the hydrogens of the ammonium ion have moreover been found to be compatible with the lattice energies of NH_4Cl, NH_4Br and NH_4I, which have the alternative CsCl structure (Goodliffe, Jenkins, Martin & Waddington, 1971).

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References

ADRIAN, H. W. W. & FEIL, D. (1969). *Acta Cryst.* A**25**, 438–444.
BENTLEY, J. J. & STEWART, R. F. (1976). *Acta Cryst.* A**32**, 910–914.
BIANCHI, R., CREMASCHI, P., MOROSI, G. & SIMONETTA, M. (1977). *Chem. Phys.* **22**, 267–271.
CLEMENTI, E. (1965). *Tables of Atomic Functions*. Suppl. to *IBM J. Res. Dev.* **9**, 2.
COPPENS, P. (1972). *Acta Cryst.* B**28**, 1638–1640.
COPPENS, P., CSONKA, L. & WILLOUGHBY, T. V. (1970). *Science*, **167**, 1126–1128.
COULSON, C. A. & THOMAS, M. W. (1971). *Acta Cryst.* B**27**, 1354–1359.
CROMER, D. T., LARSON, A. C. & STEWART, R. F. (1976). *J. Chem. Phys.* **65**, 336–349.
DAWSON, B. (1975). *Adv. Struct. Res. Diffr. Methods*, **6**, 97–111.
GOODLIFFE, A. L., JENKINS, H. D. B., MARTIN, S. V. & WADDINGTON, T. C. (1971). *Mol. Phys.* **21**, 761–767.
GROENEWEGEN, P. P. M. & FEIL, D. (1969). *Acta Cryst.* A**25**, 444–450.
HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* B**31**, 162–172.
HEHRE, W. J., DITCHFIELD, R., STEWART, R. F. & POPLE, J. A. (1970). *J. Chem. Phys.* **52**, 2769–2773.
International Tables for X-ray Crystallography (1959). Vol. II, p. 241. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.
IWATA, M. (1977). *Acta Cryst.* B**33**, 59–69.
KRAUSS, M. (1963). *J. Chem. Phys.* **38**, 564–565.
KUESTER, J. L. & MIZE, J. H. (1973). *Optimization Techniques with Fortran*. New York: McGraw-Hill.
MACKENZIE, J. K. (1974). *Acta Cryst.* A**30**, 607–616.
PRICE, P. F., VARGHESE, J. N. & MASLEN, E. N. (1978). *Acta Cryst.* A**34**, 203–216.
STEVENS, E. D., RYS, J. & COPPENS, P. (1977). *Acta Cryst.* A**33**, 333–338.
STEWART, R. F. (1973). *J. Chem. Phys.* **58**, 1668–1676.
STEWART, R. F. DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
ZACHARIASEN, W. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1978). A**34**, 662–666

The Magnetic Structure of $Bi_2Fe_4O_9$ – Analysis of Neutron Diffraction Measurements

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The compound $Bi_2Fe_4O_9$ belongs to the space group *Pbam* (D_{2h}^9), with two formula units per unit cell. Neutron diffraction measurements showed that it is paramagnetic at room temperature and undergoes a transition to an antiferromagnetic state at $T_N = (264 \pm 3)$ K in agreement with previous susceptibility and Mössbauer measurements. Analysis of the 80 K neutron diffraction pattern yielded a magnetic structure with the following features: (*a*) The basic translations $\mathbf{a}_o$, $\mathbf{b}_o$, $\mathbf{c}_o$ of the chemical lattice change into antitranslations in the magnetic lattice. (*b*) The spins are perpendicular to $\mathbf{c}_o$. (*c*) The magnetic structure belongs to the P_C2/m space group and is a basis vector to an irreducible space under the *Pbam* irreducible representations, in accord with Landau's theory of second-order phase transition. The position parameters of the Fe^{3+} ions in the unit cell were refined. The magnetic moment of the compound was found to be $(4\cdot95 \pm 0\cdot08)\mu_B$, compared with the value of $5\mu_B$ for the Fe^{3+} free ion. The temperature dependence of the $\{131\}$ magnetic reflection peak intensity was measured and found to be in agreement with the sublattice magnetization predicted by the molecular field approximation.

