

**Antiferromagnetic Resonance in NiO:Co<sup>2+</sup> and NiO:Fe<sup>2+</sup>**

By

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The antiferromagnetic resonance (AFMR) in NiO doped with either Fe<sup>2+</sup> or Co<sup>2+</sup> was studied at liquid helium temperatures in the far infrared. A strong frequency shift of the AFMR line was observed in Co<sup>2+</sup>-doped crystals. In the case of the Fe<sup>2+</sup>-doped crystals, this shift was much smaller. In addition, a second absorption line was found at larger Co<sup>2+</sup> concentrations (5% to 7%), the nature of which has not yet definitely been established. A simple model calculation which primarily employs the single ion anisotropies of the Co<sup>2+</sup> and Fe<sup>2+</sup> ions was performed for a qualitative interpretation of the experimental results.

Die antiferromagnetische Resonanz (AFMR) wurde untersucht bei Temperaturen des flüssigen Heliums an NiO, dotiert mit Fe<sup>2+</sup> oder Co<sup>2+</sup>, im fernen Infrarot. Für die mit Co<sup>2+</sup> dotierten Kristalle wurde eine starke Verschiebung der AFMR-Linie beobachtet. Im Falle der mit Fe<sup>2+</sup> dotierten Kristalle war die Verschiebung deutlich kleiner. Bei großen Co<sup>2+</sup>-Konzentrationen (5% bis 7%) wurde eine zusätzliche Absorptionslinie gefunden, deren Ursache bislang noch nicht restlos geklärt wurde. Einfache Modellbetrachtungen, die wesentlich den Einfluß der Einzelionenanisotropien der Co<sup>2+</sup>- oder Fe<sup>2+</sup>-Ionen berücksichtigen, dienen zu einer mehr qualitativen Deutung der Meßergebnisse.

**1. Introduction**

NiO is one of the antiferromagnetic oxides which has the NaCl structure in the paramagnetic phase. In this class of materials, NiO and MnO are fairly well understood with respect to their magnetic properties. Magnons in these materials have been studied by means of inelastic neutron scattering experiments [1, 2], Raman scattering [3, 4], and infrared spectroscopy [5, 6]. The results of these investigations can be interpreted in terms of model calculations, based on a simple Heisenberg model. This is mainly due to the fact that the ground states of Ni<sup>2+</sup> and Mn<sup>2+</sup> are singlet states (<sup>3</sup>Γ<sub>2</sub> and <sup>6</sup>Γ<sub>1</sub>) with quenched or zero orbital angular momentum. In contrast, the ground states of Co<sup>2+</sup> and Fe<sup>2+</sup> are the triplet states <sup>4</sup>Γ<sub>4</sub> and <sup>5</sup>Γ<sub>5</sub>, respectively, with an effective orbital momentum  $l = 1$ . These ground states are split by the spin-orbit interaction, the exchange field, and, possibly, by an uniaxial crystal field below the Néel temperature. The excitations in crystals containing Co<sup>2+</sup> or Fe<sup>2+</sup> are partly collective and partly single-ion in nature (see, for example, the results from KCoF<sub>3</sub> [7, 8]). Although CoO has been investigated intensively by various methods (neutron scattering, IR spectroscopy, and Raman effect) [9 to 13], there are still a number of unsolved problems with respect to magnetic excitations. In the case of FeO, very little experimental data are available as yet since this material is unstable. Therefore, the study of either Co<sup>2+</sup> or Fe<sup>2+</sup> as a dopant in other magnetic materials is of some value. Co<sup>2+</sup> in MnO was studied by Hughes recently [14], and the present investigation was performed on Co<sup>2+</sup> and Fe<sup>2+</sup> in NiO.

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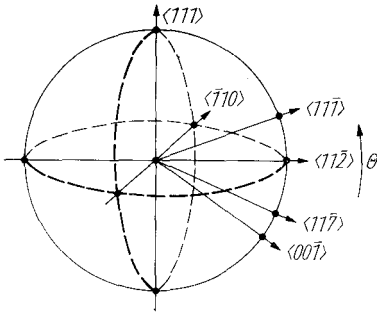


Fig. 1. Illustration of various directions which are important for the discussion of antiferromagnetic oxides with NaCl structure

