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

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The magnetic properties of antiferromagnetics, FeO and CoO, are investigated from the standpoint of the one-ion approximation. In their crystalline field of cubic symmetry the orbital degeneracies of Fe^{++} and Co^{++} are not completely removed and the residual orbital angular momenta play an important role through the presence of the spin-orbit coupling and through the direct effect of the orbital magnetic moments. After deriving the effective Hamiltonian for these degenerate cases, which corresponds to the Hamiltonian derived by Pryce for the non-degenerate case, we discuss the paramagnetic susceptibility, the Néel temperature and the state of each ion at absolute zero. We can give a reasonable quantitative interpretation of the susceptibility of CoO in paramagnetic state and obtain a good agreement with experiment for the magnetic moment of CoO in antiferromagnetic state. For FeO, sufficiently reliable data to compare with theory are not available at present, but a preliminary comparison is made. Further, in connection with the investigation of the validity of our theory, the origins of the crystalline field are discussed and it is pointed out that the covalent effect may make an appreciable contribution to the crystalline field.

§ 1. Introduction

Iron-group monoxides are known to be antiferromagnetic substances[1]. Their powder susceptibilities[2] show typical behaviours of antiferromagnetism and their spin arrangements have been determined by Shull, Strauser and Wollan[3] by neutron diffraction. They all have the structure of NaCl type except for a slight deformation[4] which takes place below the Néel temperature. The purpose of this paper and the succeeding one is to make a theoretical investigation of ferrous and cobaltous oxides from the standpoint of the one-ion approximation which seems to be appropriate when applied to these ionic crystals.

Each metallic ion of these oxides can be regarded as being placed in a strong electric field arising from other ions. Above the Néel temperature this crystalline field has cubic symmetry. Below the Néel temperature there is a crystalline field of a lower symmetry produced by a deformation; however, as will be discussed fully in the next paper, this deformation is caused mainly by magnetostriction and has a smaller effect on the energy levels than the spin-orbit coupling energy. A particular situation with ferrous and cobaltous ions as compared with manganous and nickelous ions is that their orbital angular momenta are not completely quenched by the Stark effect due to the cubic field. As shown in Fig. 1, when a cubic field is present, the ground orbital states of the free ferrous and cobaltous ions are split into two and three sublevels[5], respectively, of which the lowest ones, Γ_5 and Γ_4, respectively, are triply degenerate. Therefore, the residual orbital angular momentum plays an important role for their magnetic properties through the spin-orbit coupling and directly through the orbital magnetic moment.

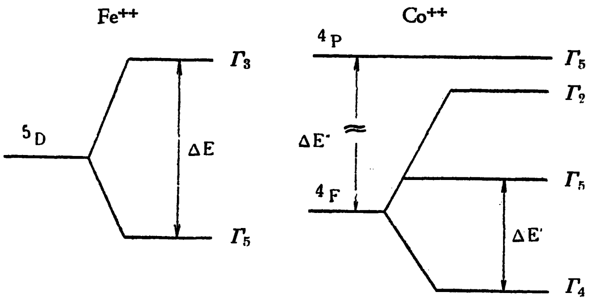

Fig. 1. Orbital level schemes of Fe^{++} and Co^{++} in the cubic electric field.

Néel[6] and Anderson[7] discussed the antiferromagnetic ordering of spins in these substances. Extending Anderson's calculation, Smart[8] has however, found a difficulty in interpreting the paramagnetic susceptibility of CoO, as will be referred to in § 4. These treatments do not take into account the presence of the residual orbital angular momentum.

Measurement[3] of the absolute intensity of the neutron diffraction in antiferromagnetic state shows that, in CoO, there is a significant contribution arising from the orbital angular momentum. However, the data could not be interpreted quantitatively[3] by the simple classical picture that the spin and the residual orbital angular momentum of each cation are parallel with each other. This difficulty can be removed by taking account of the spin-orbit coupling energy quantum-mechanically, as will be shown in § 6.

Recently, Li[9] has analysed the neutron diffraction data of iron group monoxides and discussed the relation between the magnetic anisotropy and the deformation below the Néel temperature, but his discussions indicate nothing of the origin of the magnetic anisotropy energy and of the mechanism of the deformation below the Néel temperature.

We shall give in this and the next papers a reasonable interpretation of the susceptibility, magnitude of the magnetic moment of each cation in antiferromagnetic state, magnetic anisotropy energy and deformation of these two oxides by considering the presence of the residual orbital angular momentum. In § 2 of this paper we discuss the form of the effective Hamiltonian of the spin-orbit coupling energy and the Zeeman energy for the degenerate orbital levels which corresponds to the Hamiltonian derived by Pryce[10] for the nondegenerate case. The paramagnetic susceptibility is discussed in § 3 and § 4; the effect of the orbital angular momentum on the Néel temperature in § 5; the state of each metallic ion at the absolute zero of temperature in § 6. Finally, in § 7, we discuss the origins of the crystalline field and thereby investigate the validity of our theory. In the next paper we shall discuss the magnetic anisotropy energy and deformation below the Néel temperature.

§ 2. Effective Hamiltonian for the lowest orbital state

Pryce[10] derived the effective Hamiltonian for the non-degenerate ground orbital state, assuming that the energy separations between the ground orbital state and upper ones are so large that one can treat the spin-orbit coupling energy as perturbation. We shall here derive the corresponding effective Hamiltonian for the degenerate orbital state under a similar assumption that the energy separations caused by the cubic field are so large that other terms of the Hamiltonian can be treated as perturbations.

