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Abstract. A model calculation of the spin-canting effect for Li–Zn ferrite is presented here to improve the existing calculations and to determine an accurate relationship between the magnetic moment at 0 K and the Zn substituent level. It is assumed that, although the B sublattice can be subdivided into two commensurate sublattices B' and B" regarding the spin orientations because of the spin-canting effect, the spin orientation is actually random at local sites. In contrast with previous calculations, the exchange integral ratio J_{AB}/J_{BB} in this paper is expressed in terms of correlated molecular-field coefficients. By self-consistent iterative computation, excellent agreement between the theory and the experimental results is realised, which we consider to be the best of those published.

1. Introduction

Investigations of Li ferrite are receiving increasing interest from researchers. The reason is obvious, since on the one hand materials of this kind have found wide applications in microwave devices and on the other hand the study of their magnetic structures is of theoretical significance.

It appears from the experiments so far reported on the non-magnetic Zn^{2+}-substituted Li–Zn ferrite that the magnetic moment increases with increasing Zn concentration and it begins to decrease and deviate gradually from what is predicted by Néel's collinear ferrimagnetic theory when the Zn content reaches 0.35 atoms/formula unit [1]. The general explanation of this phenomenon is based on the so-called spin-canting hypothesis.

The earliest quantitative discussion of this phenomenon was given by Yafet and Kittel (YK) [2]. In their YK model, they assumed that the replacement of some ions in one of the two opposing A and B magnetic sublattices with non-magnetic ions might cause a spin-canting effect on the other sublattice and proposed that the B sublattice could accordingly be divided into two identical sublattices B' and B", each canting symmetrically about the direction of net magnetisation M. Further study [3] showed that the local environment of a spin should be responsible for its canting. More recent calculation results taking into account the influence of different possible local environments of the spins were subsequently published [4–6]. However, even if the calculated curves in [4] could fit the experimental results of $M(z, T = 0\ K)$ against z to a certain degree, the model calculation itself was implausible since the ratio J_{AB}/J_{BB} adopted in
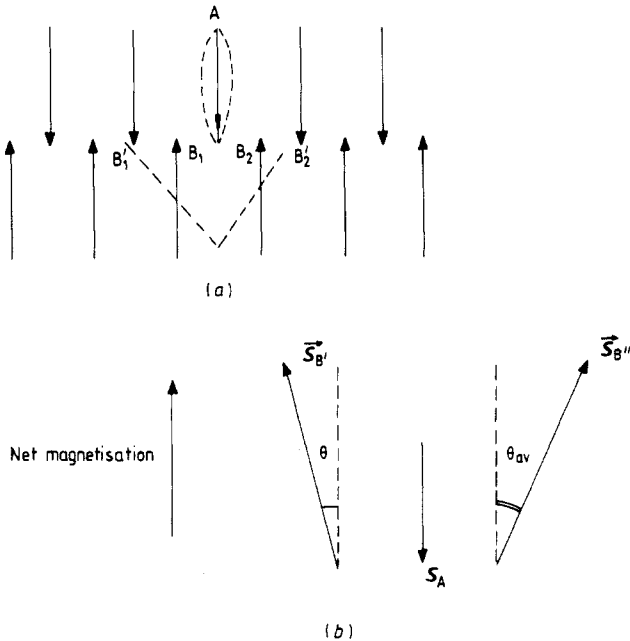
Figure 1. Model configuration showing spin canting in Li–Zn ferrite.

the calculation was unreasonable in comparison with practical values. The same situation recurred in the calculation in [5]. It is believed here that J_{AB} or J_{BB} reflects the strength of spin interaction and hence is an intrinsic property, a function of the doping level.

This paper is therefore aimed at improving the existing model calculations. By adopting a more rational computational plan and, more realistically, expressing the exchange integral ratio J_{AB}/J_{BB} in terms of the associated molecular-field coefficients, derived from the experimental results of M against T, we expect to estimate more reliably the canting effect at different doping levels and reach better agreement between the theoretical predictions and experimental data on $M(z, T = 0 \text{ K})$ against z.