In all these materials, the antiferromagnetic ordering below the Néel temperature is accompanied by a uniaxial distortion which lowers the symmetry. The magnetic structure is type II f.c.c. The magnetic moments lie in (111) planes and there is considerable evidence that they are oriented in  $\langle 11\bar{2} \rangle$  directions in NiO and MnO [15] (see Fig. 1). The confinement to (111) planes is energetically favoured by the magnetic dipole interactions [16] which are the dominant contributions to the anisotropy energy in these materials. For these reasons, the distortion in NiO and MnO is a trigonal one, a contraction of the lattice along any of the four  $\langle 111 \rangle$  axes which is caused mainly by exchange striction [18]. In CoO, a comparatively strong tetragonal distortion is observed below  $T_N$  [19] in addition to a weaker trigonal distortion [20]. In CoO, the main contributions to the anisotropy energy are expected to arise from single ion effects [18]. In particular, the tetragonal distortion is attributed to magnetoelastic effects [14, 18]. Both collinear [21, 22] and canted [23] spin arrangements have been proposed for CoO. Experimental evidence is somewhat in favour of a collinear model with the spins pointing in a direction somewhere between  $\langle 11\bar{2} \rangle$  and  $\langle 00\bar{1} \rangle$ . Roth assigned the preferred spin direction to be parallel to  $\langle 11\bar{7} \rangle$  [21]. On the other hand, Reichtin and Averbach [22] reported that the spins are tipped away from  $\langle 11\bar{2} \rangle$  by only  $7.83^\circ$  toward the tetragonal axis (see Fig. 1).

For NiO, MnO, and CoO, the strength of the exchange interaction is known from the results of neutron scattering experiments [1, 2, 10]. In NiO, the interaction is very strong in comparison to the other materials (see Table I), and correspondingly, the Néel temperature is rather high. On the other hand, only estimates of the exchange interaction are available for FeO [17]. Given the

Table I

Effective exchange and anisotropy fields for some magnetic ions in pure and doped crystals

ion	Ni <sup>2+</sup>	Co <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Co <sup>2+</sup>
host crystal	NiO	NiO	NiO	MnO	MnO
$J_{\text{eff}}$ (cm <sup>-1</sup> )	71.3 <sup>a)</sup>	29.6 <sup>b,c)</sup>	27.3 <sup>b,d)</sup>	6.77 <sup>e)</sup>	9.06 <sup>b,c)</sup>
$H_E = 2zSJ_{\text{eff}}$ (cm <sup>-1</sup> )	856 <sup>a)</sup>	604 <sup>b,c)</sup>	656 <sup>b,d)</sup>	203 <sup>e)</sup>	185 <sup>b,c)</sup>
$H_A$ (cm <sup>-1</sup> )	0.75 <sup>f)</sup>	18 <sup>h)</sup>	2.5	1.9 <sup>f)</sup>	38.6 <sup>g)</sup>
$H_A/H_E$	$8.8 \times 10^{-4}$	$3 \times 10^{-2}$	$4 \times 10^{-3}$	$9.4 \times 10^{-3}$	0.21

a) From [1];

b)  $J^{\text{II D}}$  for explanation see text;

c)  $J^{\text{D D}}$  from [10];

d)  $J^{\text{D D}}$  from [17];

e) from [2];

f) from  $\nu_{\text{AFMR}}$ , [5];

g) from [14];

h) present investigation.

values of the exchange parameters, far infrared antiferromagnetic resonance (AFMR) experiments yield essentially the effective anisotropy field  $H_A$  since

$$\omega_{\text{AFMR}} \sim \sqrt{H_E H_A},$$

where  $H_E$  is the exchange field. Since NiO and MnO are easy-plane antiferromagnets, two AFMR modes are expected. One of them, with frequencies of 36.6 and 27.7 cm<sup>-1</sup> in NiO and MnO [5], respectively, involves mainly a motion of the spins out of the easy plane. The other AFMR mode involving mainly in-plane motion of the spins occurs at much lower energies. In MnO, this mode has only been observed in high magnetic fields [24]. If MnO and NiO, which have relatively small anisotropy fields, are doped with Co<sup>2+</sup> or Fe<sup>2+</sup>, a considerable shift of the AFMR frequencies is expected even at impurity concentrations of a few percent. This shift can be attributed to the large single ion anisotropy energies of these ions. Therefore, the investigation of the AFMR in NiO doped with Co<sup>2+</sup> and Fe<sup>2+</sup> will provide information about the single ion anisotropy energies of these ions.

