

Theory of the Magnetic Properties of Ferrous and Cobaltous Oxides, II

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The origins of the magnetic anisotropy energies of the crystals of FeO and CoO in the state of antiferromagnetic ordering and the mechanism of the deformation they suffer when the antiferromagnetic ordering sets in are investigated from the atomistic point of view, following the line developed in the preceding paper. It is concluded that the most effective part of the magnetic anisotropy energy in the deformation-free state of the crystals originates from orbital multipole (or van Vleck's orbital valence) interactions arising from both the coulomb and exchange interactions between cations. The deformation of the crystals, however, is caused mainly by magnetostriction arising from linearly strain-dependent terms of the crystalline field energies. It is shown that the theoretical determination of the axis and magnitude of the deformation, using the point charge model for the calculation of the crystalline field, can give results which are semi-quantitatively consistent with the experimental results. It is shown that in CoO the deformation-dependent anisotropy energy overcomes other anisotropy energies and determines the direction of the magnetization to be the direction of the tetragonal axis of deformation, [001], while in FeO the deformation-independent anisotropy energies are predominant in determining that direction, which coincides with the crystalline trigonal axis, [111]. Discussions are also given for other kinds of deformations which do not depend on the orientation of the magnetic moments, that is, the volume striction and the trigonal deformation suggested by Greenwald and Smart. A brief comment is given to the magnetic anisotropies of MnO, MnS and NiO.

§ 1. Introduction

In this paper we investigate the origins of the magnetic anisotropy energies of FeO and CoO in their antiferromagnetic state and look for the mechanism of their deformation below the Néel temperature. MnO, MnS and NiO will also be discussed briefly.

FeO, MnO, MnS and NiO deform into trigonal symmetry^{1),2)} below their Néel temperatures. In the case of FeO, the angle α that specifies the fundamental rhombohedron is smaller than 60° , whereas for MnO and NiO α is greater than 60° . CoO^{2),3)} deforms into tetragonal symmetry and a contraction occurs along the c -axis. X-ray data for this oxide show that the contraction takes place gradually from the Néel temperature with decreasing temperature and its magnitude amounts to about 1 percent at the lowest temperature of the measurements.

According to neutron diffraction experiments,⁴⁾ the antiferromagnetic spin arrangement in FeO is that proposed by Néel,⁵⁾ Fig. 1 (a), which we shall call structure [A] after Li.⁶⁾ This arrangement can be obtained by attaching alternately $+$ spins and $-$ spins to hexagonal close-packed layers which compose the cubic face-centred lattice of the cations. It has trigonal symmetry. In the following, we shall take [111] as the trigonal

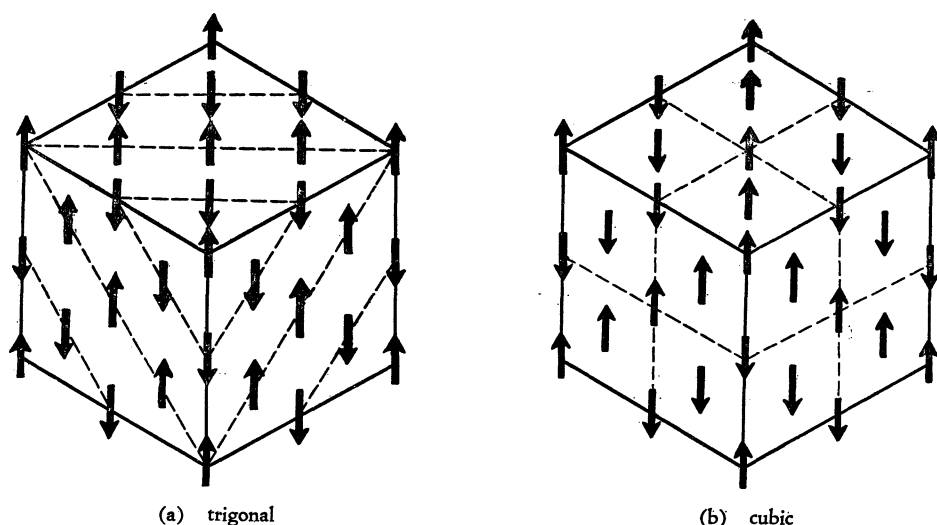


Fig. 1

axis. The orientation of the magnetic moments in FeO was definitely determined to be $[111]$ by neutron diffraction. For CoO, MnO and NiO, the neutron diffraction experiments with powder specimens could not decide whether the spin arrangement has structure [A] or another cubic structure [B], Fig. 1 (b). Li⁽⁶⁾ showed that for structure [A] the orientation consistent with neutron diffraction data is $[001]$ and for structure [B] the orientation cannot be determined at all. As will be shown in later sections, the tetragonal deformation of CoO can reasonably be interpreted as a magnetostriction originating in the effect of the crystalline field on the residual orbital angular momentum of Co^{++} , so that it is highly probable that the orientation of magnetic moments in CoO is $[001]$.^{*} For MnS, neutron diffraction experiment⁽⁷⁾ determined the spin arrangement to be the structure [A] and the orientation of the magnetic moments to be in the (111) plane. In NiO, recent magnetic measurements indicate the orientation of magnetic moments to be likely in the (111) plane, as will be referred to in the last section.

Theoretically speaking, we can distinguish between two kinds of the mechanisms of deformation: one is exchange striction which arises from the dependence of the exchange energies on inter-ionic distances and does not depend on the orientation of the magnetic moments; another is magnetostriction which arises from the anisotropy energies and depends on the orientation of the magnetic moments. In structure [A], the exchange striction can cause a deformation of trigonal symmetry, as well as a volume striction, as suggested by Greenwald and Smart.⁽⁸⁾ In structure [B], it causes only a volume striction. The present investigation will show that, in both FeO and CoO, the magnetostriction predominates due to the presence of a residual orbital angular momentum. In FeO, the

^{*} Note added in proof. Recently, Roth has found by neutron diffraction that the orientation of the magnetic moments in MnO, CoO and NiO is probably in the (111) plane. (W. L. Roth, Annual Meeting, American Crystallographic Association, June, 1956 (unpublished).) His result for CoO is at variance with the conclusion of this study. However, the result of Singer's⁽²³⁾ magnetic measurements on a single crystal of CoO is favourable to our conclusion.

magnetostriction elongates the crystal along the trigonal axis, overcoming the exchange striction which contracts the crystal along the same trigonal axis.

So far, the studies of the origins of the anisotropy energies of antiferromagnetics⁹⁾ have been limited to the non-degenerate orbital case. In cubic crystals of FeO and CoO, however, the orbital state is degenerate. From a new standpoint, we can divide the origins of their magnetic anisotropy energies into four categories: 1. the magnetic dipole-dipole interaction; 2. the spin-orbit interactions; 3. the orbit-orbit interactions; 4. the anisotropy energy arising from deformation.

In the first category, we include intra-ionic magnetic spin-spin interaction as well as inter-ionic magnetic dipole-dipole interaction. The latter was calculated for structure [A] by Kaplan¹⁰⁾; it makes (111) the easy plane of magnetization. In cubic structure [B], it makes no first order contribution to the anisotropy energy. The intra-ionic spin-spin interaction in a free atom or an ion was discussed by Araki¹¹⁾ and Pryce¹²⁾; modified by cubic crystalline field, it gives rise to an anisotropy energy of cubic symmetry.

The spin-orbit coupling energy modified by cubic crystalline field was calculated in the preceding paper,* using the second order perturbation theory. Anisotropy energies of other origins, to be included in this second category are such as anisotropic exchange energy derived by Moriya and Yosida,¹³⁾ but they are negligible in our case.

The anisotropy energies belonging to the third category were discussed generally by van Vleck¹⁴⁾ for the case of ferromagnetism, but we shall attempt to make more specific calculations in later sections. These energies arise from that the cations act as multipoles on their surrounding cations which are also multipoles. In the case of degenerate orbital level, in which the residual orbital angular momentum drags the spin moment, these energies contribute to the anisotropy energy in the first order of perturbation. Classically they can be calculated as the multipole part of the coulomb interactions between the cations. In addition to it, however, there are contributions arising from the exchange part. Also, two cations intervened by an oxygen ion can interact via covalent electron configuration and this produces an anisotropy energy (§ 5).

The magnetostriction is caused by anisotropy energies which depend linearly on strain components. The anisotropy energies belonging to the above three categories have parts which are linearly dependent on strain components, but it can be shown that they cannot produce as large deformations as those observed in FeO and CoO. On the other hand, the crystalline field energy arising from deformation acts directly on the residual orbital angular momentum and produces spontaneous deformations of a right order of magnitude.

Since the change of energy by magnetostriction depends on the orientation of the magnetic moments, it contributes also to the anisotropy energy. This anisotropy energy is important in the present case, particularly in CoO. There is also an anisotropy energy arising from a combination of the exchange striction and magnetostriction. These anisotropy energies are included in the fourth category.

The calculations of the following sections are based on the molecular field approxi-

* Cited as [I], in the following.

mation, or the one-ion approximation, in which the Hamiltonian of each ion is derived from the total Hamiltonian by averaging the operators relating to other ions. We mostly confine ourselves to the absolute zero of temperature, so that the average is taken over the zero-point motion of the spins. We treat the anisotropy Hamiltonians as perturbations and calculate their first order contributions using the wave functions calculated in § 6 of [I] as the unperturbed wave functions. The orbital multipole interactions turn out to have the magnitude not very small compared with the exchange energy and spin-orbit coupling energy, and one might question if it is allowable to treat them as perturbations. It can be shown, however, that their non-diagonal elements are small within the scheme of the one-ion approximation and therefore this procedure is allowable.

In performing these calculations, we meet difficulties for precise evaluations, and some ambiguities as regards the numerical magnitudes will inevitably be introduced. Nevertheless, it is believed that all the conceivable important origins of the anisotropy energies and deformations are considered in the present paper and an essentially correct picture of the antiferromagnetic oxides is obtained.

In § 2, magnetic dipole-dipole interactions and spin-orbit interactions are investigated; in § 3, 4 and 5, orbit-orbit interactions are calculated; in § 6 theory of magnetostriction is developed; in § 7, calculation is made of the magnetostriction using the point charge model for the crystalline field; in § 8 exchange striction is considered; § 9 summarises the anisotropy energies including that which arises from deformation; the last section is a brief discussion of the magnetic anisotropy energies and deformations of MnO, MnS and NiO.

