ANISOTROPY OF Ni2+ AND Ni3+ IONS IN CUBIC SITES

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Résumé. — On a préparé des monocristaux de ferrite de nickel avec (a) les ions Ni^{3+} dans l'état 4 F sur les sites octaédriques et (b) les ions Ni^{2+} dans l'état 3 F sur les sites tétragonaux. Les niveaux les plus bas de ces deux ions se subdivisent en trois niveaux par les composants non cubiques du champ cristallin. On peut représenter cette subdivision au moyen d'un Hamiltonien de spin qui inclut l'énergie de couplage spin-orbite et les termes trigonaux (ou tétragonaux) du champ. On a déterminé les contributions à la constante d'anisotropie, K_1 (du fait des deux ions) en fonction de la température et on les a ajustées aux paramètres de l'Hamiltonien en utilisant un ordinateur. On a fait une comparaison avec l'ion Co^{2+}.

Abstract. — Single crystals of nickel ferrite have been prepared containing (a) F-state Ni^{3+} ions on B-sites, and (b) F-state Ni^{2+} ions on A-sites. The ground state triplet levels of both these ions are split by non-cubic components of the crystal field. This splitting can be represented by means of a Spin Hamiltonian which includes the spin-orbit coupling energy and trigonal (or tetragonal) field splitting terms. The contributions to the anisotropy constant K_1, due to the two ions, have been determined as a function of temperature and fitted to the parameters of the Hamiltonian by computer. A comparison has been made with the F-state ion Co^{2+}.

1. **Introduction.** — A large amount of effort has been devoted in recent years to the study of the anisotropy of the magnetocrystalline energy introduced by Co^{2+} ions on the B-sites (octahedral sites) of magnetic spinel lattices. With the lattice site of the Co^{2+} ion as shown in figure 1 the crystal field will

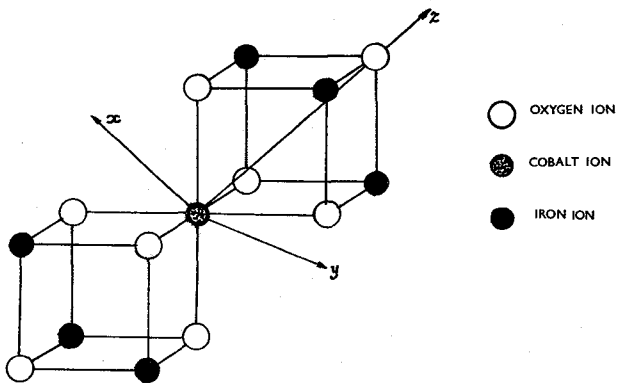

FIG. 1. — Configuration of cations neighbouring a Co^{2+} ion in the B-sites of the spinel lattice.

have both cubic and trigonal components, the sources of which are thought to be well understood. Since the Co^{2+} ion exists in a ^4F state, its ground state will be an orbital triplet which is split by the trigonal field while the spin levels are split by the exchange field $\mathbf{H}_{ex}$ and the spin-orbit coupling. The effective spin Hamiltonian may thus be written as

$$\mathcal{H}_s = \Delta_t(1 - L_z^2) + g\beta\mathbf{H}_{ex}.\mathbf{S} - \alpha\lambda\mathbf{L}.\mathbf{S} \qquad (1)$$

where Δ_t is the splitting of the $L_z = 0$ and $L_z = \pm 1$ states due to the trigonal field (the z-direction being taken along the trigonal axis). The quantity $\alpha\mathbf{L}$ is the effective orbital angular momentum [1] and λ is the spin-orbit coupling constant.

Approximate solutions of this Hamiltonian for the lower energy levels of the Co^{2+} ion in the B-sites have been undertaken by Slonczewski [2] and Tachiki [3] on the assumption that $\Delta_t \gg g\beta H_{ex} \gg \alpha\lambda$ and the values of the magnetocrystalline energy constant, K_1, so predicted have been compared with experiment. An attempt to fit the experimental values of K_1 over the whole temperature range by computer has been made by Sturge et al. [4] with fair success. A comparison of the various theoretical curves and the experimental results is shown in figure 2 together with the respective values chosen for the parameters in the Hamiltonian. It is observed that, with these parameters, it is not reasonable to carry out a first order calculation.