## 2. Experimental

The samples were cut from flame-grown single crystals.<sup>3)</sup> Both pure and doped crystals were black in colour indicating an excess of O<sup>2-</sup> ions. The impurity concentration of each sample was determined by means of a X-ray fluorescence method. With this method, the homogeneity of the impurity distribution could also be checked. Samples with a considerably inhomogenous distribution were omitted. Within the limits of accuracy ( $\pm 0.2$  at%), no other impurities could be detected.

Optical measurements in the far infrared were carried out at 4.2 K with a typical resolution of 1 cm<sup>-1</sup>. In addition, some transmission measurements were performed between 800 and 3500 cm<sup>-1</sup> at room and liquid helium temperatures.

The results of the AFMR measurements are shown in Fig. 2 and 3. The frequency of the upper AFMR mode (out-of-plane) is shifted with increasing impurity concentration to higher frequencies, strongly for Co<sup>2+</sup> and moderately for Fe<sup>2+</sup>. Also, the width of the AFMR absorption line increases as can be seen in Fig. 2. The same behaviour, a shift of frequency and an increase in linewidth, has been observed for Co<sup>2+</sup> in MnO [14]. And in both cases, the squares of the resonance frequencies are almost a linear function of the impurity concentrations. But there are deviations from such a linear behaviour which are outside the experimental uncertainty.

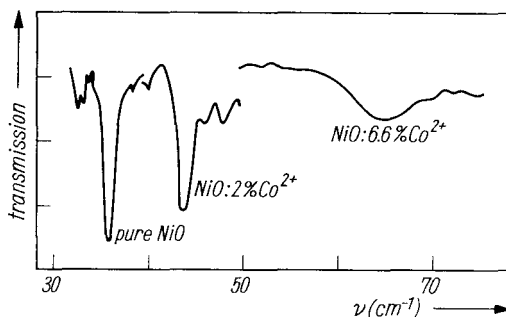


Fig. 2. AFMR lines (transmission) of some Co<sup>2+</sup>-doped NiO samples

<sup>3)</sup> The crystals were purchased from Siltronix, S. A., Geneva; except for one Fe<sup>2+</sup> doped sample obtained from Marubeni Company Japan.

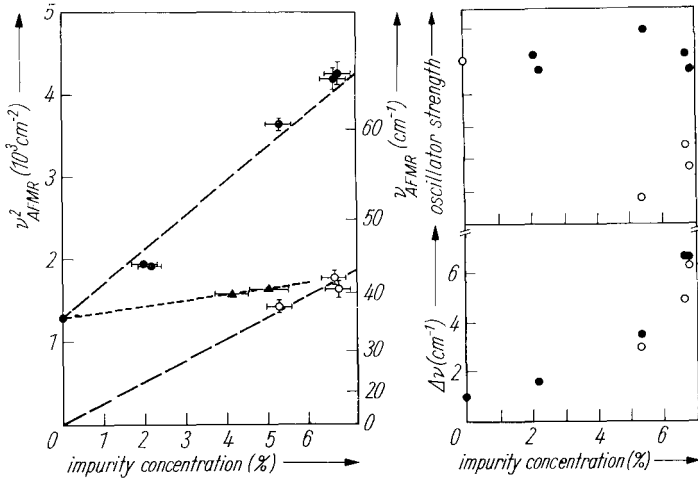


Fig. 3. Square of the AFMR frequency ( $v_{AFMR}^2$ ), oscillator strength, and half-width  $\Delta\nu$  of the AFMR lines versus impurity concentration for NiO doped with  $\text{Co}^{2+}$  (● upper mode and ○ lower mode) and for NiO doped with  $\text{Fe}^{2+}$  (▲)

In addition to the absorption line due to the out-of-plane AFMR mode, we have found for  $\text{Co}^{2+}$  concentrations of 5.3, 6.6, and 6.7% a second absorption line at lower frequencies (see Fig. 3). Both frequency and oscillator strength of this line depend strongly on the impurity concentration. The behaviour of the former is similar to that of the upper mode and is what one would expect for an AFMR mode. The latter dependence is in contrast to that of the upper mode and is what one would expect for an impurity mode (see Fig. 3).