§ 2. Magnetic dipole-dipole interaction and spin-orbit coupling energy

The contribution of the inter-ionic magnetic dipole-dipole interaction energy in structure [A] to the total energy can be written in the following form of uniaxial symmetry;

$$E_D = T_D (\alpha_x \alpha_y + \alpha_y \alpha_z + \alpha_z \alpha_x), \quad (1)$$

where α_x , α_y and α_z are the direction cosines of the sublattice magnetizations in antiferromagnetic state referred to the cubic principal axes. According to Kaplan,¹⁰⁾ T_D at absolute zero is given by

$$T_D = (114.82/a_0^3) \mu^2 \text{ erg per ion}, \quad (2)$$

where μ is the magnitude of the magnetic moment of the cation, a_0 the lattice constant of the magnetic unit cell.

For FeO, assuming the value $4.44 \mu_B$ of μ calculated in § 6 of [I] and 8.664 \AA for a_0 , we obtain

$$T_D = 1.5 \text{ cm}^{-1} \text{ per ion}. \quad (3)$$

For CoO, using the value $3.7 \mu_B$ of μ deduced from the neutron scattering data and 8.50 \AA for a_0 , we obtain

$$T_D = 1.1 \text{ cm}^{-1} \text{ per ion}. \quad (4)$$

These energies stabilize the magnetization in the plane (111).

The effective Hamiltonian of the intra-ionic spin-spin interaction in the Russel-Saunders scheme of coupling is given by

$$\mathcal{H}_{ss} = -\rho[(\mathbf{L} \cdot \mathbf{S})^2 + (1/2)(\mathbf{L} \cdot \mathbf{S})]. \quad (5)$$

According to Pryce,¹²⁾ the value of ρ^* is 0.95 cm^{-1} for Fe^{++} and 1.5 cm^{-1} for Co^{++} . We rewrite this Hamiltonian using the following relations between the orbital angular momentum and the pseudo-orbital angular momentum \mathbf{l} in subspace Γ_5 (for FeO) or Γ_4 (for CoO) :

$$L_x^2 = 4 - 3l_x^2, \quad L_x L_y + L_y L_x = 3(l_x l_y + l_y l_x), \quad \text{etc. for FeO}; \quad (6)$$

$$L_x^2 = 6l_x^2, \quad L_x L_y + L_y L_x = -(3/2)(l_x l_y + l_y l_x), \quad \text{etc. for CoO}. \quad (7)$$

Then (5) becomes

$$\mathcal{H}_{ss} = +\rho[6(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) - (3/2)(\mathbf{l} \cdot \mathbf{S}) - 3(\mathbf{l} \cdot \mathbf{S})^2] \quad \text{for FeO}; \quad (8)$$

$$\mathcal{H}_{ss} = -\rho[(15/2)(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) - (3/4)(\mathbf{l} \cdot \mathbf{S}) - (3/2)(\mathbf{l} \cdot \mathbf{S})^2] \quad \text{for CoO}. \quad (9)$$

\mathcal{H}_{ss} gives an anisotropy energy of cubic symmetry, since \mathbf{l} is antiparallel to \mathbf{S} in antiferromagnetic state. In numerically evaluating the anisotropy constant, we average \mathcal{H}_{ss} using the wave function of the ground state, (49) and (50) of [I], and assuming an arbitrary direction of the axis of magnetization. The part dependent on this direction can be written in the form,

$$E_{ss} = K_{ss}(\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2).$$

K_{ss} is determined from the difference of E_{ss} for the direction [100] and the direction [111]. The results are

$$K_{ss} = -1.9 \text{ cm}^{-1} \quad \text{per ion for FeO}; \quad (10)$$

$$K_{ss} = 0.78 \text{ cm}^{-1} \quad \text{per ion for CoO}. \quad (11)$$

Further, as calculated in § 2 of [I], the anisotropic spin-orbit coupling energy is given by the following Hamiltonian :

$$\mathcal{H}_{LS} = (\lambda^2/\Delta E)[6(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) - (\mathbf{l} \cdot \mathbf{S}) - (\mathbf{l} \cdot \mathbf{S})^2] \quad \text{for FeO}; \quad (12)$$

$$\mathcal{H}_{LS} = -(1-\beta^2)(\lambda^2/\Delta E)[(15/2)(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) - (15/4)(\mathbf{l} \cdot \mathbf{S})^2] \quad \text{for CoO}. \quad (13)$$

These have the same form as the intra-ionic spin-spin interaction. By a similar calculation, the anisotropy energies are obtained as

* As Pryce points out, these values of ρ include second order effect arising from non-diagonal elements of the spin-orbit coupling energy between multiplets of $3d^n$ configuration. This effect may be larger than the spin-spin interaction in Fe^{++} and Co^{++} . Therefore, in the cubic field, the value of ρ will be somewhat modified due to the change of the energy separations between multiplets. In Co^{++} , another modification comes from the hybridization of 4F and 4P . However, we neglect these minor effects in the following evaluation of the anisotropy energy.

$$E_{LS} = K_{LS} (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2),$$

with

$$K_{LS} = -1.85 \text{ cm}^{-1} \text{ per ion for FeO}, \quad (14)$$

$$K_{LS} = 2.0 \text{ cm}^{-1} \text{ per ion for CoO}. \quad (15)$$

In the actual calculations, use was made of the spectroscopic data of λ in both ions, experimental values of ΔE and β in CoO and the value of ΔE calculated with the point charge model in FeO.

If we evaluated K_{SS} and K_{LS} by using the wave function corresponding to $S_z = S$, $L_z = -1$, we would have obtained considerably larger absolute values for them. Since the states $S_z = S-1$, $L_z = 0$ and $S_z = S-2$, $L_z = 1$ are mixed by spin-orbit coupling, the interference effects reduce the values of K_{SS} and K_{LS} to those given above.

§ 3. Orbital multipole interactions I: the coulomb interactions

In this section, we discuss the coulomb part of the multipole interactions between cations. The coulomb interaction between two cations can be expanded in a series of multipole interactions, of which only the quadrupole-quadrupole, quadrupole-hexadecapole and hexadecapole-hexadecapole interactions appear in the first order, since the multipole clouds are formed of d -electrons. The dipole-dipole interaction gives the van der Waals force in the second order, which, however, can be neglected in our case since the polarizabilities of the cations are small.

First we derive formulas for the multipole interactions between two charge clouds which do not overlap with each other. We denote by 1 and 2 the lattice points at which the two charge clouds are located and specify by \mathbf{r}_i the position of electron i belonging to charge cloud 1, the origin being taken at the lattice point 1, and by \mathbf{r}_j the position of electron j belonging to charge cloud 2, the origin being taken at the lattice point 2. The coulomb interaction between these electrons can be expanded in a power series of \mathbf{r}_i and \mathbf{r}_j . The part proportional to the product $r_i^2 r_j^2$ represents the quadrupole-quadrupole interaction, the part proportional to $r_i^2 r_j^4$ or $r_i^4 r_j^2$ the quadrupole-hexadecapole interaction and the part proportional to $r_i^4 r_j^4$ the hexadecapole-hexadecapole interaction. If we adopt the coordinate system whose z -axis is the line joining the lattice points 1 and 2, the general forms of these interactions are as follows;

the quadrupole-quadrupole interaction

$$(\epsilon^2 r_i^2 r_j^2 / R_{12}^5) [6 P_2(\cos \vartheta_i) P_2(\cos \vartheta_j) - (4/3) P_2^1(\cos \vartheta_i) P_2^1(\cos \vartheta_j) \cos(\varphi_i - \varphi_j) + (1/12) P_2^2(\cos \vartheta_i) P_2^2(\cos \vartheta_j) \cos 2(\varphi_i - \varphi_j)]; \quad (16)$$

the quadrupole-hexadecapole interaction

$$(\epsilon^2 r_i^2 r_j^4 / R_{12}^5) [15 P_2(\cos \vartheta_i) P_4(\cos \vartheta_j) - 2 P_2^1(\cos \vartheta_i) P_4^1(\cos \vartheta_j) \cos(\varphi_i - \varphi_j) + (1/12) P_2^2(\cos \vartheta_i) P_4^2(\cos \vartheta_j) \cos 2(\varphi_i - \varphi_j)] \quad (17)$$

and a similar expression with i and j interchanged;

the hexadecapole-hexadecapole interaction

$$\begin{aligned}
 & (e^2 r_i^4 r_j^4 / R_{12}^9) [70 P_4(\cos \vartheta_i) P_4(\cos \vartheta_j) - (28/5) P_4^1(\cos \vartheta_i) P_4^1(\cos \vartheta_j) \cos(\varphi_i - \varphi_j) \\
 & + (7/45) P_4^2(\cos \vartheta_i) P_4^2(\cos \vartheta_j) \cos 2(\varphi_i - \varphi_j) - (1/315) P_4^3(\cos \vartheta_i) P_4^3(\cos \vartheta_j) \\
 & \times \cos 3(\varphi_i - \varphi_j) \\
 & + (1/2016) P_4^4(\cos \vartheta_i) P_4^4(\cos \vartheta_j) \cos 4(\varphi_i - \varphi_j)] . \quad (18)
 \end{aligned}$$

In these formulas, R_{12} is the distance between 1 and 2, and e the elementary charge.

