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## Magnons and sublattice magnetisations in hexagonal Ba ferrite

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**Abstract.** Magnon spectra in the hexagonal ferrite  $\text{BaFe}_{12}\text{O}_{19}$  are calculated using the exchange integrals obtained from the analysis of the temperature dependence of NMR corresponding to  $^{57}\text{Fe}$  nuclei in magnetic domains. From the magnon spectra the zero-point spin deviations and the temperature dependence of sublattice magnetisations are determined. For comparison all calculations are also performed with an alternative set of the exchange integrals taken from the literature.

### 1. Introduction

Hexagonal ferrites  $\text{MFe}_{12}\text{O}_{19}$  ( $\text{M} \equiv \text{Ba}, \text{Sr}, \text{Pb} \dots$ ) play an increasingly important role as materials for permanent magnets, recording media and microwave devices. At the same time they provide a unique opportunity to study the behaviour of the  $\text{Fe}^{3+}$  ion in different oxygen environments. In stoichiometric  $\text{MFe}_{12}\text{O}_{19}$   $\text{Fe}^{3+}$  ions fully occupy five cation sublattices with three different ligand coordination numbers.

Our long term goal is to understand the magnitude  $B_{\text{HF}}$  of the hyperfine field on the nuclei of  $\text{Fe}^{3+}$  ion in magnetic insulators and a thorough analysis of  $B_{\text{HF}}$  in  $\text{MFe}_{12}\text{O}_{19}$  would clearly contribute much to the understanding of this problem. However, several questions must be answered before such a task is attempted. It is generally believed (Sawatzky and van der Woude 1974) that the dominating term, which in the crystal modifies  $B_{\text{HF}}$  of the free  $\text{Fe}^{3+}$  ions is the covalency ( $\text{Fe}^{3+}$ –ligand electron transfer). There are, however, at least three other mechanisms which ought to be also considered: the dipolar field from magnetic moments of other ions present in the system, cation–cation electron transfer and the zero point spin deviation (ZPSD). The ZPSD is of special interest, as to our knowledge no corresponding quantitative calculation in ferrimagnetic compounds has ever been attempted.

In the present paper the ZPSD in  $\text{BaFe}_{12}\text{O}_{19}$  will be calculated by integration over the spin-wave spectrum. The solution of the spin-wave problem requires knowledge of the exchange integrals. These were determined recently for  $\text{BaFe}_{12}\text{O}_{19}$  by Isalgue *et al* (1986) (hereafter denoted as I) by fitting the temperature dependences of the sublattice

**Table 1.** Fe<sup>3+</sup> sublattices in BaFe<sub>12</sub>O<sub>19</sub>. Two alternative notations for sublattices, used in literature, are given.

Sublattice	Fe1 2a	Fe2 4e (2b)	Fe3 4f1	Fe4 4f2	Fe5 12k
Coordination	Octahedral	Bipyramidal	Tetrahedral	Octahedral	Octahedral
Spin	Up	Up	Down	Down	Up

magnetisations by the molecular field theory with exchange integrals as free parameters. The analysis in I was based on the Mössbauer (Albanese *et al* 1974) and NMR (Streever 1969, Hareyama *et al* 1970) measurements of the temperature dependence of the hyperfine field on <sup>57</sup>Fe nuclei. We note that both these NMR measurements correspond to <sup>57</sup>Fe nuclei in domain walls—the same also holds for the more detailed work of Petrov and Kunevitch (1971). We report here the temperature dependence of <sup>57</sup>Fe NMR in the domains, the lines being much narrower compared with the domain wall signal. A sample enriched by <sup>57</sup>Fe isotope to 87% was used, which enabled us to follow the NMR in domains to relatively high temperatures. Section 3 of the present paper is devoted to repetition of analysis given in I using the data obtained on the <sup>57</sup>Fe enriched sample. This calculation resulted in a new set of parameters describing the exchange interactions in BaFe<sub>12</sub>O<sub>19</sub>.

The spin-wave excitations are then calculated using the standard method (§ 4) and by integration over the Brillouin zone the ZPSD are determined (§ 5). The experimental data revealed that at low temperatures the NMR frequencies do not follow the  $T^{3/2}$  law expected for ferrimagnetic systems with small magnetocrystalline anisotropy. We therefore also calculate the sublattice magnetisations in the non-interacting spin-wave approximation and compare the results with experimental data.

