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An EPR Study of Magnetic Interactions in Solid Solutions Between MgO and Antiferromagnetic Oxides. I. MgO–NiO

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We have studied by EPR the solid solutions between magnesium oxide and nickel oxide. The spectrum observed in powder samples does not change very much with concentration. A study of its main features, however, provides indications about the relative importance of the contributions from isolated and from exchange-coupled ions. At high concentrations, a clear antiferromagnetic behaviour of the samples is observed, and a definite Néel transition is obtained as a function of the nickel concentration.

Introduction

Both magnesium oxide and nickel oxide have a face-centered cubic structure, and they give a continuous series of solid solutions (*1*). The Ni^{2+} ions in MgO occupy substitutional sites, and they give an EPR spectrum at room temperature (*2*) whose features are affected by the nickel concentration (*3*). These changes are to be mainly attributed to the decrease in the average distance between nickel ions in solution when their concentration increases. The decrease produces a development of magnetic interactions between neighboring ions.

The pure nickel oxide NiO is a typical antiferromagnetic compound, with a Néel temperature $T_N = 523$ K (*4*). From the magnetic point of view its structure is composed by four simple cubic sublattices of nickel ions. The magnetic moments in it are aligned according to the so-called second kind of ordering (*5*). Every ion in it is coupled by direct exchange interactions of ferromagnetic type to the twelve nearest neighbors (n.n.), six of them having the magnetic moments parallel and six antiparallel to the central one. At a slightly larger distance there are six next-nearest neighbors (n.n.n.) with the magnetic moments antiparallel to the central one and indirect antiferromagnetic exchange interactions through an oxygen ion. The strongest interactions in NiO are between n.n.n. ions, while those between n.n. ions are relatively weak. Recent measurements of inelastic neutron scattering on NiO have given for the exchange interaction constant J the values -16 K for an n.n. pair and 221 K for an n.n.n. pair (*4*).

In the MgO–NiO solid solutions the structure of NiO is preserved and the exchange interactions remain substantially the same. Besides the exchange interactions, the classical magnetic dipole–dipole interaction between neighboring ions also effects the EPR spectrum of solid solutions.

The dipole–dipole interactions between magnetic ions mainly produce a broadening of the spectrum of the isolated ions. The exchange interaction, on the contrary, may have a much more substantial effect on the EPR spectrum. This effect has been widely studied by analysing the spectrum of pairs of ions coupled by exchange (*6–8*).

The analysis of the EPR spectrum of solid solutions between a diamagnetic and an antiferromagnetic oxide in a wide range of compositions allows one to obtain important information on the progressive development of the interactions between magnetic ions in solution as a function of their concentration.

Experimental

The MgO–NiO solid solutions have been prepared starting from pure oxides (Baker Anal. Reag.) mixing and grinding them with care and then firing the mixture for 24 hr at 1200°C. The analysis of several samples has shown that the final nickel content was the same as the starting

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one. The concentration of nickel is given as the mole fraction f of NiO in the solution.

EPR spectra have been measured with a Varian V-4502-12 spectrometer working at X-band frequency ($\nu \approx 9.52$ kMHz) with a 100 kHz modulation. The temperature of the sample could be varied in the range 100–573 K with a commercial variable temperature unit. The intensity of the spectra has been obtained by first moment calculation of the first derivative of the absorption curve (*9*). The g values have been obtained by comparison with polycrystalline DPPH.

Results and Discussion

1. Assignment of the EPR Spectrum

The EPR spectrum of the MgO–NiO solid solutions, for any nickel concentration, consists of a single isotropic signal of nearly Lorentzian shape, with a g value $g = 2.226 \pm 0.002$ at low nickel concentration ($f < 0.01$) and $g = 2.246 \pm 0.002$ for high concentration ($f > 0.4$). However, some of the signal characteristics change with nickel concentration, showing the gradual appearance of magnetic interactions between Ni^{2+} ions as the concentration increases.

For low nickel concentrations ($f < 0.01$) the observed spectrum is undoubtedly due to isolated ions replacing Mg^{2+} ions in the lattice sites (*2*). For higher concentrations the presence of clusters of two or more Ni^{2+} ions close enough to give strong exchange interactions becomes increasingly more probable. At the same time the concentration of the isolated ions becomes less than the total concentration. It is interesting to know the total nickel concentration at which the isolated ions concentration is maximum. This value in fact is related to the number m of cation sites close to a Ni^{2+} ion that must be free from nickel ions so that the former can act as isolated. In effect the mole fraction of isolated Ni^{2+} ions in solution, which we define as $f_0 = n_0/N$ (where n_0 is the number of isolated nickel ions in a given sample and N is the total number of cation sites in the same sample) is connected to the total mole fraction of nickel f by the equation (*10*):

$$f_0 = f(1-f)^m \qquad (1)$$

if the distribution of the ions in solution is assumed to be completely random. From the last equation it follows that f_0 will have a maximum for a value of f which is function of m and is given by:

$$f = 1/(1+m) \qquad (2)$$

as may be seen by differentiating the Eq. (1) with respect to f. The experimental determination of this particular value of f allows an estimate of m to be obtained.