To calculate the anisotropy energy, we rewrite the above formulas referring to the cubic axes and sum the results over all the pairs of cation. Further, we make the approximation of molecular field, that is, we assume that all the cations have the same average spacial distribution of electrons around each of their nuclei. It is convenient to replace the spacial coordinates of a representative electron of each cation by the total orbital angular momentum of that cation, which in our case, is further replaced by the pseudo-orbital angular momentum \mathbf{l} , using relations (6), (7) and the relations connecting the 4th order polynomials of \mathbf{L} with the quadratic forms of \mathbf{l} . Details are given in App. I. In terms of the pseudo-orbital angular momentum \mathbf{l} , all these interactions become effectively quadrupole-quadrupole interactions, since, in the lowest triplet, the hexadecapole reduces to quadrupole. Thus we obtain the following expression for the effective Hamiltonian of these interactions:

$$\begin{aligned}
 \mathcal{H}_{LL} = & \kappa_1 [l_{x1}^2 l_{x2}^2 + l_{y1}^2 l_{y2}^2 + l_{z1}^2 l_{z2}^2] + (\kappa_2/2) [(l_{x1} l_{y1} + l_{y1} l_{x1})(l_{x2} l_{y2} + l_{y2} l_{x2}) \\
 & + (l_{y1} l_{z1} + l_{z1} l_{y1})(l_{y2} l_{z2} + l_{z2} l_{y2}) + (l_{z1} l_{x1} + l_{x1} l_{z1})(l_{z2} l_{x2} + l_{x2} l_{z2})] . \quad (19)
 \end{aligned}$$

For the details of the calculation of κ_1 and κ_2 the reader is referred to Appendix I. The contribution from this to the anisotropy energy is obtained by averaging (19) with the wave function of the ground state. As easily be shown, we can replace the operators by the direction cosines α_i of the magnetization through the following relations:

$$\begin{aligned}
 (l_x^2 - 2/3) &= (1/2)(a^2 + c^2 - 2b^2)(\alpha_x^2 - 1/3), \text{ etc., and} \\
 l_x l_y + l_y l_x &= (a^2 + c^2 - 2b^2) \alpha_x \alpha_y , \quad (20)
 \end{aligned}$$

where a , b and c are defined by the relation,

$$\psi_\theta = a\psi_{S,-1} + b\psi_{S-1,0} + c\psi_{S-2,1} .$$

The factor $(a^2 + c^2 - 2b^2)$ represents the reducing effect of the spin-orbit coupling on the anisotropy constant. This factor tends approximately to zero for increasing strength of the spin-orbit coupling. This factor is 0.531 in FeO and 0.402 in CoO.

In quantitatively estimating the anisotropy energy, however, we meet some difficulties. Firstly, the average values of r^2 and r^4 , $\langle r^2 \rangle$ and $\langle r^4 \rangle$, which enter into the calculation through (16), (17) and (18), depend sensitively on the radial distribution function and in particular, on its tail at far distances from the ion core. Secondly, there are overlap regions of charge clouds between nearest neighbouring cations, which, though include only a few percent of the total density, give appreciable effects on the final results, since r^2 and r^4 have large values there and thus formulas (16), (17) and (18) are not justified

To take these features into account precisely is not easy. Therefore, in order to obtain a semi-quantitative idea of these effects, we made two calculations: in one calculation we ignored the fact of the overlaps but still used in (16), (17) and (18) the values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ of the free ion calculated with the Slater function¹⁵⁾; in the other calculation we cut off, for the interactions between nearest neighbours, the charge clouds outside the spheres of a radius equal to half the nearest neighbour distance drawn around each of the lattice points, and assumed for other interactions the free ion values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ calculated with the Slater function. These free ion values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are

$$\begin{aligned} \langle r^2 \rangle &= 0.903 \text{ \AA}^2 & \langle r^2 \rangle &= 0.741 \text{ \AA}^2 \\ \langle r^4 \rangle &= 1.310 \text{ \AA}^4 & \langle r^4 \rangle &= 0.882 \text{ \AA}^4 \end{aligned} \quad \text{for FeO, and} \quad \text{for CoO;} \quad (21)$$

while the cut-off values are

$$\begin{aligned} \langle r^2 \rangle_c &= 0.759 \text{ \AA}^2 & \langle r^2 \rangle_c &= 0.669 \text{ \AA}^2 \\ \langle r^4 \rangle_c &= 0.853 \text{ \AA}^4 & \langle r^4 \rangle_c &= 0.664 \text{ \AA}^4 \end{aligned} \quad \text{for FeO, and} \quad \text{for CoO.} \quad (22)$$

The first calculation gives for the anisotropy constant

$$\begin{aligned} K_{LL} &= -72.9 \text{ cm}^{-1} \text{ per ion for FeO,} \\ K_{LL} &= -18.0 \text{ cm}^{-1} \text{ per ion for CoO,} \end{aligned} \quad (23)$$

and the second calculation gives

$$\begin{aligned} K_{LL} &= -33.7 \text{ cm}^{-1} \text{ for FeO,} \\ K_{LL} &= -11.1 \text{ cm}^{-1} \text{ for CoO.} \end{aligned} \quad (24)$$

As shown in Appendix I, it is found that in both oxides, the quadrupole-hexadecapole interactions make the largest contribution to the anisotropy energy. The quadrupole-quadrupole interactions favour the directions $\{100\}$ in both oxides but they are overcome by the quadrupole-hexadecapole interactions which favour $\{111\}$. The hexadecapole-hexadecapole interactions make a much smaller contribution.

It might be remarked that a contribution to the one-ion Hamiltonian for atom 1 is obtained from (19) by replacing the operators having suffix 2 by their average values, but these average values have to be determined self-consistently since it has non-diagonal elements between those states which are determined from the one-ion Hamiltonian consisting only of exchange energy and spin-orbit energy. However, it can be shown that these non-diagonal elements are small compared with the unperturbed energy separations and therefore we can neglect them. A crude estimation shows that these non-diagonal elements affect the value of the anisotropy constant by about 10 percent.

To conclude, we obtain from the multipole interactions a large anisotropy energy favouring the directions $\{111\}$ and overcoming K_{SS} and K_{LS} . This is consistent with the neutron diffraction result in FeO, but not so with that in CoO. The latter discrepancy will be removed in a later section (§ 9).

§ 4. Orbital multipole interactions II: the direct exchange part

In this section we shall investigate the direct exchange interactions between the cations. In [I], it was concluded from the analysis of the paramagnetic susceptibility data that there are significant exchange interactions between nearest neighbouring cations. Whether these exchange interactions are of the direct type or of an indirect type, similar to superexchange interactions, is a question to be settled before treating the anisotropy problem. If they arise by an indirect mechanism, we may expect that the magnitude of the exchange integral will change proportionally to the magnitude of the superexchange interaction constant between second neighbours when we go from MnO to CoO or from MnO to MnS.¹⁶⁾ In going from MnO to MnS, θ decreases from 610°K to 528°K and the Néel temperature T_N increases from 122°K to 165°K, θ corresponding to a certain sum of the superexchange interaction constant and the exchange integral in question and T_N to the superexchange interaction constant alone. Thus the exchange interaction in question does not behave in the same way as the superexchange. It decreases with increasing interionic distance. As regards MnO and CoO, we concluded in paper [I] from the analysis of the paramagnetic susceptibility of CoO that the magnitude of the exchange integral in CoO is about the same as that in MnO, while the magnitude of the superexchange is at variance, the Néel temperature being 122°K and 293°K for MnO and CoO, respectively. One may therefore reasonably assume that the exchange interactions between nearest neighbours are mainly of the direct type.

The exchange interaction can be divided into the spin-independent part and the spin-dependent part. We define the latter as $-2J_2\mathbf{S}_1\cdot\mathbf{S}_2$, where J_2 is the average exchange integral (J_2 has the opposite sign to that defined in [I]). We shall first discuss the spin-independent part.

We consider a cluster composed of one central cation and its twelve nearest neighbours (see Fig. 2), and denote the doubly occupied d -orbits of the central cation by suffix μ , those of the nearest neighbours by suffix ν , and the singly occupied d -orbits of the central cation by suffix ρ , those of the nearest neighbours by suffix σ . Then the spin-independent part of the exchange energy between the central cation and one of its nearest neighbours is given by

$$-(1/2) \sum_{\rho, \sigma} J_{\rho\sigma} - \sum_{\rho, \nu} J_{\rho\nu} - \sum_{\mu, \sigma} J_{\mu\sigma} - 2 \sum_{\mu, \nu} J_{\mu\nu}.$$

We have to pick up only the part of the exchange energy which depend simultaneously on the doubly occupied orbits, since the sum of the exchange integrals taken over all the d -orbits of one of the participant cations depends only on the d -orbit belonging to the other cation and further when this sum is summed over the cations surrounding the latter cation, the result becomes isotropic, i.e. independent of the kind of that d -orbit. Therefore the anisotropic part can be expressed as a certain sum of the interaction between one of the electrons in each μ and one of the electrons in each ν :

$$\mathcal{E}_{ex} = -(1/2) \cdot (1/2) \cdot \sum_{\mu, \nu} J_{\mu\nu}, \quad (25)$$

where the factor $1/2$ is inserted in order to get the energy per one ion. In FeO, only one d -orbit is doubly occupied, so we shall at first investigate this case in detail and then go over to the case of CoO, making use of the results obtained for FeO.

We assume that the wave function of the doubly occupied orbit μ is given by

$$\phi_\mu = a_1 \phi_1 + a_2 \phi_2 + a_3 \phi_3 \quad (26)$$

and that of the orbit ν by

$$\phi_\nu = b_1 \phi_1' + b_2 \phi_2' + b_3 \phi_3', \quad (26')$$

where ϕ_i are the wave function given in § 7 of [I] and a prime is attached to the orbits of the surrounding cations. Then the exchange energy (25) between the central cation and one of the nearest neighbours is written as

$$\mathcal{E}_{ex} = -(1/4) \sum_{k,l,m,n} a_k^* a_l b_m^* b_n (km | \mathcal{V} | nl), \quad (27)$$

where

$$(km | \mathcal{V} | nl) = \int \phi_k^* (I) \phi_n' (II) \mathcal{V} \phi_l' (I) \phi_l (II) d\tau_I d\tau_{II}, \quad (28)$$

\mathcal{V} being the interacting potential. (27) can be written in operator form by the following relations:

$$\begin{aligned} a_k^* a_l &= -l_{kl}, & b_m^* b_n &= -l_{mn}, \\ a_k^* a_k &= 1 - l_{kl}^2, & b_m^* b_m &= 1 - l_{m2}^2; \end{aligned} \quad (29)$$

$k, l=1, 2, 3$; $m, n=1, 2, 3$ and $1, 2, 3=\gamma, z, x$, where the suffices 1 and 2 of l 's specify respectively the central ion and the participant nearest neighbour. When the summation is taken over all the nearest neighbours, we obtain two different anisotropy Hamiltonians: one has cubic symmetry and is similar to that for the coulomb interaction, (19), and the other is uniaxial. However, lack of our knowledge on the magnitudes of the individual integrals forbids us to make a precise estimation. Here a rough estimate of their order of magnitude will be given. We first discuss the cubic anisotropy Hamiltonian.