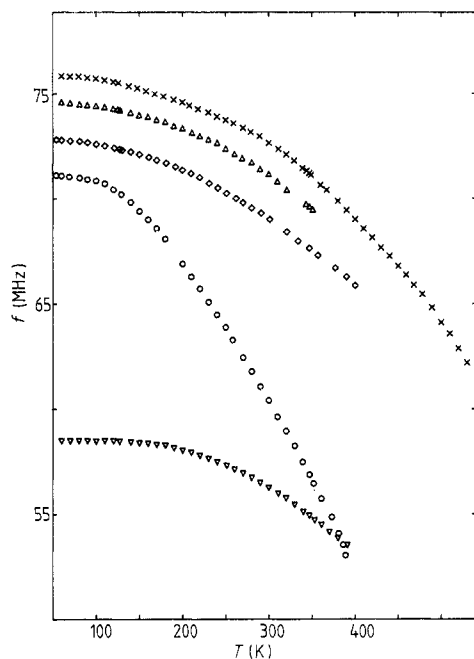
## 2. Experimental procedure

NMR was studied by the spin-echo technique using the variable-frequency pulsed spectrometer. The same single crystal as in our previous study (Zalesskij *et al* 1987) was used. The crystal was grown by the zone-fusion technique with the radiation heating (Balbashov *et al* 1971).

The experimental conditions under which NMR is excited in the domains only are described by Zalesskij *et al* (1982). In particular the RF field was directed perpendicular to the ‘easy’ *c*-axis and high RF power was used. The temperature was controlled by the evaporation of liquid helium or nitrogen and was automatically held constant to accuracies of  $\pm 0.05$  K (4.5–80 K) and  $\pm 0.3$  K (80–400 K).

In table 1 we summarise the basic data concerning the five magnetic sublattices of BaFe<sub>12</sub>O<sub>19</sub>. In figure 1 we show the temperature dependences of the <sup>57</sup>Fe NMR frequencies.

If the Fe<sup>3+</sup>–Fe<sup>3+</sup> electron transfer, dipolar field and the ZPSD are neglected, the NMR frequency is proportional to the electronic magnetic moment *m* localised on corresponding Fe<sup>3+</sup> ion. Simple spin-wave theory predicts that at low temperatures *m* varies



**Figure 1.** Temperature dependence of  $^{57}\text{Fe}$  NMR frequencies in  $\text{BaFe}_{12}\text{O}_{19}$ . The symbols used correspond to Fe1 ( $\Delta$ ), Fe2 ( $\nabla$ ), Fe3 ( $\diamond$ ), Fe4 ( $\times$ ) and Fe5 ( $\circ$ ).

**Table 2.** Parameters describing the temperature dependence of the sublattice magnetisations.

	Fe1	Fe2	Fe3	Fe4	Fe5
$B_{\text{HF}}(0)$ (MHz)	74.50	58.50	72.75	75.86	71.06
$10^3\alpha$ (MHz)	1.159	2.025	1.094	0.904	4.177
$\Delta$ (meV)	6.81	27.44	4.38	3.20	7.89

as  $T^{3/2}$  and we have tried therefore to fit the experimental  $B_{\text{HF}}(T)$  dependence using the formula