2. Spin-canting model and related interaction Hamiltonian

In Li–Zn ferrite, non-magnetic Zn^{2+} ions prefer to substitute for the Fe^{3+} ions in the A sublattice. This leads to a reduction in the A–B antiferromagnetic interaction at the corresponding localities and therefore to spin canting of the Fe^{3+} ions at the adjacent B sites to maintain the energy minimisation condition of the spin system, as schematically illustrated in figure 1(*a*).

At a particular lattice site where an Fe^{3+} A ion is replaced by a Zn^{2+} ion, the spins of the two adjacent B ions will cant and assume two canting directions θ and θ_{av} (figure 1(*b*)). The B sublattice would accordingly split into two further sublattices: B' and B".

For Li–Zn ferrite $((Zn_zFe_{1-z})_A[Li_{0.5-z/2}Fe_{1.5+z/2}]_BO_4)$ the nearest-neighbour (NN) interaction Hamiltonian of the spin system can be expressed as

$$H = - \sum_{ij} J_{ij} S_i \cdot S_j \tag{1}$$

where the J_{ij}-values (i, j = A, B' and B'') are the NN exchange integrals of i–j spin interaction, which obey the following relations [4]:

$$J_{B'B'} = J_{B''B''} = J_{B'B''} = J_{B''B'} = J_{BB} \tag{2}$$

$$J_{AB'} = J_{AB''} = J_{B'A} = J_{B''A} = J_{AB}. \tag{3}$$

The spin system has thus an extra spin-canting-related energy

$$E(\theta) = -J_{AB}(L_A n_{AB'} + L_{B'} n_{B'A})S^2 \cos \theta$$
$$- J_{BB}(L_{B'} n_{B'B''} + L_{B''} n_{B''B'})S^2 \cos(\theta + \theta_{av}) \tag{4}$$

where S is the absolute value of S_i (i $\equiv$ A, B' and B''), the L_i-values are the numbers of Fe^{3+} ions per formula unit in A, B' and B'' sublattices and the n_{ij}-values (i, j $\equiv$ A, B' and B'') denote the NN numbers of Fe^{3+} j ions for an Fe^{3+} i ion. Obviously, both L_i and n_{ij} change with doping level.

The canting angle can therefore be calculated by energy minimisation:

$$\partial E(\theta)/\partial \theta = 0 \tag{5}$$

$$\cot \theta = \{[J_{AB}(L_A n_{AB'} + L_{B'} n_{B'A})/J_{BB}(L_{B'} n_{B'B''} + L_{B''} n_{B''B'})] \cos \theta_{av}\}/\sin \theta_{av} \tag{6}$$

from which it follows that the canting angle of B' spin depends on the local distribution of its neighbouring ions when the canting angle of B'' spin is designated as θ_{av}.

3. The NN exchange interaction parameters

A crystallographic study shows that the maximum number of the NN B ions is 12 for an A ion in the spinel structure. An Fe^{3+} ion in Li–Zn ferrite has an average number of B ion neighbours given by

$$\langle n_{AB} \rangle = 12(1 - p) \tag{7}$$

where p ($=(0.5 - z/2)/2$) denotes the proportion of non-magnetic B ions, per formula unit, in the Li–Zn ferrite. It turns out that

$$\langle n_{AB} \rangle = 6(1.5 + z/2)$$

and so

$$\langle n_{AB'} \rangle = 3(1.5 + z/2).$$

Similarly

$$\langle n_{B'A} \rangle = 6(1 - z)$$

and

$$\langle n_{B'B''} \rangle = \langle n_{B''B'} \rangle = 3(1.5 + z/2)/2.$$

The above formulae represent the average NN numbers for cation constituents of Li–