Before proceeding, we have to examine the main aspects of the EPR spectrum of the isolated and the associated ions.

a. Isolated ions. The EPR spectrum of isolated Ni^{2+} ions in solution in MgO has been studied in single crystals (*2*) as well as in powders (*3*). Since in this structure the cation lies at the center of a regular octahedron of oxygen ions, the crystal field has cubic symmetry and the EPR spectrum is isotropic. In fact, the spectrum of the powders also shows a single signal about 170 G wide, depending on nickel concentration as well as on the thermal treatment of the samples (*3, 11*).

For low nickel concentrations ($f < 0.002$), at the center of this main broad signal a narrow one is observed at the same g value, attributed to a transition between the levels $|+1\rangle$ and $|-1\rangle$ due to a simultaneous absorption of two quanta (*12*).

The width of the nickel spectrum in MgO is also unusually large in single crystals. This behaviour has been chiefly ascribed to local departures from cubic symmetry due to random strains in the crystal introducing zero field terms in the spin Hamiltonian and making the spectrum anisotropic (*11, 12*).

b. Pairs of ions. When two or more paramagnetic ions are placed at short distance in a diamagnetic matrix, they undergo a dipolar magnetic interaction producing a broadening of the EPR spectrum in absence of other interactions. If, however, the distance of the two ions is short enough and their positions suitable, an exchange interaction may result that modifies deeply the spectrum. In fact, if the exchange interaction between two ions $Js_1 . s_2$ of spin s_1 and s_2 is greater than the Zeeman interaction $g\beta H$, the pair will behave as a single unit. It will assume various energy levels defined by the values of the total spin quantum number S, which can take the values $S = s_1 + s_2, s_1 + s_2 - 1, \ldots, 0$ if $s_1 = s_2$ (*6*). Each of these levels has a population varying with temperature according to the Boltzmann distribution law and shows an anisotropic EPR spectrum described by the spin Hamiltonian (*13*):

$$\mathscr{H} = \beta g H \cdot S + \tfrac{1}{2}J\{S(S+1) - 2s(s+1)\} + D_S\{S_z^2 - \tfrac{1}{3}S(S+1)\} + E_S(S_x^2 - S_y^2). \tag{3}$$

We have dropped the term related to the hyperfine interaction, which does not exist for nickel ions. In this expression the first term represents the Zeeman interaction, the second the isotropic exchange interaction, the third and fourth the fine structure terms of axial and rhombic symmetry respectively, and include the contributions from the dipolar and anisotropic exchange interactions. Following the usual notation, we have (*13*):

$$D_S = 3\alpha_S D_e + \beta_S D_c \quad \text{and} \quad E_S = \alpha_S E_e + \beta_S E_c \tag{4}$$

where $D_e = D_E$ (exchange) + D_d (dipole–dipole) is the axial parameter of zero field splitting due to pair interactions; D_c is the axial parameter of zero field splitting of the isolated ion; E_e is the rhombic parameter of zero-field splitting due to the pair interactions and E_c is the rhombic parameter of zero field splitting of the isolated ion. Finally, α_S and β_S are two parameters defined in function of the total spin of the pair S and the single-ion spin s_i (*13*). For a pair of ions Ni^{2+} ($s_i = 1$) these parameters exhibit the following values:

$$\alpha_0 = -\tfrac{4}{3} \quad \alpha_1 = 1 \quad \alpha_2 = \tfrac{1}{3}$$
$$\beta_0 = \tfrac{11}{3} \quad \beta_1 = -1 \quad \beta_2 = \tfrac{1}{3}.$$