We consider the nearest neighbours in the xy -plane. The cubic anisotropy Hamiltonian represents effectively a kind of quadrupole-quadrupole interaction. Thus, integrals which do not change its sign when we go from the nearest neighbours in the first quadrant to that in the second quadrant contribute to it. The most effective integral in (27) will be $(22 | \mathcal{V} | 22)$, because the pertinent wave function has the largest overlap, and the corresponding term in (27) will be $-(1/4) (22 | \mathcal{V} | 22) (1 - l_{x1}^2) (1 - l_{z2}^2)$. Neglecting other integrals and summing this over all the twelve nearest neighbours of the cation 1, we obtain for the total cubic anisotropy Hamiltonian

$$\mathcal{H}'_{ex} = -(22 | \mathcal{V} | 22) (l_{x1}^2 l_{x2}^2 + l_{y1}^2 l_{y2}^2 + l_{z1}^2 l_{z2}^2), \quad (30)$$

the suffix 2 now indicating any representative one of the nearest neighbours. If we assume the magnitude of $(22 | \mathcal{V} | 22)$ to be about 6 times the magnitude of the average exchange integral, which can be estimated from the data of MnO and CoO, we obtain

$(22|\mathcal{H}|22) = -30\text{cm}^{-1}$.* Then the anisotropy constant K_{ex} becomes about -4.2 cm^{-1} .

The uniaxial anisotropy Hamiltonian represents a kind of dipole-dipole interaction. It comes from such integrals that change their sign when we go from the nearest neighbour in the first quadrant of the xy -plane to that in the second quadrant. In (27), terms which contribute to this anisotropy energy are

$$-(1/4)[(21|\mathcal{H}|23)(a_2^*a_3b_1^*b_2+a_3^*a_2b_2^*b_1+a_1^*a_2b_2^*b_3+a_2^*a_1b_3^*b_2) \\ + (22|\mathcal{H}|13)(a_2^*a_3b_2^*b_1+a_3^*a_2b_1^*b_2+a_1^*a_2b_3^*b_2+a_2^*a_1b_2^*b_3)],$$

which can also be written as

$$-(1/8)[\{(21|\mathcal{H}|23)+(22|\mathcal{H}|13)\}\{(a_2^*a_3+a_3^*a_2)(b_1^*b_2+b_2^*b_1) \\ + (a_1^*a_2+a_2^*a_1)(b_2^*b_3+b_3^*b_2)\} \\ + \{(21|\mathcal{H}|23)-(22|\mathcal{H}|13)\}\{(a_2^*a_3-a_3^*a_2)(b_1^*b_2-b_2^*b_1) \\ + (a_1^*a_2-a_2^*a_1)(b_2^*b_3-b_3^*b_2)\}]. \quad (31)$$

The first term of (31) makes no contribution, because it vanishes when summed over all the nearest neighbours. The second term can be written in the operator form as

$$+(1/8)\{(21|\mathcal{H}|23)-(22|\mathcal{H}|13)\}(l_{y1}l_{x2}+l_{x1}l_{y2}).$$

For spin-structure [A], this energy gives a uniaxial anisotropy, since, if we go from the nearest neighbour of plus spin to that of minus spin, the direction of \mathbf{l} and the sign of the integrals are simultaneously reversed. Adding similar terms coming from the nearest neighbours in the yz - and zx -plane and summing over twelve nearest neighbours, we obtain

$$(1/2)\{(21|\mathcal{H}|23)-(22|\mathcal{H}|13)\}\{(l_{x1}+l_{y1}+l_{z1})(l_{x2}+l_{y2}+l_{z2}) \\ - (\mathbf{l}_1 \cdot \mathbf{l}_2)\}. \quad (32)$$

Here we took the cation 2 in the first quadrant of the xy -plane as the representative nearest neighbour. In (32), the integral $(21|\mathcal{H}|23)$ is much larger than $(22|\mathcal{H}|13)$ in absolute magnitude and its sign is positive, since the pertinent wave functions, ϕ_1' and ϕ_3 have different signs. Assuming that the absolute magnitude of $(21|\mathcal{H}|23)$ is equal to that of the average exchange integral, we obtain the uniaxial anisotropy given by

$$E''_{ex} = T'_{ex}(\alpha_x\alpha_y + \alpha_y\alpha_z + \alpha_z\alpha_x),$$

with

$$T'_{ex} = -4\text{ cm}^{-1} \text{ per ion.} \quad (33)$$

It is the present author's opinion that this anisotropy energy as well as that obtained from the spin-dependent exchange energy to be discussed later are most important in

* This estimation is based on the following consideration. If we define ϕ_4, ϕ_5 after the definition of § 7 of [I], the effective integrals contained in the average exchange integral will be $(44|\mathcal{H}|44), (22|\mathcal{H}|22), (42|\mathcal{H}|24)$ and $(24|\mathcal{H}|42)$. Assuming that they are approximately equal, and considering the weight of the state, 2, in paramagnetic state, we obtain this value,

determining the favourable direction of the aligned magnetic moments in FeO, since, had we not these anisotropy energies, the strong cubic anisotropy derived in the preceding section favours four directions $\{111\}$ equally and the weak magnetic dipole-dipole interaction, E_D , calculated by Kaplan excludes the trigonal axis itself and leaves only the remaining three $\{111\}$ as favourable directions, whereas the experiment shows that the magnetic moments are in $[111]$.

In the case of CoO, two of the three d -orbitals, ϕ_1 , ϕ_2 and ϕ_3 are almost doubly occupied. If, moreover, the remaining one were also doubly occupied, there would be no contribution to the anisotropy energy. Therefore the anisotropic exchange interaction can be interpreted as the interaction arising from a hole which occupies one of the three orbitals. Thus the Hamiltonian takes the same form as (27). However, the absolute magnitude of the anisotropy constants would be smaller than in FeO, because, for the cubic anisotropy constant, the factor $(1/2)(a^2 + c^2 - 2b^2)$ is smaller in CoO and also because, influenced by 4P , the electrons tends to occupy the three d -orbitals equally in order to lower the internal coulomb energy.

Next, we shall discuss the spin-dependent part of the direct exchange interactions. This part is usually considered as being cancelled out in antiferromagnetic state, since there are equal numbers of nearest neighbours with parallel and antiparallel spins (see Fig. 2). However, if the spin arrangement is of structure [A], there is a possibility that this exchange energy gives rise to an anisotropy energy of trigonal symmetry. Qualitatively speaking, this comes out in the following way. Since the pseudo-orbital angular momentum l points antiparallel to the spin, the shape of the cation charge cloud depends on the orientation of its spin, and since the lines connecting parallel spin-pairs

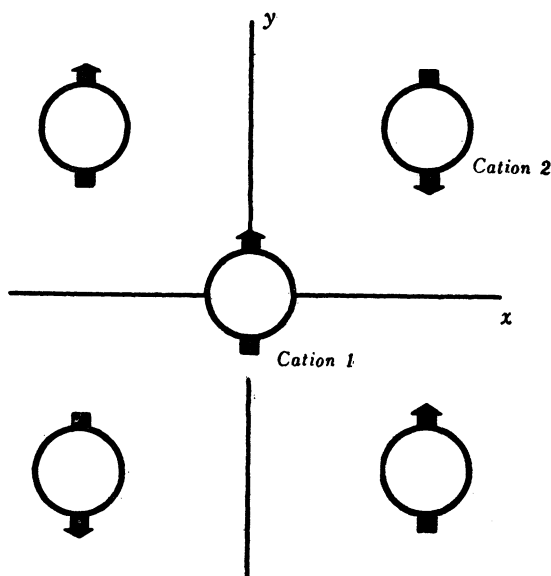


Fig. 2

and those connecting antiparallel spin-pairs have different directions (the former being perpendicular to the trigonal axis and the latter oblique), the sum of the exchange integrals for parallel spin-pairs are different from those for antiparallel spin-pairs, this difference depending on the orientation of the magnetic moments. Further, since the exchange energy changes its sign for these two kinds of pairs, the total exchange energy is proportional to this difference and so it has trigonal symmetry.

Quantitative calculation of this anisotropy energy is difficult, because it requires the knowledge of various complicated integrals. We attempt, however, to estimate its order

of magnitude by a crude calculation similar to that already made in this section.

First we discuss the case of FeO. If J_{km} is the exchange integral between the k -th orbit of the central cation and the m -th orbit of one of the nearest neighbours and suffices μ and ν mean, as before, the electron paired orbits, the average exchange integral J_2 is written as

$$J_2 = (1/16) \left\{ \sum_{k,m} J_{km} - \sum_m J_{\mu m} - \sum_k J_{k\nu} + J_{\mu\nu} \right\}, \quad (34)$$

where the sums are taken over all the five d -orbits. The first sum does not contribute to the anisotropy energy, since it does not depend on the orbital states of the participant cations.

The other sums can be expanded in a way similar to (27). When summing the exchange energy over the four nearest neighbours in the xy -plane, it is clear that only those integrals that change their signs in going from plus spin to minus spin give finite contributions. Such integrals, referred to the cation in the first quadrant of the xy -plane and the central cation, are

$$(1m | \mathcal{H} | m3), (22 | \mathcal{H} | 13), (21 | \mathcal{H} | 23),$$

and those integrals which become equivalent to these by interchanges of the indices. So the sum of the exchange energy over the four nearest neighbours in the xy -plane is expressed as follows:

The part arising from the sum, $\sum_m J_{\mu m}$, is given by

$$(1/2) (S_1 \cdot S_2) (a_1^* a_3 + a_3^* a_1) \sum_m (1m | \mathcal{H} | m3), \quad (35)$$

the part arising from $J_{\mu\nu}$ is given by

$$\begin{aligned} & - (1/2) (S_1 \cdot S_2) [(12 | \mathcal{H} | 23) b_2^* b_3 (a_1^* a_3 + a_3^* a_1) + (11 | \mathcal{H} | 13) (b_1^* b_1 + b_3^* b_3) \\ & \quad \times (a_1^* a_3 + a_3^* a_1) \\ & + (1/4) \{ (22 | \mathcal{H} | 13) + (21 | \mathcal{H} | 23) \} \\ & \quad \times \{ (a_2^* a_3 + a_3^* a_2) (b_1^* b_2 + b_2^* b_1) + (a_1^* a_2 + a_2^* a_1) (b_2^* b_3 + b_3^* b_2) \}]. \end{aligned} \quad (35')$$