I. Introduction

The crystallographic structure of the compound $Bi_2Fe_4O_9$ at room temperature, revealed by X-ray diffraction (Koizumi, Niizeki & Ikeda, 1964; Tutov, Mylnikova, Parfenova, Bokov & Kizhaev, 1964; Niizeki & Wachi, 1968; Tutov & Markin, 1970), belongs to the orthorhombic space group *Pbam* (D^9_{2h}). The dimensions of the unit cell, which contains two formula units, are (Niizeki & Wachi, 1968): $a_o = 7{\cdot}950$, $b_o = 8{\cdot}428$, $c_o = 6{\cdot}005$ Å. The Fe^{3+} ions occupy (*International Tables for X-ray Crystallography*, 1952) the special positions 4(*h*) and 4(*f*) with point symmetries m_z and 2_z respectively. The 4(*h*) position Fe^{3+} ions occupy the centres of O^{2-} tetrahedra while those in the 4(*f*) positions occupy the centres of O^{2-} octahedra.

A transition from para- to antiferromagnetism at $T_N = 265$ K was found in the magnetic susceptibility (Tutov *et al.*, 1964) and Mössbauer effect (Bokov, Novikov, Trukhtanov & Yushchuk, 1970; Kostiner & Shoemaker, 1971; Bokov, Yushchuki, Popov, Parfenova & Tutov, 1971; Bokov, Kamzin & Karapet'yan, 1973) studies of this compound. A transition to a $k \neq 0$ magnetic structure was predicted by Bokov *et al.* (1971). Measurements of the magnetoelectric effect (Gorodetsky, 1972) failed to detect any magnetoelectricity.

The purpose of the present study was to determine the magnetic structure of $Bi_2Fe_4O_9$ with the neutron diffraction technique.

II. Experimental data

A powder sample of the compound $Bi_2Fe_4O_9$ was prepared at the Weizmann Institute of Science with the method of Koizumi *et al.* (1964). Neutron ($\lambda = 2{\cdot}4$ Å) diffraction patterns of this sample were obtained at 298 and 80 K (Fig. 1). The 298 K pattern is indexed according to the chemical unit cell given by Niizeki & Wachi (1968). Several lines of α-Fe_2O_3 contamination, some of which are temperature dependent (Shull, Strauser & Wollan, 1951), are also observed. The calculated reflection intensities, using the position parameters of Niizeki & Wachi (1968), are in agreement with the 298 K measured intensities.

The 80 K neutron diffraction pattern (Fig. 1*b*), exhibits 12 magnetic reflections which do not appear in the 298 K pattern. The indices of these reflections on the basis of the chemical unit cell are characterized by $h/2,k/2,l/2$ where *h*, *k* and *l* are odd numbers. This

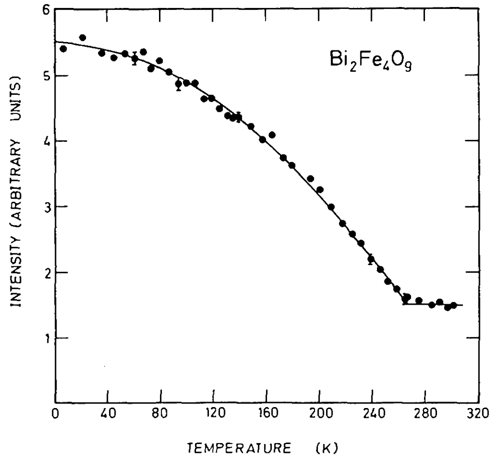

Fig. 2. The peak intensity of the magnetic reflection {131} *versus* temperature.