To predict the EPR spectrum of pairs, the values of the zero-field splitting parameters should be known. For pairs of Ni^{+2} ions in MgO, the terms D_c and E_c are zero because of the cubic symmetry of the cation sites in the oxide. However, one should recall that possible lattice strains due to imperfections, or to the presence of nickel in substitutional sites, may introduce terms D_c and E_c in the spin Hamiltonian (*12*). The term D_e is made up of dipolar and anisotropic exchange contributions, the former usually prevailing (*6*). This is given by $D_d = -(g^2\beta^2/r^3)$ (*6*) and is easily computed if the interionic distance r is known. To estimate D_E, we use the expression of Kanamori (*14*) for the anisotropic exchange interaction constant of the n.n.n. pairs of Ni^{2+} ions in MgO:

$$C_{ij} = (2\lambda^2/\Delta E^2)J \tag{5}$$

where λ is the spin–orbit coupling and ΔE is the energy difference between the ground orbital level and the first excited level. Since in this case $\lambda/\Delta E = \Delta g/8$ (*15*), where $\Delta g = g - 2$ is the g shift from the free electron value, one has:

$$C_{ij} = (\Delta g^2/32)J. \tag{6}$$

By comparison of the Eq. (3.41) of Kanamori (*16*) with the Eq. (2) of Owen (*6*) one also gets $C_{ij} = D_E$.

Using for J the value of 221 K recently obtained instead of the value of 91 cm^{-1} previously used (*14*), we have $D_E = 0.243$ cm^{-1}, which represents a considerable contribution to the final D value of the pair. For the n.n. pairs D_E seems to be zero (*14*), while for pairs at a distance higher than the n.n.n. D_E should be small because it is proportional to $\Delta g^2 J$ (*17*) and, therefore, we will neglect it.

It is not possible, on the contrary, to estimate theoretically the value of the rhombic term of zero field splitting, which must be determined experimentally. One may recall, however, that the n.n. pairs are aligned along the [1,1,0] directions and may have a term $E_e \neq 0$. For the n.n.n. pairs aligned along the crystallographic axis, E_e must be zero by symmetry (*6*). For pairs at higher distances E_e can be neglected, since it should decrease rapidly with distance, as the exchange interaction does. As we cannot predict the value of E_e for the pairs, let us neglect the rhombic term of zero-field splitting and consider only the axial term.

Having obtained the D values for the pairs, we may now predict the EPR spectrum of the states $S = 1$ and $S = 2$ (the state $S = 0$ is diamagnetic) for the pairs. In the EPR spectrum of powders containing paramagnetic species in axial symmetry sites, the strongest absorptions correspond to the orientations of the external, static magnetic field perpendicular to the local symmetry axis, because these orientations are the most favourable in the powders (*18*). The magnetic field values in which these absorptions fall for the different kind of pairs can be computed for the states with $S = 1$ using the equations giving the energy of the three sublevels as a function of the magnetic field for these particular orientations (*19*). For the $S = 2$ levels of the pairs more distant than the n.n.n. for which $g\beta H \gg D$, we used the second-order perturbation formula (*20*). For n.n. and n.n.n. pairs, where the above condition is not fulfilled, we used the plots recently published (*21*) to explain the spectra of powders of systems with $S = 2$. The results we obtained for $S = 1$ pair levels are shown in Table I, where we give the

TABLE I

SHIFTS ΔH (IN GAUSS) OF THE EPR ABSORPTIONS DUE TO THE $S = 1$ LEVELS OF THE Ni^{2+} PAIRS IN MgO WHEN $H_\perp$ TO THE PAIR AXIS (ΔH_1 = SHIFT FOR THE TRANSITION $M = -1 \leftrightarrow 0$, ΔH_2 = SHIFT FOR THE TRANSITION $M = 0 \leftrightarrow 1$) FROM THE ISOLATED IONS SPECTRUM

Pair	n.n.	2 n.n.	3 n.n.	4 n.n.	5 n.n.	6 n.n.	7 n.n.
Distance (Å)	2.978	4.212	5.159	5.957	6.660	7.295	7.880
ΔH_1	1011.1	no abs	217.5	142.5	103.6	78.4	62.9
ΔH_2	−1594.6	2257.8	−234	−149.6	−107.3	−80.5	−64.3

shifts ΔH in gauss of the absorptions for the different pairs from the position of the isolated nickel ions spectrum at the same frequency. The short distance pair absorptions fall too far from the central signal of the isolated ions to give a significant contribution to the observed spectrum, taking into account the width of the latter. The spectra of more distant pairs may, on the contrary, give some contribution to the wings of the observed spectrum. For the $S = 2$ levels of the pairs the predicted ΔH shifts are of the same order as those of the corresponding $S = 1$ levels, and therefore the same conclusions hold.

