Localized canting effect in Zn-substituted Ni ferrites

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Abstract

A model of three sublattices (A, B and B′) to describe the magnetic behavior of mixed Ni–Zn ferrites is presented. It is proposed that only sublattice B′ is affected by canting, due to the substitution of Zn^{2+} ions in sublattice A. The cases where: (i) only Fe^{3+} ions are found in B′, and (ii) B′ is occupied by Fe^{3+} and Ni^{2+} ions are considered. The two-sublattice model with canting in sublattice B is presented for comparison with cases (i) and (ii). The canting angle θ_L is calculated from energetic considerations, assuming that the J_{ij} ion-to-ion interaction energies are not modified by the substitution of Zn^{2+} ions in sublattice A. The number of Bohr magnetons per molecule, n_B, and the Curie temperature, T_c, are predicted as a function of Zn content, z. The experimental values of n_B as well as the results for T_c are satisfactorily reproduced by the model described in (i). Results on Zn-substituted Li ferrite are also mentioned. It is found that additional considerations on the interactions are needed for this system, as lithium acts as a non-magnetic dilution in the octahedral sublattice. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that when adding Zn ions (which are non-magnetic) to spinel ferrites their magnetization increases with Zn content, z [1]. This is observed up to values of $z \sim 0.5$ at/formula unit. The magnetization drops for higher z.

It is accepted [2–6] that this fact is due to the so-called *canting effect*, in which the magnetization of one of the sublattices in the crystalline structure is led to depart from collinearity with the net magnetization direction as a consequence of a 'loosening' in the interactions between the sublattices.

Many attempts have been made to provide an acceptable explanation to this phenomenon. Yafet and Kittel [2] proposed an approach in which one sublattice is divided into two halves each oppositely canted at some uniform canting angle relative to the average magnetization. They were the first to argue that non-magnetic substitutions on one sublattice could lead to a non-collinear arrangement on the other. Geller [3,4] gave a localized canting approach in which individual moments on one sublattice are canted at different angles, depending

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on the characteristics of the local magnetic environment. This concept was formalized by Dionne [7] in a refinement of the Néel molecular-field model. Patton and Liu [5] provided a mathematical formulation of the random localized canting proposed by Geller starting from a nearest-neighbor Heisenberg–Hamiltonian and considering average values of some involved quantities. They used local effective fields to evaluate average canting angles.

In this paper, the idea of a uniform canting angle is considered and a modification of the mathematical formulation proposed by Patton and Liu is used for modeling the canting effect in the system $Zn_zNi_{1-z}Fe_{1+z}O_4$. Localized average surroundings are taken into account in the description, bearing in mind Dionne's idea of canting [7–9]. The results obtained by Bercoff and Bertorello [10] for the ion-to-ion exchange constants of different spinel ferrites are used in this work for the evaluations. The calculations performed do not require any adjustable parameter. The results are compared with the experimental values given by Gorter [1], Smit and Wijn [11], and Pauthenet [12], obtaining a good agreement between the theory and experimental data for the magnetization curves and Curie temperature as a function of z.

The model proposed is also used for Li–Zn ferrites, obtaining a good agreement for the magnetization curves.

2. Theoretical framework

The magnetic structure of Ni ferrite, $NiFe_2O_4$, is that of two opposing magnetic sublattices — A (tetrahedral sites) and B (octahedral sites) — , in which the magnetic ions are all coupled antiferromagnetically. The A–B coupling is the strongest and dominates the interactions. There are more B sites than A sites so the net magnetization is simply the difference between the B sublattice magnetization and the A sublattice magnetization.

The crystalline structure of Ni ferrite is the 'inverted' spinel, where the A sublattice contains half of the Fe^{3+} ions and the other half together with all the Ni^{2+} ions are in the B sublattice. Zn ferrite belongs to the 'normal' type of spinels, that is, all the Zn^{2+} ions are in A sites. In a mixed Ni–Zn

ferrite, $Zn_zNi_{1-z}Fe_{1+z}O_4$ (z being the Zn content per formula unit), the Zn^{2+} ions stay in A sites and the Ni^{2+} ions in B sites [11].

When the Fe^{3+} ions concentration in the A sublattice is diluted by low concentrations of diamagnetic substitutions (like Zn^{2+}), the net magnetization increases. However, at higher doping levels, a decrease in magnetization occurs. The reason for this is that low Zn concentrations lead to a decrease in the number of spins occupying the A sublattice causing an increase of the net magnetization. As the Zn content is increased the exchange interactions are weakened and the B spins are no longer held rigidly parallel to the few remaining A spins. The decrease in the B-sublattice moment, interpreted as a spin departure from collinearity, causes the effect known as *canting*.

