DISTANCE BETWEEN MAGNETIC IONS AND FUNDAMENTAL PROPERTIES IN FERRITES

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Résumé. — A partir du ferrite spinelle de base $NiFe_2O_4$, on a introduit des ions de rayon ionique de plus en plus grand, Zn^{2+} et Cd^{2+}, avec une concentration x de plus en plus forte. Ces matériaux de composition $Ni_{1-x}Zn_xFe_2O_4$ et $Ni_{1-x}Cd_xFe_2O_4$ ont été préparés en utilisant une technologie spéciale. Le pas du réseau croît linéairement avec le rayon moyen d'ion en site tétraédrique.

La variation de température de Curie due à une variation de distance entre les ions magnétiques est évaluée. La contribution à la température de Curie due à la distribution des porteurs magnétiques est mise en évidence par une courbe unique *hypothétique* intercomposition. De la même façon, l'influence de la variation de distance entre les ions magnétiques sur l'aimantation M_s a été déterminée. Enfin les résultats obtenus sur les spinelles sont comparés avec ceux déduits de la littérature pour les grenats.

Abstract. — In the basic spinel $NiFe_2O_4$, ions of larger and larger ionic radius, Zn^{2+} and Cd^{2+}, have been introduced with higher and higher concentrations. The corresponding materials of composition $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Cd_xFe_2O_4$ have been prepared by using a special technologic process. The lattice constant increases linearly with the mean ionic radius in tetrahedral site.

The variation of the Curie temperature due to a variation of the distance between magnetic ions is evaluated. The contribution to the Curie temperature due to the magnetic carriers distribution is shown by plotting a single intercomposition *hypothetic* curve. In the same way the influence upon the magnetization value of the variation of the distance between magnetic ions has been evaluated. Results obtained on spinels have been compared with those deduced from literature data in the case of garnets.

1. **Introduction.** — We have previously shown the role plaid by the concentration in the tetrahedral sites of non magnetic ions larger than Fe^{3+}, as well upon the components of the total anisotropy [1] as upon the expansion anomaly [2].

The present paper investigates the influence upon the fundamental properties of ferrimagnets of introducing in the oxygen lattice ions with larger and larger ionic radius and concentration.

As it is well known, spinels and garnets are ionic compounds with localized magnetic moments; moments values are determined by the electronic state of ions ; the exchange interactions between moments are of super exchange type, depending on the interatomic distance, which controls the intensity of the interactions.

We have chosen to use $NiFe_2O_4$ as the basic spinel ferrite. In such an inverse spinel the cation distribution is given by :

$$Fe^{3+}[Ni^{2+}Fe^{3+}]O_4 .$$

The tetrahedral sites are occupied by Fe^{3+} ions which present the same diameter as the site (0.49 Å, calculated from the lattice constant $a = 8.339$ Å and the oxygen parameter $u = 0.381$ [3]) ; the octahedral sites are occupied by Ni^{2+} and Fe^{3+} ions.

Starting from this basic ferrite, M^{2+} non magnetic ions, with an ionic radius larger than that of Fe^{3+}, Zn^{2+} or Cd^{2+}, have been substituted for the Ni^{2+} magnetic ions. Zn^{2+} and Cd^{2+} ions are known to occupy preferably the tetrahedral sites [4] resulting in a displacement of Fe^{3+} ions towards the empty octahedral sites left by Ni^{2+} ions. This process results in a new cation distribution as follows

$$Fe^{3+}_{1-x}M^{2+}_x[Ni^{2+}_{1-x}Fe^{3+}_x, Fe^{3+}]O_4 .$$

The ionic radius of Fe^{3+}, Zn^{2+} and Cd^{2+} ions on tetrahedral sites are respectively 0.49 Å, 0.60 Å and 0.84 Å [5].

There is a correlation between the ionic radius and the lattice constant [6] : the increase of the lattice constant is proportional to the increase of the ionic radius. So the introduction of larger and larger ions results in an increase of the distance between the magnetic ions, which means that it is possible to investigate the influence of the distance between the magnetic ions upon the fundamental properties such as Curie temperature and magnetization.