A second reason to exclude that the pairs of ions will give a significant contribution to the observed spectrum is based on the behavior of the V^{2+} ion pairs in magnesium oxide (*8*). It has been found that the transitions within the levels of the n.n.n. pairs with $S = 1$ and $S = 3$ are not observable even in single crystals, and this has been attributed to the presence of random strain fields introducing D and E terms in the spin Hamiltonian of the isolated ion. These terms are introduced also in the spin Hamiltonian of the pair through Eqs. (3) and (4) and produce a broadening of the spectra of the levels $S = 1$ and

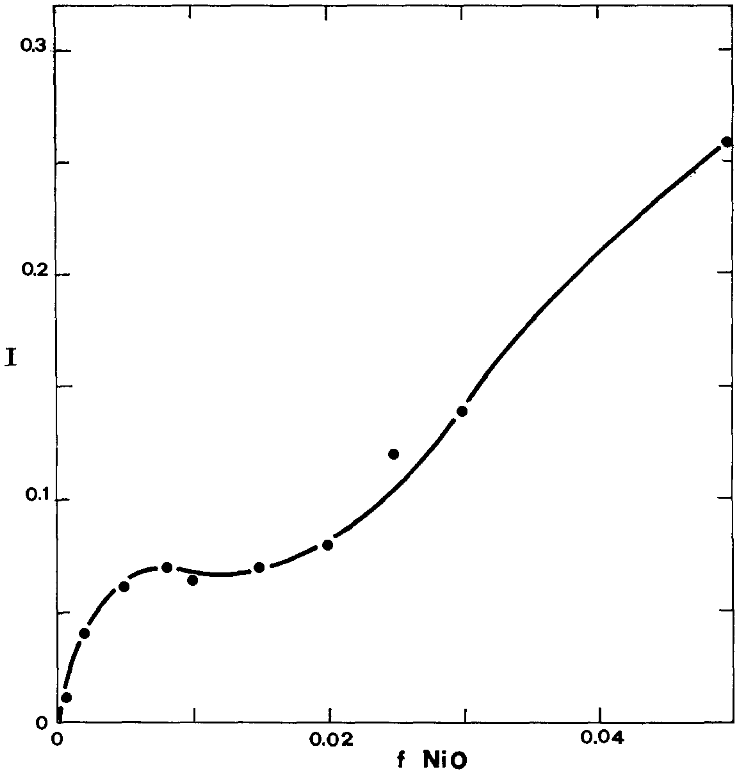

FIG. 1. Relative intensity of the EPR spectrum at room temperature in function of the nickel concentration for diluted samples.

$S=3$, which have $\beta_S \neq 0$. On the contrary, the level $S=2$, which has $\beta_2=0$, is not affected by this mechanism, and its spectrum is easily observed. For pairs of nickel ions, both β_1 and β_2 values differ from zero, and this broadening effect can act for both levels. Taking into account the great sensitivity of the EPR spectrum of the isolated ions to the presence of lattice strains, one can predict that the spectra of pairs of nickel ions are not observable in MgO powders.

c. Clusters of ions. When the nickel concentration is sufficiently high there will be in solution, besides the pairs, also groups of more than two ions coupled by exchange. The analysis of the EPR spectrum of clusters of three ions has been carried out only for one system (*22*), while for different kinds of triads of Cr^{3+} ions in corundum only the manifold of energy levels has been studied (*23*). However, it is possible to predict that a system made of many identical ions coupled by strong exchange interactions will give an isotropic EPR spectrum centered near the g value of the isolated ion for ions without fine structure terms in the spin Hamiltonian, as happens for Ni^{2+} in MgO (*24*).

Therefore, we conclude that the EPR spectrum observed in MgO–NiO solid solutions for $f > 0.02$ has to be attributed mainly to clusters of many ions coupled by exchange, while for lower concentrations it is made up of the sum of contributions from the isolated and the associated ions, excluding the pairs. The previous discussion shows that the EPR spectrum of the isolated ions falls in the same position as that of the associated ones, with the exception of the pairs and possibly of small groups of ions, whose spectrum is hardly seen in powders because of its anisotropy. It is therefore difficult to separate the contribution of the isolated ions from that of the associated ones in the experimental spectrum. A feature of the spectrum giving an indication as to the relative importance of the isolated and associated-ion spectra is the intensity dependence of the spectrum on the nickel concentration at room temperature for low concentration samples (Fig. 1). The plot shows a range of concentrations (from $f=0.008$ to $f=0.015$) where the intensity is nearly constant. For higher concentrations the intensity increases again.