The Hamiltonian of each metallic ion consists of the following terms:

$$\mathcal{H} = (\text{potential energy due to the crystalline field}) + (\text{exchange energy}) + \lambda \boldsymbol{L}\cdot\boldsymbol{S} + \mu_B \boldsymbol{H}\cdot(2\boldsymbol{S}+\boldsymbol{L}). \tag{1}$$

Here we assume that the so-called crystalline field can be represented by the electrostatic potential which depends on one-electron coordinates. This assumption will be discussed in a later section (§ 7) in connection with the theory of the origin of the crystalline field. Further, we assume cubic symmetry for the potential energy. Leaving the discussion of the exchange energy to later sections, we calculate here the effective Hamiltonian of the $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling and Zeeman energy for the degenerate ground state by using the perturbation theory.

In (1), we have neglected the internal spin-spin coupling because of its smallness and also the orbit-orbit interactions between the cations (which are not necessarily small), because they make no contribution in paramagnetic state where the orbital momenta of the cations have random orientations. The detailed discussion of these interactions will be given in the next paper in relation to the calculation of the anisotropy energy in antiferromagnetic state. We shall treat the ferrous ion and the cobaltous ion separately.

The ground state of a free ferrous ion is ^5D. We denote the orbital magnetic quantum number by M and the corresponding orbital function by φ_M. The three orbital wave functions which are degenerate in the cubic field are given by

$$\psi_1 = -(1/\sqrt{2})(\varphi_1 - \varphi_{-1}),\ \psi_2 = (1/\sqrt{2}i)(\varphi_2 - \varphi_{-2}) \text{ and } \psi_3 = (i/\sqrt{2})(\varphi_1 + \varphi_{-1}). \tag{2}$$

These functions give the representation Γ_5 of the octahedral group. The other two wave functions, which belong to Γ_3, are given by

$$\psi_4 = (1/\sqrt{2})(\varphi_2 + \varphi_{-2}) \quad \text{and} \quad \psi_5 = \varphi_0. \tag{3}$$

The matrices of the orbital angular momentum with respect to these ψ_i are

$$L_z = \begin{bmatrix} 0 & 0 & -i & 0 & 0 \\ 0 & 0 & 0 & 2i & 0 \\ i & 0 & 0 & 0 & 0 \\ 0 & -2i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad \text{and} \quad L_x + iL_y = L^+ = \begin{bmatrix} 0 & i & 0 & 1 & -\sqrt{3} \\ -i & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & -i & -\sqrt{3}i \\ -1 & 0 & i & 0 & 0 \\ \sqrt{3} & 0 & \sqrt{3}i & 0 & 0 \end{bmatrix}. \tag{4}$$

The submatrices of $\boldsymbol{L}$ in space of Γ_5 are therefore connected with the matrices of the angular momentum operator $\boldsymbol{l}$ of magnitude 1 by the relation[11]:

$$\boldsymbol{L} = -\boldsymbol{l}. \tag{5}$$

Using (5), the first order terms of the spin-orbit coupling energy and Zeeman energy for the ground orbital states are written as

$$\lambda' \boldsymbol{l}\cdot\boldsymbol{S}(\lambda'=-\lambda) \quad \text{and} \quad \mu_B \boldsymbol{H}(2\boldsymbol{S}-\boldsymbol{l}). \tag{6), (7}$$

The second order terms are produced by those matrix elements of $\boldsymbol{L}$ which connect Γ_5 and Γ_3. Using the perturbation theory, the second order term of $\lambda\boldsymbol{L}\cdot\boldsymbol{S}$ can be expressed by the following matrix of the Γ_5 space:

$$\mathcal{H}_1=2(\lambda^2/\Delta E)\begin{bmatrix} -2S_y^2 & S_yS_z & S_yS_x \\ S_zS_y & -2S_z^2 & S_zS_x \\ S_xS_y & S_xS_z & -2S_x^2 \end{bmatrix},$$

where ΔE is the energy separation between Γ_5 and Γ_3. In operator form this matrix can be written as

$$\mathcal{H}_1=-(4\lambda^2/\Delta E)\cdot S(S+1)+(2\lambda^2/\Delta E)$$
$$\times\{3(l_x^2S_x^2+l_y^2S_y^2+l_z^2S_z^2)-(\boldsymbol{l}\cdot\boldsymbol{S})^2-(\boldsymbol{l}\cdot\boldsymbol{S})\}. \tag{8}$$

Similarly, the cross term of $\lambda\boldsymbol{L}\cdot\boldsymbol{S}$ and $\mu_B\boldsymbol{H}\cdot\boldsymbol{L}$ gives rise to

$$\mathcal{H}_2=(8|\lambda|/\Delta E)\cdot\mu_B(\boldsymbol{H}\cdot\boldsymbol{S})-(2|\lambda|/\Delta E)\mu_B$$
$$\times[6(H_xl_x^2S_x+H_yl_y^2S_y+H_zl_z^2S_z)-\{(\boldsymbol{H}\cdot\boldsymbol{l})(\boldsymbol{l}\cdot\boldsymbol{S})+(\boldsymbol{l}\cdot\boldsymbol{S})(\boldsymbol{H}\cdot\boldsymbol{l})\}]. \tag{9}$$

$\mathcal{H}_2$ corresponds to the $(g-2)$-tensor of the non-degenerate case. The second order perturbation $\mu_B\boldsymbol{H}\cdot\boldsymbol{L}$ is given by

$$\mathcal{H}_3=-(4\mu_B^2H^2/\Delta E)+(2\mu_B^2/\Delta E)$$
$$\times\{3(H_x^2l_x^2+H_y^2l_y^2+H_z^2l_z^2)-(\boldsymbol{H}\cdot\boldsymbol{l})^2\}. \tag{10}$$

This corresponds to that term of the non-degenerate case which gives the temperature-independent susceptibility.

