Equivalence of ion-size effect and hydrostatic-pressure effect on exchange coupling in spinels and garnets

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The equivalence of ion-size effect and hydrostatic-pressure effect on the superexchange coupling is quantitatively established by using experimental results published in the literature for spinel and garnet ferrimagnetic materials. The method of investigation is based on the introduction in $NiFe_2O_4$ and in $Y_3Fe_5O_{12}$ of two kinds of nonmagnetic ions with different ionic radii r and with low concentrations x: the volume variation ΔV and the Curie-temperature variation ΔT_C due to the ion-size effect permit one to find the value of $\beta = (\Delta T_C/T_C)/\Delta V/V$ of the law $T_C \sim V^\beta$. These values of β also agree with those obtained from the thermal-expansion measurements by using the expression of the volume anomaly deduced from molecular-field theory.

INTRODUCTION

It is known that the exchange magnetic energy of Heisenberg type between two neighboring magnetic ions i and j with magnetic moments S_i and S_j is given by $-2J_{ij}(a)S_iS_j$, where $J(a)$ is the exchange parameter which depends on the overlapping of ion orbitals and, hence, strongly depends on the distance between the two ions. The magnetic ordering temperature T_C is directly proportional to the exchange parameter J. Assuming a volume dependence of J of the form V^β and considering a small volume variation ΔV, T_C ($\sim J$) can be written as[1]

$$T_C = T_0 \left[1 + \beta \frac{\Delta V}{V} \right] . \tag{1}$$

β is the slope of the dependence of J on volume:

$$\beta = \frac{\Delta T_C/T_C}{\Delta V/V} . \tag{2}$$

The spatial variation of exchange interactions can be studied by measuring the variation ΔT_C of the magnetic ordering temperature corresponding to a small volume variation ΔV. Experimentally, one can obtain small volume changes ΔV by the following:

(1) Application of hydrostatic pressure, which is the simple method for varying the interatomic distance. In the case of insulating cubic magnetic materials, Bloch states precisely the law for the volume dependence of the superexchange interactions.[2]

(2) Using the magnetoelastic interactions corresponding to the exchange striction.[3] The experimental volume anomaly of $Y_3Fe_5O_{12}$ and $NiFe_2O_4$ permits the determination of the volume dependence of the exchange interactions, through the theoretical expression deduced from molecular-field theory.[4]

Another method of varying the distance between magnetic ions consists of introducing nonmagnetic ions with different sizes and concentrations. However, this method is more delicate because not only the interionic distance changes, but also the ionic and crystallographic structures

may change, which makes difficult the interpretation of the results. Therefore, we have searched experimental conditions of ion substitution in $Y_3Fe_5O_{12}$ and $NiFe_2O_4$ allowing the evaluation of the volume dependence of exchange coupling by the ion-size effect.

METHOD OF INVESTIGATION

The use of the ion-size effect as a way to change the interionic distance is based on the fact that there exists in ionic compounds a linear dependence between the lattice constant and the ionic radii of the constituent ions: the introduction of larger and larger ions with higher and higher concentrations results in an increased distance between lattice ions. Hence, it is possible to investigate the influence of the distance between magnetic ions upon fundamental properties such as the magnetic ordering Curie temperature.

The $NiFe_2O_4$ spinel and $Y_3Fe_5O_{12}$ garnet materials are ionic compounds with magnetic moments localized on two sublattices corresponding to tetrahedral d sites and octahedral a sites. The magnetic order is governed by the superexchange interaction energy between magnetic cations via oxygen anions. Generally, one assumes the antiferromagnetic interaction between the two sublattices a and d to be dominant. Then the magnetic ordering Curie temperature is proportional to the superexchange interaction energy of Fe_d^{3+}—O^{2-}—Fe_a^{3+} linkages and to the number of linkages.[5]

The method of investigation is to consider two series of substituted materials containing two kinds of nonmagnetic ions located in the same reference lattice. These two kinds of nonmagnetic ions are located in the same type of site, but are characterized by two different ionic radii. Then, we compare, for a same concentration x, two materials with a same number of Fe_d^{3+}—O^{2-}—Fe_a^{3+} linkages and differing only by the distance between magnetic ions.