In (35') we have omitted the term corresponding to the second term of (31), because it cancels out at the summation. Also terms which are obtained from (35) and (35') by interchanging a and b are omitted; they make the same contribution as that of (35) and (35') and can be dropped for the calculation of the anisotropy energy per ion. As before, we express a and b in terms of the components of angular momenta l_1 , l_2 and obtain the anisotropy Hamiltonian for the cluster in the xy -plane as

$$\begin{aligned} & - (1/2) (S_1 \cdot S_2) \left[\sum_m (1m | \mathcal{H} | m3) - (12 | \mathcal{H} | 23) \right] (l_{x1} l_{y1} + l_{y1} l_{x1}) \\ & + \{ (12 | \mathcal{H} | 23) - (11 | \mathcal{H} | 13) \} (l_{x1} l_{y1} + l_{y1} l_{x1}) l_{z2}^2 \\ & + (1/4) \{ (22 | \mathcal{H} | 13) + (21 | \mathcal{H} | 23) \} \{ (l_{x1} l_{x1} + l_{x1} l_{x1}) (l_{y2} l_{x2} + l_{x2} l_{y2}) \\ & + (l_{y1} l_{x1} + l_{x1} l_{y1}) (l_{x2} l_{x2} + l_{x2} l_{x2}) \}]. \end{aligned} \quad (36)$$

In (36), the first term makes the largest contribution. Neglecting the other terms and adding to it two similar expressions with x, y, z cyclically interchanged, we obtain for the total anisotropy Hamiltonian of the central cation

$$\mathcal{H}_{ex}''' = -(1/2) (\mathbf{S}_1 \cdot \mathbf{S}_2) \left\{ \sum_m (1m | \mathcal{H} | m3) - (12 | \mathcal{H} | 23) \right\} \\ \times (l_x l_y + l_y l_x + l_y l_z + l_z l_y + l_z l_x + l_x l_z). \quad (37)$$

In all the above formulas \mathbf{S}_1 and \mathbf{S}_2 are antiparallel spins. In order to estimate the order of magnitude of the anisotropy energy, we replace the sum $\left\{ \sum_m (1m | \mathcal{H} | m3) - (12 | \mathcal{H} | 23) \right\}$ by half the average exchange integral, $J_2/2$, and use the value of -5 cm^{-1} for J_2 . Then we obtain the trigonal (uniaxial) anisotropy energy as

$$E_{ex}''' = T_{ex}'' (\alpha_x \alpha_y + \alpha_y \alpha_z + \alpha_z \alpha_x), \\ T_{ex}'' = -3 \text{ cm}^{-1} \text{ per ion.} \quad (38)$$

The argument above contains quantitatively somewhat dubious points, but it can safely be said that the uniaxial anisotropy energies, (33) and (38), can overcome the inter-ionic dipole-dipole interactions.

The case of CoO is much more difficult because of its more complicated electron configuration. Even the sign of the anisotropy constant cannot be inferred. Roughly speaking, however, the magnitude of the anisotropy energy obtainable from the spin-dependent part will be reduced considerably as compared with that of FeO. We may suppose that this anisotropy energy is not so much important in CoO to determine the direction of the magnetic moments.

Finally, it may be remarked that there is a possibility that the second order perturbation energy, arising from the transition matrix elements between the ground state and those excited states in which an electron is transferred from the cation to one of its nearest neighbours, makes some contribution to the anisotropy energy. But this energy can be expressed in the same form as the exchange energy, so that the above calculation effectively includes this energy.

§ 5. Orbital multipole interactions III: the indirect interactions; summary of the results of this and previous sections

Under the heading of the indirect multipole interactions, we include those orbit-orbit interactions which are related to the covalent electron configuration between one of the cations and an intervening oxygen ion, as in superexchange mechanism. We consider for instance two cations intervened by an oxygen ion which is located midway on the line joining the cations. We take this line as the z -axis. Since the interaction energies are obtained in the third order process of the perturbation scheme, they consist of two quantities of which one is the degree of the covalency between the oxygen and one of the cations and the other is the interaction between the other cation and the oxygen in covalent state with the first cation. As discussed in § 7 of [I], the degree of covalency

depends on the orbital state of the participant cation via the magnitude of the excitation energy of the electron transfer, the availability of the bonding orbit and the magnitude of the transfer integral. The interaction between the covalently bonded oxygen ion and the other cation consists of coulomb and exchange interactions. Though precise calculations are not feasible, we shall show in the following that these interactions make no important contributions to the anisotropy energy.

In both oxides, the dependence of the covalent degree on the orbital state of the cation is considered to be small, since the predominant bond, specified by t_1 (see § 7 of [I]), can be formed almost irrespectively of the orbital state of the cation and also the dependence of the excitation energy on the orbital state is small. On the other hand, a large contribution to the interaction between O^- and the non-covalently bonded cation will arise from the coulomb interaction between them. We may assume that the dependence of the covalent degree on the cation orbital state is given by

$$(t/\Delta W)^2(1+c_1I_{s1}^2) \quad (t \approx t_1)$$

and that the interaction of the oxygen with other cation is given by $c_2I_{s2}^2$. Somewhat arbitrarily $|c_1|$ will be assumed to be 10 percent, while $|c_2|$ is roughly estimated to be at most 3000 cm^{-1} . Then we obtain a contribution of about $1\sim 2\text{ cm}^{-1}$ to the cubic anisotropy constant. This is negligible in both oxides.

Summarizing the calculations made in this and the previous sections, we obtain the following conclusion as to the origins of the anisotropy energy which are effective in the deformation-free state of the crystal. In FeO, a large cubic anisotropy energy arising mainly from orbit-orbit coulomb interactions favours the directions $\{111\}$, and a uniaxial anisotropy energy pertinent to structure [A] arising mainly from direct exchange interactions favours the trigonal axis $[111]$. The latter overcomes the uniaxial anisotropy energy arising from the magnetic dipole-dipole interactions, which favours the plane (111) . In this way we obtained a result consistent with the experiment in the case of FeO. In CoO, the cubic anisotropy energies arising from intra-ionic spin-spin energy and spin-orbit coupling energy in cubic crystalline field favour the directions $\{100\}$, but a larger orbit-orbit coulomb energy makes the directions $\{111\}$ more favourable. The uniaxial anisotropy energy arising from the dipole-dipole interactions favours the plane (111) , but it was not investigated in detail whether another uniaxial anisotropy arising from the direct exchange interactions makes the direction $[111]$ more favourable or not. The latter is possibly smaller than in FeO. However, we shall find in § 9 that magnetostrictive anisotropy energy is most effective in CoO and that this energy deforms crystal tetragonally in one of the $\{100\}$ directions and makes the magnetic moments align along this tetragonal axis. In FeO, such does not occur.

§ 6. Theory of the magnetostriction

In the following sections, we shall investigate the deformation of the crystal in antiferromagnetic state. In the first place, we discuss the mechanism of the magnetostriction of FeO and CoO,

The magnetostriction is caused by an anisotropy energy which depends linearly on the strain components of the crystal. Its general form for a cubic crystal can be written¹⁷⁾ as

$$E_{ME} = B_1(\alpha_x^2 e_{xx} + \alpha_y^2 e_{yy} + \alpha_z^2 e_{zz}) + B_2(\alpha_x \alpha_y e_{xy} + \alpha_y \alpha_z e_{yz} + \alpha_z \alpha_x e_{zx}), \quad (39)$$

neglecting terms of higher powers of the direction cosines, α_x , α_y , α_z , of the magnetization. One might suspect that the anisotropy energies discussed in previous sections would also make contributions to this magnetoelastic energy. However, the observed deformations of FeO and CoO amount to as large as about 1 percent, which requires that B_1 or B_2 is at least about 10^3 cm⁻¹ per ion, since the elastic constants have a magnitude of $10^{12} \sim 10^{13}$ ergs per c.c. or $10^5 \sim 10^6$ cm⁻¹ per ion. Such a large value of B_1 or B_2 cannot be expected from the origins hitherto investigated. We shall show that the crystalline field energy dependent on deformation is the predominant origin of the magnetostriction and that it can give the required magnitudes of the coupling constants B_1 and B_2 . The residual orbital angular momentum l of magnitude 1 of each cation can freely take any direction if only the cubic field acting on it is present and the exchange interactions are neglected; a deformation will, however, remove the three-fold degeneracy and stabilize a certain direction or substate of the momentum, or inversely, a spontaneous deformation in a certain direction, a Jahn-Teller effect, will occur.* In the present case, however, the spins of the cations are coupled with one another by exchange interactions and each spin is coupled to the residual orbital angular momentum of the same cation. The crystalline field acts directly on this residual angular momentum. A deformation in a certain direction will here also stabilize the crystal and this direction will further determine the direction of the antiparallel magnetic moments. We shall show that this actually occurs in CoO, the axis of the deformation and magnetization being one of the cubic axes. In FeO, it seems that the deformation-independent anisotropy energy first determines the direction of the magnetic moments and the deformation then follows.

Other conceivable origins, such as spin-dependent indirect exchange interactions, whose strength is anisotropic since it depends on the orbital state of the cation, or also certain complicated second order effects, are of minor importance, and we shall neglect them and focus here our attention to the crystalline field effect.