$$B_{\text{HF}}(T) = B_{\text{HF}}(0) - \alpha_0 T^{3/2}. \quad (1)$$

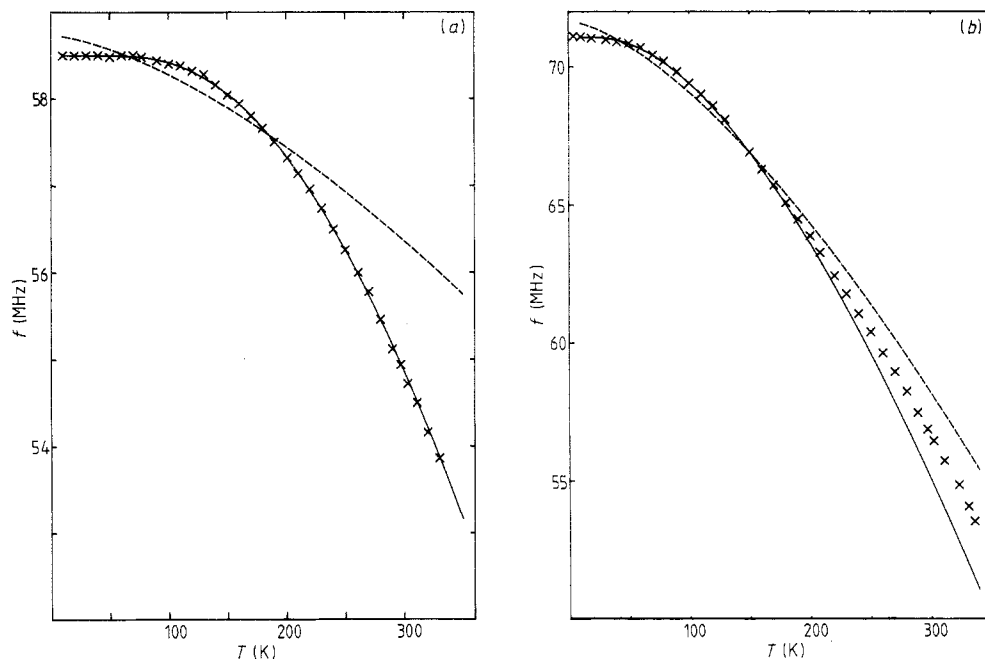
This, however, describes the experiment poorly, especially for Fe2. The fit was not much improved even when the term  $\beta T^{5/2}$  was added to (1). For temperatures below about 200 K the results may, however, be reasonably well fitted by

$$B_{\text{HF}}(T) = B_{\text{HF}}(0) - \alpha \exp(-\Delta/kT) T^{3/2}. \quad (2)$$

It is usually thought that in (2) the exponential pre-factor reflects the effect of magnetocrystalline anisotropy. In our case  $\Delta$  comes out rather large (table 2) and it can hardly be associated with this mechanism. In figure 2 the fits of  $B_{\text{HF}}(T)$  for Fe1 and Fe2 to (1) and (2) are shown.

### 3. Exchange integrals

To calculate the exchange integrals we follow closely the method based on the molecular field approximation which was described in I. In particular, proportionality between the



**Figure 2.** The fits of the temperature dependence of the NMR frequency for (a) Fe2 and (b) Fe5. Broken curve, equation (1); full curve, equation (2).

**Table 3.** Exchange integrals (in K) in  $\text{BaFe}_{12}\text{O}_{19}$ .

	$J_{13}$	$J_{15}$	$J_{24}$	$J_{25}$	$J_{33}$	$J_{35}$	$J_{44}$	$J_{45}$	$J_{55}$
This work	-25.3	-2.4	-20.2	0.0	-8.8	-13.5	-14.2	-21.4	-4.4
I	-22	-3	-22	-3	-9	-16	-18	-25	-10

sublattice magnetisations and corresponding NMR frequencies is assumed and nine nonzero exchange integrals  $J_{ik}$  are considered. In most cases  $J_{ik}$  corresponds to the interaction between nearest neighbour  $\text{Fe}^{3+}$  ions from sublattice  $i$  and  $k$  but  $J_{24}$ ,  $J_{25}$  and  $J_{35}$  represent an effective mean value for interaction between nn and nnn  $\text{Fe}^{3+}$  ions (corresponding geometry of nn and nnn pairs differ only slightly in these cases) and  $J_{55}$  is an effective mean value for the interaction between four different but similar pairs of  $\text{Fe}^{3+}$  ions from the sublattice 5.

Program MINUIT from the CERN library was used to find  $J_{ik}$  which minimise the sum of squares of differences between theory and experiment. As the Curie temperature is not known for our sample, we assumed that it lies in the region  $720 \leq T_C \leq 745$  K and a penalty function was added into the minimalisation procedure when  $T_C$  falls outside this interval. In table 3 such obtained  $J_{ik}$  are compared with those given in I.

