
101	$1-2\delta, \delta, 1$	9.176	9.179	205	$2-2\delta, \delta, 5$	3.649	3.650
	$1-\delta, \delta, 1$				$2-\delta, -\delta, 5$		
	$1-\delta, 2\delta, 1$	9.125	9.124		$2-\delta, 2\delta, 5$	3.642	3.643
	$1+\delta, -2\delta, 1$				$2+\delta, -2\delta, 5$		
	$1+2\delta, -\delta, 1$	9.067	9.069		$2+2\delta, -\delta, 5$	3.636	3.636
	$1+\delta, \delta, 1$				$2+\delta, \delta, 5$		
105	$1-2\delta, \delta, 5$	4.818	4.819	211	$2-\delta, 1-\delta, 1$		3.639
	$1-\delta, \delta, 5$				$2-2\delta, 1+\delta, 1$		3.627
	$1-\delta, 2\delta, 5$	4.810	4.811		$2+\delta, 1-2\delta, 1$		3.624
	$1+\delta, -2\delta, 5$				211	3.619	3.620
	$1+2\delta, -\delta, 5$	4.801	4.802		$2-\delta, 1+2\delta, 1$		3.617
	$1+\delta, \delta, 5$				$2+2\delta, 1-\delta, 1$		3.614
					$2+\delta, 1+\delta, 1$		3.610
113 +201	$1-\delta, 1-\delta, 3$	4.791	4.791	116	116	3.559	3.559
	$1+\delta, 1-2\delta, 3$	4.784	4.784				
	$1-2\delta, 1+\delta, 3$						
	113	4.776	4.776				
	$2-2\delta, \delta, 1$	4.774	4.774				
	$2-\delta, -\delta, 1$	4.768	4.768				
	$1-\delta, 1+2\delta, 3$						
	$1+2\delta, 1-\delta, 3$						
	$1+\delta, 1+\delta, 3$						
	$2-\delta, 2\delta, 1$	4.760	4.759				
	$2+\delta, -2\delta, 1$						
	$2+2\delta, -\delta, 1$	4.741	4.743				
	$2+\delta, \delta, 1$						

magnetic diffraction peaks. Quite generally, the intensity of the satellite peaks depends on the angle φ between the diffraction plane and the spin rotation plane (see e.g. Bacon 1975) and is given by:

$$I_{sat} \propto (1 + \cos^2 \varphi). \tag{3}$$

If we represent these two planes by their normal vectors $\boldsymbol{\tau}$ and $\boldsymbol{n}$ in the reciprocal space and describe their orientation by angles (ξ, η) and (α, γ) as shown in figure 7, the intensity of a satellite can be written as:

$$I_{sat} \propto 1 + \sin^2 \eta \cos^2(\xi - \alpha) + \cos^2 \gamma[\cos^2 \eta - \sin^2 \eta \cos^2(\xi - \alpha)] + \tfrac{1}{2} \sin 2\eta \sin 2\gamma \cos(\xi - \alpha). \tag{4}$$

The sum over all satellite intensities of equivalent reflections depends only on the angles η and γ:

$$\sum_{\xi} I_{sat} \propto j[1 + \tfrac{1}{2}\sin^2 \eta + \cos^2 \gamma(\cos^2 \eta - \tfrac{1}{2} \sin^2 \eta)] \tag{5}$$

where j is the multiplicity factor.

From the intensity ratio of the (003) peak and the (101) triplet one can derive the angle γ between the spin-plane vector and the c^* axis. In the experiment we found $I_{003}/I_{101} = 0.25 \pm 0.01$ for sample no 1 and $I_{003}/I_{101} = 0.236 \pm 0.006$ for sample no 2; for $\gamma = 90°$ the theoretical intensity ratio is 0.23. This means that the spin rotation plane is perpendicular to the hexagonal base plane.

Then for $\gamma = 90°$ equation (4) simplifies and from the intensity ratio R within the (101) triplet one can derive the angle α giving the orientation of the normal to the spin rotation plane with respect to the a^* axis:

$$R = \frac{I_{\text{central}}(101)}{\Sigma_{\xi} I_{\text{side}}(101)} = \frac{1 + \sin^2\eta\cos^2(120 - \alpha)}{2 + \sin^2\eta[\cos^2(240 - \alpha) + \cos^2\alpha]} \tag{6}$$

where the ξ of equivalent reflections were properly chosen according to their contribution to the different peaks in the (101) triplet.