As discussed in § 7 of [I], the crystalline field appears as a combined result of several effects which cause splittings of the orbital state. If we expand its potential equivalent in a power series of strain components, we can write its first order terms as

$$\begin{aligned} V_1 = & K_1(e_{xx} + e_{yy} + e_{zz}) + D_1(e_{xx} + e_{yy} + e_{zz})(x^4 + y^4 + z^4 - 3/5 \cdot r^4) \\ & + A_1\{e_{xx}(3x^2 - r^2) + e_{yy}(3y^2 - r^2) + e_{zz}(3z^2 - r^2)\} \\ & + C_1\{e_{xy}xy + e_{yz}yz + e_{zx}zx\} + F_1\{e_{xx}(7x^4 - 6x^2y^2 + 3/5 \cdot r^4) \end{aligned}$$

* However, such a deformation does not occur in paramagnetic state, because orbital level splitting due to the deformation is smaller than kT .

$$\begin{aligned}
& +e_{yy}(7\gamma^4-6\gamma^2r^2+3/5\cdot r^4)+e_{zz}(7z^4-6z^2r^2+3/5\cdot r^4)\} \\
& +H_1\{e_{xy}(\kappa^3\gamma+\gamma^3\kappa-6\kappa\gamma z^2)+e_{yz}(\gamma^3z+z^3\gamma-6\gamma z\kappa^2) \\
& +e_{zx}(z^3\kappa+\kappa^3z-6z\kappa\gamma^2)\}.
\end{aligned} \tag{40}$$

As done in the calculation of orbital multipole interactions, the spacial coordinates in this formula can be replaced by the corresponding components of the pseudo-orbital angular momentum, l , of the cation. Terms quartic in l reduce to quadratic terms. Thus, the general form of the magnetoelastic Hamiltonian can be expressed as

$$\begin{aligned}
\mathcal{H}_{ME} = & b_1\{e_{xx}l_x^2+e_{yy}l_y^2+e_{zz}l_z^2-(2/3)(e_{xx}+e_{yy}+e_{zz})\} \\
& +b_2\{e_{xy}(1/2)(l_xl_y+l_yl_x)+e_{yz}(1/2)(l_yl_z+l_zl_y) \\
& +e_{zx}(1/2)(l_zl_x+l_xl_z)\},
\end{aligned} \tag{41}$$

where we dropped those terms which do not affect the cubic symmetry of the crystal.

The relations between b_1 , b_2 and A_1 , C_1 , F_1 , H_1 can be obtained by a calculation similar to that made in the case of orbital multipole interactions (see Appendix I, (Ap. 4) and (Ap. 5)). The results are

$$\begin{aligned}
b_1 = & N\{(6/7)A_1\langle r^2 \rangle - (8/21)F_1\langle r^4 \rangle\}, \\
b_2 = & N\{-(2/7)C_1\langle r^2 \rangle + (8/21)H_1\langle r^4 \rangle\},
\end{aligned} \quad \text{for FeO,} \tag{42}$$

$$\begin{aligned}
b_1 = & N[-\{(12/35) + (72/35)\alpha\beta - (54/35)\beta^2\}A_1\langle r^2 \rangle \\
& + \{(2/7) + (8/21)\alpha\beta - (2/7)\beta^2\}F_1\langle r^4 \rangle], \\
b_2 = & N[\{(1/35) + (16/35)\alpha\beta + (13/35)\beta^2\}C_1\langle r^2 \rangle \\
& - \{(4/7) - (4/21)\alpha\beta - (4/7)\beta^2\}H_1\langle r^4 \rangle].
\end{aligned} \quad \text{for CoO.} \tag{43}$$

Here N is the total number of the cation per c.c.

From (41), the magnetoelastic coupling constants B_1 and B_2 are calculated to be

$$B_1 = (1/2)(a^2 + c^2 - 2b^2)b_1 \quad \text{and} \quad B_2 = (1/2)(a^2 + c^2 - 2b^2)b_2$$

by taking necessary averages with respect to the wave function of the ground state.

The equilibrium strain components e_{ij} are

$$e_{ii} = B_1\{(1/3) - \alpha_i^2\}/(c_{11} - c_{12}), \tag{44}$$

$$e_{ij} = -B_2\alpha_i\alpha_j/c_{44}, \quad (i, j = x, y, z). \tag{44'}$$

§ 7. Calculation of A_1 , C_1 , F_1 and H_1

The calculation A_1 , C_1 , F_1 and H_1 presents the same difficult problem as that we encountered in the calculation of the strength of the crystalline field in § 7 of [I]. In the case of cubic field, we saw that the simplest model of point charges located on lattice sites gave a good result. According to the discussion in § 7 of [I], this comes out from the compensation of various other effects. Though the same situation cannot necessarily

be expected here, we shall still use this model with a hope of obtaining a semiquantitative idea of A_1 , etc.

Deferring the details of the calculation to Appendix II, we describe here the results. The following values of A_1 , C_1 , F_1 and H_1 are obtained:

$$\begin{aligned} A_1 &= -5.96 (e^2/a^3), & C_1 &= 11.93 (e^2/a^3), \\ F_1 &= -16.61 (e^2/a^5), & H_1 &= 10.21 (e^2/a^5), \end{aligned} \quad (45)$$

where a is the distance between neighbouring cation and oxygen. Using these values and the values (21) of $\langle r^2 \rangle$ and $\langle r^4 \rangle$, the coupling constants B_1 and B_2 are obtained as

$$\begin{aligned} B_1 &= -8660 \text{ cm}^{-1} \text{ per ion or } -8.42 \times 10^{10} \text{ erg per c.c.}, \\ B_2 &= -6050 \text{ cm}^{-1} \text{ per ion or } -5.89 \times 10^{10} \text{ erg per c.c.}, \end{aligned} \quad \text{for FeO,} \quad (46)$$

$$\begin{aligned} B_1 &= 3930 \text{ cm}^{-1} \text{ per ion or } 4.07 \times 10^{10} \text{ erg per c.c.}, \\ B_2 &= 200 \text{ cm}^{-1} \text{ per ion or } 0.21 \times 10^{10} \text{ erg per c.c.}, \end{aligned} \quad \text{for CoO.} \quad (47)$$

These results predict in CoO a contraction along one of the $\{100\}$ directions if the magnetization is assumed to point in this direction, because B_1 is positive, and in FeO an elongation along $[111]$ if the magnetization is assumed to point in this direction, because B_2 is negative. These are in agreement with the experimental results. For quantitative calculations, we need the elastic constants of the crystals. Since they are not available, we use the following data of $\text{MgO}^{(18)}$:

$$\begin{aligned} 1/(c_{11} - c_{12}) &= s_{11} - s_{12} = 4.94 \times 10^{-13} \text{ c.c./erg}, \\ 1/c_{44} &= s_{44} = 6.46 \times 10^{-13} \text{ c.c./erg}, \\ 1/(c_{11} + 2c_{12}) &= s_{11} + 2s_{12} = 2.15 \times 10^{-13} \text{ c.c./erg}. \end{aligned} \quad (48)$$

Then our theory gives $e_{xy} = 1.3$ percent for FeO and $(a-c)/a = 2.0$ percent for CoO. Experiment on FeO at 95°K gives a rhombohedral angle $\alpha = 59^\circ 32',^{(2)}$ which gives $e_{xy} = 0.705$ percent ($\delta\alpha = -2/\sqrt{3} e_{xy}$). Data for $\text{CoO}^{(2),(3)}$ are available at several temperature; extrapolating them to 0°K , we obtain about 1.2 percent for $(a-c)/a$.

We see that the point charge model gives fairly good results again in this case. Though the present calculation contains quantitatively ambiguous points, still it might not be useless to point out that the point charge approximation overestimates the coupling constants. As discussed in § 7 of [I], the covalent effect makes an important contribution to the strength of the cubic field in the direction cancelling the overlap effect of the electron clouds, but this effect will make a less important contribution to magnetoelastic coupling, because the predominant bond specified by t_1 can be formed almost irrespectively of the orbital state which the cation can take, and thus it cannot produce a large crystal-line field of lower symmetry than cubic in the deformed crystal. Therefore, in the case of the magnetoelastic coupling, the point charge effect will considerably be reduced by the electron overlap effect. The anisotropy energy arising from magnetostriction will be discussed in § 9.

§ 8. Discussion of the exchange striction

As mentioned in introduction, there is another mechanism of the deformation, i.e. that arising from the exchange interactions between the spins. We shall estimate its order of magnitude in this section.

We shall first discuss the volume striction which arises from the exchange interactions between next-nearest neighbouring cations. In the molecular field approximation, the respective total energy is given by

$$-6N|J_1|\langle S \rangle^2,$$

of which the strain-dependent part can be written

$$-2N\langle S \rangle^2(\partial |J_{1z}|/\partial e_{zz})(e_{xx}+e_{yy}+e_{zz}), \quad (49)$$

J_{1z} being the exchange integral between next-nearest neighbouring cations which lie along the z -direction. The volume striction arising from this elasto-exchange coupling is given by

$$\Delta V/V = (e_{xx}+e_{yy}+e_{zz}) = 6N\langle S \rangle^2(\partial |J_{1z}|/\partial e_{zz})/(c_{11}+2c_{12}). \quad (50)$$

From this formula we obtain a contribution to the thermal expansion coefficient as

$$\beta = 6N(\partial |J_{1z}|/\partial e_{zz})(\partial \langle S \rangle^2/\partial T)/(c_{11}+2c_{12}). \quad (51)$$

If we assume the simple spin-only molecular field theory, $(\partial \langle S \rangle^2/\partial T)$ at the Néel temperature is given by

$$(\partial \langle S \rangle^2/\partial T)_{T=T_N} = -(k/6 |J_1|)[40S^2(S+1)^2/\{(2S+1)^4-1\}]. \quad (52)$$

Using this relation, the anomalous expansion coefficient at the Néel temperature is given by

$$\begin{aligned} \beta|_{T=T_N} = & -(Nk/c_{11}+2c_{12})[40S^2(S+1)^2/\{(2S+1)^4-1\}] \\ & \times (\partial |J_{1z}|/\partial e_{zz})/|J_1|. \end{aligned} \quad (53)$$

M. Foex¹⁰⁾ measured the thermal expansion coefficients of the monoxides of Iron group elements in the temperature range between -200°C and 400°C which covers the Néel temperatures of these oxides. The anomaly at Néel temperature is about 5×10^{-5} for MnO, 3×10^{-5} for FeO, 2×10^{-5} for CoO and 1.5×10^{-5} for NiO. Using the value of $(c_{11}+2c_{12})$ for MgO, we can deduce the values of $(\partial |J_{1z}|/\partial e_{zz})/|J_1|$ from these data. The results range from -5 for NiO to -15 for MnO. On the other hand, if we assume for the exchange integral and for the square of the transfer integral between cation and oxygen the same exponential dependence on distance as that we know in Born-Mayer's repulsive potential (see ref. 20), we obtain for this quantity a value of about -6 , since the covalent degree and the exchange integral will contribute respectively about -3 to it.

In the second place, we shall discuss the deformation arising from the direct exchange interactions between nearest neighbouring cations. As Greenwald and Smart³⁾ suggested,

this mechanism will produce a deformation of trigonal symmetry in structure [A]. However, it might be mentioned that, if the interaction were of indirect nature similar to superexchange, it would not produce such a deformation, because a trigonal strain would not produce any large difference between the exchange integral relating parallel spins and that relating antiparallel spins.