The sum of squares of differences between theory and experiment is 2.06 times bigger when the values of  $J_{ik}$  from I are taken. The Curie temperature calculated with our set of  $J_{ik}$  is 726 K.

#### 4. Spin waves

To describe the magnetic interactions in the system considered, we used the Hamiltonian

$$H = - \sum_{p,l} A_l S_{pl}^{(z)} - \frac{1}{2} \sum_{p,l,qm} J_{pl,qm} S_{pl} S_{qm} \quad (3)$$

where  $A_l$  corresponds to the anisotropy field. In what follows we take  $z$  parallel to the hexagonal axis, as this is the easy direction for magnetisation in  $\text{BaFe}_{12}\text{O}_{19}$ .  $S_{pl}$  is the spin of  $l$ th  $\text{Fe}^{3+}$  ion ( $l = 1, 2, \dots, M$ ) in the  $p$ th unit cell ( $p = 1, 2, \dots, N$ ).  $M = 24$  is the number of  $\text{Fe}^{3+}$  ions in the unit cell, while  $N$  is the total number of unit cells.  $J_{pl,qm}$  are the exchange integrals which—if nonzero—reduce to one of the nine quantities listed in table 3.

In order to diagonalise (3) the Bogolyubov—Tyablikov method as described in Tyablikov (1967) was used. We give here only the main steps of the procedure. For the derivation and full discussion the reader is referred to Tyablikov (1967).

The  $S_{pl}$  are approximated by the localised Bose operators

$$\begin{aligned} S_{pl}^{(x)} &= \sqrt{S}(a_{pl}^+ + a_{pl})/\sqrt{2} \\ S_{pl}^{(y)} &= i\varepsilon_l \sqrt{S}(a_{pl}^+ - a_{pl})/\sqrt{2} \\ S_{pl}^{(z)} &= \varepsilon_l(S - a_{pl}^+ a_{pl}) \end{aligned} \quad (4)$$

where  $S = \frac{5}{2}$  is the spin of  $\text{Fe}^{3+}$  ion,  $\varepsilon_l = +1$  ( $-1$ ) if the spin is parallel (antiparallel) to the  $z$  axis,  $a_{pl}^+$  and  $a_{pl}$  are Bose creation and annihilation operators localised on the site  $pl$ .

The operators  $a_{pl}$  are transformed into  $\mathbf{k}$  space

$$a_{pl} = (1/\sqrt{N}) \sum_{\mathbf{k}} A_{kl} \exp(i\mathbf{r}_p \cdot \mathbf{k}). \quad (5)$$

Here  $N$  is the number of unit cells,  $\mathbf{r}_p$  is the lattice translation vector by which  $p$ th cell is obtained from the reference cell.

The final transformation is

$$A_{kl} = \sum_j [u_{lj}(\mathbf{k}) \xi_{kj} + v_{lj}^*(\mathbf{k}) \xi_{kj}^+] \quad (6)$$

where the coefficients  $u_{lj}(\mathbf{k})$ ,  $v_{lj}(\mathbf{k})$  are chosen so that the Hamiltonian (3) expressed in terms of operators  $\xi_{kj}$ ,  $\xi_{kj}^+$  is diagonal.

$u_{lj}(\mathbf{k})$ ,  $v_{lj}(\mathbf{k})$  are eigenvectors of the eigenvalue problem which may be symbolically written as

$$\begin{pmatrix} \mathbf{P}(\mathbf{k}) & \mathbf{R}(\mathbf{k}) \\ -\mathbf{R}(\mathbf{k}) & -\mathbf{P}(\mathbf{k}) \end{pmatrix} \begin{pmatrix} u(\mathbf{k}) \\ v(-\mathbf{k}) \end{pmatrix} = E \begin{pmatrix} u(\mathbf{k}) \\ v(-\mathbf{k}) \end{pmatrix} \quad (7)$$

where  $\mathbf{P}$  and  $\mathbf{R}$  are Hermitian matrices with elements

$$\begin{aligned} P_{lm} &= \left( \varepsilon_l A_l + \sum_{l'} \varepsilon_{l'} \varepsilon_l S I_{ll'}(0) \right) \delta_{lm} - \varepsilon_l \varepsilon_m S I_{lm}(\mathbf{k}) (\varepsilon_l \varepsilon_m + 1)/2 \\ R_{lm} &= -\varepsilon_l \varepsilon_m S I_{lm}(\mathbf{k}) (\varepsilon_l \varepsilon_m - 1)/2 \end{aligned} \quad (8)$$

