# Contribution to Magnetic Anisotropy from Cations Which Locally Distort the Crystal Lattice

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The energy states of the $Ni^{2+}$ ion on the tetrahedral sites of the spinel lattice have been calculated as a function of tetragonal distortions from cubic symmetry. The computed first- and second-order contributions from tetrahedral $Ni^{2+}$ to the cubic anisotropy of magnetic spinels have been compared with experiment. Less than 0.1% tetrahedral $Ni^{2+}$ could be responsible for the anisotropy of $NiFe_2O_4$. Computed values for the zero-field splitting of $Cr^{3+}$ in $MgAl_2O_4$ and the anisotropy of octahedral $Co^{2+}$ in magnetic spinels are consistent with experiment for a trigonal field 10% of the cubic field in strength and with a sign corresponding to that due to the nearest neighbor oxygen ions. The single-ion first- and second-order contributions to the cubic anisotropy from octahedral $Ni^{3+}$ have also calculated and found to be very large and positive.

## 1. Introduction

The crystalline electric fields, experienced by the magnetic ions in oxides, play a major role in determining the contribution such ions have to the net magnetic anisotropy. Calculations on single-ion contributions to the magnetic anisotropy have heretofore been restricted to certain ions which permit great simplifications in the theory. However, little concern has been expressed for the many ions which could not be considered before and yet which should have very large contributions to the magnetic anisotropy. This paper is a preliminary report on work directed toward the calculation of the single-ion contributions to magnetic anisotropy for the transition metal ions including those ions which tend to distort their local environment. The method of treatment is first outlined and the some of the more important results obtained for $d^2, d^3, d^7$ and $d^8$ ions are discussed.

## 2. Method of Treatment

### A. The Isolated Ion

The first step in the anisotropy calculation is to obtain the electronic states of the ion in the crystalline electric field as if the ion were magnetically isolated from the lattice. The magnetic exchange is subsequently introduced as a perturbation.

The Hamiltonian, $H_0$, for the isolated $d^N$ or $d^{10-N}$ ion is

$$H_0 = \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i}^{N} \lambda L_i \cdot S_i + \sum_{i}^{N} V_i, \quad (1)$$

where the $V_i$ are the crystalline electric field

potentials for each electron. The last term of $H_0$ can be conveniently expressed in terms of the tensor operator, $T_i^m$, which operate directly on the space coordinate of the many electron wave function;

$$T_i^m = \sqrt{\frac{4\pi}{2l+1}} Y_i^m, \quad (2)$$

where the $Y_i^m$ are the usual spherical harmonics. For example, an ion on a lattice site having tetragonal symmetry would have the potential:

$$\sum_i V_i = 21Dq\left\{T_4^\circ + \sqrt{\frac{5}{7}}\left(\frac{T_4^{+4} + T_4^{-4}}{\sqrt{2}}\right)\right\}$$
$$+ 21Qq\left\{T_4^\circ - 3\sqrt{\frac{5}{7}}\left(\frac{T_4^{+4} + T_4^{-4}}{\sqrt{2}}\right)\right\}$$
$$+ 210ApT_2^\circ, \quad (3)$$

where the $Dq$, $Qq$, and $Ap$ are the cubic and tetragonal crystalline field parameters. The first term of $H_0$ is the internal electron exchange of the ion, which can be expressed in terms of the Racah[1] parameters $B$ and $C$.

The electronic states (45 for $d^2$ or $d^8$, and 120 for $d^3$ or $d^7$ ions) produced by the Hamiltonian $H_0$ can be obtained for any arbitrary set of parameters. The secular determinant is first factored according to the symmetry of the problem and then exact diagonalization is carried out for each factor. Parameters are so chosen as to be consistent with optical spectra measured for the particular ion in a similar diamagnetic lattice.

### B. Magnetic Exchange

Once the electronic states for the isolated ion are found, one must include the magnetic

exchange between the given ion and all the remaining magnetic ions in the crystal. At the present time this has been accomplished using the molecular field approximation. Thus, we add to the Hamiltanian $H_0$ the perturbation:

$$H_1 = 2\mu_B \mathbf{S} \cdot \mathbf{H}_e , \qquad (4)$$

where $\mu_B$ = Bohr magneton and $H_e$ is the effective exchange field. The electronic states in the presence of exchange are then obtained by diagonalization of the secular determinant for the lowest manifold of states.