Taking into account the ionic character of the chemical bond and considering only nonmagnetic ions located in

tetrahedral sites, with four nearest-neighbor O^{2-} ions (even number of neighbors), we choose bivalent or tetravalent nonmagnetic ions. From the literature, we have selected the pairs of nonmagnetic ions satisfying best the above-described conditions.

ION-SIZE EFFECT IN SPINEL LATTICE

Let us consider the $NiFe_2O_4$ spinel lattice as the reference structure. The investigation is based on the introduction of nonmagnetic ions Zn^{2+} and Cd^{2+}: it is known that these two cations enter in tetrahedral sites with ionic radii of 0.60 and 0.84 Å, respectively.[6] We use the results obtained for these two series by Globus et al.[7] (Fig. 1). Consider a given concentration x and compare the two materials $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Cd_xFe_2O_4$. In these materials the ion distribution in the sites is the same. Then the difference ΔT_C is the contribution to T_C due to the change of the distance between magnetic ions.

If we plot the variation of ΔT_C as a function of $\Delta V/V = 3\Delta a/a$ for different concentrations x, we obtain a linear dependence (Fig. 2: solid line) until $x \lesssim 0.50$, whose slope at the origin permits one to determine the β value of the law $J \sim V^\beta$: from $\beta = (\Delta T_C/T_C)/\Delta V/V$, where $\Delta V/V = 3(\Delta a/a)$, we find $\beta = -2.3$.

Now we can compare the results obtained from the hydrostatic-pressure and ion-size effects. A hydrostatic pressure ΔP leads to a volume variation ΔV:

$$\frac{\Delta V}{V} = -\chi \Delta P \ , \tag{3}$$

where χ is the compressibility.

FIG. 2. Relations between the Curie temperature variation ΔT_C and the relative volume variation $\Delta V/V$, in $NiFe_2O_4$ spinel lattice, deduced from the ion-size effect (bottom solid line) and from the hydrostatic pressure effect [top solid line (Ref. 8)]. The dashed line corresponds to the extrapolated relation in the case of the hydrostatic-pressure effect.

Then β is given by

$$\beta = -\frac{\Delta T_C/T_C}{\chi \Delta P} \ . \tag{4}$$

In the case of $NiFe_2O_4$, Foiles and Tomizuka found a variation ΔT_C under a hydrostatic pressure ΔP: $\Delta T_C/\Delta P \simeq +1.16$ K/kbar.[8] Thus with the value of $\chi \simeq 0.54 \times 10^{-12}$ $dyn^{-1}cm^2$ (Ref. 9) the expression (4) gives $\beta = -2.4$, in good agreement with the value found from the ion-size effect.

ION-SIZE EFFECT IN GARNET LATTICE

Consider the substitution of Si^{4+} and Ge^{4+} ions in $Y_3Fe_5O_{12}$: it is known that these two cations enter tetrahedral sites for small concentrations x (≤ 0.50) with ionic radii of 0.26 and 0.39 Å, respectively.[6] The two series are

$$Y_{3-x}Ca_xFe_{5-x}Si_xO_{12}$$

and

$$Y_{3-x}Ca_xFe_{5-x}Ge_xO_{12} \ ,$$

in which nonmagnetic bivalent Ca^{2+} ions are located in dodecahedral sites, which ensures the crystal electrical equilibrium.