Having in mind previous results of Dionne [7–9], in the present work it is considered that there are two octahedral sublattices — B and B′ — , and only B′ is affected by the canting effect. It is assumed that the B′ sublattice is formed only by the nearest neighbors to the A sites which have been occupied by Zn^{2+} ions. In this way the amount of B′ sites will increase with higher z values. The B′ spins will be canted from the direction of net magnetization an angle θ, forming an angle of 2θ between them, as depicted in Fig. 1.

Two cases are studied:

(i) *B′ is occupied only by Fe^{3+} ions:* As Zn^{2+} ions replace Fe^{3+} ions in A sites it can be argued that, in order to locally keep the total charge neutral, all the ferric ions that had been displaced will tend to stay near the Zn^{2+} ions that have taken their place. In this way, B′ sites will be occupied by Fe^{3+} ions. In
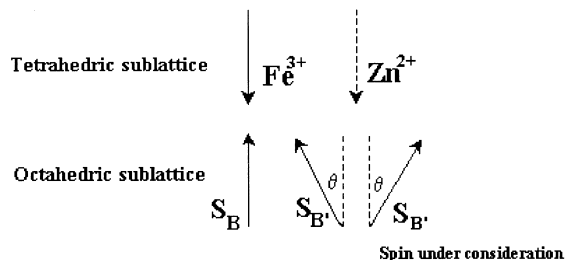

Fig. 1. Model spin configuration of a Zn-substituted ferrite (after Dionne [7]).

this case it is considered that all B′ sites have ferric ions; therefore, in sublattice B there will be equal proportion of Fe^{3+} and Ni^{2+}.

(ii) *B′ is occupied by Fe^{3+} and Ni^{2+} ions:* It can be thought that all the ions in octahedral sites which are nearest-neighbors of Zn ions keep an 'average character', so B′ sites are occupied by Fe^{3+} and Ni^{2+} ions in the proportion given by the average composition of the ferrite.

Geller [3,4] proposed a localized canting approach, in which individual moments on one sublattice are canted at different angles, depending on the specifics of the local magnetic environment. Patton and Liu [5] provided a mathematical formulation of random localized canting, starting from a nearest-neighbor Heisenberg–Hamiltonian

$$H = - \sum_i \sum_{NN \ to \ i} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where J_{ij} are the i–j nearest-neighbor exchange constants and $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins of the ions on the i and j sites.

The model spin configuration of a Zn-substituted ferrite is shown in Fig. 1.

Having this idea in mind, the free energy can be written in terms of the canting angle θ in the form

$$H = a \cos \theta + b \cos 2\theta + c, \tag{2}$$

where

$$a = - |J_{AB'}| S_A S_{B'} (q_A n_{AB'} + q_{B'} n_{B'A})$$
$$+ |J_{BB'}| S_B S_{B'} (q_B n_{BB'} + q_{B'} n_{B'B})$$

$$b = |J_{B'B'}| S_{B'}^2 q_{B'} n_{B'B'}$$

and q_i = number of magnetic ions per formula unit in sublattice i (i = A, B, B′), n_{ij} = number of nearest-neighbor j-ions to an i-ion (i, j = A, B, B′).

The values of q_i and n_{ij} are the same for cases (i) and (ii), and are shown in Table 1.

Table 2
Values of S_i for cases (i) and (ii)

	S_A	S_B	$S_{B'}$
Case (i)	2.5	$\frac{1}{2}[2.5 + 1]$	2.5
Case (ii)	2.5	$\frac{1}{2}[2.5(1 - z) + (1 - z)]$	S_B

When $z \ll 1$, q_B and $q_{B'}$ are $2(1 - z)$ and $2z$, respectively. This is not accurate for all z; the number of ferric ions with more than z Zn^{2+} nearest-neighbors varies as a function of z due to the overlapping of neighboring B′ zones produced when the amount of Zn ions increases. In order to take this fact into account $q_B = 2(1 - z + 2z^2 - 2.5z^3)$ and $q_{B'} = 2(z - 2z^2 + 2.5z^3)$ are used on empirical grounds.