*C. Anisotropy*

The magnetic anisotropy energy is associated with the anisotropic part of the total free energy of the crystal. The total first-order anisotropy constant for a cubic material can then be expressed[2] as

$$K_1 = 4(F_{<110>} - F_{<100>}) , \qquad (5)$$

where $F_{<110>}$ is the free energy of the magnetic crystal with the magnetization along a $<110>$ direction, and similarly for $F_{<100>}$.

If now the given ion of interest is sufficiently dilute in the lattice, the net contribution of all such ions should then have the same form as Equation (5) except that the free energies indicated are the partial free energies for these given ions. For an example, let us consider the case of an ion which has tetragonal symmetry so that there is a unique "z" direction along one of the cubic axes, there are three such sets of ions in the cubic lattice each having a different unique axis. For each set of ions there will be a contribution having the form of Equation (5), and after summing over each of these sets one obtains:

$$K_1(T, H) = \frac{-4N}{3}$$
$$\times kT \left\{ \ln\left(\frac{Z_{xz}}{Z_z}\right) + \ln\left(\frac{Z_{xz}}{Z_x}\right) + \ln\left(\frac{Z_{xy}}{Z_x}\right) \right\}, \qquad (6)$$

where $N$ is the total number of the given ions and $Z_{xy}(T, H)$ is the single-ion partition function for the given ion at the temperature $T$ with an exchange field $H$ in the $xy$ direction, etc. Similar expressions can also be developed for the single-ion contribution to the second-order anisotropy.

All phases of this treatment from the solution of the states of the isolated ion to the actual anisotropy calculation have been pro-grammed for successive operation on the IBM 7090 computer.

## 3. The Tetrahedral $Ni^{2+}$ Ion

The treatment described above has been applied to the $d^2, d^3, d^7$, and $d^8$ ions ($V^{3+}$, $Cr^{3+}$, $Ni^{3+}$, $Co^{2+}$, and $Ni^{2+}$). However, because of space limitations only one important case will be discussed in any detail; namely, that for the $Ni^{2+}$ ion when it occupies the tetrahedral sites, or $A$ sites, of the spinel lattice.

The $Ni^{2+}$ ion on the $A$ sites tends to distort its local environment from cubic to tetragonal symmetry. Therefore, the tetragonal crystalline field potential given in Equation (3) may be used. The lowest states of the isolated ion are given in Fig. 1, for the set of parameters; $B = 1030$ cm$^{-1}$, $C = 4.5B$, $\lambda = -618$ cm$^{-1}$
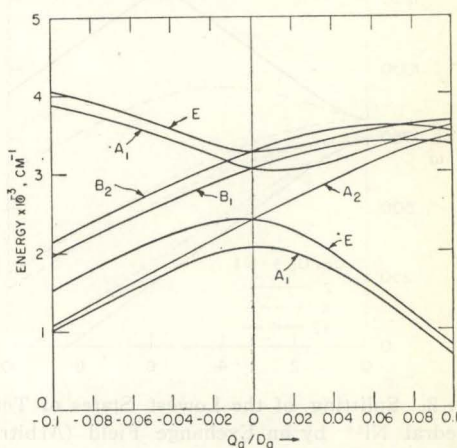


Fig. 1. Lowest States of Tetrahedral $Ni^{2+}$ with Tetragonal Distortion (Symbols Refer to the Irreducible Representations of the $D_{4h}$ Double Group).

$Dq = 412$ cm$^{-1}$, $Ap = -Qq$ which are consistent with the optical spectra. The values of the distortion parameters $Qq/Dq = -0.1, 0, +0.1$ correspond to a local $c/a = 1.18, 1.0, 0.92$, respectively. The energy of the ground state in Fig. 1 is lowered by about the same amount by both signs of the distortion parameter. Without a knowledge of the nuclear potential it is thus difficult to predict the sign of the distortion. The local distortions about the concentrated $Ni^{2+}$ ions in the compound $NiCr_2O_4$ appear to be such that $c/a > 1$[3]. Nevertheless, the local distortions about very dilute tetrahedral $Ni^{2+}$ ions in a cubic structure could be either prolate or oblate.