The behavior of the spectrum intensity is in

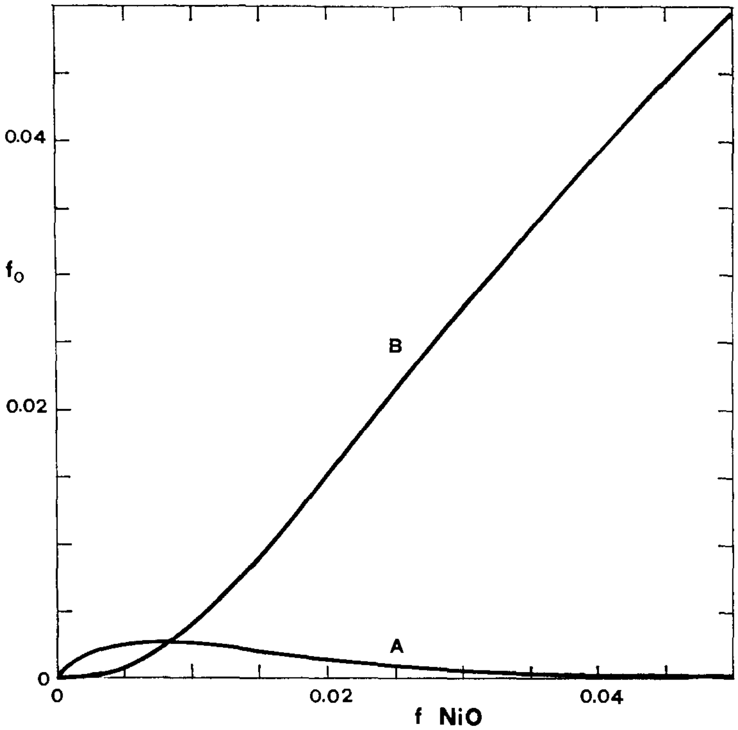

FIG. 2. The mole fraction of isolated Ni^{2+} ions f_0 (curve A) and of the Ni^{2+} ions in clusters of more than two ions $f-(f_0+f_1)$ (curve B) in function of the total nickel concentration ($m=124$).

agreement with the assumption that the experimental spectrum has no contribution from the ion pairs, otherwise the intensity would increase regularly with the nickel concentration. Since the isolated-ion concentration f_0 depends on the total concentration f through Eq. (1), which predicts the existence of a maximum in the plot of f_0 against f, we can assume that the range of nearly constant intensity corresponds to the maximum of f_0. For higher concentrations f_0 will decrease, but the associated-ion concentration will increase so that the total intensity increases. If we assume that the maximum of f_0 corresponds to the beginning of the constant intensity range of Fig. 1 ($f_0 \approx 0.008$) one gets, from Eq. (2), for m a value of 124. This value is in satisfactory agreement with the conclusions drawn from the acoustic resonance spectra of pairs of nickel ions in MgO, showing that the exchange interactions are still of the order of 0.3 cm^{-1} (the magnitude of the microwave quantum used in our measurements) for pairs as far apart as approx. 8 Å (*25*). The number of cation sites around a given cation at distances less than 8 Å in the MgO lattice is 86 including the sites up to the sixth nearest neighbors ($r = 7.29$ Å) and 134 including the seventh nearest neighbors ($r = 7.88$ Å), assuming for the dilute solid solutions a lattice constant identical to that of the pure oxide ($a = 4.212$ Å) (*26*).

Figure 2 shows a plot of f_0 and the concentration of the ions belonging to groups of more than two ions as a function of f taking $m = 124$. This concentration is given by $f - (f_0 + f_1)$, where f_0 is the isolated-ion concentration and f_1 is the concentration of ions in pairs, given by (10):

$$f_1 = mf^2(1 - f)^{m-1} \tag{7}$$

Figure 2 shows that the isolated ions predominate over the ions in groups of more than two when $f < 0.008$, while the mole fraction of associated ions becomes nearly linear with f when $f > 0.02$, in agreement with the experimental dependence of the intensity on the concentration (Fig. 1).

2. *Features of the EPR Spectrum*

a. Dependence of intensity on temperature. The values of the product IT, where I is the relative