We use the experimental results obtained for these two series by Geller et al.[10] and by Winkler et al.[11] and summarized on Fig. 3. Consider a given concentration x and compare the two materials $Y_{3-x}Ca_xFe_{5-x}Si_xO_{12}$ and $Y_{3-x}Ca_xFe_{5-x}Ge_xO_{12}$. In these materials the ion distri-
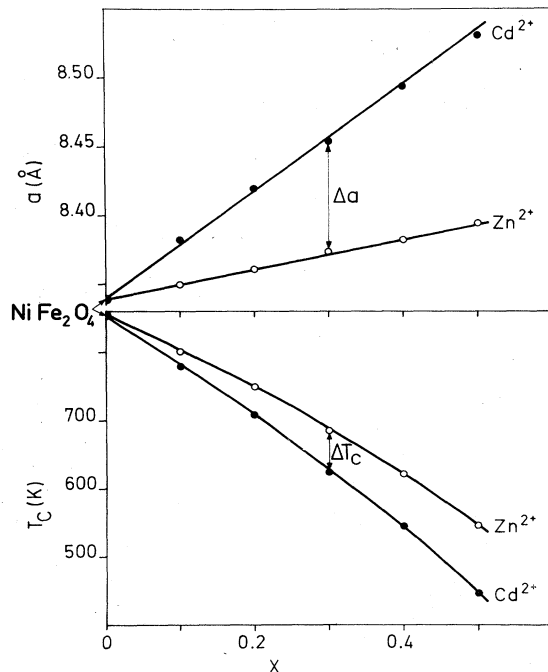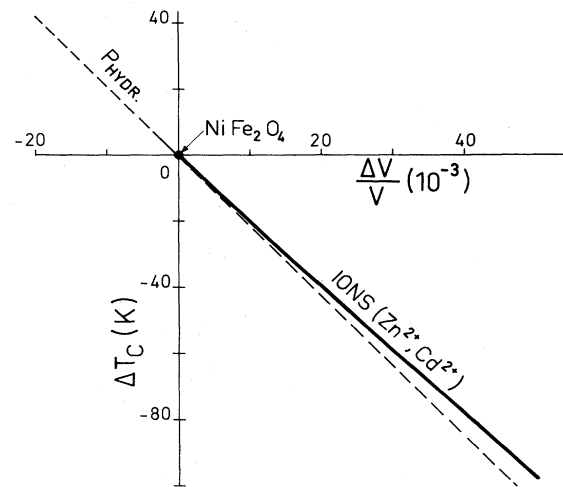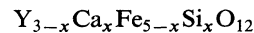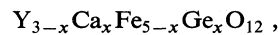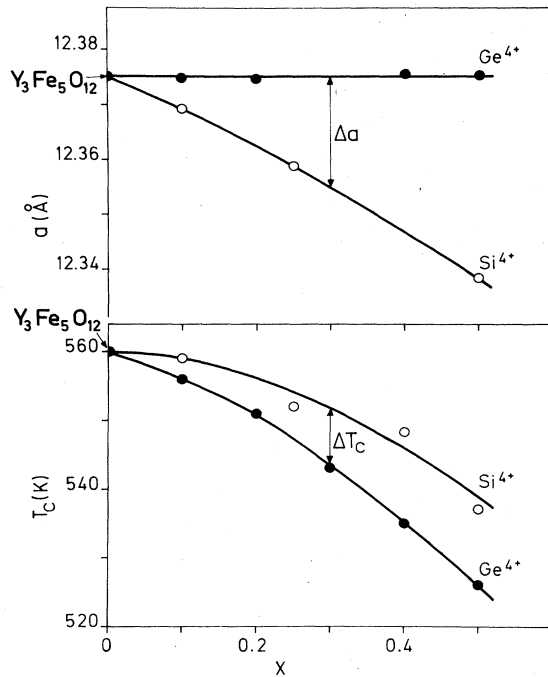
FIG. 1. Lattice constant a and Curie temperature T_C, versus Zn^{2+} and Cd^{2+} concentration x, in $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Cd_xFe_2O_4$ (Ref. 7).

FIG. 3. Lattice constant a and Curie temperature T_C, versus Ge^{4+} and Si^{4+} concentration x, in $Y_{3-x}Ca_xFe_{5-x}Si_xO_{12}$ and $Y_{3-x}Ca_xFe_{5-x}Ge_xO_{12}$ (Refs. 10 and 11).

bution in the sites is the same. Consequently they only differ in that their lattice constant is not the same. Then, the difference ΔT_C is the contribution to T_C caused by the change of the distance between magnetic ions.