2. **Sample preparation.** — Preparing Ni-Zn ferrites is now classical, although the volatility of Zn may often result in poor quality and poor ionic structure homogeneity ; as far as cadmium ferrites are concerned, the problem appears more difficult, not only because of the higher volatility of Cd but also since the large Cd ions enter with difficulty the tetrahedral sites which are smaller. Materials obtained are neither stoichio-

metric nor homogeneous. Cd volatilization results in an increase of the Curie temperature as it can be seen by comparing other results [7] to ours.

The technology which has been used is based on the following principles :

— chosing the right oxide powder fineness, obtained by a specific milling process which does not affect the purity [8] ;

— homogeneizing the mixture during the drying process ;

— sintering at relatively low temperatures choosen according to the chemical and granular characteristics of the material.

The high fineness obtained by using very long milling durations and a very good mixture of the powders result in an increase of the chemical reactivity ; such a fact allows us to use lower sintering temperatures ($\lesssim$ 1 000 °C) in order to minimize the volatization ; despite the low temperatures used a high chemical homogeneity is achieved by using long sintering times, up to several days, which results in obtaining a total formation of the compound as far as the ionic distribution is concerned.

3. **Testing the ionic structure.** — The initial magnetic susceptibility, which is directly related to the magnetization and to the anisotropy — then to the ionic structure — is well known to be the most sensitive among the magnetic properties ; that explains why we use the thermal spectra of susceptibility as a test of the formation and homogeneity of the ionic structure of the samples [9]. Classically it is well known that the thermal spectra of the initial susceptibility present a maximum just below the Curie temperature.

A sample well formed with a good ionic structure homogeneity shows a sharp peak followed by a vertical downfall of the susceptibility value which gives an accurate value of T_c (Fig. 1).

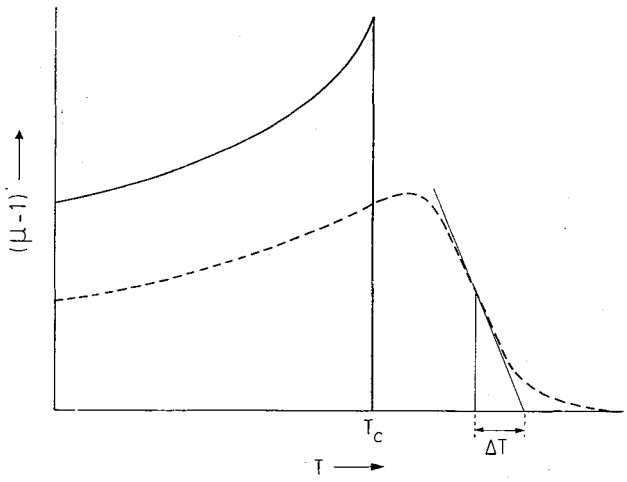

FIG. 1. — Typical thermal variations of the initial susceptibility (μ — 1) : continuous line : homogeneous material well formed ; dashed line : inhomogeneous material uncompletely formed.

A poor ionic structure homogeneity may be due to an uncomplete formation of the sample or to other reasons, such as for example a partial vaporization of an element [10]. In such a case the spectrum shows a less sharp peak which is shifted as a function of temperature and often followed by a *susceptibility tail* around T_c ; the degree of ionic quality of the material may be then characterized by the parameter ΔT (refer to dashed line on Fig. 1).

4. **Experimental results.** — 4.1 LATTICE CONSTANT. — All the samples of composition $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Cd_xFe_2O_4$ with $0 \leqslant x \leqslant 1$ have been investigated by X-ray diffraction at room temperature. The diffraction patterns as a function of the incident angle agree very well with a spinel structure.

Figure 2 shows the variation of the lattice constant as a function of the concentration x.