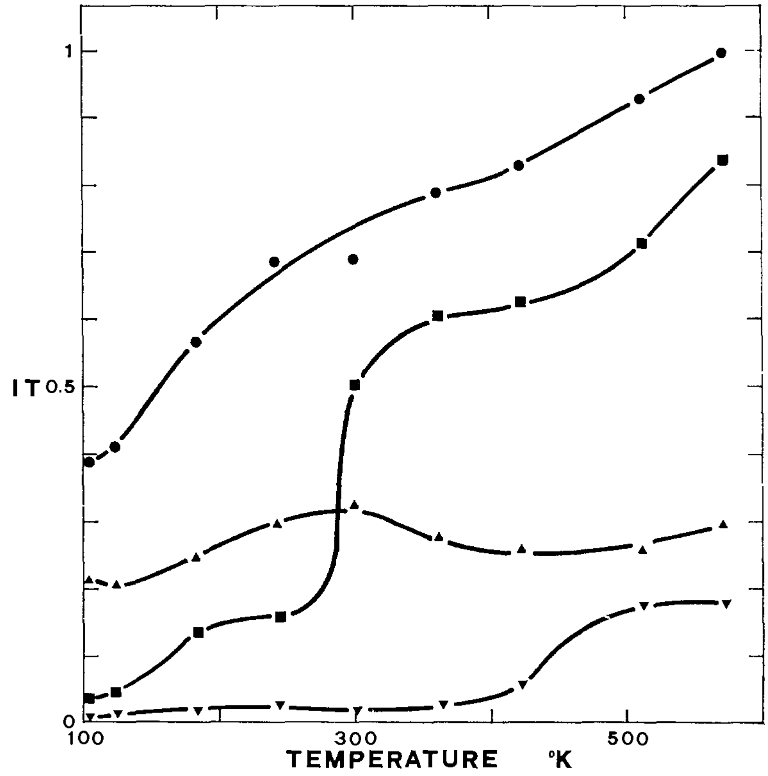

FIG. 3. Dependence of the product IT on temperature for different samples: ▲$f = 0.20$; ●$f = 0.30$; ■$f = 0.40$; ▼$f = 0.80$.

intensity of the EPR spectrum and T the absolute temperature, are plotted in Fig. 3 as a function of T for several samples. For isolated paramagnetic ions with a ground level well below the excited states the EPR spectrum intensity is inversely proportional to the absolute temperature T, in so far as the condition $h\nu \ll kT$ is observed (*27*), so that IT should be independent of temperature. The pairs of exchange-coupled paramagnetic ions, on the contrary, give rise to a manifold of different energy levels among which the total population of the pairs is distributed. The temperature dependence of the EPR spectrum intensity of the various levels of the pairs has often been used to obtain the value of the exchange interaction constant J. For pairs with a value of $J > 0$ (antiferromagnetic interaction) the product IT tends to zero at sufficiently low temperatures (*6*).

We have already observed that for $f > 0.02$ the spectrum is mainly due to the contributions from groups of more than two ions coupled by exchange, and not from pairs, at least for short-distance pairs. A detailed prediction of the EPR spectrum dependence on temperature for these systems is impossible because they are formed by a different number of ions in various positions. However, one may forecast that in the systems where antiferromagnetic interactions predominate, the product IT should decrease toward lower temperatures, as has been observed in some similar systems (*10*, *28*, *29*).

Figure 3 shows that at higher nickel concentrations the decrease of the product IT at low temperature becomes stronger. In similar cases the abrupt fall of IT taking place in a given range of temperature has been considered an indication of a general antiferromagnetic behavior of the system, and the temperature at which this effect is observed has been taken as the Néel temperature of the sample (*28*). In fact, it is known that the antiferromagnets do not give EPR absorptions at temperatures lower than their T_N (*30*). The solid solutions of a diamagnetic and an antiferromagnetic compound may also show the paramagnetic-antiferromagnetic transition at a given T_N. For these systems T_N depends on the composition, being lowered when the concentration of the antiferromagnetic compound decreases (*28*, *31*). The values of T_N for solid

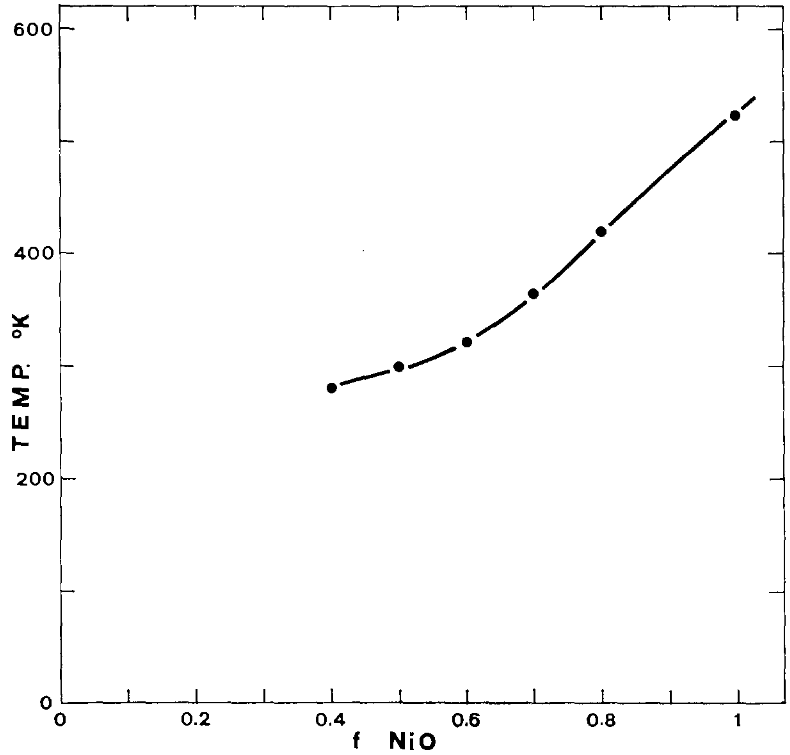

FIG. 4. Dependence of the Néel temperature T_N on the nickel concentration.