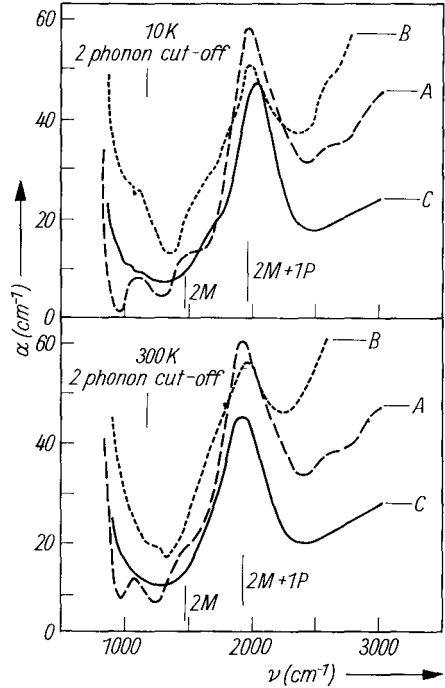
The results of the transmission measurements between 800 and  $3500 \text{ cm}^{-1}$  are shown in Fig. 4. A sharp decrease in absorption occurs at about  $800 \text{ cm}^{-1}$ , which is below the two-phonon cut-off (see Table 2). At  $2000 \text{ cm}^{-1}$ , a broad absorption band is found which is due to the simultaneous excitation of two magnons and one phonon [3, 6]. This band is nearly unaffected by the impurities. A shift of this band to lower frequencies would have been expected since the exchange field of the  $\text{Co}^{2+}$  ions is much smaller than that of the  $\text{Ni}^{2+}$  ions (see Table 1). Because of the high symmetry of the NaCl structure, no absorption band due to two-magnon processes is observed (cf. Table 2). These are Raman-but not infrared-active, and only if the cubic symmetry is sufficiently distorted,

Table 2  
Optical data of pure NiO

type of excitation	$\text{cm}^{-1}$	references
antiferromagnetic resonance	36	[5]
TO phonon at $q = 0$	400	[25]
LO phonon at $q = 0$	580	[25]
high-energy magnons	$\approx 900$	[1]
sharp decrease in ir absorption	$\approx 800$	see Fig. 4
two-phonon cut-off	1160	[25]
peak of two-magnon processes (Raman)	1570	[3, 4]
peak of (two-magnon + one-phonon) processes (ir)	2035	[3, 6]

Fig. 4. Absorption coefficient  $\alpha$  versus frequency for three samples at 10 K (upper part) and at 300 K (lower part). The samples are A (pure NiO, source: Japan), B (NiO: 5% Fe<sup>2+</sup>, source: Japan), and C (NiO: 5% Fe<sup>2+</sup>, source: Grenoble)

can these processes become infrared-active [26]. The absorption spectrum of one of the samples shows a pronounced shoulder at 1600 cm<sup>-1</sup> which coincides with the two-magnon band found in Raman scattering. This shoulder may be due to an impurity-induced two-magnon ir absorption. All samples investigated show a "background" absorption which depends on the impurity concentration of the samples and on their origin (see Fig. 4). All Co<sup>2+</sup>-doped samples were opaque in this spectral region, even with concentrations as low as 2%. The "background" absorption is probably a result of the excess oxygen.



### 3. Discussion

The fact that the AFMR modes are  $q = 0$  or "uniform" modes, suggests that one may employ, in a first approximation, a simple average model. Such a model has already been used by Hughes in connection with his results on MnO:Co<sup>2+</sup> [14]. Although our model is similar, the notation will be somewhat different. There will be an important difference in treating the anisotropy energy of the Co<sup>2+</sup> ions. The host ions and the defect ions have different preferred directions in the doped crystal. If we could switch off the exchange interaction, all magnetic moments would point along their preferred directions. If the exchange field alone were acting on the magnetic ions, they would all be antiferromagnetically aligned. Since the exchange interaction usually is taken to be isotropic, there would be no preferred direction in the absence of the anisotropy field. In reality, both the exchange and the anisotropy fields act on the ions. For small impurity concentrations, most of the host ions will point along their preferred directions. But the defect ions are rotated toward their preferred direction by reason of their high single-ion anisotropy energy. The change in orientation from a defect to the unperturbed lattice far away, takes place gradually, minimizing the free energy of the whole system. The angle between the orientations of two neighbouring spins will depend on the ratio  $H_A/H_E$  of the anisotropy field and the exchange field (see Table 1). Hughes assumed in his average model [14] that practically each ion points in its own preferred direction because the ratio  $H_A/H_E$  is rather large especially for Co<sup>2+</sup> ions in MnO. For NiO, with its extremely high exchange interaction, the corresponding values