In order to establish the values of n_{ij} it is considered an average surrounding the A sites so that the number of B′ nearest-neighbors to an A ion is the number of B neighbors to an A site, multiplied by the fraction of Zn per formula unit, i.e. $n_{AB'} = 12z$. The number of B′ neighbors to a B ion is taken as the number of B neighbors to a B site, multiplied by the fraction of Zn per formula unit, i.e. $n_{BB'} = 6z$. Both $n_{B'B}$ and $n_{B'B'}$ are corrected by the factor z^2.

The values of S_B and $S_{B'}$ are different in cases (i) and (ii) because the ionic distribution changes. The criterion followed to set the values of S_B and $S_{B'}$ in each case considered was to take the mean of the spin numbers of the ions that were in the same sublattice (see Table 2).

A straightforward minimization of Eq. (2) leads to the following expression for a 'local' canting angle θ_L:

$$\cos \theta_L = \frac{- a}{4b}. \tag{3}$$

Table 1
Values of q_i and n_{ij}

q_A	q_B	$q_{B'}$	$n_{AB'}$	$n_{BB'}$	$n_{B'A}$	$n_{B'B'}$	$n_{B'B}$
$1 - z$	$2 - q_{B'}$	$2(z - 2z^2 + 2.5z^3)$	$12z$	$6z$	$5(1 - z)$	$2(1 - z^2)$	$6 - n_{B'B'}$

Table 3
Exchange constants J_{ij}, estimated from the ion-to-ion constants $J_{ij}^{\text{ion-ion}}$

	Case (i)	Case (ii)
$J_{AB'}$	$J_{AB}^{Fe^{3+}-Fe^{3+}}$	$\frac{1}{2}[(1+z)J_{AB}^{Fe^{3+}-Fe^{3+}} + (1-z)J_{AB}^{Fe^{3+}-Ni^{2+}}]$
$J_{BB'}$	$\frac{1}{2}(J_{BB}^{Fe^{3+}-Fe^{3+}} + J_{BB}^{Fe^{3+}-Ni^{2+}})$	$\frac{1}{4}[(1+z)^2 J_{BB}^{Fe^{3+}-Fe^{3+}} + 2(1-z)(1+z)J_{BB}^{Fe^{3+}-Ni^{2+}} + (1-z)^2 J_{BB}^{Ni^{2+}-Ni^{2+}}]$
$J_{B'B'}$	$J_{BB}^{Fe^{3+}-Fe^{3+}}$	$J_{BB'}$

Table 4
Values of the ion-to-ion constants

(K)	Bercoff and Bertorello [10]	Srivastava et al. [14]
$J_{AB}^{Fe^{3+}Fe^{3+}}$	− 12.0	− 28.0
$J_{AB}^{Fe^{3+}Ni^{2+}}$	− 29.8	− 27.4
$J_{BB}^{Fe^{3+}Fe^{3+}}$	− 8.8	− 5.4
$J_{BB}^{Fe^{3+}Ni^{2+}}$	− 13.6	− 2.7
$J_{BB}^{Ni^{2+}Ni^{2+}}$	+ 0.8	+ 30.0

The exchange constants J_{ij} were estimated from the ion-to-ion constants $J_{ij}^{\text{ion-ion}}$ in the way shown in Table 3. It was considered that the J_{ij} ion-to-ion interaction energies are not modified by the substitution of Zn^{2+} ions in sublattice A, similarly to the assumptions made by Dionne in his work about dilution effect in magnetic garnets [7,13].

Two sets of ion-to-ion constants are listed in Table 4 and both were used for the calculation of $\cos\theta_L$. One of the sets was obtained from Bercoff and Bertorello [10] who considered $J_{AA} = 0$ in spinel ferrites, based on arguments that led to the conclusion that superexchange interaction between A ions is very unlikely. The other set of ion-to-ion exchange constants was obtained from a paper on the subject by Srivastava and coworkers [14], who estimated them by a three-sublattice model for magnetization and susceptibility, which involves six exchange constants.

The total magnetization of a spinel ferrite can be written in the form

$$M_T(T) = M_B(T) + M_{B'}(T)\cos\theta_L - M_A(T), \quad (4)$$

where $M_A(T)$, $M_B(T)$ and $M_{B'}(T)$ are the magnetizations of the A, B and B' sublattices, respectively.

The number of Bohr magnetons per formula unit, n_B as a function of Zn content can then be expressed for $T = 0$ K in the way shown in Table 5. The expressions are for cases (i) and (ii), and for comparison the case was included in which there are only two sublattices, A and B, and the entire sublattice B is affected by canting.