solutions MgO–NiO are reported in Fig. 4 for some samples. For samples with $f < 0.4$ there is no definite Néel temperature. Figure 4 shows that T_N is approximately a linear function of the mole fraction of nickel up to $f = 0.6$. This dependence has been anticipated theoretically for concentrated solid solutions on the grounds of different models (*32–34*). Some of these theories predict that T_N is defined only for concentrations of magnetic ions higher than a minimum value, in agreement with the behavior of our system. In particular according to the constant-coupling approximation theory it has been found that the critical concentration below which the magnetic order disappears and T_N is no more defined is:

$$f = p/z - 1 \tag{8}$$

where z is the number of nearest neighbors in the structure under consideration and p is approximately $(s + \frac{1}{2})/s$, where s is the spin of a single ion (*33*). Recalling that in the NiO structure the strongest interactions are between n.n.n. ions and taking $z = 6$, one gets from Eq. (8) $f = 0.5$, close enough to the experimental value 0.4.

b. Dependence of intensity on concentration. In Fig. 5, the relative intensity of the EPR spectrum of solid solutions MgO–NiO measured at room temperature is plotted as a function of the mole fraction of NiO f for high concentration samples. The dependence of the intensity on f when $f < 0.1$ has already been discussed. For $f > 0.1$, the intensity increases at first in a linear way up to $f = 0.15$, it reaches a maximum when $f = 0.25$ and then decreases falling to zero when $f \approx 1$.

The linear increase of intensity up to $f = 0.15$ may be explained assuming that in these samples practically all the nickel contributes to the observed spectrum, which is mainly due to the associated ions. When f ranges between 0.15 and 0.20, the increase is no longer linear, in agreement with the plot of IT against T which shows a large drop near room temperature for these samples. This behavior indicates the presence of strong antiferromagnetic interactions, and the fraction of nickel taking part in antiferromagnetic

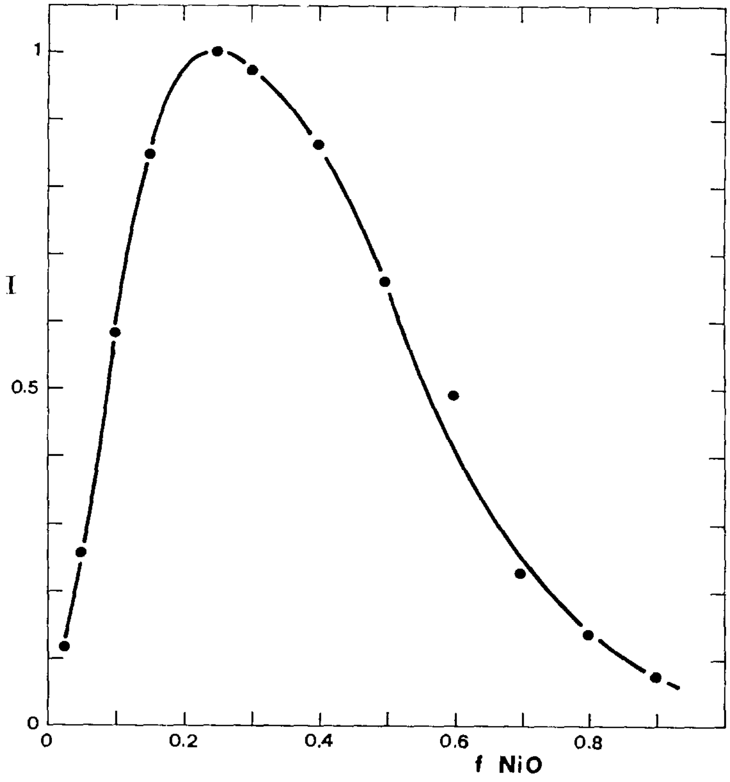

FIG. 5. Relative intensity of the EPR spectrum at room temperature in function of the nickel concentration for concentrated samples ($f > 0.025$).

clusters does not contribute to the spectrum at temperatures lower than their T_N. When $f > 0.20$ the intensity decreases towards higher concentrations. The plots of IT against T show for these samples the existence of a well defined Néel temperature increasing with concentration. For $f > 0.9$ the spectrum tends to disappear because the T_N of these samples are higher than the room temperature (see Fig. 5).

c. Dependence of linewidth on concentration. The dependence of linewidth measured at room temperature on nickel concentration is shown in Fig. 6. The plot shows that, starting from low concentrations, the linewidth first decreases up to $f = 0.02$, then increases up to $f = 0.6$ and finally decreases again when $f > 0.6$.