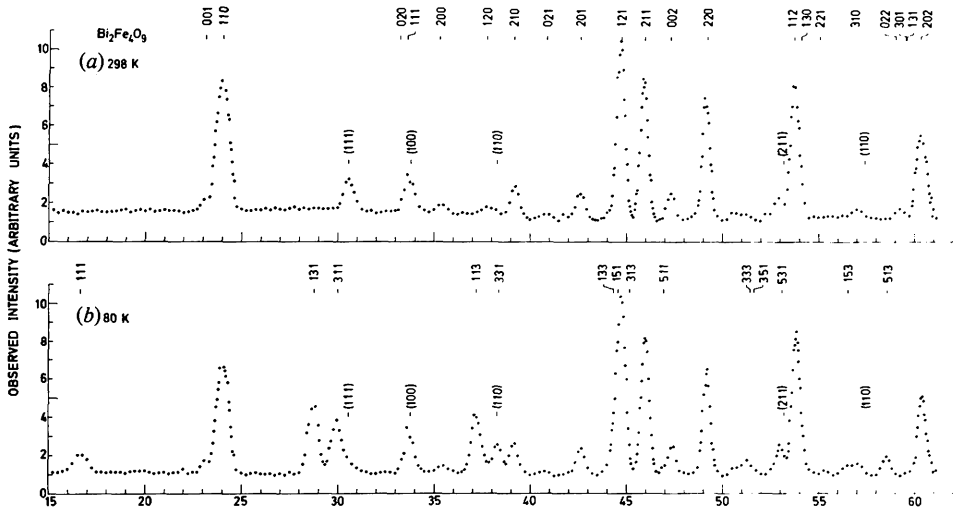

Fig. 1. Neutron ($\lambda = 2{\cdot}4$ Å) diffraction patterns of $Bi_2Fe_4O_9$ at: (*a*) 298 K; the indexing is according to the crystallographic unit cell (Niizeki & Wachi, 1968); (*b*) 80 K; only the magnetic reflections are marked, and the indexing is according to the extended $k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$ unit cell. The indices in parentheses in both spectra are of α-Fe_2O_3 contamination (Shull, Strauser & Wollan, 1951).

corresponds to a magnetic unit cell with $\mathbf{a} = 2\mathbf{a}_o$, $\mathbf{b} = 2\mathbf{b}_o$ and $\mathbf{c} = 2\mathbf{c}_o$. (This fact explains the lack of magnetoelectricity in $Bi_2Fe_4O_9$.) It should be noted that the intensity of the line {110} as well as that of the group {301, 131, 202} has decreased at 80 K, possibly because of changes in the position parameters of the magnetic ions (see data analysis).

The peak intensity of the strongest magnetic reflection {131}, was measured as a function of temperature (Fig. 2). The intensity–temperature curve thus obtained yielded $T_N = (264 \pm 3)$ K, in good agreement with susceptibility (Tutov *et al.*, 1964) and Mössbauer effect (Bokov *et al.*, 1970) measurements. The temperature dependence of the magnetization (Fig. 3) derived from the intensity–temperature curve, is in good agreement with molecular field calculations for $J = \frac{5}{2}$ (Brillouin curve).

III. Symmetry considerations

In the special case of a second-order phase transition, Landau & Lifshitz (1969) showed that the magnetic structure has to belong to an irreducible representation of the pre-transition symmetry group. In the $Bi_2Fe_4O_9$ case, the pre-transition group is D^9_{2h}. To concur with the observed magnetic lattice, the irreducible representations must be taken at the point $k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$ in reciprocal space. The space group D^9_{2h} has eight one-dimensional imaginary irreducible representations at the point $k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$ (Zak, Casher, Gluck & Gur, 1969). In describing magnetic structures, only real representations are used. Hence, a real two-dimensional space is constructed from a one-dimensional space and its complex conjugate. Four two-dimensional real representations Γ_1, Γ_2, Γ_3 and Γ_4 are constructed in this way. The characters of the two operations, at the origin of the extended unit cell, 2_z and m_z in these representations are listed in Table 1. The magnetic lattice which corresponds to these representations is monoclinic P_C (Opechowski & Guccione, 1965) as shown in Fig. 4. The P_C unit cell is given by the vectors $2\mathbf{a}_o$, $2\mathbf{c}_o$, $-\mathbf{a}_o - \mathbf{b}_o$.