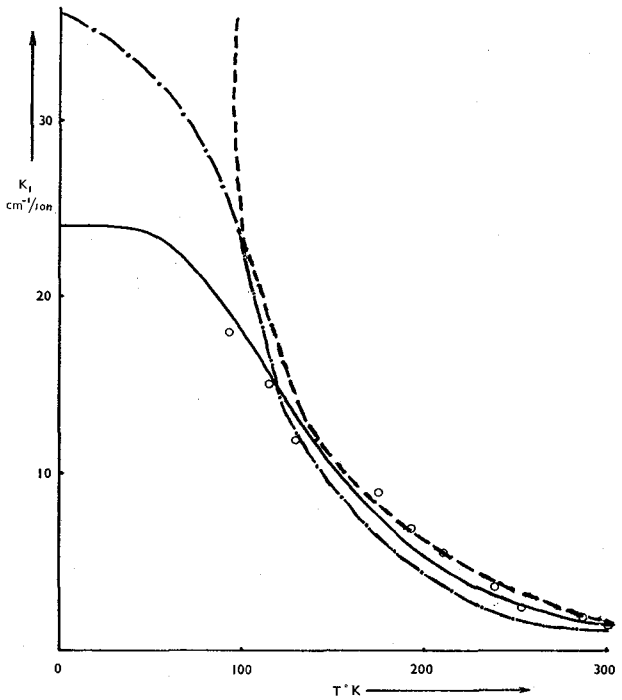

FIG. 2. — Temperature dependence of the cubic anisotropy constant K_1 for octahedral Co^{2+}. o, experimental results of Okada et al. [5]; - - - -, Slonczewski's theory [2] with $\alpha\lambda = 100$ cm^{-1} · - · - · -, Sturge's theory [4] using parameters $g\beta Hex = 150$ cm^{-1}, $\alpha\lambda = -200$ cm^{-1}, $\Delta_t = 650$ cm^{-1}. ——, theory of present work with parameters $g\beta H_{ex} = 180$ cm^{-1}, $\alpha\lambda = -300$ cm^{-1}, $\Delta_t = 800$ cm^{-1}.

In the present work, attention is directed to the Ni^{3+} and Ni^{2+} ions in the spinel lattice. The Ni^{3+} ion is isoelectronic with the Co^{2+} ion and, as a ^4F ion on the B-site of a spinel lattice, will be expected to obey a Hamiltonian similar to that of Eq. (1). On the other hand the ^3F Ni^{2+} ion has an orbital triplet ground state when situated on the A-site (tetrahedral site) of the spinel lattice which is energetically unfavourable for this ion. In this case, since the tetrahedral site is expected to be a good cubic site, the splitting, Δ_t, is expected to be small and, depending on its origin, could define either a trigonal or tetragonal axis.

2. **The Ni^{3+} ion.** — Crystals of nickel ferrite containing Ni^{3+} ions on octahedral sites have been produced by means of the fluxed melt technique in two ways. In the first case, crystals have been grown from a fluxed-melt containing an excess of nickel oxide such that, when an oxygen pressure of about 4 atmospheres was maintained over the melt, crystals of composition $(Fe_1^{3+})_A(Ni_1^{2+}Ni_x^{3+}Fe_{1-x}^{3+})_BO_4^{2-}$ were produced with x of the order of 0.01. In the second, lithium carbonate was added to the melt such that a small fraction of Li^+ ions could be substituted for Ni^{2+} ions on the B-sites of the ferrite, thus forcing an equal fraction of the nickel ions within the ferrite into the Ni^{3+} form in order to maintain charge neutrality. The resultant crystals would have the nominal composition $(Fe_1^{3+})_A(Li_x^+Ni_{1-x}^{2+}Ni_x^{3+}Fe_1^{3+})_BO_4^{2-}$ with x limited by the solubility of the lithium to values below about 0.01 also [6]. In both cases the flux used was approximately 1.5 moles of $(B_aO)_3B_2O_3$ to 1 mole of $NiFe_2O_4$, and the crystals were grown by slow cooling the fluxed melt at 1 °C/h from 1 330 °C.

The anisotropy constant, K_1, of the various Ni^{3+} ions containing crystals was measured from the variation of ferromagnetic resonance field with orientation in the (110) plane. Measurements were made at a microwave frequency of 8.921 GHz at room temperature and over a temperature range 4.2 °K to 300 °K. The difference between these values of K_1 and those for crystals of pure nickel ferrite were used for comparison with the values predicted by Eq. (1) using the parameters

$$g\beta H_{ex} = 110\ cm^{-1};\quad \alpha\lambda = -425\ cm^{-1};\quad \Delta_t = 300\ cm^{-1}$$

and the resultant curves are shown in figure 3. (The values of x, the fraction of Ni^{3+} ions present, have been checked both by the curve fitting and by analysis.) The values of $g\beta H_{ex}$ and $\alpha\lambda$ giving this fit are in fair agreement with those found for Co^{2+} but the value of Δ_t is much smaller. This would be explained if, in agreement with the calculations of Sturge et al. the splitting of the Ni^{3+} levels were partially quenched by a Jahn-Teller distortion.