of  $H_A/H_E$  are smaller by an order of magnitude. Thus, the region where the host ions are rotated out of their preferred direction will be ten times greater for NiO:Co<sup>2+</sup> than for MnO:Co<sup>2+</sup>. Therefore, we believe that a better approximation for NiO:Co<sup>2+</sup> would be to allow all magnetic moments to rotate to a new equilibrium direction corresponding to a minimum in the free energy. In order to have a simple, easily calculable model, we assume, however, that all magnetic moments are rotated by the same angle.

The effective exchange parameter for spin wave modes in NiO<sup>4)</sup> for  $q = 0$  (AFMR) is  $J = J_1^+ + J_2$ . At this point, we assume that the effective exchange energy in the doped crystals is the average of the contributions from the host ions and the defect ions:

$$\mathcal{H}_{\text{ex}} = (1-x)^2 2zN J^{\text{HH}} \mathbf{S}_a^{\text{H}} \cdot \mathbf{S}_b^{\text{H}} + (1-x)x2zN J^{\text{HD}} (\mathbf{S}_a^{\text{H}} \cdot \mathbf{S}_b^{\text{D}} + \mathbf{S}_a^{\text{D}} \cdot \mathbf{S}_b^{\text{H}}) + x^2 2zN J^{\text{DD}} \mathbf{S}_a^{\text{D}} \cdot \mathbf{S}_b^{\text{D}}. \quad (1)$$

The indices H, D, a, and b refer to the host ions, defect ions, and to the two magnetic sublattices, respectively.  $N$ ,  $x$ , and  $z$  are the number of magnetic ions per sublattice, the impurity concentration, and the number of effective neighbours, i.e. 6, respectively.  $J^{\text{HH}}$ ,  $J^{\text{HD}}$ , and  $J^{\text{DD}}$  are the parameters for the exchange interaction between host ions, between host and defect ions, and between defect ions, respectively. In our model,  $J^{\text{HD}}$  was always taken to be equal to  $\sqrt{J^{\text{HH}}J^{\text{DD}}}$  [27] since reliable experimental data were not available. The quantities  $J^{\text{HH}}$  and  $J^{\text{DD}}$  are known from neutron scattering experiments on pure crystals except for FeO. In Table 1, values of the effective exchange fields  $J^{\text{HH}}$  or  $J^{\text{HD}}$  are compiled for a number of systems. Quite recently, results of inelastic neutron scattering on mixed crystals  $\text{Co}_x\text{Ni}_{1-x}$  were obtained [28] which indicate that the actual value of  $J^{\text{HD}}$  for Co<sup>2+</sup> in NiO is slightly higher ( $J^{\text{HD}} \approx 32 \text{ cm}^{-1}$ ) than that calculated from the square root of  $J^{\text{HH}}J^{\text{HD}}$  (see Table 1).

In our phenomenological model, no effort was made to include a microscopic theory of the anisotropy energy and of its various physical origins [18]. We have formulated the anisotropy energy of the doped crystals as follows:

$$\mathcal{H}_{\text{ani}} = N(1-x) \mathcal{H}_{\text{ani}}^{\text{H}} + Nx \mathcal{H}_{\text{ani}}^{\text{D}}. \quad (2)$$

$\mathcal{H}_{\text{ani}}^{\text{H}}$  contains only a term of trigonal symmetry (see Table 3) with parameter  $T^{\text{H}}$  in accordance with theoretical results for the magnetic dipole interactions

Table 3

Some properties of contributions to the anisotropy energy

symmetry	type	maximum for positive parameter	minimum for positive parameter
trigonal	$T(\alpha_x\alpha_y + \alpha_y\alpha_z + \alpha_z\alpha_x)$	$\langle 111 \rangle$	$(111)$
tetragonal	$-\frac{3}{2}R\alpha_z^2$	$(001)$	$\langle 001 \rangle$
cubic	$K(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2)$	$\langle 111 \rangle$	$\langle 100 \rangle$
cubic	$-U\alpha_x^2\alpha_y^2\alpha_z^2$	$\langle 100 \rangle, \langle 110 \rangle$	$\langle 111 \rangle$ and all equivalent directions

<sup>4)</sup> For details see [1].