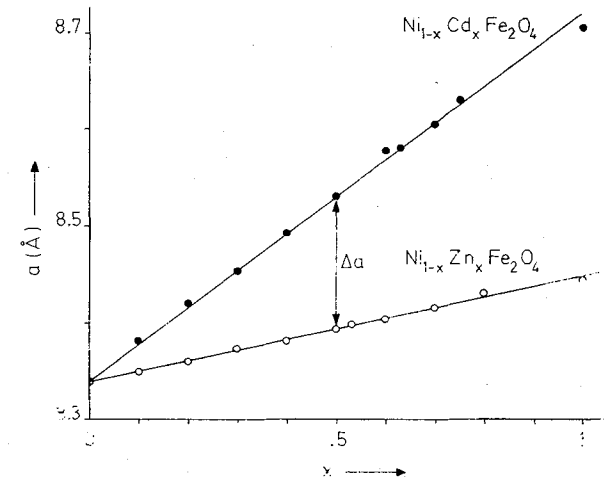

FIG. 2. — Lattice constant a (at room temperature) *versus* the non magnetic ion concentration x.

It can be seen that the lattice constant increases linearly with x, the slope being higher for Cd samples than for Zn samples. Zn^{2+} and Cd^{2+} ions occupy tetrahedral sites ; then for a given concentration x :

— the ion distribution in the sites is similar ;

— the magnetic carrier distribution is the same ;

— Δa measures the lattice constant difference at a given x value.

4.2 CURIE TEMPERATURE. — T_c is determined from the thermal spectra of the initial susceptibility, recorded on toroidal samples, as mentionned above (Fig. 1).

Figure 3 shows the variations of T_c as a function of the concentration x. It can be seen that for a given x value the Curie temperature is lower for Ni-Cd than for Ni-Zn samples (the difference is denoted ΔT_c) : then the larger is the distance between the magnetic ions, the lower is the Curie temperature.

4.3 SPONTANEOUS MAGNETIZATION. — The magnetization is measured by using a vibrating sample magne-

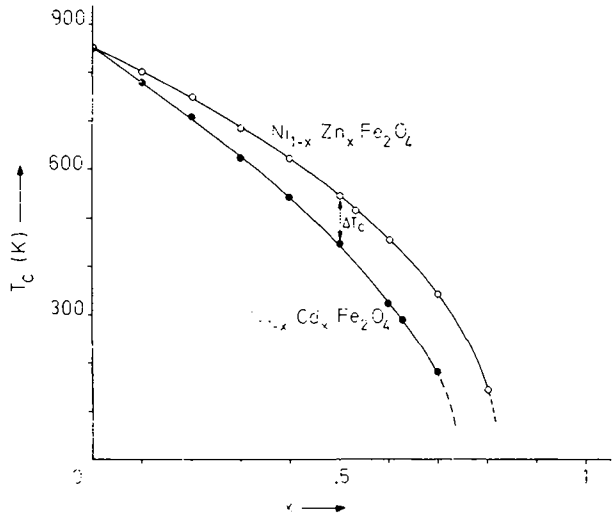

FIG. 3. — Curie temperature T_c versus the non magnetic ion concentration x.

tometer in the temperature range 4.2 or 77 K to T_c, the magnetizing field varying from 0 to around 13 kOe. The spontaneous magnetization is determined by extrapolating to $H = 0$ the linear part of the curves $M = f(H)$ at a given temperature.

Figure 4 shows the variations of the spontaneous magnetization M_s, extrapolated at 0 K, as a function of x.

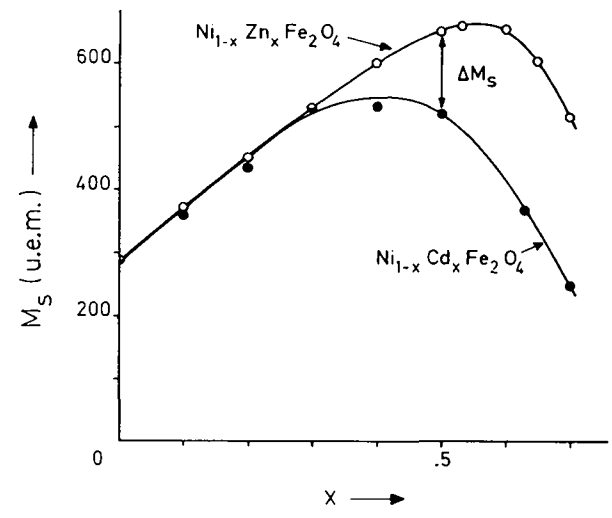

FIG. 4. — Spontaneous magnetization M_s, extrapolated at 0 K, *versus* the non magnetic ion concentration x.