For cobaltous ion, the situation is a little more complicated, because the ground state ^4F of a free cobaltous ion is perturbed by a ^4P state through the cubic crystalline field. For the time being, we neglect this effect; however, the effect can be taken into account by a certain multiplicative factor as will be shown a little later. The ground orbital state of ^4F in the cubic crystalline field is given by

$$\psi_1=(1/4i)\{\sqrt{5}(\varphi_3+\varphi_{-3})+\sqrt{3}(\varphi_1+\varphi_{-1})\},\ \psi_2=\varphi_0,$$
$$\psi_3=-(1/4)\{\sqrt{5}(\varphi_3-\varphi_{-3})-\sqrt{3}(\varphi_1-\varphi_{-1})\}. \tag{11}$$

They give the representation Γ_4. The triply degenerate state, which gives the representation Γ_5 and is separated in energy by ΔE from the ground state, is given by

$$\psi_4=(1/4)\{\sqrt{3}(\varphi_3-\varphi_{-3})+\sqrt{5}(\varphi_1-\varphi_{-1})\},$$
$$\psi_5=(1/\sqrt{2})(\varphi_2+\varphi_{-2}),$$
$$\psi_6=(1/4i)\{-\sqrt{3}(\varphi_3+\varphi_{-3})+\sqrt{5}(\varphi_1+\varphi_{-1})\}. \tag{12}$$

The highest non-degenerate state is given by

$$\psi_7=(1/\sqrt{2i})\,(\varphi_2-\varphi_{-2}). \tag{13}$$

The matrices of L with respect to ψ_i are

$$L_z=\begin{bmatrix} 0 & 0 & -3i/2 & \sqrt{15}i/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 3i/2 & 0 & 0 & 0 & 0 & -\sqrt{15}i/2 & 0 \\ -\sqrt{15}i/2 & 0 & 0 & 0 & 0 & i/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -2i \\ 0 & 0 & \sqrt{15}i/2 & -i/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2i & 0 & 0 \end{bmatrix},$$

$$L^+=\begin{bmatrix} 0 & 3i/2 & 0 & 0 & \sqrt{15}i/2 & 0 & 0 \\ -3i/2 & 0 & -3/2 & -\sqrt{15}/2 & 0 & -\sqrt{15}i/2 & 0 \\ 0 & 3/2 & 0 & 0 & -\sqrt{15}/2 & 0 & 0 \\ 0 & \sqrt{15}/2 & 0 & 0 & -1/2 & 0 & -2i \\ -\sqrt{15}i/2 & 0 & \sqrt{15}/2 & 1/2 & 0 & -i/2 & 0 \\ 0 & \sqrt{15}\,i/2 & 0 & 0 & i/2 & 0 & -2 \\ 0 & 0 & 0 & 2i & 0 & 2 & 0 \end{bmatrix}. \tag{14}$$

The submatrices of L in the space of Γ_4 can be expressed by $\boldsymbol{l}$ of magnitude 1 as

$$\boldsymbol{L}=-(3/2)\,\boldsymbol{l}. \tag{15}$$

Corresponding to (6), we obtain the first order energy as

$$\lambda'\boldsymbol{l}\cdot\boldsymbol{S}\,(\lambda'=-(3/2)\lambda) \quad \text{and} \quad \mu_B\boldsymbol{H}(2\boldsymbol{S}-(3/2)\boldsymbol{l}). \tag{16), (17}$$

Corresponding to (8), (9) and (10), the second order energies are given by

$$\mathcal{H}_1=-(15/4)\,(\lambda^2/\Delta E)\,\{2\,(l_x^2S_x^2+l_y^2S_y^2+l_z^2S_z^2)-(\boldsymbol{l}\cdot\boldsymbol{S})^2\}, \tag{18}$$

$$\mathcal{H}_2=(15/4)\,(|\lambda|\mu_B/\Delta E)\,\{4\,(H_xl_x^2S_x+H_yl_y^2S_y+H_zl_z^2S_z) \\ -(\boldsymbol{H}\cdot\boldsymbol{l})\,(\boldsymbol{l}\cdot\boldsymbol{S})-(\boldsymbol{l}\cdot\boldsymbol{S})\,(\boldsymbol{H}\cdot\boldsymbol{l})\}, \tag{19}$$

$$\mathcal{H}_3=-(15/4)\,(\mu_B^2/\Delta E)\,\{2\,(H_x^2l_x^2+H_y^2l_y^2+H_z^2l_z^2)-(\boldsymbol{H}\cdot\boldsymbol{l})^2\}. \tag{20}$$