Since the $Ni^{2+}$ ion has a unique "$z$" axis along one of the cubic axes of the crystal, we can use the expression for the anisotropy contribution given in Equation (6). For the case of $T=0°K$, Equation (6) reduces to a much simpler form for the $Ni^{2+}$ ion:

$$K_1(0, H) = \frac{4N}{3}(2E_{xz}^o - E_x^o - E_z^o), \quad (7)$$

where $E_{xz}^o(H)$ is the ground state when the exchange field is in the $xz$ direction, and the fact that, for this ion, $E_{xy}^o = E_x^o$ has been used to simplify the expression. In Fig. 2 is shown a typical example of how the exchange field splits the lower states of $Ni^{2+}$ on the A-sites
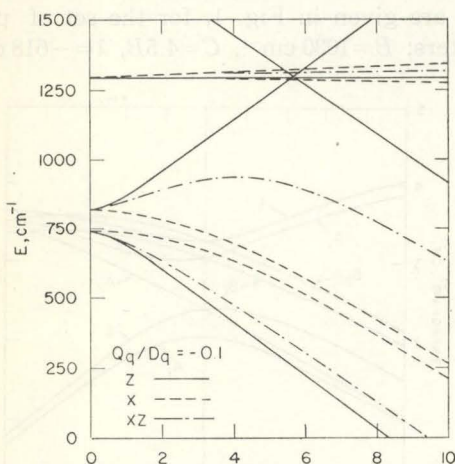


Fig. 2. Splitting of the Lowest States of Tetrahedral $Ni^{2+}$ by an Exchange Field (Arbitrary Origin for Energy).
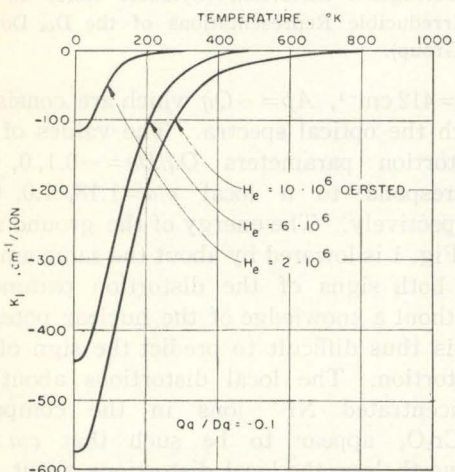


Fig. 3. Single-Ion Contribution of Tetrahedral $Ni^{2+}$ to the First-Order Cubic Anisotropy.

of the spinel lattice. Using Equation (7) one can by inspection of Fig. 2 see qualitatively the behavior of the single-ion contribution to $K_1$ at $T=0$; $K_1$ is negative and large, increasing monotonically toward a limiting value at high fields.

Equation (6) and a similar one for the second-order anisotropy has been used to calculate the temperature dependence of the single-ion anisotropy contribution. The first and second order contribution for $Ni^{2+}$ on A-sites with a prolate local distortion are given in Figs. 3 and 4. Similar results were obtained for $Ni^{2+}$ on A-sites with a oblate local distortion except that the contribution to the second order anisotropy is positive and much smaller. These single-ion contributions are so large that a very small fraction of $Ni^{2+}$ on the A-sites of magnetic spinels would have a profound influence on the anisotropy.
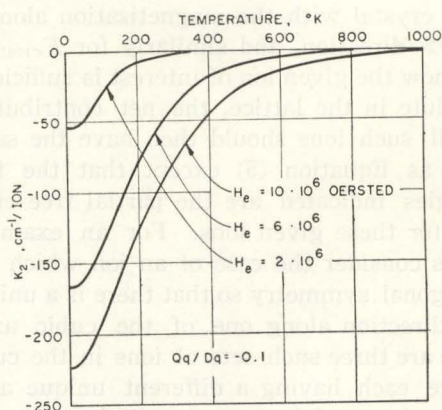


Fig. 4. Single-Ion Contribution of Tetrahedral $Ni^{2+}$ to the Second-Order Cubic Anisotropy.