For $0 \leqslant x \leqslant 0.30$ the M_s value is identical for Zn and Cd ferrites and in a rather good agreement with the classical theory of substituting non magnetic metallic ions for Fe^{3+} in tetrahedral A sites, which confirms that the amount of magnetic ions Fe^{3+} displaced from tetrahedral to octahedral sites are equal in both the composition series.

The increase of M_s when substituting progressively non magnetic Zn^{2+} or Cd^{2+} ions for Fe^{3+} ions on A sites is shown experimentally up to $x \simeq 0.30$ for Cd and $x \simeq 0.50$ for Zn ; above these values, M_s diverges from the straight line corresponding to the theoretical magnetic moment value of 10 μB which would be reached for a total substitution on A sites.

Concentration values of 0.30 for Cd and 0.50 for Zn are those where the magnetic moments on octahedral sites become to diverge from parallelism : they correspond to the appearance of Yaffet-Kittel *triangular* interactions [11].

So the influence upon the magnetization of the variations of the distance between magnetic ions is revealed by the fact that the triangular Yaffet-Kittel interactions occur for x values lower in the case of Ni-Cd than in the case of Ni-Zn (0.30 instead of 0.50). For $x > 0.30$ and for a given x value, M_s is smaller for Ni-Cd than for Ni-Zn : the difference is denoted ΔM_s.

5. **Interpretation.** — 5.1 LATTICE CONSTANT. — A correlation can be established between the lattice constant and the ionic radius of the cations in tetrahedral sites.

For a given composition x a mean ionic radius on tetrahedral site per molecule may be defined as follows :

$$r_{\text{tetra ion}} = (1 - x)\, r_{\text{tetra } Fe^{3+}} + x r_{\text{tetra } M^{2+}} .$$

Figure 5 shows that the lattice constant increases linearly as a function of the mean ionic radius on tetrahedral site. A single intercomposition curve is obtained, which shows that an increase of mean ionic radius of 0.1 Å produces an increase of lattice constant of about 0.1 Å, which confirms reference [6].

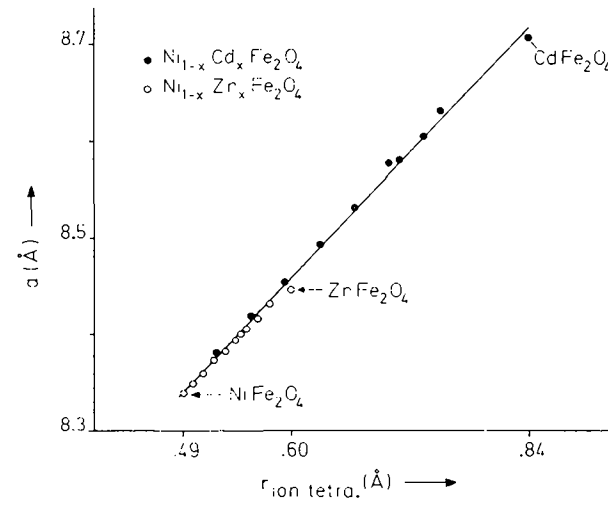

FIG. 5. — Lattice constant a *versus* the mean ionic radius of ions in tetrahedral sites $r_{\text{tetra ion}}$.

As already mentionned, introducing in the lattice bigger and bigger ions with concentration higher and higher results in an increase of the distance between the magnetic ions which can be controlled.

5.2. CURIE TEMPERATURE. — From figure 2 and figure 3 one can deduce, for a given concentration x, the Curie temperature variation ΔT_c corresponding to a lattice constant variation Δa.

ΔT_c is really the contribution to T_c due to the increase of the distance between the magnetic ions, since the magnetic carrier distribution is the same for a given x value as well for Zn ferrites as for Cd ferrites.

Results are shown on figure 6.