For the (101) reflection $\eta = 70.8°$ and the maximum for this ratio becomes $R = 0.774$ for $\alpha = -60°$. From our experiment we find $R = 0.79 \pm 0.08$ and thus $\alpha = -60°$. Then $\boldsymbol{n}$ is perpendicular to the $\boldsymbol{q}$ direction, which means that $\boldsymbol{q}$ lies in the spin rotation plane. This is a cycloidal spiral. [110] is the spiral direction and (110) is the spin rotation plane. Figure 8 shows schematically the antiferromagnetic spiral ordering in $BiFeO_3$.

From different details in the experiment we could thus derive individual features of the spin structure: the length of the spiral is derived from the span of the (101) triplet, the orientation of $\boldsymbol{q}$ from the shape of the magnetic peaks and the type of spiral from the intensities of (003) and (101) peaks. To check the model as a whole and to find out optimum parameters we calculated spectra based on that model and compared them with the experimental data. For the distribution of $\boldsymbol{q}$ directions in the basal plane we assumed a Gaussian. The atomic positions were taken from Fischer *et al* (1980), the magnetic form factors from Watson and Freeman (1961), and the magnetic moment we took to be 4 μ_B. The best agreement, which is shown by the full curves in figures 2–5 we

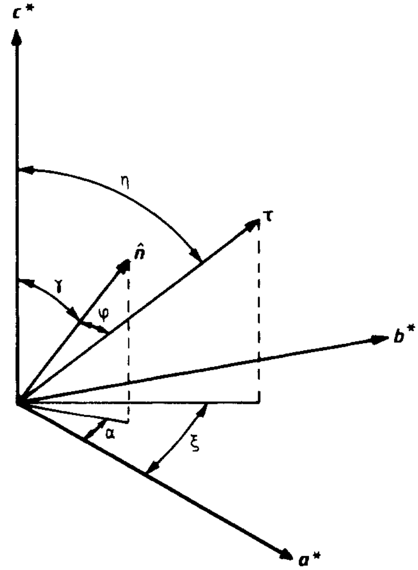

Figure 7. Definition of orientation angles of the normal to the spin-rotation plane $\boldsymbol{n}$ and the normal to the scattering plane $\boldsymbol{\tau}$ in the reciprocal space.

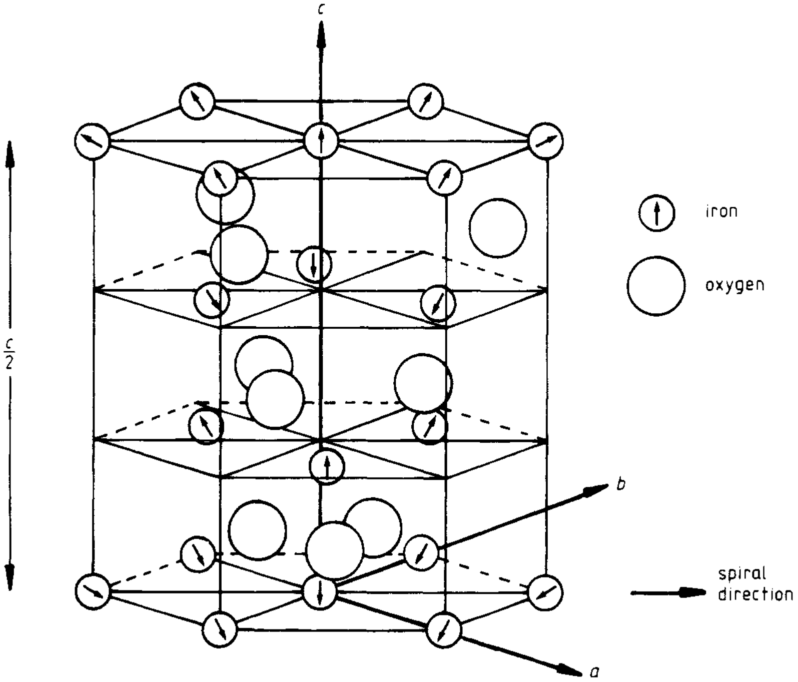

Figure 8. Portion of the $BiFeO_3$ lattice with only iron and oxygen ions shown. The arrows indicate the Fe^{3+} moment direction of our model. The spiral period is reduced for illustration purpose.