We now calculate the effect of the hybridization of ^4P into the ground orbital sublevels. Attaching a prime to the wave functions of ^4P, we define ψ_i' by the relation:

$$\psi_1'=(i/\sqrt{2})\,(\varphi_1'+\varphi_{-1}'),\ \psi_2'=\varphi_0' \quad \text{and} \quad \psi_3'=-(1/\sqrt{2})\,(\varphi_1'-\varphi_{-1}'). \tag{21}$$

The symmetry property of these wave functions is the same as that of ψ_1, ψ_2, ψ_3. Therefore, we obtain the wave functions of the ground orbital state in the form,

$$\Psi_i=\alpha\psi_i+\beta\psi_i' \quad (\alpha^2+\beta^2=1,\ i=1,2,3). \tag{22}$$

Since the matrices of $\boldsymbol{L}$ in the space of ^4P are the same as those of $\boldsymbol{l}$, (15) is modified to

$$\boldsymbol{L}=-(3/2)\alpha^2\boldsymbol{l}+\beta^2\boldsymbol{l}=-(3/2)\boldsymbol{l}+(5/2)\beta^2\boldsymbol{l}, \tag{23}$$

and (16) and (17) now become

$$\lambda'=-(3/2)(1-(5/3)\beta^2)\lambda \quad \text{and} \quad \mu_B\boldsymbol{H}\{2\boldsymbol{S}-(3/2)(1-(5/3)\beta^2)\boldsymbol{l}\}. \qquad (24),\ (25)$$

Furthermore, since (18), (19) and (20) operate only on ψ_i, each of them must now acquire a factor $(1-\beta^2)$ each.

If we adopt the one-electron approximation, the energy matrix of the cubic crystalline field potential[11),12)] constructed between $\psi_i(i=1, 2, 3)$ and $\psi_i'(i=1, 2, 3)$ becomes

$$\begin{bmatrix} -(3/4)\Delta E' & -(1/2)\Delta E' \\ -(1/2)\Delta E' & \Delta E'' \end{bmatrix}, \tag{26}$$

where $\Delta E'$ is now the energy separation between Γ_4 and Γ_5 of ^4F and $\Delta E''$ the separation between ^4F and ^4P of free ion. $\Delta E''$ is about 14,800 cm^{-1} according to the spectroscopic data.[13)] From (26) β is given, in the first approximation, by

$$\beta=\frac{(1/2)\Delta E'}{\Delta E''+(3/4)\Delta E'} \tag{27}$$

and the true separation ΔE between Γ_4 and Γ_5 is given by

$$\Delta E=(1+\beta/2)\Delta E'. \tag{27'}$$

In actual calculations, β, though small, cannot be neglected.

§ 3. Theory of the paramagnetic susceptibility

In the paramagnetic state above the Néel temperature the energy levels of each ion are determined mainly by the first order spin-orbit coupling energy (6) or (16), and they are specified by the magnitude of the resultant angular momentum $\boldsymbol{j}=\boldsymbol{l}+\boldsymbol{S}$. In the case of CoO, there are three energy levels which correspond to $\boldsymbol{j}=1/2$, $3/2$ and $5/2$. Adopting the value $-180\ \text{cm}^{-1}$ for the coefficient λ of the spin-orbit coupling, we obtain the separations of these levels as

$$E_{3/2}-E_{1/2}=405\ \text{cm}^{-1} \quad \text{and} \quad E_{5/2}-E_{1/2}=1080\ \text{cm}^{-1}.$$

Here we neglected the effect of ^4P. Since the Néel temperature of CoO is about 293°K or 204 cm^{-1}/k (k: Boltzmann constant), there are appreciable contributions from the higher levels to the paramagnetic susceptibility, and this makes the calculation rather complicated. A similar situation occurs in the case of FeO.

For the exchange energy we adopt the molecular field approximation and write it as

$$\mathcal{H}_{\text{ex}}=2Jz\langle \boldsymbol{S}\rangle\cdot\boldsymbol{S}. \tag{28}$$

$\langle S \rangle$ means the average vector of each spin. Since we have orbital degeneracy, it is in general open to question whether we can adopt the same form, (28), for the exchange energy as in the non-degenerate case. Above the Néel temperature, however, the exchange field has cubic symmetry on the average so that the assumption (28), which depends only on spins, is justified. This problem will be discussed further in the next paper. The value of $2Jz$ alone cannot determine the Néel temperature, because the exchange energies among geometrically nearest neighbours are ineffective in antiferromagnetic state[7], whereas they are effective in paramagnetic state and is included in $2Jz$. Thus we take $2Jz$ as an adjustable parameter and determine it by comparing the calculated paramagnetic susceptibility with the corresponding experimental data.