If we plot the variation of ΔT_C with $\Delta V/V$ for different concentrations $x \lesssim 0.50$, we obtain the curve in Fig. 4, whose slope at the origin permits one to determine the β value of the law $J \sim V^{\beta}$: from $\beta = (\Delta T_C/T_C)/\Delta V/V$ we find $\beta \simeq -3.6$.

Now we can compare the results obtained from the hydrostatic-pressure and ion-size effects. For $Y_3Fe_5O_{12}$, Bloch et al. found $\Delta T_C/\Delta P \simeq +1.2$ K/kbar.[12]

With the value of $\chi = 0.63 \times 10^{-12}$ dyn^{-1} cm^2,[13] the expression (4) gives $\beta \simeq -3.6$, in very good agreement with the value found from the ion-size effect.

COMPARISON WITH THE β VALUE DEDUCED FROM THE VOLUME ANOMALY EFFECT

It is interesting to compare the β values obtained for $NiFe_2O_4$ and $Y_3Fe_5O_{12}$ from the ion-size and hydrostatic-pressure effects with those obtained by using the magnetoelastic interactions corresponding to the exchange striction. The experimental volume anomaly $(\Delta V/V)_0$ of $Y_3Fe_5O_{12}$ and $NiFe_2O_4$ permits one to determine β, with the expression deduced from the molecular-field theory. The general expression relating β to $(\Delta V/V)_0$ is given by[15]

$$\beta = \frac{(\Delta V/V)_0}{\chi(\frac{1}{2}k_BT_C)N[3S/(S+1)]} , \qquad (5)$$

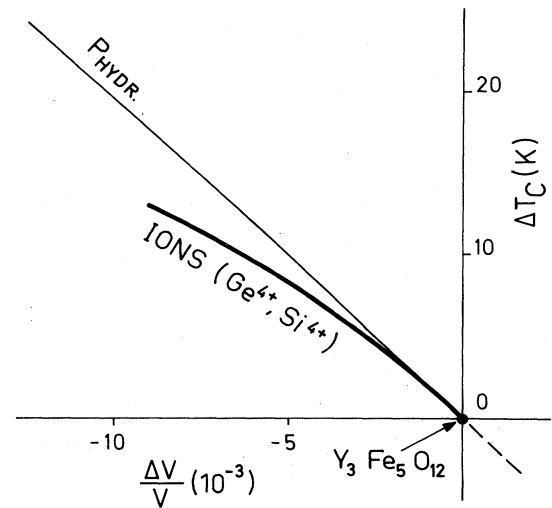where N is the number of magnetic ions per unit volume

FIG. 4. Relations between the Curie temperature variation ΔT_C and the relative volume variation $\Delta V/V$, in $Y_3Fe_5O_{12}$ garnet lattice, deduced from the ion-size effect (bottom curve) and from the hydrostatic-pressure effect (top straight line) (Refs. 12 and 14).

and S the spin of the magnetic ion.

With the experimental volume anomaly values found from thermal-expansion measurements[4] and the expression (5) adapted to the case of ferrimagnetic materials with two sublattices,[16] we find $\beta = -3.5$ for $Y_3Fe_5O_{12}$ and $\beta = -2.3$ for $NiFe_2O_4$, in very good agreement with the values found from the ion-size effect.

CONCLUSIONS

The equivalence is verified with bivalent and tetravalent nonmagnetic ions, in tetrahedral sites, both with an increased and decreased volume of the lattice, by using experimental results published in the literature on substitution of nonmagnetic ions and the comparison of two materials which differ by the nonmagnetic ion radius. The results of the ion-size effect also agree with those obtained from thermal-expansion measurements by using the expression of the volume anomaly deduced from the molecular-field theory.

Furthermore, from another method of investigation, it is confirmed: for $Y_3Fe_5O_{12}$ the $\frac{10}{3}$ law for the superexchange volume dependence,[2] for $NiFe_2O_4$ the existence of a different law for the superexchange volume dependence, which is related to a different spatial overlapping of ionic orbitals.

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