[16, 29, 30]. In Table 3,  $\alpha_x, \alpha_y, \alpha_z$  are the direction cosines of the magnetic moments under consideration with respect to the cubic axes.

Other possible contributions to  $\mathcal{H}_{\text{ani}}^{\text{H}}$  are neglected, e.g. a sixth-order cubic term (parameter  $U^{\text{H}}$ ) from which the small but finite anisotropy field of the in-plane mode originates. For the defect ions terms of trigonal symmetry ( $T^{\text{D}}$ ), of tetragonal symmetry ( $R^{\text{D}}$ ), and of cubic symmetry ( $K^{\text{D}}, U^{\text{D}}$ ) are considered. Of course, one would expect the dominant contributions to the single ion anisotropy to have cubic symmetry. However, the trigonal distortion of the host lattice below  $T_{\text{N}}$  and the magnetic dipole interactions will give rise to contributions of trigonal symmetry. Furthermore, it may be useful to consider also a contribution of tetragonal symmetry in view of the tetragonal distortion in CoO.

By minimizing the total energy  $\mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{ani}}$ , with respect to the spin orientation for a given concentration  $x$ , the equilibrium direction of the magnetic moments was determined, assuming all ions are rotated by the same angle. Without losing too much generality, the rotation is restricted to the (110) plane (see Fig. 1) and described by an angle  $\theta$ . After inserting the equilibrium position into  $\mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{ani}}$ , the equations of motion for the transverse spin components were derived in the usual spin wave approximation. The frequencies of the two AFMR modes for small impurity concentrations are

$$(\hbar\omega)_i^2 = 4zJ^{\text{HH}} [(1-x)S^{\text{H}}H_{\text{Ai}}^{\text{H}} + xS^{\text{D}}H_{\text{Ai}}^{\text{D}}] + 8xzJ^{\text{HH}}H_{\text{Ai}}^{\text{H}}S^{\text{D}} \left(1 - \frac{J^{\text{HH}}}{J^{\text{HD}}}\right), \quad (3)$$

where  $i = 1$  or  $2$ .

The higher-order corrections are proportional to  $x^3$  and can be ignored. This formula is very similar to that derived by Hughes [14], except for the term which takes into account the different exchange field acting on impurities. This term is important for the systems NiO:Co<sup>2+</sup> and NiO:Fe<sup>2+</sup>, but can be neglected for MnO:Co<sup>2+</sup> (see Table I). The two frequencies (equation (3)) correspond to the out-of-plane and in-plane AFMR modes in pure NiO.  $H_{\text{Ai}}^{\text{H}}$  and  $H_{\text{Ai}}^{\text{D}}$  are the anisotropy fields derived from (2) for small deviations from the equilibrium direction. In general, there are two different anisotropy fields corresponding to the two AFMR modes. The dependence on the rotation angle  $\theta$  is shown in Fig. 5 for the various contributions to  $H_{\text{Ai}}^{\text{H}}$  and  $H_{\text{Ai}}^{\text{D}}$ . It should be noted that our average model as well as that of Hughes is very similar to the REI (random element isodisplacement) model [31]. This has been used successfully for the interpretation of the  $q = 0$  lattice modes of mixed crystals [32]. In addition to the two AFMR modes discussed so far, there are two other solutions to the equations of motion which are degenerate in frequency. This frequency is independent of  $x$  for small  $x$ :

$$(\hbar\omega)^2 = (2zS^{\text{H}}J^{\text{HD}} + H_{\text{A1}}^{\text{D}}) (2zS^{\text{H}}J^{\text{HD}} + H_{\text{A2}}^{\text{D}}). \quad (4)$$

For these modes, Hughes [14] obtained a similar expression. They are predominantly a precession of the impurity spins about their effective magnetic field. If its frequency is far above the spin wave band of the host crystal, these modes are localized. Such localized excitations, magnons [33, 34] as well as phonons [35], have been studied both theoretically and experimentally. The frequency of the local magnon mode in MnF<sub>2</sub>:Fe<sup>2+</sup> is satisfactorily described by an expression as given in (4) [36]. Unfortunately, the extremely high exchange field in NiO does not favour local magnon modes [37]. For Co<sup>2+</sup> and Fe<sup>2+</sup> in