We shall here discuss the case of CoO. The second order terms of the Zeeman and spin-orbit coupling energies (18), (19) and (20) have anisotropic forms of cubic symmetry and they produce a cubic anisotropy of the paramagnetic susceptibility. Therefore, in order to compare our calculation with the measured powder susceptibility, which is the only available magnetic data of CoO at present, it is necessary to take the average of the susceptibility over the direction of the external field. For the sake of convenience, however, we adopt the following simplified procedure which is correct in the first order of $|\lambda|/\Delta E$ and $\mu_B H/\Delta E$. We divide each of the Hamiltonians (18), (19) and (20) into two parts: an isotropic part and an anisotropic part. For the latter, we choose a form such that transforms under coordinate transformation in the same manner as the spherical harmonics of the fourth degree; then this anisotropic part makes no contribution to the powder susceptibility in the first order, since it vanishes when averaged, and we can confine ourselves to the isotropic part. Thus, we write (18) in the following form:

$$\begin{aligned}\mathcal{H}_1 = -(15/4)(\lambda^2/\Delta E)[&\{2(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) \\ &-(2/5)(S(S+1)l(l+1) + (\boldsymbol{l}\cdot\boldsymbol{S}) + 2(\boldsymbol{l}\cdot\boldsymbol{S})^2)\} \\ &+\{(2/5)(S(S+1)l(l+1) + (\boldsymbol{l}\cdot\boldsymbol{S}) + 2(\boldsymbol{l}\cdot\boldsymbol{S})^2) - (\boldsymbol{l}\cdot\boldsymbol{S})^2\}].\end{aligned}$$

The first curled bracket is the anisotropic part which is constructed in the form of the spherical harmonic $x^4+y^4+z^4-(3/5)r^4$. We can mit this part and also the constant terms. The remaining part is

$$\mathcal{H}_1' = -(3/4)(\lambda^2/\Delta E)\{2(\boldsymbol{l}\cdot\boldsymbol{S}) - (\boldsymbol{l}\cdot\boldsymbol{S})^2\}.$$

In the same way, we have for (19) and (20) the effective parts

$$\mathcal{H}_2' = (|\lambda|\mu_B/\Delta E)\{6(\boldsymbol{H}\cdot\boldsymbol{S}) - (3/4)((\boldsymbol{H}\cdot\boldsymbol{l})(\boldsymbol{l}\cdot\boldsymbol{S}) + (\boldsymbol{l}\cdot\boldsymbol{S})(\boldsymbol{H}\cdot\boldsymbol{l}))\}$$

and

$$\mathcal{H}_3' = -(3/4)(\mu_B^2/\Delta E)\{4H^2 - (\boldsymbol{H}\cdot\boldsymbol{l})^2\}.$$

The total Hamiltonian effective for the calculation of the powder susceptibility, including the effect of ^4P, is

$$H=-(3/2)(1-(5/3)\beta^2)\lambda \boldsymbol{l}\cdot\boldsymbol{S}+2Jz\langle\boldsymbol{S}\rangle\cdot\boldsymbol{S}+\mu_B\boldsymbol{H}\{2\boldsymbol{S}-(3/2)(1-(5/3)\beta^2\boldsymbol{l}\}$$
$$+(3/4)(1-\beta^2)(\lambda^2/\Delta E)\{(\boldsymbol{l}\cdot\boldsymbol{S})^2-2(\boldsymbol{l}\cdot\boldsymbol{S})\}$$
$$+(1-\beta^2)(|\lambda|\mu_B/\Delta E)\{6(\boldsymbol{H}\cdot\boldsymbol{S})-(3/4)((\boldsymbol{H}\cdot\boldsymbol{l})(\boldsymbol{l}\cdot\boldsymbol{S})+(\boldsymbol{l}\cdot\boldsymbol{S})(\boldsymbol{H}\cdot\boldsymbol{l}))\}$$
$$-(3/4)(1-\beta^2)(\mu_B^2/\Delta E)\{4\boldsymbol{H}^2-(\boldsymbol{H}\cdot\boldsymbol{l})^2\}. \tag{29}$$

In the following, we give the method of calculation of the susceptibility neglecting ^4P; in our actual calculation we took ^4P into account. We also drop the last term of (29) for a moment, which gives the temperature-independent susceptibility.

We specify the energy of each level by W_{jm}, where the suffix m means the magnetic quantum number of j. To the second power of H, W_{jm} is given by

$$W_{jm}=W_{0j}+2Jz\langle S\rangle\cdot S_{jm}+\mu_B H\{(2+6(|\lambda|/\Delta E))S_{zjm}-(3/2)l_{zjm}+g_{jm}\}$$
$$+\sum_{j'\neq j}(1/\Delta W_{jj'})[\{2Jz\langle S\rangle+((7/2)+6(|\lambda|/\Delta E))\mu_B H\}^2|S_{zjj'm}|^2$$
$$+\mu_B H\{2Jz\langle S\rangle+((7/2)+6(|\lambda|/\Delta E))\mu_B H\}(g_{jj'm}S_{zj'jm}+S_{zjj'm}g_{j'jm})], \tag{30}$$

where W_{0j} is the energy for vanishing field and g is defined by

$$g=-(3/4)(|\lambda|/\Delta E)\{l_z(\boldsymbol{l}\cdot\boldsymbol{S})+(\boldsymbol{l}\cdot\boldsymbol{S})l_z\}.$$