where  $I_{lm}(\mathbf{k}) = \sum_p J_{pl,qm} e^{-i\mathbf{k} \cdot (\mathbf{r}_p - \mathbf{r}_q)}$ . It may be shown that following relations hold:

$$u_{lj}(-\mathbf{k}) = u_{lj}^*(\mathbf{k}) \quad v_{lj}(-\mathbf{k}) = v_{lj}^*(\mathbf{k}). \quad (9)$$

The matrix of the eigenvalue problem has order  $2M \times 2M$  and it is nonsymmetrical and

**Table 4.**  $z$  components of the anisotropy field in  $\text{BaFe}_{12}\text{O}_{19}$  (all values in T).

Contribution	Fe1	Fe2	Fe3	Fe4	Fe5
Dipolar	1.289	0.945	0.041	0.604	-0.555
Single ion	-0.043	0.592	0.025	0.047	0.082
Total	1.246	1.537	0.066	0.651	-0.473

nonhermitian. If we note that  $R_{lm} = 0$  when  $S_{lm} = 0$  and vice versa, we may easily block diagonalise it to two  $M \times M$  matrices, however.

A remark should be made concerning the values of the anisotropy fields. It is generally accepted (Obradors *et al* 1986) that the dipolar interaction gives the main contribution to the magnetocrystalline anisotropy in hexagonal ferrites, though the single-ion contribution may modify it, especially for Fe2 whose polyhedron is strongly distorted. We have calculated the dipolar contribution to the anisotropy fields by direct summation over all  $\text{Fe}^{3+}$  ions in a sphere of radius 1200 nm (estimated error is less than 1%). For rough estimation of the single-ion contribution the superposition model of the zero-field splitting with the data given by Yeung (1988) was used. The results are summarised in table 4.

In all following calculations the total anisotropy is used. It should be emphasised, however, that if the anisotropy fields are kept within reasonable limits, their values have only small effect on the magnon dispersion curves and in particular they do not influence any of the results described in the § 5.

In figures 3(a) and 3(b) the spin-wave dispersion spectra are shown for two sets of exchange parameters listed in table 3. An interesting feature to be noted is the existence of a gap in the magnon spectra which persists for both sets of the exchange integrals. The magnetocrystalline anisotropy gap amounts to 0.14 meV which is much smaller than the values of  $\Delta$  (table 2).

## 5. ZPSD and temperature dependence of the sublattice magnetisations in the spin-wave approximation

What we would like to determine is the mean value of the  $z$  component of the  $\text{Fe}^{3+}$  spin for each of the five sublattices. Using (4)–(6) and (9) we get

$$|\langle S_{pl}^{(z)} \rangle| = S - (1/N) \sum_{k,m} \{ [ |u_{lm}(\mathbf{k})|^2 + |v_{lm}(\mathbf{k})|^2 ] \langle \xi_{km}^+ \xi_{km} \rangle + |v_{lm}(\mathbf{k})|^2 \}. \quad (10)$$