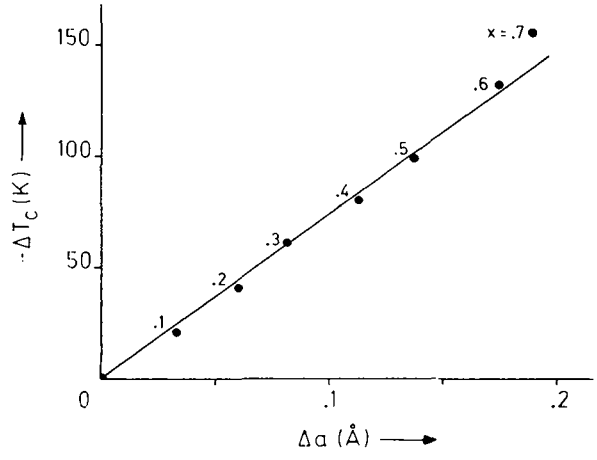

FIG. 6. — Relation between the Curie temperature variation $-\Delta T_c$ and the corresponding increase of the lattice constant Δa. The slope $\beta = \Delta T_c/\Delta a$ is equal to — 74 K/0.1 Å.

ΔT_c varies linearly with the lattice constant increase up to high concentrations ($x \simeq 0.7$). The slope $\beta = \Delta T_c/\Delta a$ is about $-$ 74 K/0.1 Å, i. e. $-$ 6.2 K for a relative interatomic distance variation of 1×10^{-3}.

Such a result can give an information about the variation of the exchange energy as a function of the distance between magnetic ions.

a) It is of interest to compare this value to that obtained by measuring the Curie temperature variations as a function of the hydrostatic pressure in $NiFe_2O_4$ [12] : 1.16 K/kbar.

By using the volume variation $\Delta V/V$ per kbar for $NiFe_2O_4$ equal to 0.54×10^{-3} [13], one finds a Curie temperature variation of 6.4 K per a relative length variation of $\frac{1}{3}\frac{\Delta V}{V} = 10^{-3}$.

This is in very good agreement with our own result $-$ 6.2 K/10^{-3} (the opposite sign corresponds to an expansion instead of a compression).

b) The linearity between ΔT_c and Δa that we have obtained allows us to separate the contribution to T_c due to the distance between magnetic ions from that due to the magnetic carrier distribution, considering $NiFe_2O_4$ as the basic reference structure. Then, for each composition, a hypothetic Curie temperature can be calculated by substracting from the measured Curie temperature the contribution due to the distance variation between the magnetic ions, $NiFe_2O_4$ being the reference :

$$T_{c_{hypoth}} = T_{c_{measured}} - \beta(a_x - a_{NiFe_2O_4}) .$$

Values obtained for Ni-Zn and Ni-Cd are roughly the same for each composition x : then a single inter-composition hypothetic curve can be plotted as shown on figure 7.

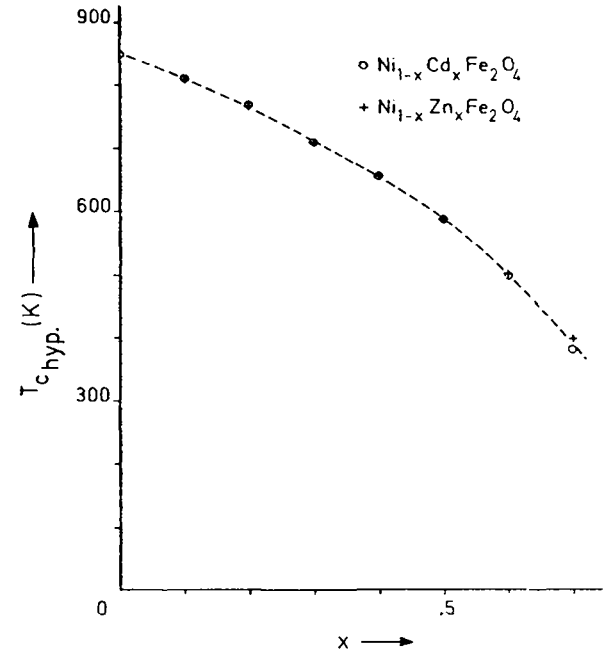

FIG. 7. — Hypothetic Curie temperature $T_{c_{hypoth}} = T_{c_{measured}} - \beta(a_x - a_{NiFe_2O_4})$ *versus* the non magnetic ion concentration x.