Zn ferrite at a definite substituent concentration while the number m of NN magnetic ions at a typical local site should be an integer ranging from 0 to m_{max}, the maximum number of the NNs possibly occupied. For instance, $n_{B'A}$ could be any integer from 0 to 6. The probability that these different numbers occur, however, is determined by the doping level z:

$$P_{B'A}(m, z) = (1 - z)^m z^{(6-m)} \binom{6}{m} \tag{8}$$

where $\binom{6}{m} = 6!/m!(6 - m)!$. The same procedure can be applied to assessing $n_{B'B''}$, $n_{B''B'}$ and $n_{AB'}$, $n_{AB''}$.

$n_{B'B''}$, $n_{B''B'}$ and $n_{AB'}$, $n_{B'A}$ can be approximated by their average values for simplification. This is feasible since the proportion of non-magnetic A ions at a normal substituent concentration is generally lower for the ferrite in question. And therefore the canting angle of Li–Zn ferrite can be re-expressed as

$$\cot \theta(m) = \{-q[m + 6(1 - z)]/3(1.5 + z/2) - \cos \theta_{av}\}/\sin \theta_{av} \tag{9}$$

where q is the absolute value of the ratio J_{AB}/J_{BB} and has a form in terms of correlated molecular-field coefficients N_{AB} and N_{BB} [4]:

$$q = |J_{AB}/J_{BB}| = 0.5 N_{AB}/N_{BB}. \tag{10}$$

The expressions for the molecular-field coeffients as functions of z have been deduced for Li–Zn ferrite [7] from the experimental fitted curves of M against T. They have the following forms:

$$N_{AB} = 273(1 - 0.2z) \text{ mol cm}^{-3} \tag{11}$$

$$N_{BB} = -60(1 - z/3) \text{ mol cm}^{-3} \tag{12}$$

so that we have

$$q = 2.29(1 - 0.2z)/(1 - z/3) \tag{13}$$

and hence

$$\cot \theta(m) = \{0.765[m + 6(1 - z)](1 - 0.2z)/(1 - z/3)(1.5 + z/2)$$
$$- \cos \theta_{av}\}/\sin \theta_{av}. \tag{14}$$

4. Calculation procedure

The numerical calculation of the canting effect for Li–Zn ferrite is performed with an initial guess for θ_{av}, calculating the canting angle $\theta(m) = \cot^{-1} \theta(m)$ over different possible values of m, i.e.

$$\theta(m) = \cot^{-1} [\{0.764[m + 6(1 - z)](1 - 0.2z)/(1 - z/3)(1.5 + z/2)$$
$$- \cos \theta_{av}\}/\sin \theta_{av}] \tag{15}$$

averaging $\cos \theta(m)$ over different m-values, i.e.

$$\langle \cos \theta(m) \rangle = \sum_{m=0}^{6} P_{B'A}(m, z) \cos \theta(m) \tag{16}$$

and finally comparing $\langle \cos \theta(m) \rangle$ with $\cos \theta_{av}$. If the two values are unequal, we then let

$$\theta_{av} = \cos^{-1}[\langle \cos \theta(m) \rangle]$$

and substitute it into equation (15). The computational process is repeated until a self-consistent result is reached.

Table 1. The calculated canting angles for Li–Zn ferrite under different doping conditions.

z (Zn atoms/formula unit)	θ_{av} (deg)	$\cos \theta_{av}$
0.1	0.0	1.000
0.2	11.5	0.980
0.3	19.9	0.940
0.4	31.8	0.850
0.5	43.9	0.720
0.6	58.1	0.528
0.7	66.7	0.395