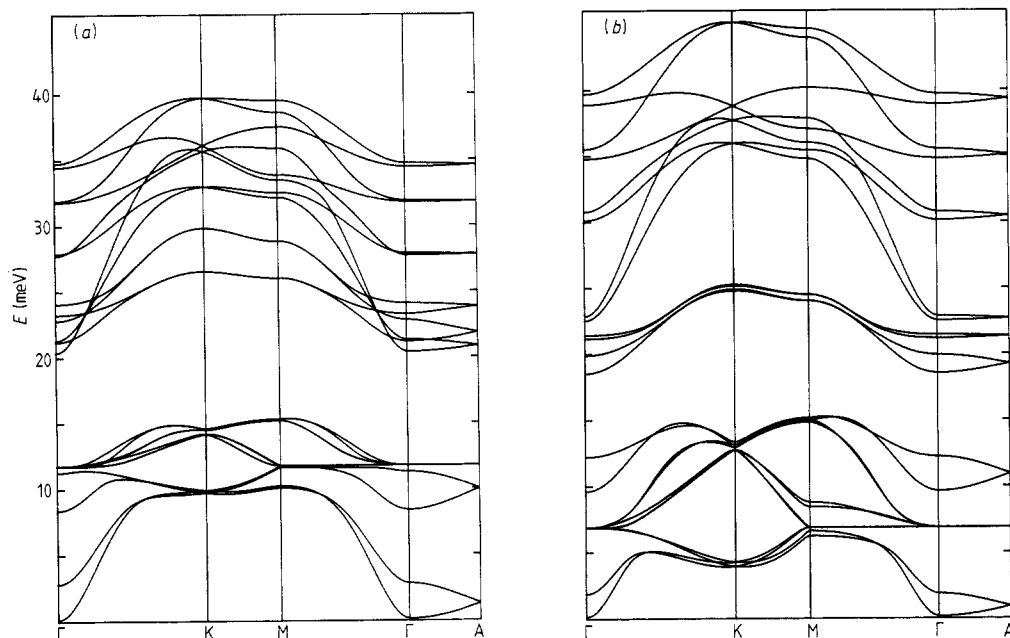
As in the ground state  $\langle \xi_{km}^+ \xi_{km} \rangle = 0$ , we obtain for the ZPSD the expression

$$\delta_l = S - |\langle S_{pl}^{(z)} \rangle| = (1/N) \sum_{k,m} |v_{lm}(\mathbf{k})|^2. \quad (11)$$

At nonzero temperatures

$$\langle \xi_{km}^+ \xi_{km} \rangle = n_m(\mathbf{k}) = 1/(e^{-E_m(\mathbf{k})/k_B T} - 1). \quad (12)$$

In (10) and (11) the summation over  $\mathbf{k}$  vectors may be approximated by an integration over all  $\mathbf{k}$  vectors in the first Brillouin zone. Using the symmetry of the Brillouin zone of the close packed hexagonal lattice, the integration region may be reduced to  $\frac{1}{24}$  of its



**Figure 3.** Magnon dispersion curves calculated (a) with our set of  $J_{ik}$  and (b) with  $J_{ik}$  given in I.

**Table 5.** Zero-point spin deviations (ZSPDs) for the two sets of  $J_{ik}$ .

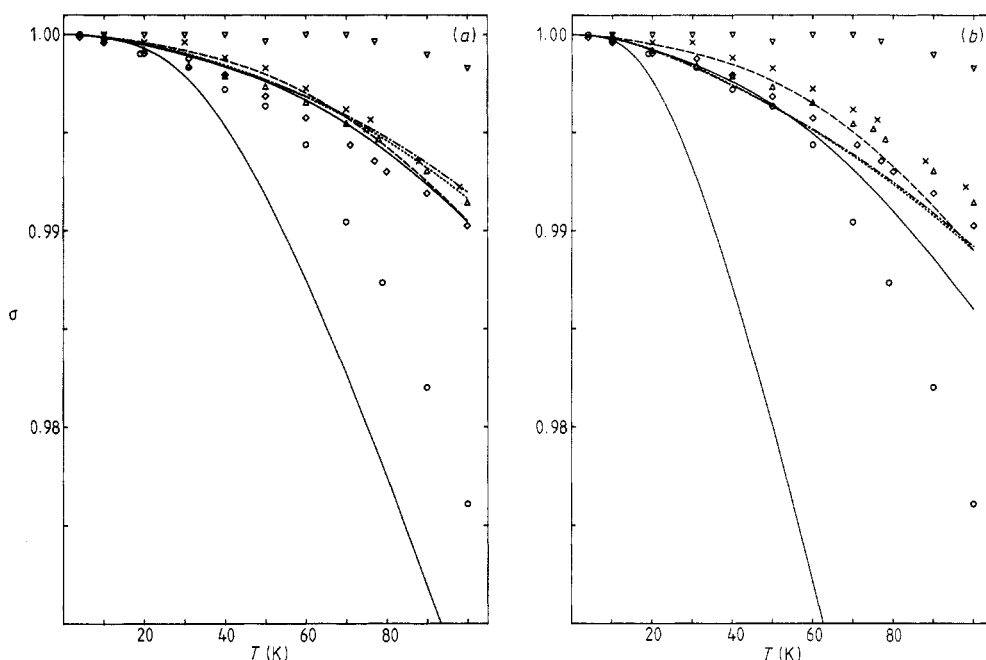
	Fe1	Fe2	Fe3	Fe4	Fe5
$J_{ik}$ from this work	0.0117	0.0078	0.0150	0.0182	0.0078
$J_{ik}$ from I	0.0095	0.0080	0.0169	0.0219	0.0098