First, we must determine self-consistently the value of $\langle S\rangle$. $\langle S\rangle$ is calculated by

$$\langle S\rangle=\mathrm{Tr}\left[\frac{\partial\mathcal{H}}{\partial(2Jz\langle S\rangle)}e^{-\mathcal{H}/kT}\right]\Big/\mathrm{Tr}[e^{-\mathcal{H}/kT}],$$

which becomes, using (30),

$$\langle S\rangle=-(1/\sum_{j,m}e^{-W_{0j}/kT})\cdot\sum_{j,m}e^{-W_{0j}/kT}[\{2Jz\langle S\rangle+((7/2)+6(|\lambda|/\Delta E))\mu_B H\}$$
$$\times\{(S_{zjm}^2/kT)+2\sum_{j'\neq j}(|S_{zjj'm}|^2/\Delta W_{j'j})\}$$
$$-(3/2)\mu_B H(S_{zjm}m/kT)+$$
$$\mu_B H\{(S_{zjm}g_{jm}/kT)+\sum_{j'\neq j}(S_{zjj'm}g_{j'jm}+g_{jj'm}S_{zj'jm})/\Delta W_{j'j}\}]. \tag{31}$$

From (31), the self-consistent value of $\langle S\rangle$ is obtained as

$$\langle S\rangle=-\mu_B H[\sum_{j,m}e^{-W_{0j}/kT}\{((7/2)+(6|\lambda|/\Delta E))((S_{zjm}^2/kT)+2\sum_{j'\neq j}|S_{zjj'm}|^2/\Delta W_{j'j})$$
$$-(3/2)(mS_{zjm}/kT)+(S_{zjm}g_{jm}/kT)$$
$$+\sum_{j'\neq j}(S_{zjj'm}g_{j'jm}+g_{jj'm}S_{zj'jm})/\Delta W_{j'j}\}]$$
$$\div[\sum_{j,m}e^{-W_{0j}/kT}+2Jz\sum_{j,m}e^{-W_{0j}/kT}\{(S_{zjm}^2/kT)+2\sum_{j'\neq j}|S_{zjj'm}|^2/\Delta W_{j'j}\}]. \tag{32}$$

Defining C by the relation,

$$\langle S\rangle=(\mu_B H/2Jz)C, \tag{33}$$

the susceptibility is given by

$$\chi=(N/H)\mathrm{Tr}(-\frac{\partial\mathcal{H}}{\partial H}e^{-\mathcal{H}/kT})/\mathrm{Tr}(e^{-\mathcal{H}/kT})+(N\mu_B^2/2Jz)C^2. \tag{34}$$

We must have the second term of (34), because in the molecular field approximation we count the exchange interactions doubly. In the absence of any orbital angular momentum (34) gives the ordinary Curie-Weiss law. More explicitly, (34) is written as

$$\chi = (N\mu_B^2/\sum_{j,m} e^{-W_{0j}/kT})[\sum_{j,m} e^{-W_{0j}/kT}\{((7/2)+C+6(|\lambda|/\Delta E))^2$$

$$\times((S_{zjm}^2/kT)+2\sum_{j\neq j'}|S_{zjj'm}|^2/\Delta W_{j'j})$$

$$+2((7/2)+C+6(|\lambda|/\Delta E))$$

$$\times((S_{zjm}g_{jm}/kT)+\sum_{j'\neq j}(S_{zjj'm}g_{j'jm}+g_{jj'm}S_{zj'jm})/\Delta W_{j'j})$$

$$-3((7/2)+C+6(|\lambda|/\Delta E))(mS_{zjm}/kT)+(9/4)(m^2/kT)-(3mg_{jm}/kT)\}]$$

$$+(N\mu_B^2/2Jz)C^2. \qquad (35)$$

In our actual calculation we took into account the effect of ^4P and also added to (35) the constant susceptibility due to the last term of (29). The resulting susceptibility is a very complicated function of temperature, as already seen in (35), but numerical calculations give apparently the Curie-Weiss law above 500°K irrespectively of the values of the parameters, $2Jz$ and $\Delta E'$, contained in (35). Roughly speaking, the effect of the residual orbital angular momentum manifests itself in two way: in the first place it gives rise to a change in the apparent g-value through the accompanying magnetic moment, and in the second place it gives rise to a change in the apparent paramagnetic Curie temperature θ through the spin-orbit coupling. The latter effect makes θ smaller than that would be expected from the value of $2Jz$ when orbital momentum is absent. The apparent g-value depends mainly on the value of the parameter, $\Delta E'$, which relates to the previously stated small correction terms of the second order. The apparent paramagnetic Curie temperature θ depends on both parameters, $2Jz$ and $\Delta E'$. We can thus determine these two parameters by comparison with experiment.

§ 4. Comparison of the theory of the preceding paragraph with experiment.

The powder susceptibility of CoO was measured by several authors.[2),14),15)] Their results are consistent with one another within experimental errors; we adopt here the result of La Blanchetais[14)], whose measurements cover the widest temperature range, i. e. 100-750°K. The susceptibility obtained by this experiment was found to follow the Curie-Weiss law

$$\chi_{\mathrm{mol}} = 3.0546/(T+280). \qquad (36)$$

This corresponds to our

$$2Jz = 295\ \mathrm{cm}^{-1} \quad \text{and} \quad \Delta E' = 7560\ \mathrm{cm}^{-1}. \qquad (37),\ (37')$$

With these values it is shown that our calculation agrees with experiment within errors of 0.3 percent above 500°K. The results are given in Fig. 2 in which three curves corresponding to different sets of two parameters are drawn for comparison. With the value (37′), β, the measure of hybridization of ^4P, is calculated to be $\beta=0.185$.