The moment at 0 K, per formula unit, of Li–Zn ferrite can thus be calculated from

$$M = M_B \cos \theta_{av} - M_A \tag{17}$$

where

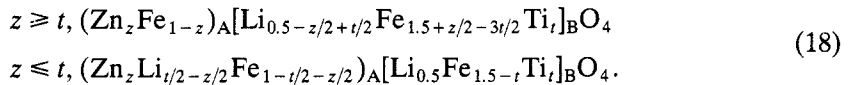$$M_B = 2gS\mu_B(1 - k_B)$$

and

$$M_A = gS\mu_B(1 - k_A)$$

while

$$k_B = 0.5 - 0.5z$$

and

$$k_A = z.$$

The same procedure can be applied for double-substituted Li–Ti–Zn ferrite with a Ti substituent level t, if the particular ion distribution in this ferrite [8] is taken into account:

$$z \geq t, \ (Zn_z Fe_{1-z})_A[Li_{0.5-z/2+t/2}Fe_{1.5+z/2-3t/2}Ti_t]_B O_4$$
$$z \leq t, \ (Zn_z Li_{t/2-z/2}Fe_{1-t/2-z/2})_A[Li_{0.5}Fe_{1.5-t}Ti_t]_B O_4. \tag{18}$$

It follows from equation (14) that

$$z \geq t, \ \theta(m) = \tan^{-1}[\{q[m + 6(1 - z)]/3(1.5 + z/2 - 3t/2) - \cos \theta_{av}\}/\sin \theta_{av}] \tag{19}$$

where $q = 2.29(1 - 0.4tz - 0.2z)/(1 - z/3)$ and

$$z \leq t, \ \theta(m) = \tan^{-1}[\{q[m + 6(1 - 0.5z - 0.5t)]/3(1.5 + 0.5z - 1.5t)$$
$$- \cos \theta_{av}\}/\sin \theta_{av}] \tag{20}$$

where $q = 2.29[1 - 0.2t(t + z) - 0.2z]/(1 - t/2 + z/6)$.

5. Results and discussion

Table 1 enumerates the calculational results for the canting effect in Li–Zn ferrite under different doping conditions and table 2 shows how the canting angle changes with the

Table 2. The calculated canting angles for Li–Ti–Zn ferrite at different substituent levels t of Ti when the Zn concentration is kept at 0.4 atoms/formula unit.

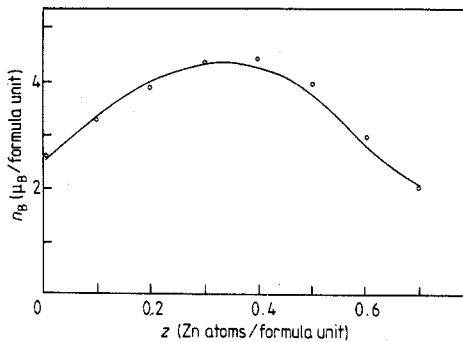| t (Ti atoms/formula unit)	θ_{av} (deg)	$\cos \theta_{av}$
0.0	31.8	0.850
0.1	28.9	0.875
0.2	19.9	0.940
0.3	11.5	0.980
0.4	2.56	0.999
0.5	0.0	1.000

Figure 2. The magnetic moment at 0 K plotted against the doping level z of Zn for Li–Zn ferrite: ——, model calculation; ○, experimental data [1].
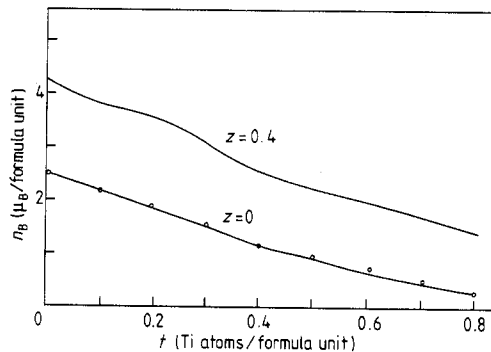

Figure 3. The magnetic moments at 0 K plotted against the substituent concentration t of Ti for Li–Ti–Zn ferrite with the doping content z of Zn being 0.4 atoms/formula unit and for Li–Ti ferrite: ——, model calculation; ○, experimental data [7].

doping level t for Ti–Zn-doped Li ferrite when the Zn substituent concentration is kept at 0.4 atoms/formula unit.