When a shear strain e_{xy} is present, the change of distance between antiparallel spins is given by (see Fig. 2)

$$\delta r = (e_{xy}/2) \sqrt{2} a,$$

and the change of distance between parallel spins is $-\delta r$. The corresponding change of the total exchange energy is

$$-2N\langle S \rangle^2 e_{xy} \sqrt{2} a (\partial |J_2| / \partial r),$$

and therefore the total elasto-exchange energy is

$$-2N\langle S \rangle^2 \sqrt{2} a (\partial |J_2| / \partial r) (e_{xy} + e_{yz} + e_{zx}). \quad (54)$$

From (54), the equilibrium shear strains become

$$e_{xy} = e_{yz} = e_{zx} = -B_3/c_{44}, \quad (55)$$

where $B_3 = -2N\langle S \rangle^2 \sqrt{2} a (\partial |J_2| / \partial r)$. Assuming $\sqrt{2} a (\partial |J_2| / \partial r) / |J_2| = -3^*$ and $J_2 = -5 \text{ cm}^{-1}$, the following equilibrium values of e_{xy} are obtained for the four oxides:

$$\begin{aligned} e_{xy} = & -11 \times 10^{-4} \text{ for MnO, } -6 \times 10^{-4} \text{ for FeO,} \\ & -3 \times 10^{-4} \text{ for CoO, } -2 \times 10^{-4} \text{ for NiO.} \end{aligned} \quad (56)$$

The observed rhombohedral deformation of $\text{NiO}^{(71)}$ at room temperatures corresponds to $e_{xy} = -1.2 \times 10^{-3}$, which is larger by a factor of 6 than the value above. The discrepancy might be due to ambiguities about the assumed values of $(\partial |J_2| / \partial r)$ and c_{44} . However, it is reported⁽⁷²⁾ that the deformation of NiO increases at lower temperatures to $e_{xy} = -3 \times 10^{-4}$ at -183°C . Such a large temperature dependency cannot be expected by the present calculation, since the Néel temperature of NiO is as high as 520°K .

§ 9. Discussion of the total anisotropy energies

Using (44), (44') and (55), the energy gain arising from deformation is obtained as

$$\begin{aligned} \Delta E = & -(1/2) (B_1^2 / (c_{11} - c_{12})) \sum_x \{ (1/3) - \alpha_x^2 \}^2 - (1/2) (B_2^2 / c_{44}) \sum_{x,y} \alpha_x^2 \alpha_y^2 \\ & - (B_2 B_3 / c_{44}) \sum_{x,y} \alpha_x \alpha_y - (3/2) (B_3^2 / c_{44}). \end{aligned} \quad (57)$$

Consequently, the anisotropy energy arising from the deformation is given by

$$E_{ME} = K_{ME} (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) + T_{ME} (\alpha_x \alpha_y + \alpha_y \alpha_z + \alpha_z \alpha_x),$$

with

*) In going from MnO to MnS, the change $|J_2|$ is smaller than that calculated from this ratio under the assumption of the exponential form. However, the superexchange-type interaction will make some contribution to $|J_2|$. The increase of this interaction will compensate to some extent the decrease of the direct exchange interaction. Considering these circumstances, we have tentatively assumed the value of $\partial |J_2| / \partial r$ mentioned in the text.

$$K_{ME} = B_1^2 / (c_{11} - c_{12}) - B_2^2 / 2c_{44} \text{ and } T_{ME} = -B_2 B_3 / c_{44}. \quad (58)$$

From experimental data for CoO, an estimate of $B_1 = 2.4 \times 10^{10}$ erg per c.c.* is obtained. Using this value, $B_1^2 / (c_{11} - c_{12})$ is calculated to 29.2×10^7 erg per c.c. or 28.2 cm^{-1} per ion. In the calculation of § 7 we obtained a much smaller value of B_2 than that of B_1 for CoO. Though we are not perfectly certain of this, we may neglect B_2 and obtain for the anisotropy constant $K_{ME} = 28.2 \text{ cm}^{-1}$. This corresponding anisotropy energy can easily overcome the anisotropy energy investigated in § 2-5, which amounted to values of the anisotropy constants of $-8 \sim -15 \text{ cm}^{-1}$, though minor neglected effects will affect these values to some extent. In particular, if the values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ estimated by using the Slater function were too large compared with their actual values, these values would have been somewhat reduced. We may conclude, however, that the magnetic moments orient along one of the directions $\{100\}$ in CoO, these directions being favoured by K_{ME} and other opposing anisotropy energies being overcome by it.

In FeO, we obtain $B_2^2 / 2c_{44} = 34.6 \times 10^7$ erg/c.c. or 35.5 cm^{-1} per ion, using experimental data. If we use this value and assume the calculated value for the ratio, B_1/B_2 , we obtain $K_{ME} = 75.7 \text{ cm}^{-1}$. This value favours the directions $\{100\}$ and is comparable in absolute magnitude with the largest value obtained for the anisotropy constant in deformation-free state. However, since experiment shows that the magnetic moments are in $[111]$, the total anisotropy energy must favour the direction $[111]$. Thus the above value of K_{ME} would have been overestimated. Nevertheless, considering the reliability of our numerical estimations, we might conclude that the anisotropy energy in deformation-free state is more important in determining the direction of the magnetic moments in FeO.

In (58), there is a uniaxial anisotropy term arising from a combined action of exchange striction and magnetostriction. In FeO, this anisotropy energy favours the plane (111) , since the sign of B_2 is opposite to that of B_3 . If we assume the exchange striction to be $e_{xy} = -0.1$ percent and the magnetostriction to be $e_{xy} = 0.7$ percent, the magnitude of T_{ME} will be about 3 cm^{-1} . This energy, as well as the energy given by T_D , is overcome by the anisotropy energy arising from the exchange energy.

If we assume spin-structure [A] for CoO, there must be a small deviation of the easy axes from the cubic axes. This arises from a combined action of the trigonal and cubic anisotropies. The angle of deviation ϑ is given by $T/\sqrt{2}K$ in the first order. Adopting $K = 20 \text{ cm}^{-1}$ and $T = 1 \text{ cm}^{-1}$, ϑ turns out to be about 2° . It would be interesting to verify this experimentally, though perhaps very difficult.

§ 10. Remarks about the magnetic anisotropy of MnO, MnS and NiO

In this final section we shall briefly discuss the magnetic anisotropies of MnO, MnS

* This value leads to $c = 140 \text{ cm}^{-1}$, where c is defined as the coefficient of the tetragonal crystalline field in § 6 of [I]. There we assumed a value $c = 100 \text{ cm}^{-1}$, which was obtained assuming a contraction of 1 percent. The difference does not affect the results obtained there.

and NiO. Since orbital degeneracy is completely removed in these substances, their magnetic anisotropy energies must be considerably smaller as compared with those of FeO and CoO. Though several origins of the anisotropy energy are conceivable, one concludes in the present stage of the theory that the inter-ionic magnetic dipole-dipole interactions make the largest contribution to it if structure [A] is valid for them. The lowering of the energy by an amount of the order of 0.1 cm^{-1} per ion due to a rhombohedral exchange striction in structure [A] favours this structure. Further, if the spins orient in the direction favoured by the inter-ionic magnetic dipole-dipole interactions, a further energy reduction of 0.9 cm^{-1} per ion occurs in the case of MnO. Also, by using the spin-wave theory, the present author has found that the zero-point energy of the spins prefers structure [A] to structure [B], though the energy difference is very small. Therefore, it can theoretically be concluded that these oxides have spin-structure [A] and their spins lie in the plane (111). This conclusion might appear to contradict with the experimental results of Shull et al.⁴⁾ for MnO and NiO. However, a recent neutron diffraction experiment on MnS supports the above conclusion.*) Furthermore, Singer's susceptibility measurements²³⁾ on a single crystal of NiO, annealed by applying a pressure along one of the trigonal axes, appear to indicate that the spins lie in the plane perpendicular to this axis, i.e., in the (111) plane. Also, torque measurements made by Uchida and Kondoh²⁴⁾ on a single crystal of NiO in magnetic field and an analysis of their results exclude the possibilities {100} and {111} for the direction of the spin axis.

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Appendix I. Calculation of the anisotropy energy arising from the classical orbital multipole interactions

The quadrupole-quadrupole interaction, (16), can be written in cartesian coordinates as

$$\begin{aligned} & (e^2/R_{12}^5) \left[(3/2) (3z_i^2 - r_i^2) (3z_j^2 - r_j^2) + 12z_i^2 z_j^2 - 12z_i z_j (\mathbf{r}_i \cdot \mathbf{r}_j) \right. \\ & \left. + (3/4) \{ (r_i^2 - z_i^2) (r_j^2 - z_j^2) - 2(x_i y_j - y_i x_j)^2 \} \right]. \end{aligned} \quad (\text{Ap. 1})$$

We define n_1 , n_2 and n_3 as the direction cosines of the z -axis (which we take along the line joining the two cations) referred to the cubic axes, and denote the coordinates of the electrons referred to the same cubic axes by X , Y and Z . Then summation of (Ap. 1) over all the equidistant neighbours of the cation 1 yields

$$\begin{aligned} & (e^2/R_{12}^5) \left[\left\{ - (315/4) \sum n_1^2 n_2^2 + (63/4) \sum n_1^2 \right\} (X_i^2 X_j^2 + Y_i^2 Y_j^2 + Z_i^2 Z_j^2) \right. \\ & + \left\{ (105/2) \sum n_1^2 n_2^2 - (21/2) \sum n_1^2 \right\} (2X_i Y_i X_j Y_j + 2Y_i Z_i Y_j Z_j + 2Z_i X_i Z_j X_j) \\ & \left. + \left\{ (105/4) \sum n_1^2 n_2^2 - (21/4) \sum n_1^2 \right\} R_i^2 R_j^2 \right]. \end{aligned} \quad (\text{Ap. 2})$$

As mentioned in the text, we do not distinguish between the coordinates of the electrons

* See also the footnote on page 2 of this paper.

belonging to different neighbouring cations, since they have the same spatial distribution relative to each of their nuclei. Further, summation must be taken over all the pairs of the d -electrons belonging to the interacting cations, but we dispensed with this summation in the above formulas for the sake of simplicity.