The magnetic anisotropy of $NiFe_2O_4$ is a case in point for which previous investigations[4] have entirely neglected the role of the $Ni^{2+}$ on the A-sites. The measured[5] first-order anisotropy, $K_1 = -0.04$ cm$^{-1}$/molecule, has been previously attributed to the $Fe^{3+}$ ion, but is more likely due to less than 0.1% of $Ni^{2+}$ on the A-sites. Measurements[5],[6] of the second-order anisotropy of $NiFe_2O_4$ vary in magnitude, but all are negative. The negative second order anisotropy would indicate that the influence of $Ni^{2+}$ on prolately distorted A-sites predominates even though both types of local distortion may exist in this compound.

## 4. Octahedral $d^3$ and $d^7$ Ions

Other significant results have been computed for the case of the ions $Cr^{3+}$, $Co^{2+}$, and $Ni^{3+}$ on the B-sites of the spinel lattice. The large zero field splitting observed[7] for $Cr^{3+}$ in $MgAl_2O_4$ was found consistent with a trigonal field which is 10% of the cubic field strength and which has the sign associated with the field of the nearest neighbor oxygen ions. The anisotropy contribution from the $Co^{2+}$ ion, in a trigonal field of the same sign as that for $Cr^{3+}$, was obtained and found consistent with experiment (for $H_e = 4 \cdot 10^6$ oersted, $T = 0°K$; $K_1 = +48 cm^{-1}$/ion and $K_2 = -150 cm^{-1}$/ion). Similarly for $Ni^{3+}$ the anisotropy con-

tribution was found to be very large (for $H_e = 4 \cdot 10^6$ oersted, $T = 0°K$; $K_1 = +80 cm^{-1}$/ion and $K_2 = +800 cm^{-1}$/ion).

### References

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## DISCUSSION

S. KRUPIČKA: I would like to make a remark on the existence of local distortions in cubic spinels. About one year ago we attempted to get some evidence of the existence of such distortions by X-ray investigation. As there are some indications of the presence of some $Mn^{3+}$ ions in stoichiometric manganese ferrite we determined the mean-square displacement of ions in this ferrite and compared it with m.s. displacements in other binary ferrites (Zn, Mg, Ni). It was found that displacements in Mn ferrite are greater about 0.06Å which was interpreted in agreement with a rough computation as due to Jahn-Teller distortions of $Mn^{3+}$ octahedra (J. Phys. Chem. Solids **20** (1961), 167). More recently Mr. Červinka from our Institute has made a refinement of that study using the monochromatic radiation. His results agree excellently with the previous ones; in addition, if we plot the logarithm of the integrated intensities (divided by $|F_{hkl}|^2$ and corrected for usual factors) against $\sin^2 \theta/\lambda^2$ we get two straight lines with different slopes each of which belongs to different systems of $\{hkl\}$. The slope of one line is the very same as for other ferrites studied but the others is pointing to a greater displacement of certain ions. So we believe that it will be possible to determine which ions are displaced by distortion.

P. K. BALTZER: I have no comment with regard to Dr. KRUPIČKA's remark. However, I would like to add that the reason the energy of the orbital singlet, for $Ni^{2+}$ on $A$-sites, is lowered with an *oblate* distortion is that the second-order tetragonal crystalline field parameter $Ap$ has the sign opposite to the fourth order tetragonal parameter $Qq$ (this is opposite to that for ions on $B$ sites).

K. SIRATORI: If $Ni^{2+}$ on $A$ site is the main cause of the magnetic anisotropy in $NiFe_2O_4$, we can expect that the magnitude of the anisotropy depends not only on oxidation or reduction of the sample, as was discovered by Mr. and Mrs. SEKIZAWA, but also on heat treatment even in a stoichiometric state. Do you know any experimental data on this point?

P. K. BALTZER: The dependence of the anisotropy of $NiFe_2O_4$ on the amount of $Ni^{2+}$ on the 4-fold sites has not been investigated. If it is possible by proper heat treatment to vary the amount of $Ni^{2+}$ on the $A$ sites while keeping the chemistry invarient it should be possible to verify the dependence of the anisotropy of $NiFe_2O_4$ on tetrahedral $Ni^{2+}$.