By replacing the canting angle in equation (14) with the calculated values and performing the calculations in equation 17, the relationship between the moment at 0 K and the doping level for either Li–Zn ferrite or Li–Ti–Zn ferrite can thus be determined in the framework of our model. The results are illustrated by the curves in figures 2 and 3.

Table 3. The variation in exchange integral ratio $|J_{AB}/J_{BB}|$ with doping concentration z of Zn.

z (Zn atoms/formula unit)	$|J_{AB}/J_{BB}|$
0.1	2.306
0.2	2.340
0.3	2.376
0.4	2.415
0.5	2.457
0.6	2.503
0.7	2.552

It is remarkable that the theoretical curve in this paper, as shown in figure 3, fits the experimental data excellently, forming a striking contrast to the reported computational results obtained from existing model calculations [4, 5]. It is not only their fits that are not very successful, but also the ratio J_{AB}/J_{BB} which is taken as a fixed value in the work in [4, 5] that is unrealistic. The best result was attained in [4] by setting $|J_{AB}/J_{BB}| = 1.5$ while 2.5, 3.5 and 4.5 were selected in [5] as the value of $|J_{AB}/J_{BB}|$ to meet the situation. This ratio, as a function of doping level, should nevertheless take some more reasonable values, as listed in terms of absolute value in table 3, so that the result obtained in either [4] or [5] seems of little importance even if it were in good agreement with the experimental data.

In addition, as far as the computational plan is concerned, our calculation is also distinct from that in [5], where $\theta(m)$ was regarded as the convergent, i.e. in contrast with equation (16) in this paper the equation

$$\langle \theta(m) \rangle = \sum_{m=0}^{6} P_{B'A}(m, z)\theta(m) \tag{21}$$

was used to calculate the average canting angle and the result was considered as self-consistent when $\langle \theta(m) \rangle = \theta_{av}$. It is important to emphasise, however, that what equation (16) represents differs completely from what equation (21) represents from both a physical and a purely mathematical meaning. Since the model itself requires the $\langle \cos \theta(m) \rangle$ form to be used in calculating the moment, not equation (21) but equation (16) should be adopted in the iterative computation with the convergent surely being $\langle \cos \theta(m) \rangle$ rather than $\langle \theta(m) \rangle$. Furthermore, when the distribution $P_{B'A}(m, z)$ is taken into account, we have

$$\langle \cos \theta(m) \rangle \neq \cos\langle \theta(m) \rangle. \tag{22}$$

Figure 3 depicts the theoretical curve of the moment at 0 K against the doping level t of Ti for Ti–Zn-doped Li ferrite when the Zn content is 0.4 atoms/formula unit, a theoretically fitted curve for Li–Ti ferrite, along with its experimental counterpart, is also shown.

Although a comprehensive analysis cannot be carried out at present owing to lack of a complete set of experimental data for Li–Ti–Zn ferrite, we can still make some inferences at this stage from both our model calculation and the information available. It follows from figure 3 that no canting effect exists in Li–Ti ferrite over the entire concentration range of substitution under discussion ($t \leqslant 0.8$ atoms/formula unit) and

the moment n_B decreases almost monotonically and linearly with increasing doping level, while n_B for Li–Ti–Zn ferrite substituted with a definite quantity of Zn does not manifest a similar pattern of change until $t \geq z$, indicating the intervention of the canting effect in the latter ferrite. It seems from our model calculations that the introduction of Ti into the Li–Zn ferrite can reduce the canting effect or even suppress it completely when $t \geq z$. This implies that the double substitution at both A and B sites with a suitable proportion of substituents can maintain the spin system in a magnetically ordered and energetically favourable state even without invoking spin canting, which confirms theoretically a reported experimental conclusion [7].

Acknowledgment

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