The quadrupole-hexadecapole interaction can be transformed in a similar way. Except for isotropic terms, the result is given by

$$15(e^2/R_{12}^5) \left[\left\{ (693/16) \sum n_1^2 n_2^4 - (63/4) \sum n_1^2 n_2^2 - (9/16) \sum n_1^2 \right\} \right. \\ \times \{ Z_i^2 (X_j^4 + Y_j^4 - 6X_j^2 Y_j^2) + X_i^2 (Y_j^4 + Z_j^4 - 6Y_j^2 Z_j^2) + Y_i^2 (Z_j^4 + X_j^4 - 6Z_j^2 X_j^2) \} \\ \left. + \left\{ (231/2) \sum n_1^2 n_2^4 - 42 \sum n_1^2 n_2^2 - (3/2) \sum n_1^2 \right\} \{ X_i Y_i (X_j^3 Y_j + Y_j^3 X_j - 6X_j Y_j Z_j^2) \right. \\ \left. + Y_i Z_i (Y_j^3 Z_j + Z_j^3 Y_j - 6Y_j Z_j X_j^2) + Z_i X_i (Z_j^3 X_j + X_j^3 Z_j - 6Z_j X_j Y_j^2) \} \right]. \quad (\text{Ap. 3})$$

We can obtain a similar formula for the hexadecapole-hexadecapole interactions, but we shall not write it down here.

The operator-equivalence relations²⁴⁾ between spacial coordinates and orbital angular momenta are well known in the calculation of crystalline field splittings. In our case, the orbital momenta are further replaced by pseudo-orbital angular momenta l_i . The relations between them are easily obtained by calculating the matrix elements. Thus, the spacial coordinates in (Ap. 2) and (Ap. 3) are replaced by the following relations:

for FeO,

$$Z^2 = (2/7) \langle r^2 \rangle l_z^2, \quad XY = -(1/7) \langle r^2 \rangle (l_x l_y + l_y l_x), \quad (\text{Ap. 4})$$

$$X^4 + Y^4 - 6X^2 Y^2 = (8/21) \langle r^4 \rangle l_x^2,$$

$$X^3 Y + Y^3 X - 6XY Z^2 = (4/21) \langle r^4 \rangle (l_x l_y + l_y l_x),$$

and for CoO,

$$Z^2 = \{ -(4/35) - (24/35) \alpha \beta + (18/35) \beta^2 \} \langle r^2 \rangle l_z^2,$$

$$XY = \{ (1/70) + (8/35) \alpha \beta + (13/70) \beta^2 \} \langle r^2 \rangle (l_x l_y + l_y l_x),$$

$$X^4 + Y^4 - 6X^2 Y^2 = \{ -(2/7) - (8/21) \alpha \beta + (2/7) \beta^2 \} \langle r^4 \rangle l_x^2, \quad (\text{Ap. 5})$$

$$X^3 Y + Y^3 X - 6XY Z^2 = \{ -(2/7) + (2/21) \alpha \beta + (2/7) \beta^2 \} \langle r^4 \rangle (l_x l_y + l_y l_x).$$

The constant terms which are not essential are neglected in the above formulas.

As examples, the interactions between nearest neighbouring cations in FeO are given by the following formulas:

the quadrupole-quadrupole interaction is

$$\mathcal{H}_{QQ} = (e^2 \langle r^2 \rangle^2 / R_0^5) \left[- (9/14) (l_{x1}^2 l_{x2}^2 + l_{y1}^2 l_{y2}^2 + l_{z1}^2 l_{z2}^2) \right. \\ \left. + (3/14) \{ (l_{x1} l_{y1} + l_{y1} l_{x1}) (l_{x2} l_{y2} + l_{y2} l_{x2}) \right. \\ \left. + (l_{y1} l_{z1} + l_{z1} l_{y1}) (l_{y2} l_{z2} + l_{z2} l_{y2}) \right. \\ \left. + (l_{z1} l_{x1} + l_{x1} l_{z1}) (l_{z2} l_{x2} + l_{x2} l_{z2}) \} \right]; \quad (\text{Ap. 6})$$

the hexadecapole-quadrupole interaction is

$$\begin{aligned}\mathcal{H}_{HQ} = & (e^2 \langle r^2 \rangle \langle r^4 \rangle / R_0^7) [(585/98) (l_{x1}^2 l_{x2}^2 + l_{y1}^2 l_{y2}^2 + l_{z1}^2 l_{z2}^2) \\ & + (195/49) \{ (l_{x1} l_{y1} + l_{y1} l_{x1}) (l_{x2} l_{y2} + l_{y2} l_{x2}) \\ & + (l_{y1} l_{z1} + l_{z1} l_{y1}) (l_{y2} l_{z2} + l_{z2} l_{y2}) \\ & + (l_{z1} l_{x1} + l_{x1} l_{z1}) (l_{z2} l_{x2} + l_{x2} l_{z2}) \}] ;\end{aligned}\quad (\text{Ap. 7})$$

and the hexadecapole-hexadecapole interaction is

$$\mathcal{H}_{HH} = (e^2 \langle r^4 \rangle^2 / R_0^9) (495/56) (l_{x1}^2 l_{x2}^2 + l_{y1}^2 l_{y2}^2 + l_{z1}^2 l_{z2}^2). \quad (\text{Ap. 8})$$

In these formulas, R_0 is the distance between the nearest neighbours, and each interaction was divided by 2 for the purpose of estimating the anisotropy energy per ion.

Using the values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ given by (21) or (22), the ratios between the contributions from multipole interactions (Ap. 6), (Ap. 7) and (Ap. 8) to the anisotropy constant are calculated to be

$$K'_{HQ} = \begin{matrix} -2.0 K'_{QQ} \\ -1.55 K'_{QQ} \end{matrix}, \quad K'_{HH} = \begin{matrix} -0.20 K'_{QQ} \\ -0.12 K'_{QQ} \end{matrix}, \quad (\text{Ap. 9})$$

where the upper values are obtained using (21) and the lower ones using (22). The value of K'_{QQ} is given by

$$K'_{QQ} = \begin{matrix} +53.7 \text{ cm}^{-1} \\ +37.9 \text{ cm}^{-1} \end{matrix}. \quad (\text{Ap. 10})$$

Adding the contributions from other surrounding cations, which are mainly due to quadrupole-quadrupole interactions and which amount to -8.3 cm^{-1} in total, we obtained the final results of the anisotropy constant (23) and (24).

In the case of CoO, the relations (Ap. 9) between the magnitudes of the interactions are approximately the same as in the case of FeO. Since the Hamiltonians \mathcal{H}_{QQ} , etc., can easily be obtained from those of FeO, taking account of different factors appearing in (Ap. 5), they will not here be reproduced. In this case, we obtain smaller values of the anisotropy constant, because $\langle r^2 \rangle$ and $\langle r^4 \rangle$ have a smaller value and also the factors appearing in (Ap. 4) and (Ap. 5) are different.

Appendix II. Calculation of A_1 , C_1 , F_1 , H_1 with the point charge model

In this model, in which the ions surrounding a given cation are approximated by point charges, the electrostatic potential for the electrons can be expanded in a series of spherical harmonics:

$$\begin{aligned}V = & A(3z^2 - r^2) + Cxy + F(7z^4 - 6z^2 r^2 + 3/5 \cdot r^4) \\ & + H(x^3 y + y^3 x - 6z^2 xy) + \dots\end{aligned}\quad (\text{Ap. 11})$$

The coefficients, A , C , F and H , are given by the summations,²⁶⁾

$$\begin{aligned}
 A &= -(1/4)e \sum_j' (e_j/R_j^5) (3Z_j^5 - R_j^2), \quad C = -3e \sum_j' (e_j/R_j^5) X_j Y_j, \\
 F &= -(5/64)e \sum_j' (e_j/R_j^9) [5(7Z_j^4 - 6Z_j^2 R_j^2 + (3/5)R_j^4) - 7(X_j^4 + Y_j^4 - 6X_j^2 Y_j^2)], \\
 H &= -(75/2)e \sum_j' (e_j/R_j^9) (X_j^3 Y_j + Y_j^3 X_j - 6X_j Y_j Z_j^2), \quad (\text{Ap. 12})
 \end{aligned}$$

where X_j , etc., are the coordinates of the j -th lattice point, e_j the point charge on it. A_1 , C_1 , F_1 and H_1 are the derivatives of these coefficients with respect to strain components ;

$$\begin{aligned}
 A_1 &= (\partial A / \partial e_{xx}) = -(1/4) \sum_j' e_j Z_j \cdot \partial / \partial Z_j \cdot [(3Z_j^2 - R_j^2) / R_j^5] \\
 &= (3e/4) \sum_j' (e_j/R_j^7) (5Z_j^4 - R_j^4), \\
 C_1 &= (\partial C / \partial e_{xy}) = -(3e/2) \sum_j' e_j (X_j \cdot \partial / \partial Y_j + Y_j \cdot \partial / \partial X_j) X_j Y_j / R_j^5 = -2A_1, \\
 F_1 &= -(35/2) (7e/8) \sum_j' (e_j/R_j^9) (5Z_j^4 - R_j^4) \\
 &\quad + (135e/16) \sum_j' (e_j/R_j^{11}) (7Z_j^6 - R_j^6), \\
 H_1 &= 25(7e/8) \sum_j' (e_j/R_j^9) (5Z_j^4 - R_j^4) - (45e/4) \sum_j' (e_j/R_j^{11}) (7Z_j^6 - R_j^6). \quad (\text{Ap. 13})
 \end{aligned}$$

These formulas are obtained by considering the cubic symmetry of the lattice. The sum $D = -(7e/8) \sum_j' (e_j/R_j^9) (5Z_j^4 - R_j^4)$ is the coefficient of the cubic crystalline field, which was calculated by Bethe²⁷⁾ to be

$$D = 7.16 (e^2/a^5),$$

a being the distance between the nearest neighbouring cation and anion. Other two sums appearing in (Ap. 13) are calculated by the direct summation method to be

$$\begin{aligned}
 \sum_j' (ee_j/R_j^7) (5Z_j^4 - R_j^4) &= -7.95 (e^2/a^3), \\
 \sum_j' (ee_j/R_j^{11}) (7Z_j^6 - R_j^6) &= -16.819 (e^2/a^5). \quad (\text{Ap. 14})
 \end{aligned}$$

Using these values, (45) of the text is obtained.

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