In the samples with low nickel concentration ($f < 0.02$) the spectrum has an important contribution from the isolated ions. The theory developed for the effect of the dipolar interaction on the linewidth of the isolated ion spectrum predicts a linear increase with f for low concentrations ($f < 0.01$) and a dependence on the square root of f for $f > 0.1$ (*35*). The experimental behavior of ΔH as a function of f is therefore in disagreement with the theory. However, we recall that the EPR spectrum of Ni^{2+} ions in MgO has a very large linewidth compared to other species in the same oxide, and it is very sensitive to the sample treatment (*3*, *12*). The anomalous dependence of ΔH on f observed on dilute samples is then probably related to a variable degree of distortion around the isolated nickel ions in this concentration range.

The linewidth increase when $f > 0.02$ must be attributed to the increasing importance of dipolar interactions inside the clusters of ions giving the observed spectrum. Indeed, the factors influencing the linewidth in magnetically concentrated systems are two, namely the dipolar interaction giving a broadening and the exchange interaction giving a narrowing of the spectrum (*35*). However, for the exchange-narrowing to be effective, every ion must be exchange-coupled to many neighbors (*35*). The observed dependence of ΔH on f suggests that for $f < 0.6$ the dipolar interaction predominates, producing a broadening, and only for $f > 0.6$ the exchange narrowing sets in. Assuming a completely random distribution of the nickel ions in solution, it is possible to

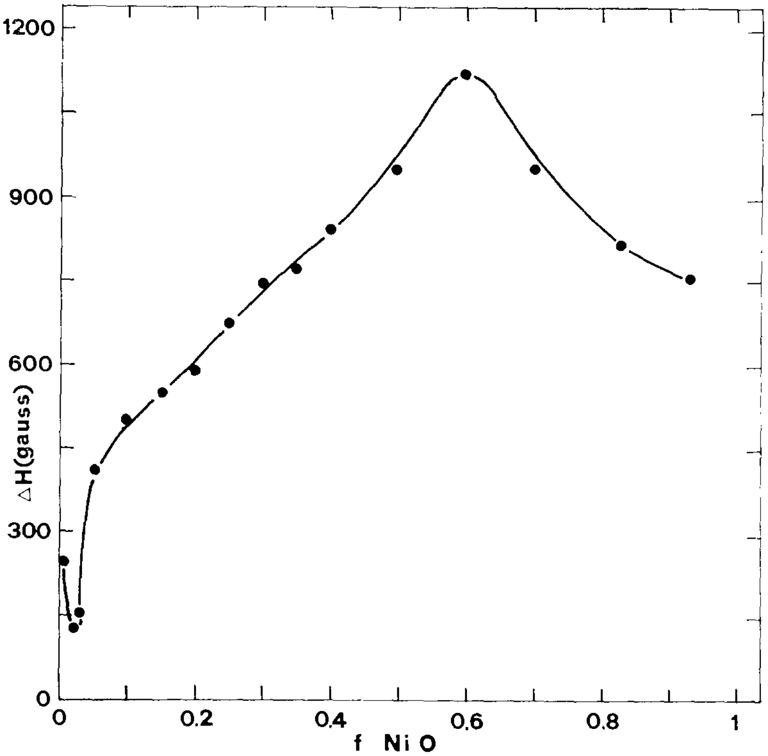

FIG. 6. Dependence of the room-temperature EPR spectrum linewidth ΔH on the nickel concentration.

calculate the average number of Ni^{2+} neighbors that an ion has when the narrowing begins to appear.

The average number of interactions per nickel ion in a solution of mole fraction f is given by:

$$\bar{\nu} = \sum_{0}^{m} in_i / \sum_{0}^{m} n_i, \qquad (9)$$

where n_i represents the number of ions having i identical neighbors among the m nearest sites and is (10):

$$n_i = N\binom{m}{i} f^{i+1}(1-f)^{m-i}, \qquad (10)$$

where N is the total number of cations in the sample. Introducing Eq. (10) into Eq. (9), it may be shown that the latter assumes the simple form $\bar{\nu} = mf$. If we take into account only the strongest interactions, i.e. those with the n.n. and the n.n.n. sites, m is 18. Then Eq. (9) for $f = 0.6$ gives $\bar{\nu} = 10.8$. This means that in the system MgO–NiO every nickel ion must have more than about eleven nickel ions among the n.n. and the n.n.n. sites for the exchange narrowing to be effective. One may notice that the concentration at which the exchange narrowing begins to appear is higher than that required to observe an antiferromagnetic behavior of the samples.

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