3. Results

In Fig. 2, n_B versus z is plotted for case (i) when only ferric ions are found in B', case (ii) in which B' is occupied by Fe^{3+} and Ni^{2+} ions in equal proportions compared to that in B, and for the two-sublattice model where all the ions in octahedral sites are affected by canting. The results obtained for any of these cases with the exchange constants given by Srivastava [14] are also included. Experimental values are also shown in the same figure taking data from Gorter [1], Smit and Wijn [11] and Pauthenet [12].

Analyzing Fig. 2 it can be seen that:

- The two-sublattice model predicts very low values of n_B which disagrees with the experimental results.
- Using the values obtained by Srivastava and others [14] for the ion-to-ion exchange constants, no canting is predicted as z varies in any of the cases considered.
- When case (i), having only ferric ions in B', is considered, the magnetization (n_B) as a function of Zn content drops too abruptly and the values of n_B are below the experimental data. Canting is present for all z, even for $z \ll 1$, and this does not agree with the experiments.

Table 5
Number of Bohr magnetons per formula unit, n_B as a function of Zn content, z for $T = 0$ K. $g^{Fe^{3+}}$ and $g^{Ni^{2+}}$ are the Landé factors and $S^{Fe^{3+}}$ and $S^{Ni^{2+}}$ are the spin numbers for Fe^{3+} and Ni^{2+} ions, respectively

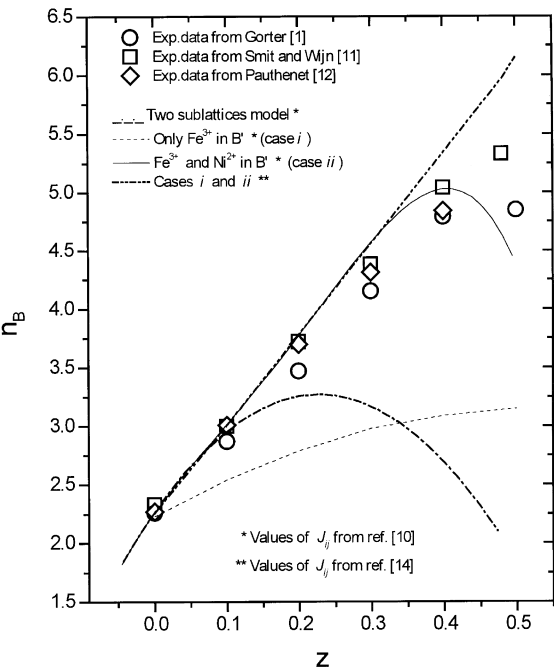|	n_B
Case (i)	$\dfrac{q_B}{2}[g^{Fe^{3+}}S^{Fe^{3+}} + g^{Ni^{2+}}S^{Ni^{2+}}] + q_{B'}\cos\theta_L g^{Fe^{3+}}S^{Fe^{3+}} - q_A g^{Fe^{3+}}S^{Fe^{3+}}$
Case (ii)	$\left(\dfrac{q_B}{2} + \dfrac{q_{B'}}{2}\cos\theta_L\right)[g^{Fe^{3+}}S^{Fe^{3+}}(1+z) + g^{Ni^{2+}}S^{Ni^{2+}}(1-z)] - q_A g^{Fe^{3+}}s^{Fe^{3+}}$
Two sublattices	$[g^{Fe^{3+}}S^{Fe^{3+}}(1+z) + g^{Ni^{2+}}s^{Ni^{2+}}(1-z)]\cos\theta_L - q_A g^{Fe^{3+}}S^{Fe^{3+}}$

Fig. 2. Number of Bohr magnetons per formula unit as a function of Zn content, for Ni–Zn ferrite. Cases (i) and (ii) are compared with the results of the two-sublattice model and experimental data from Refs. [1,11,12].
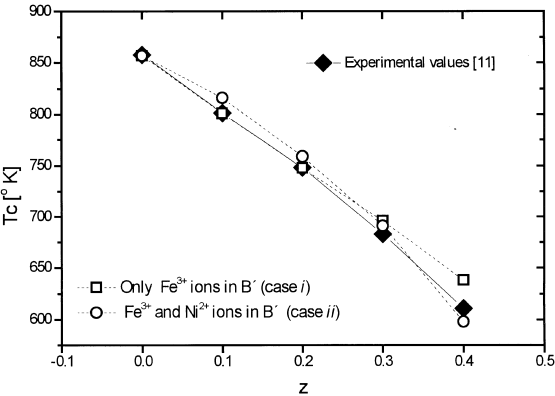

Fig. 3. Curie temperature as a function of Zn content. Cases (i) and (ii) are compared with experimental data from Ref. [11].