This curve shows how the displacement of Fe^{3+} ions from tetrahedral to octahedral sites and the substitution of non magnetic ions for Ni^{2+} ions would result in a change of the Curie temperature if it could be possible to avoid the increase of the distance between magnetic ions (assuming it would be possible to keep the lattice-constant value equal to that of $NiFe_2O_4$).

5.3 MAGNETIZATION. — From figure 2 and figure 4, one can deduce, for a given concentration x, the magnetization variation ΔM_s corresponding to the lattice constant variation Δa.

For $x > 0.30$, ΔM_s would represent the contribution to M_s due to the increase of the distance between the magnetic ions, since the magnetic carrier distribution is the same in Zn and Cd ferrites for a given x value.

Results are shown on figure 8.

For $x > 0.30$, ΔM_s varies linearly with Δa. The slope $\gamma = \Delta M_s/\Delta a$ is about $-$ 260 uem/0.1 Å.

Such a linear relation between ΔM_s and Δa allows us to separate the contribution to M_s due to the distance variation between magnetic ions from the contribution to M_s due to the magnetic carrier distribution.

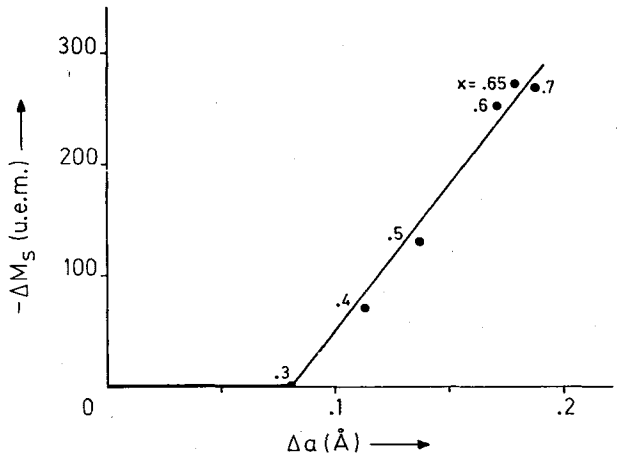

FIG. 8. — Relation between the magnetization variation $-\Delta M_s$ and the corresponding increase of the lattice constant Δa. The slope $\gamma = \Delta M_s/\Delta a$ is equal to — 260 uem/0.1 Å for $x > 0.3$.

For each composition corresponding to $x > 0.3$, one can calculate an hypothetic magnetization value by substracting the contribution due to the distance between magnetic ions from the measured magnetization value, the composition $x = 0.30$ being the reference :

$$M_{s_{hypoth}} = M_{s_{measured}} - \gamma(a_x - a_{x=0.30}) .$$

As above in the case of Curie temperatures, a single intercomposition hypothetic curve can be plotted as shown on figure 9.

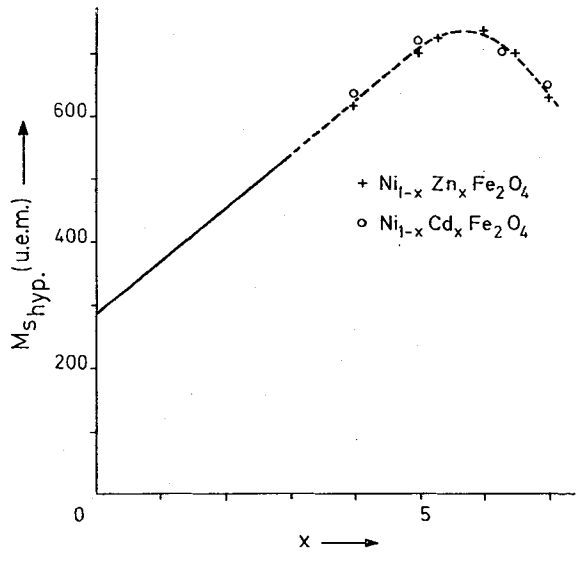

FIG. 9. — Hypothetic magnetization $M_{s_{hypoth}} = M_{s_{measured}} - \gamma(a_x - a_{x=0.3})$ for $x > 0.3$. *versus* the non magnetic ion concentration x.

6. **Garnets.** — The deductions we have made from our results on spinels have been compared to the analysis which can be carried out from published works on garnets.