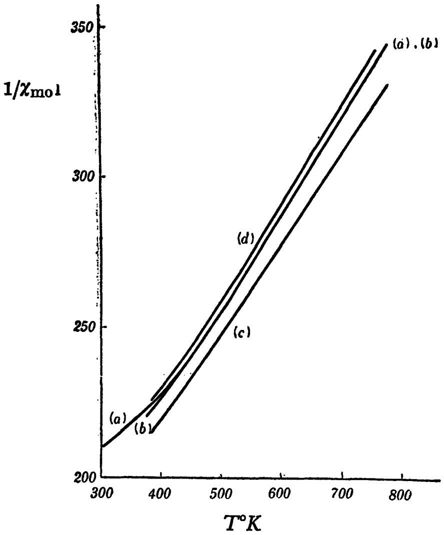

Fig. 2. Susceptibility of CoO above the Néel temperature.
Curve (a): experimental (after La Blanchetais[14]);
curve (b): calculated, assuming $2Jz=294.6\,\mathrm{cm}^{-1}$ and $\Delta E'=7560\,\mathrm{cm}^{-1}$;
curve (c): calculated, assuming $2Jz=297.5\,\mathrm{cm}^{-1}$ and $\Delta E'=6000\,\mathrm{cm}^{-1}$;
curve (d): calculated, assuming $2Jz=289.9\,\mathrm{cm}^{-1}$ and $\Delta E'=8300\,\mathrm{cm}^{-1}$.

The usual simple molecular field theory, which considers only spins, gives

$$\Theta=2JzS(S+1)/3k. \qquad (38)$$

And further, if we assume the spin-superstructure of the 2nd kind, which has been supported by neutron diffraction experiments and in which the spins of the next-nearest neighbouring pair of atoms point in the opposite directions, while there are equal number of nearest neighbouring pairs with parallel and antiparallel spins, the Néel temperature is given by

$$T_N=2J_1z_1S(S+1)/3k, \qquad (39)$$

where $2J_1z_1$ is the coefficient of the molecular field resulting from the nearest neighbours. The difference $2J_2z_2=2Jz-2J_1z_1$ is the coefficient of the molecular field resulting from the nearest neighbours. Therefore, if this simple theory could be applied to the case of CoO, we would have to interpret $2J_2z_2$ to be negative (ferromagnetic) and to be much smaller in absolute magnitude than $2J_1z_1$, since $\Theta/T=280/293$. On the other hand, this simple theory must be applicable to MnO and in this case the value of $2J_2z_2$ was found to be positive (antiferromgnetic) and larger than $2J_1z_1$. Smart[8], comparing these two cases, remarked that CoO cannot be well understood by such a simple theory. However, our value of $2Jz$, given by (37), is much larger than the value $180\,\mathrm{cm}^{-1}$ of $2J_1z_1$ to be obtained from the Néel temperature (see the next section) and, therefore, our calculation suggests that $2J_2z_2$ is antiferromagnetic and has a magnitude of $(295-180=)\ 115\,\mathrm{cm}^{-1}$, which is approximately epual to $118\,\mathrm{cm}^{-1}$ of MnO.[16]

The electrostatic potential of the cubic symmetry can be written as

$$D(r)\cdot(x^4+y^4+z^4-(3/5)\cdot r^4). \qquad (40)$$

If we assume the surrounding ions to be point charges, $D(r)$ does not depend on r, since the potential satisfies Laplace's equation. In several cases[17),18)] it was found that this model can give the correct sign and correct order of magnitude of the level splittings. In our oxides the magnitude of D with this model is given by $D=17.9\ e^2/a^5$ [19),20)], where e is the elementary charge and a the distance between O^{--} and the metallic ion. For CoO $\Delta E'$ is then given by

$$\Delta E'=(16/105)\cdot D\cdot\langle r^4\rangle, \tag{41}$$

where $\langle r^4\rangle$ means the average over the density of the d-electrons. For FeO we have

$$\Delta E=(4/21)\cdot D\cdot\langle r^4\rangle. \tag{42}$$

With these formulas and with the Slater function[21] for the d-electron wave function, we obtain

$$\Delta E'=6455\ \mathrm{cm}^{-1} \quad \text{for} \quad \mathrm{CoO} \tag{43}$$

and

$$\Delta E=10885\ \mathrm{cm}^{-1} \quad \text{for} \quad \mathrm{FeO}. \tag{44}$$

The value for CoO is very near that given by (37'). Abragam and Pryce[22] assumed 8800 cm^{-1} for $\Delta E'$ of cobalt tutton salt in order to obtain a good agreement of their calculated g-values and hyperfine splittings with the corresponding experimental results. Considering these situations, our value (37') appears to be quite reasonable.*

For FeO, we have yet no reliable experimental data, presumably because this oxide is unstable at room temperature. Measurements of the powder susceptibility above the Néel temperature (of about 186°K) up to room temperature by Bizette[23] give

$$\chi_{\mathrm{mol}}=6.24/(T+570).$$

However, this value of the Curie constant is unreasonably large. Mashiyama, Uchida and Kondoh[24] obtained

$$\chi_{\mathrm{mol}}=4.60/(T+190)$$

for the temperature region between 196°K and 460°K, and

$$\chi_{\mathrm{mol}}=2.42/(T+190)$$

for the temperature region between 973°K and 1320°K. The low temperature data which are not reliable are about 1.5 times as large as those of Bizette.