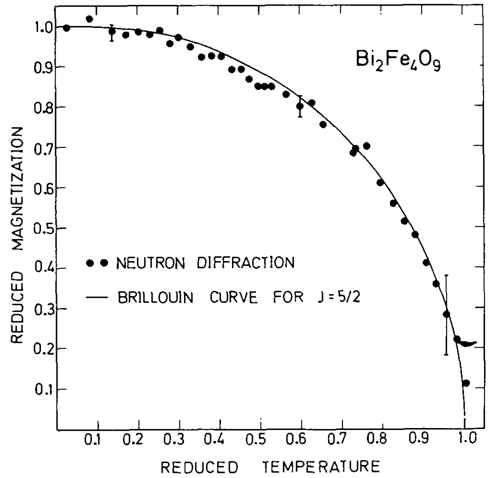

Fig. 3. The reduced magnetization of the {131} reflection *versus* reduced temperature (dots), compared with the molecular field model (Brillouin) curve (solid line).

Table 1. *The characters of the operators 2_z and m_z which are located at the origin, in the four real irreducible representations*

Representation	Characters of 2_z	m_z
Γ_1	+2	+2
Γ_2	−2	−2
Γ_3	+2	−2
Γ_4	−2	+2

Each of the two special position sets 4(*h*) and 4(*f*) of D^9_{2h} splits under the reduced magnetic symmetry into two pairs. From each pair, a set of 16 magnetic special positions (SMSP) at the extended unit cell are:

$$(0,0,0;\ \tfrac{1}{2},0,0;\ 0,\tfrac{1}{2},0;\ 0,0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\ +$$

$$4(f)\ \begin{cases} 16(f)_{\mathrm{I}} & 0,\tfrac{1}{4},z;\ 0,\bar{\tfrac{1}{4}},\bar{z} \\ 16(f)_{\mathrm{II}} & \bar{\tfrac{1}{4}},0,z;\ \tfrac{1}{4},0,\bar{z} \end{cases}$$

$$4(h)\ \begin{cases} 16(h)_{\mathrm{I}} & x,y,\tfrac{1}{4};\ \bar{x},\bar{y},\bar{\tfrac{1}{4}} \\ 16(h)_{\mathrm{II}} & \tfrac{1}{4}+x,\tfrac{1}{4}-y,\tfrac{1}{4};\ \bar{\tfrac{1}{4}}-x,\bar{\tfrac{1}{4}}+y,\bar{\tfrac{1}{4}}. \end{cases}$$

Members of each of the above pairs are connected by inversion through the origin. Such a pair will be denoted by *IOI*. Hence, for a given irreducible representation, the intra-*IOI* coupling is either ferro- or antiferromagnetic for all the *IOI*'s.

The conditions which limit reflections from the various configurations of all sets of special positions and the corresponding irreducible representations at $k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$ are listed in Table 2. The requirement that the

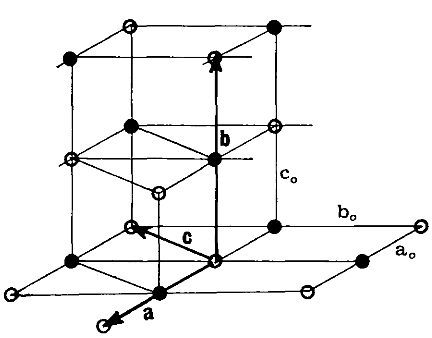

Fig. 4. The magnetic lattice P_C basic translations, according to Opechowski & Guccione (1965), (bold type) in the extended $k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$ orthorhombic unit cell (lightface type). One eighth of the magnetic P_C cell is also noted.

magnetic structure at all the SMSP's should belong to the same irreducible representation leads to intra-IOI couplings which follow from Table 2 and are listed in Table 3.