- The experimental results are well predicted only when case (ii) (with Fe^{3+} and Ni^{2+} in B′) and values of J_{ij} given in Ref. [10] are considered. The effect of canting starts to be noticeable for $z > 0.35$ which is in good agreement with Refs. [11,12]. Also, the maximum value of n_B for $z \sim 0.5$ is predicted which is in conformity with the measurements of Refs. [1,11].

- Comparing the results obtained for case (ii) using the exchange constants given by Ref. [10] with the situation where the values of J_{ij} were taken from the work of Srivastava et al. [14], it can be deduced that the effect of canting is well described when the interaction Ni^{2+}–Ni^{2+} in octahedral sites is slightly ferromagnetic, in agreement with Anderson's considerations [15] in his theory of superexchange. The value of $J_{BB}^{(Ni2+)-(Ni2+)}$ calculated by Srivastava and coworkers is too high and cannot be explained according to Anderson's theory.

In Fig. 3 the variation of the Curie temperature T_c as a function of Zn content z is shown. The
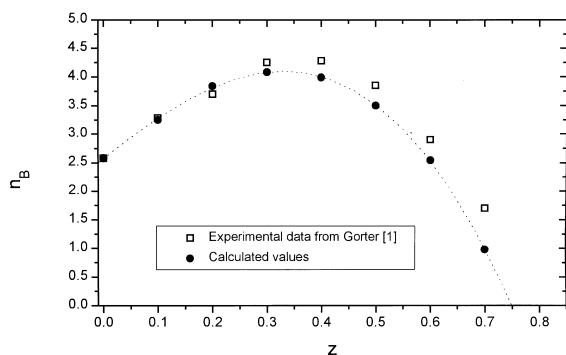
Fig. 4. Number of Bohr magnetons per formula unit as a function of Zn content, for Li–Zn ferrite. The results obtained in this work are compared with experimental data from Ref. [1].

experimental values obtained from Ref. [11] are compared with the results from cases (i) and (ii) calculated by equating the inverse susceptibility to zero for $T = T_c$ with the three-sublattice model [14], and the exchange constants given in Ref. [10].

It can be seen that the experimental results are well predicted in both cases, being impossible to infer from this, which of the two models describes more accurately the behavior of T_c versus z. However, the agreement of the results for magnetization as a function of Zn content with the experimental values lead to conclude that the model presented in case (ii) gives a more accurate representation of the system.

The behavior of lithium ferrite was also studied under the considerations described in case (i), as the only magnetic ions in this system are Fe^{3+}. A good agreement between experimental and analytic data is obtained for n_B versus z, as can be seen in Fig. 4. These results agree with the findings of White et al. [16], who describe well the experimental data of Li–Zn ferrite using a localized canting model. However, the Curie temperature as a function of Zn content is not properly described with this model.

It is thought that this is possibly due to the fact that in the system $Li_{0.5-z/2}Zn_zFe_{2.5-z/2}$ the Li^+ ions also act as a non-magnetic dilution in sublattice B, affecting both J_{AB} and J_{BB}. Further studies on this subject are being conducted.

4. Conclusions

Canting effect in Ni–Zn ferrites is appropriately described by a three-sublattice model with the supposition that the octahedral sites are 'split' into two sublattices, B and B′, and only B′ is affected by canting. Sublattice B′ is formed by the Fe^{3+} and Ni^{2+} nearest neighbors to Zn^{2+} ions (which are placed in sublattice A).

The model proposed in case (ii) gives a good description of canting in Ni–Zn ferrites as long as the exchange constants given by Bercoff and Bertorello [10] are used. These values of the constants were calculated under the assumption $J_{AA} = 0$. In contrast, using the constants given by Srivastava and others [14] canting is not predicted for any value of z. These authors obtain $J_{AA} < 0$ and $|J_{AA}| > |J_{BB}|$, which do not agree with any theory of superexchange.

The values obtained for T_c are well predicted by the model proposed in case ii. This fact, together with the results of the canting effect on the magnetization provide strong support to the assumption that $J_{AA} = 0$ in spinel ferrites.

Acknowledgements

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