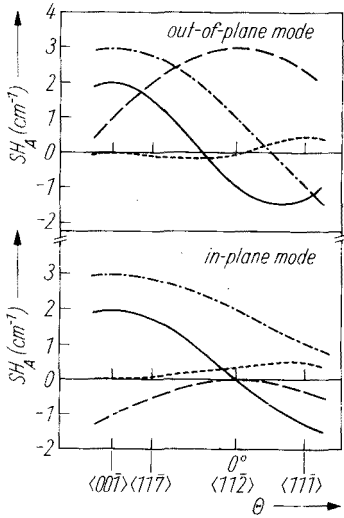


Fig. 5. Contributions  $SH_A$  to the anisotropy fields of the two AFMR modes as a function of preferred spin direction (upper part: out-of-plane mode, lower part: in-plane mode in pure NiO) for the different terms in the anisotropy energy. — Trigonal, - · - · - tetragonal, --- 4th-order cubic, and - - - - 6th-order cubic. All parameters have been set equal to +1

NiO, the frequency given by (4) falls in the spin wave band of NiO. At best we may expect resonant band modes for which equation (4) is not a good approximation.

For the anisotropy energy of the impurity ions, there are more parameters in our model considerations than can be determined from the experimental data available so far. We calculated the frequencies of the two AFMR modes by using only one or two of the four parameters and setting the others equal to zero. Our model calculation is not intended to be a fit to the experimental data, but rather a qualitative attempt to show how the frequencies of the AFMR modes

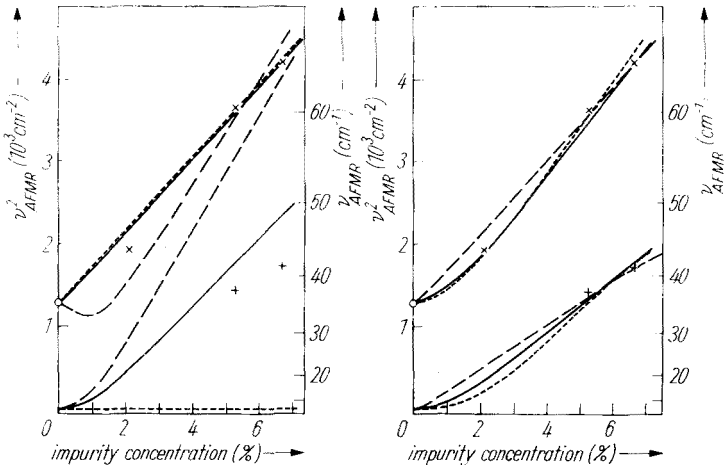


Fig. 6. Square of the AFMR frequencies for NiO doped with  $\text{Co}^{2+}$  versus impurity concentration. Experimental ( $\times$  upper mode,  $+$  lower mode) and theoretical values. On the left: models No. 1 (---), No. 2 (- · - · -), and No. 3 (—). On the right: model No. 4 (—), No. 5 (---), and No. 6 (- · - · -). The values of parameters used in these model calculations are listed in the text



depend on impurity concentration for different types of contributions to the anisotropy energy. The results of the calculations for Co<sup>2+</sup> in NiO are given in Fig. 6, as well as the experimental data. The model parameters are listed in Table 4.

As a whole, these model considerations show how the different contributions to the anisotropy field would influence the frequencies of the AFMR modes. Basically, only terms linear in the impurity concentration are taken into account. But there are deviations of  $\nu_{AFMR}^A$  versus  $x$  from a straight line caused by the angular dependence of the anisotropy fields, since the equilibrium direction depends on the concentration. In order to fit the experimental data for NiO:Co<sup>2+</sup>, values between 10 and 30 cm<sup>-1</sup> are required for the anisotropy constants. This agrees satisfactorily with  $K^D = 32.8$  cm<sup>-1</sup> for MnO:Co<sup>2+</sup> [14] and with the theoretical results of Kanamori [18]. Model No. 4 with a fourth-order cubic term and a trigonal term seems to be most favourable because of its agreement with the experimental data and its physical relevance. The cubic term is expected for symmetry reasons and has been shown to originate from magneto-elastic effects [14, 18]. However, no explanation can be offered at present for a trigonal term as large as  $T^D = 9$  cm<sup>-1</sup>, even on the grounds of the detailed theory of Kanamori [18]. On the other hand, recent results for the preferred direction in CoO ( $\theta = -7.83^\circ$ ) [22] indicate the existence of such a term. The agreement of model No. 4 with experiment includes the mode observed at lower frequencies. Although there is no direct experimental proof that the lower-frequency line is the second AFMR mode and not an impurity mode of other physical nature, the frequency of this line apparently depends on Co<sup>2+</sup> concentration as one would intuitively expect for the lower AFMR mode and as predicted by the model considerations.