Table 2. *Conditions limiting the possible magnetic reflections from the configurations and special positions of* $D_{2h}^9 k = \frac{1}{2},\frac{1}{2},\frac{1}{2}$, *with the corresponding irreducible representation and the magnetic space groups*

Wyckoff notation	Point symmetry	Conditions limiting reflections Reflections (all odd)	Configuration* + +	 + −	 − +	 − −
a	$2_z/m_z$	*h k l*	NC†	−‡	−	−
b	$2_z/m_z$	*h k l*	−	NC	−	−
c	$2_z/m_z$	*h k l*	−	−	NC	−
d	$2_z/m_z$	*h k l*	−	−	−	NC
e	2_z	*h k l*	NC	NC	−	−
f	2_z	*h k l*	−	−	NC	NC
g	m_z	*h k l*	NC	−	NC	−
h	m_z	*h k l*	−	NC	−	NC
i	1	*h k l*	NC	NC	NC	NC
Irreducible representation **S** ∥ **Z**			Γ_1	Γ_3	Γ_4	Γ_2
Magnetic space group			P_C2/m	P_C2/c	P_C2/m	P_C2/c
Irreducible representation **S** ⊥ **Z**			Γ_2	Γ_4	Γ_3	Γ_1
Magnetic space group			P_C2/c	P_C2/m	P_C2/c	P_C2/m

* The first symbol is the relative phase at the position $(2z|0).(x,y,z) = (\bar{x},\bar{y},z)$. The second symbol is the relative phase at the position $(m_z|0).(x,y,z) = (x,y,\bar{z})$ where the phase of (x,y,z) is positive.

† NC = no conditions.

‡ This mode is not allowed.

Table 3. *Intra-*IOI *couplings of magnetic structure at the SMPS* 16(*f*) *and* 16(*h*)

+ and − correspond to ferro- and antiferromagnetic intra-IOI coupling.

Irreducible representation	16(*h*) $\mu \parallel$ **c**	 $\mu \perp$ **c**	16(*f*) $\mu \parallel$ **c**	 $\mu \perp$ **c**
Γ_1		+		+
Γ_2	+		+	
Γ_3	−			−
Γ_4		−	−	

IV. Data analysis

A least-squares computer program was applied to obtain a best fit of the calculated magnetic intensities to the measured ones. The parameters of the fit were: (*a*) the ratio of the values of the magnetic moments of the $16(h)_{\text{I,II}}$ to the $16(f)_{\text{I,II}}$ ions {it was assumed that $\mu[16(f)_{\text{II}}] = \mu[16(f)_{\text{I}}]$ and $\mu[16(h)_{\text{II}}] = \mu[16(h)_{\text{I}}]$}; (*b*) the position parameters of the magnetic ions; (*c*) the direction of the magnetic moments in each SMSP.

The quality of the fit is evaluated by the weighted *R* factor, defined as:

$$R = \{\sum[(I_o - I_c)/\sigma]^2/\sum(I_o/\sigma)^2\}^{1/2} \times 100, \quad (1)$$

where I_o and I_c are the observed and calculated intensities respectively and σ the estimated error in I_o.

The best-fit computer program analysis was not restricted to magnetic structures which belong to single irreducible space.

The results of the computer program fits can be summarized as follows.

(*a*) The assumption of different values for the magnetic moments of the 4(*h*) and 4(*f*) ions does not improve the fit and can therefore be neglected.

(*b*) The changes obtained for the position parameters are small and almost independent of the fitted magnetic structure.