3. **The Ni^{2+} ion.** — If crystals of pure nickel ferrite are water-quenched from a high temperature the purely inverse structure of the ferrite will be destroyed and Ni^{2+} ions will appear on the A sites. Since the site preference energy of the Ni^{2+} ion for the B-sites has been shown by Robertson and Pointon [7] to be about

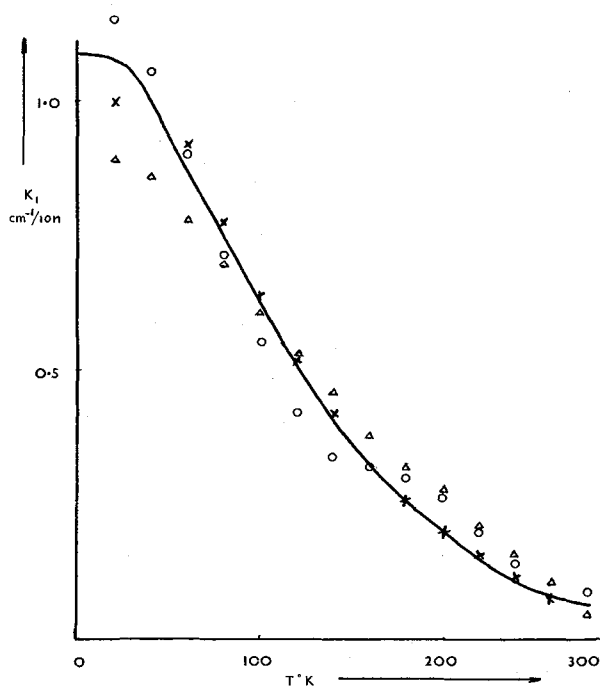

FIG. 3. — Temperature dependence of the cubic anisotropy constant K_1 for Ni^{3+} ions on B-sites. ×, lithium doped nickel ferrite with $x = 0.36$ %. o, lithium doped nickel ferrite with $x = 0.68$ %. △, nickel excess nickel ferrite with $x = 0.90$ %. ——, computer fit of the Spin Hamiltonian with the parameters $g\beta H_{ex} = 110\ cm^{-1}$, $\alpha\lambda = -425\ cm^{-1}$, $\Delta_t = 300\ cm^{-1}$.

0.80 ± 0.05 eV evenquenching from 1 300 °C will only produce a composition of the form

$$(Ni_x^{2+}Fe_{1-x}^{3+})_A(Ni_{1-x}^{2+}Fe_{1+x}^{3+})_BO_4^{2-}$$

with x about 0.4 %. The anisotropy constants, K_1, of such

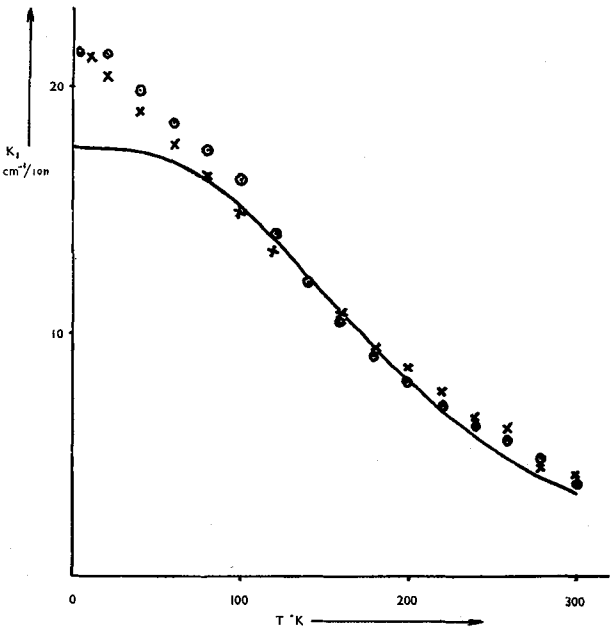

FIG. 4. — Temperature dependence of the cubic anisotropy constant K_1 for Ni^{2+} ions on A-sites. o, pure nickel ferrite water-quenched from 1 220 °C. ×, pure nickel ferrite water-quenched from 1 300 °C. ——, computer fit of Spin Hamiltonian with parameters $g\beta H_{ex} = 475\ cm^{-1}$; $\alpha\lambda = -400\ cm^{-1}$; $\Delta_t = -1\,000\ cm^{-1}$.

quenched crystals have also been determined over the temperature range 4.2 °K to 300 °K by ferromagnetic resonance and the difference, ΔK_1, between the anisotropy constant K_1 of the quenched crystals and the value for the annealed crystals has been found. The resultant curves have been fitted from Eq. (1) with the parameters

$$\Delta_t = -1\,000\ \text{cm}^{-1}\ ;\quad g\beta H_{ex} = 475\ \text{cm}^{-1}\ ;\quad \alpha\lambda = -400\ \text{cm}^{-1}$$

and are shown in figure 4. This fit has been obtained with Δ_t a trigonal splitting. (In this case the values of x have been checked by magnetic measurements.) The form of the curves is in good agreement with those obtained by Krishnan [8].

The values of the parameters are very different from those predicted by Sturge et al. and Baltzer [9], both of whom assumed that there would be a tetragonal distortion. The values of their parameters are given below

Sturge et al.

$$g\beta\,H\text{ex} = 150\ \text{cm}^{-1}\quad \alpha\lambda = -400\ \text{cm}^{-1}\quad \Delta_t = -2\,500\ \text{cm}^{-1}.$$

Baltzer

$$g\beta H\text{ex} = 600\ \text{cm}^{-1}\quad \alpha\lambda = -900\ \text{cm}^{-1}\quad \Delta_t = -40\ \text{cm}^{-1}$$

At the present time the source of the large trigonal splitting which appears to be present is not at all clear.

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