For Fe<sup>2+</sup> in NiO, analogous model calculations have been performed. In this case, only one AFMR mode was observed. The values of the anisotropy constant range

Table 4  
Model parameters for Co<sup>2+</sup> in NiO\*)

model No.	3T <sup>D</sup> (cm <sup>-1</sup> )	3RD (cm <sup>-1</sup> )	K <sup>D</sup> (cm <sup>-1</sup> )	U <sup>D</sup> (cm <sup>-1</sup> )	equilibrium direction <math>\langle\theta_0\rangle</math>	remarks
1	0.75	0	20.0	0	0	<math>\langle\theta_0\rangle</math> is close to <math>\langle 001 \rangle</math> for 5% Co <sup>2+</sup> or more <math>\langle\theta_0\rangle</math> is unchanged, frequency of in-plane mode vanishes reasonable agreement with experiment, but <math>\langle\theta_0\rangle</math> is close to <math>\langle 111 \rangle</math> <math>\langle\theta_0\rangle</math> is close to <math>\langle\theta_0\rangle</math> of Co <sup>2+</sup> in CoO <math>\langle\theta_0\rangle</math> is close to <math>\langle\theta_0\rangle</math> of Co <sup>2+</sup> in CoO <math>\langle\theta_0\rangle</math> is close to <math>\langle\theta_0\rangle</math> of Co <sup>2+</sup> in CoO
2	30.5	0	0	0	0	
3	0.75	0	-20.5	0	0	
4	27	0	16	0	0	
5	19.5	19.5	0	0	0	
6	21	0	16	-20	0	

\*) For Co<sup>2+</sup> concentrations from 0 to 6.65%

from 3 to 10  $\text{cm}^{-1}$  in order to fit the experimental data:

1.  $3T^D = 0.75 \text{ cm}^{-1}$ ,  $R^D = 0$ ,  $K^D = +11.5 \text{ cm}^{-1}$ ,  $U^D = 0$ ;
2.  $3T^D = 9.9 \text{ cm}^{-1}$ ,  $R^D = 0$ ,  $K^D = 0$ ,  $U^D = 0$ ;
3.  $3T^D = 0.75 \text{ cm}^{-1}$ ,  $R^D = 0$ ,  $K^D = -6.75 \text{ cm}^{-1}$ ,  $U^D = 0$ ;
4.  $3T^D = 5 \text{ cm}^{-1}$ ,  $R^D = 0$ ,  $K^D = -4 \text{ cm}^{-1}$ ,  $U^D = 0$ .

The numbers 1 to 4 refer to the above models explained in detail for  $\text{Co}^{2+}$  in NiO. Thus, the single ion anisotropy of  $\text{Fe}^{2+}$  turns out to be smaller than that of  $\text{Co}^{2+}$ . This is in agreement with the theory of Kanamori [18]. His results predict that the major contribution to the single ion anisotropy of  $\text{Fe}^{2+}$  in FeO arises from orbital multipole interactions ( $K^D = -34 \text{ cm}^{-1}$  to  $-73 \text{ cm}^{-1}$ ). And for these anisotropy energies, the preferred direction of  $\text{Fe}^{2+}$  would be  $\langle 111 \rangle$  or an equivalent direction (see Table 3). But these considerations do not hold for  $\text{Fe}^{2+}$  in NiO as there cannot be any orbital multipole interactions between host and defect. What we observe are some smaller contributions of unknown origin.

#### Acknowledgements

We would like to thank Prof. Dr. L. Genzel, Dr. C. Irslinger, and Dr. R. Grisar for giving us the opportunity to carry out the near infrared measurements in the M.P.I. für Festkörperforschung in Stuttgart. We gratefully acknowledge the help of Dr. E. Knauer, Mineralogisches Institut Würzburg, in determining the impurity concentrations of our samples. We are indebted to the "Deutsche Forschungsgemeinschaft" for financial support, and one of us (V.W.) gratefully acknowledges financial support of the "Bundesministerium für Forschung und Technik".

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(Received December 6, 1974)