(*c*) The demand that the moments at $16(h)_{\text{I}}$ should be collinear with those of $16(h)_{\text{II}}$ and/or the moments at $16(f)_{\text{I}}$ should be collinear with those at $16(f)_{\text{II}}$ leads to $R > 50\%$.

(*d*) All the attempts to fit the data to magnetic structures which do not belong to the Γ_1 representation yield $R > 50\%$.

(*e*) Most of the calculations restricted to Γ_1, *i.e.* in which: (1) the moments at each SMSP are collinear, (2) the moments at each IOI are ferromagnetically coupled, (3) the antiferromagnetic axis of each SMSP was allowed to change randomly in the *ab* plane, converge to the same magnetic structure yielding $R = 3{\cdot}12\%$. Besides this best fit there were some convergences to local minima with *R* in the range 6–8% yielding different magnetic structures.

The best-fitted magnetic structure thus obtained is presented in Fig. 5. The calculated and the observed integrated magnetic intensities are listed in Table 4. The obtained position parameters of the magnetic ions at 80 K are: $z = 0{\cdot}228$ for the 4(*f*) positions and $x = 0{\cdot}300$,

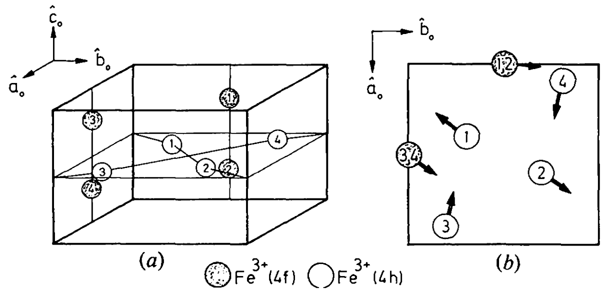

Fig. 5. The magnetic structure of $Bi_2Fe_4O_9$ obtained by the best fit. (*a*) The positions of magnetic (Fe^{3+}) ions in the crystallographic unit cell ($\frac{1}{8}$ of a magnetic cell). (*b*) The directions of the magnetic moments in a crystallographic unit cell (note that the collinear pairs of moments are not the IOI's). The angles of the magnetic moments of the ions at $16(f)_{\text{I}}$, $16(f)_{\text{II}}$, $16(h)_{\text{I}}$ and $16(h)_{\text{II}}$ with the *a* axis are 84, 51, 50 and 75° respectively.

$y = 0{\cdot}300$ for the $4(h)$ positions, in comparison to $z[4(f)] = 0{\cdot}257$, $x[4(h)] = 0{\cdot}351$ and $y[4(h)] = 0{\cdot}334$ given for room temperature by Niizeki & Wachi (1968).

The magnetic moment of the Fe^{3+} ion was calculated with the expression (Bacon, 1962):

$$n_B^2 = 13{\cdot}7\,\frac{I_o^m/I_c^m}{I_o^n/I_c^n}\,, \qquad (2)$$

where n_B is the magnetic moment per ion in μ_B, I_o^m and I_c^m are the observed and calculated magnetic intensities and I_o^n, I_c^n the corresponding nuclear intensities. The value obtained was $(4{\cdot}95 \pm 0{\cdot}08)\mu_B$ per Fe^{3+} ion, which is approximately the free Fe^{3+} value ($5\mu_B$).

V. Summary and discussion

The conclusions of the present study are as follows.

(*a*) The compound $Bi_2Fe_4O_9$ undergoes a transition to an antiferromagnetic state at $T_N = (264 \pm 3)$ K.

(*b*) The crystallographic unit-cell translations $\mathbf{a}_o$, $\mathbf{b}_o$, $\mathbf{c}_o$ change into antitranslations in the magnetic lattice.

(*c*) The magnetic moments are perpendicular to the **c** axis.

(*d*) The magnetic structure belongs to the irreducible representation Γ_1 of *Pbam*. The corresponding magnetic space group is P_C2/m.