$Y_3Fe_5O_{12}$ is considered as the reference structure. Two series of garnets are compared, $Y_3Fe_{5-x}Ga_xO_{12}$ and $Y_3Fe_{5-x}Sc_xO_{12}$, in which the Fe^{3+} ions (ionic radius in octahedral site = 0.64 Å) are replaced by either Ga^{3+} ions (ionic radius 0.62 Å) or Sc^{3+} ions (ionic radius 0.81 Å).

Figure 10 shows the lattice constant variations as a function of the Ga^{3+} or Sc^{3+} ion concentration x [14, 15].

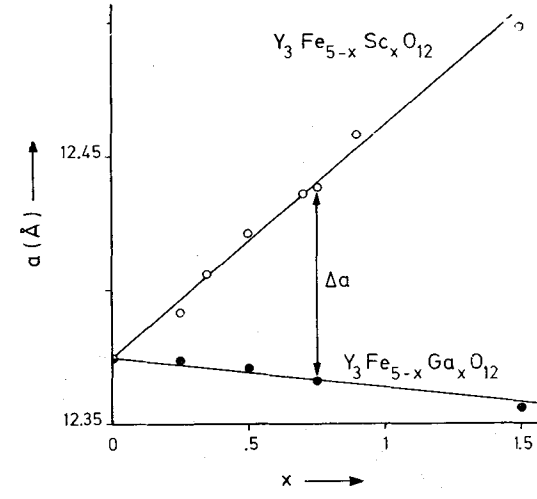

FIG. 10. — Lattice constant *a versus* non magnetic ion concentration x for garnets, from [14] and [15].

Let's assume that Sc^{3+} and Ga^{3+} ions are really placed in octahedral sites. For a given concentration x, the ion distribution is similar for both the series and then the magnetic carrier distribution is the same.

Figure 11 shows the Curie temperature variation as a function of the Ga^{3+} and Sc^{3+} ion concentration x [14, 15, 16].

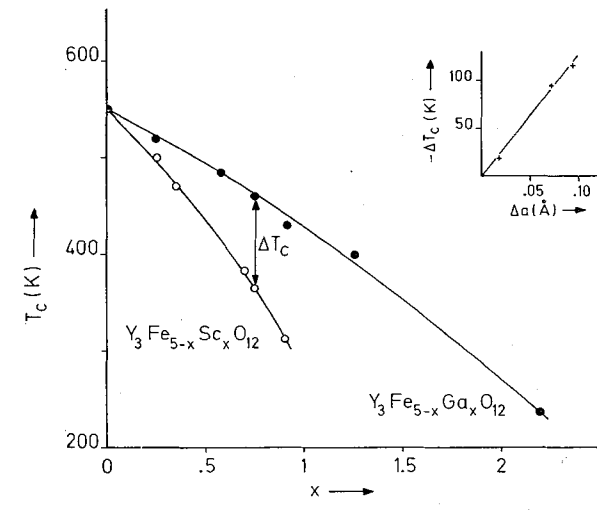

FIG. 11. — Curie temperature T_c *versus* the non magnetic ion concentration x for garnets, from [14, 15, 16]. At the top : relation between the Curie temperature variation $-\Delta T_c$ and the corresponding increase of the lattice constant Δa. The slope $\Delta T_c/\Delta a$ is equal to — 125 K/0.1 Å.

As above, the Curie temperature variation ΔT_c corresponding to the lattice constant variation Δa can be deduced from figure 10 and figure 11 for a given x value.

ΔT_c varies linearly as a function of the lattice constant increase. The variation of T_c per lattice constant unit is -125 K/0.1 Å, which value being larger than for spinels.

7. **Conclusion.** — At the whole material scale, the increase of the lattice constant due to substituting in tetrahedral sites Zn^{2+} and Cd^{2+} ions for smaller Fe^{3+} ions affects the fundamental magnetic properties such as Curie temperature and spontaneous magnetization ; such a process results not only from the ion concentration effect, but also from the ion size effect by the increase of the distance between the magnetic ions.

The fact that the lattice constant increase is proportional to ion size allows us to separate the contribution of the distance between magnetic ions to the Curie temperature and the spontaneous magnetization from the contribution due to the magnetic carrier distribution : both these contributions can be quantitatively calculated.

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