volume. For the integration the repeated Gauss–Legendre method with cylindrical coordinate system ( $k_z \parallel c$ ) has been used. Due to the smooth form of the integrands even a small number of integration points gives reliable results. In what follows, the number of points is 72 (3 for  $k_z$ , 3 for angle  $\varphi$  and 8 for  $k_\perp$ ) and we estimated that corresponding error is less than 1% for the magnetisations and 0.1% for ZPSD.

The ZPSDs are summarised in table 5. The maximum value of the ZPSD (Fe4 sublattice) amounts to 0.7–0.9%, which corresponds to the decrease in the NMR frequency of 0.6–0.7 MHz at zero temperature. The effect of ZPSDs is therefore much smaller than that of covalency (10–20 MHz), but comparable to typical values of shifts caused by dipolar fields and the cation–cation interaction (e.g. English *et al* 1985).

In figures 4(a) and 4(b) the temperature dependences of the reduced sublattice magnetisation  $\sigma_i = m_i(T)/m_i(0)$  are shown. The qualitative features are similar for both sets of the exchange integrals, though our set seems to describe the situation better. For Fe1, Fe3 and Fe4 the calculated curves do not differ much from experimental results. For Fe5 theory predicts more rapid variation than the one obtained experimentally, but here the results are very susceptible to the values of the exchange integrals.





**Figure 4.** Temperature dependence of the reduced sublattice magnetisations  $\sigma_i$  (a) calculated with our set of  $J_{ik}$ , and with (b)  $J_{ik}$  given in I. For the experimental points the same symbols as in figure 1 are used. Calculations: Fe5 (lower full curve); Fe1 (upper full curve); Fe2 (broken curve); Fe3 (chain curve); Fe4 (dotted curve).

The most interesting discrepancy concerns the Fe2 (4e) site where no reasonable choice of  $J_{ik}$  could explain why for  $T \approx 80$  K the NMR frequency is almost independent of temperature. We connect this with the character of the 4e site. It is known (see, e.g. Obradors *et al* 1985) that these sites occur in closely spaced pairs from which only one site is occupied by the Fe<sup>3+</sup> ion. The sites in each pair are related by the reflection in the mirror plane, their distance being 3.4 nm. For  $T \rightarrow 0$  the Fe<sup>3+</sup>(4e) ions are probably immobile and randomly frozen, but at elevated temperatures they begin to migrate between the two adjacent sites. This must influence their magnetic interactions—in particular a strong temperature dependence of the exchange integrals involving Fe2 ions will appear. Even more important is that due to the motion, all other mechanisms which modify  $B_{\text{HF}}$  in the crystal—in particular the covalency—become temperature dependent. We believe therefore that the anomalous temperature change of the NMR of Fe2 reflects the effect of the motion of this ion.

## 6. Conclusions

The main result of this work is the calculation of magnon spectra and the zero point spin deviations (ZSPDs) in BaFe<sub>12</sub>O<sub>19</sub>. The magnitudes of the ZSPDs were found to be 0.3–0.9% which correspond to a downward shift in the NMR frequency of 0.1–0.7 MHz.

The experimentally observed anomalous temperature dependence of the NMR frequency of Fe<sup>3+</sup> ions in the 4e sites is most probably connected with the motion of this

ion between the two adjacent equilibrium positions. This implies that the exchange integrals calculated from the temperature dependence of the NMR without taking this effect into account are necessarily inaccurate. In this situation the other approximations on the basis of which the exchange integrals were determined (molecular field approximation, neglecting dipolar field, etc) seem to be fully adequate.

### Acknowledgment

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