(*e*) The Fe^{3+} magnetic moments are $(4{\cdot}95 \pm 0{\cdot}08)\mu_B$. The temperature dependence of the moment is in agreement with the molecular field model.

(*f*) The position parameters of the magnetic ions in the antiferromagnetic phase (this study), differ quite significantly from the parameters measured in the paramagnetic phase (Niizeki & Wachi, 1968). This indicates a change of positions in the unit cell, possibly due to magnetic interactions.

(*g*) The magnetic structures obtained in computer fits with $R \sim 6$–8% resemble the one presented in Fig. 5. In all of them the magnetic moment directions are roughly along the cell axes or the cell diagonals. One pair of $4(f)$ moments is roughly parallel to one pair of $4(h)$ moments, while the other two pairs are roughly perpendicular. It should be noted that all the magnetic structures obtained yielded the same position parameters.

Table 4. *Comparison of the magnetic integrated intensities with the calculated ones in the* 80 K *pattern of* $Bi_2Fe_4O_9$

The calculated intensities were obtained with the refined parameters.

No.	$\{h\,k\,l\}$	$I_o \pm \sigma$	I_c
1	1 1 1	1600 ± 70	1637
2	1 3 1	5200 ± 90	5226
3	3 1 1	3500 ± 75	3478
4	1 1 3	3700 ± 85	3741
5	3 3 1	1400 ± 60	1406
6	1 3 3 1 5 1	1100 ± 200	1054
7	3 1 3	600 ± 150	555
8	5 1 1	300 ± 60	286
9	3 3 3 3 5 1	620 ± 70	552
10	5 3 1	740 ± 70	630
11	1 5 3	400 ± 45	327
12	5 1 3	840 ± 40	872

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References

Bacon, G. E. (1962). *Neutron Diffraction*, Ch. 6. Oxford: Clarendon Press.

Bokov, V. A., Kamzin, A. S. & Karapet'yan, G. Ya. (1973). *Sov. Phys. Solid State*, **14**, 2168–2170.

Bokov, V. A., Novikov, G. V., Trukhtanov, V. A. & Yushchuk, S. I. (1970). *Sov. Phys. Solid State*, **11**, 2324–2326.

Bokov, V. A., Yushchuk, S. I., Popov, G. V., Parfenova, N. N. & Tutov, A. G. (1971). *Sov. Phys. Solid State*, **13**, 1333–1338.

Gorodetsky, G. (1972). Private communication.

International Tables for X-ray Crystallography (1952). Vol. 1, p. 143. Birmingham: Kynoch Press.

Koizumi, H., Niizeki, N. & Ikeda, T. (1964). *Jpn. J. Appl. Phys.* **3**, 495–496.

Kostiner, E. & Shoemaker, G. L. (1971). *J. Solid State Chem.* **3**, 186–189.

Landau, L. D. & Lifshitz, E. M. (1969). *Statistical Physics*, 2nd ed. Oxford: Pergamon Press.

Niizeki, N. & Wachi, M. (1968). *Z. Kristallogr.* **127**, 173–187.

Opechowski, W. & Guccione, R. (1965). *Magnetism*, Vol. IIa, edited by G. T. Rado & H. Suhl, p. 105. New York: Academic Press.

Shull, C. G., Strauser, W. A. & Wollan, E. O. (1951). *Phys. Rev.* **83**, 333–343.

Tutov, A. G. & Markin, V. N. (1970). *Izv. Akad. Nauk USSR, Neorg. Mater.* **6**, 2014–2017.

Tutov, A. G., Mylnikova, I. E., Parfenova, N. N., Bokov, V. A. & Kizhaev, S. A. (1964). *Sov. Phys. Solid State*, **6**, 963–964.

Zak, J., Casher, A., Gluck, M. & Gur, Y. (1969). *The Irreducible Representations of Space Groups*, p. 91. New York: Benjamin.