got for a period length of 620 Å and a halfwidth of the spiral direction distribution $\Delta\psi = \pm 30°$ for sample no 1 and $\Delta\psi = \pm 13°$ for sample no 2. This means that sample no 1 has a nearly isotropic distribution of spiral directions in the *ab* plane. From figures 4 and 5 one can realise that good agreement is found for both nuclear and magnetic intensities. This model, however, cannot account for the intensity difference between the left and right side peaks of the (101) triplet.

4. Discussion and summary

Due to the high resolution of the present neutron diffraction experiment it became evident that the magnetic structure in $BiFeO_3$ is more complicated than a collinear arrangement as reported up to now. A conjecture on such a situation was made by Blauuw and van der Woude (1973) in the discussion of a Mössbauer experiment. They needed a non-uniform angle between the electric field gradient and the magnetic field in order to explain the quadrupole splitting they observed. A magnetic spiral as evidenced now produces such a variation.

The period of the spiral and the orientation of the spin rotation plane are well determined and are certainly characteristic for $BiFeO_3$. However, from our data we can conclude that the spiral direction is not a uniform parameter in both samples. This direction may vary around the [110] direction by ±13° in sample no 2 and ±30° in sample no 1. The average direction is the same for both samples, the variation a property of the individual sample and it may depend on imperfections in the lattice or some other feature in the history of the sample. No large differences in the distortions due to internal stresses in the two samples may exist, because the nuclear peaks have the same width for both samples and are about what one expects from the instrument's resolution. As we have no details about the preparation of sample no 1, no statement can be made on possible influences of the sample preparation. Recently a study of the static susceptibility and the thermal magnetic remanence was reported by Banerjee *et al* (1981). Cooling through the Néel temperature in a magnetic field as low as 20 Oe gave a significant change in the susceptibility, which however was also dependent on the sample preparation. Thus some details of the magnetic structure seem to depend on delicate internal features of the sample.

On the other hand, the spiral itself seems to be quite stable to external interactions. It was observed at 78 K, 300 K and 463 K and the period hardly changed over the temperature range. Only some slight change in the asymmetry of the (101) lines was observed, which may indicate some slight modification of the spin structure.

Quite recently measurements with a double axis spectrometer were performed at the ILL high-flux reactor (Sosnowska *et al* 1982b). As the (003) and (101) lines were not resolved, one could observe only that neither the total intensity nor the intensity ratio of the two lines (by the asymmetry of the peak) changed in a magnetic field between 6 kG and 14 kG and under pressure of 4 kbar applied at 80 K.

In no other orthoferrite has a spiral with such an extremely long period, as otherwise found only in metals, been observed up to now. The orthorhombic system $NdFeO_3$ and $PrFeO_3$, investigated with high-resolution TOF spectrometry just showed the ordinary orthorhombic splitting (Sosnowska and Steichele 1981).

The interactions responsible for such a helimagnetic structure in $BiFeO_3$ must certainly be complex. Whether the coexistence of ferroelectricity and antiferromagnetism has a direct influence on the spiral configuration is not known.

The agreement between the observed and calculated spectra is fairly good, but not yet perfect. Certainly some answers to still open questions and a completion of the present picture could be obtained if a single crystal of $BiFeO_3$ large enough for a neutron experiment could be grown.

Acknowledgments

We wish to thank all those with whom we could discuss our results during the Conferences in Argonne and Ottawa last summer. We acknowledge helpful discussions with Professors W Gläser and A Steyerl and could learn a great deal on magnetic spirals from Dr N Achiwa. Mrs Ibarra of ZTTF helped us with apparatus at the beginning of the sample preparation. One of us (IS) is indebted to Professor Gläser for the invitation to perform this work as a guest of the Physics Department of the Technical University Munich.

This work was supported by the Bundesministerium für Forschung und Technologie under project number FV 03-41E-14P.

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