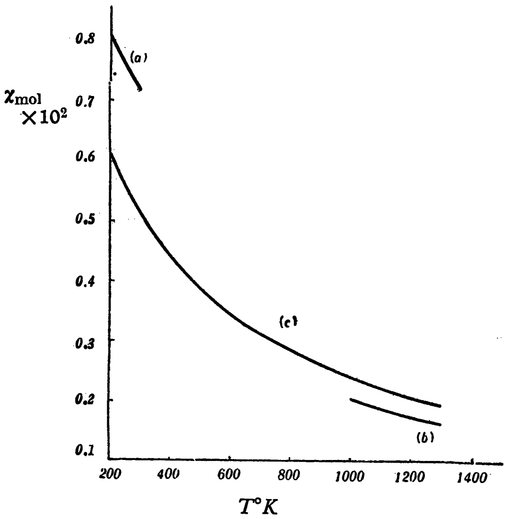

Fig. 3. Susceptibility of FeO above the Néel temperature.
Curve (a): experimental (after Bizette and Tsai[23]);
curve (b): experimental (after Mashiyama et al.[24]);
curve (c): calculated.

Since we obtained approximately the same value of $2J_2z_2$ for MnO and CoO, we may assume the same value of $2J_2z_2$ for FeO. Then, adding to this the value of $2J_1z_1$ deduced from the Néel temperature, we obtain a value of

* **Note added in proof.** Recently, the optital absorption experiment on a crystal of MgO containing Ni^{++} has been performed and it shows that the energy separation between Γ_2 and Γ_5 of ^3F of Ni^{++} is about 8600cm^{-1}. (W. Low, Bulletin Amer. Phys. Soc. 1 (1956) No. 8, 398, S11) From this value, the energy separation between Γ_5 and Γ_4, $\Delta E'$, of Ni^{++} can be estimated to be about 6900m^{-1}.

$190\ \mathrm{cm}^{-1}$ for $2Jz$ of FeO. With this value and with the simplified Hamiltonian

$$\mathcal{H}'=\lambda'\boldsymbol{l}\cdot\boldsymbol{S}+2Jz\langle S\rangle\cdot\boldsymbol{S}+\mu_B H(2\boldsymbol{S}-\boldsymbol{l}),$$

the susceptibility of FeO can be calculated. The result gives approximately the Curie-Weiss law:

$$\chi_{\mathrm{mol}}=3.15/(T+332).$$

As shown in Fig. 3, our results are somewhat below Bizette's data at low temperatures and somewhat above those of Mashiyama, Uchida and Kondoh at high temperatures. It is hoped that more reliable data are published and a better comparison can be made.

Finally, it may be mentioned that if a single crystal specimen were available and measurements of the anisotropy of its paramagnetic susceptibility could be made with it, we would be able to deduce the separation ΔE by applying our theory.

§ 5. Influence of the spin-orbit coupling on the Néel temperature

In this section we investigate the influence of the spin-orbit coupling on the Néel temperature and calculate $2J_1z_1$, i. e. the exchange coupling constant effective in the antiferromagnetic state, from the experimental data of the Néel temperature. The Néel temperature is defined as the temperature at which an infinitesimal antiferromagnetic molecular field sets in. It can be shown that the orbit-orbit interactions cannot affect the Néel temperature in the molecular field approximation, because the change of energies due to them is proportional to the fourth power of the antiferromagnetic molecular field. Then, if in (31) we put H equal to zero and attach minus sign to the left-hand side, we obtain a relation valid at the Néel temperature:

$$\langle S\rangle=2J_1z_1\langle S\rangle[\sum_{j,m}e^{-W_{0j}/kT_N}\{(S_{zjm}^2/kT_N)+2\sum_{j'\neq j}|S_{zjj'm}|^2/\Delta W_{j'j}\}]/[\sum_{j,m}e^{-W_{0j}/kT_N}].$$

From this we obtain

$$2J_1z_1=\sum_{j,m}e^{-W_{0j}/kT_N}/\sum_{j,m}e^{-W_{0j}/kT_N}\{(S_{zjm}^2/kT_N)+2\sum_{j'\neq j}|S_{zjj'm}|^2/\Delta W_{j'j}\}. \qquad (45)$$

Here we neglected the second order term of $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling and also the effect of ^4P in the case of CoO.

In the case of FeO, whose T_N is $186\,^\circ\mathrm{K}$[23),24)], we obtain from (45)

$$2J_1z_1=68.1\ \mathrm{cm}^{-1}. \qquad (46)$$

In the spin-only theory, $2J_1z_1$ is given by (39) and is $65\ \mathrm{cm}^{-1}$. Therefore, we can conclude that the spin-orbit coupling lowers the Néel temperature a little. For CoO ($T_N=293\,^\circ\mathrm{K}$[14)]), $2J_1z_1$ is obtained as

$$2J_1z_1=180.5\ \mathrm{cm}^{-1}. \qquad (47)$$

In the spin-only theory we have $2J_1z_1=162\ \mathrm{cm}^{-1}$.

§ 6. State of the ions at the absolute zero of temperature

At absolute zero the spin of each ion is subjected to a strong exchange field and is oriented in its direction. The pseudo-orbital angular momentum $\boldsymbol{l}$, connected with the spin through the spin-orbit coupling, becomes antiparallel to this direction. This is the classical picture of the ground state. Quantum mechanically, we have to start with the following Hamiltonian:

$$\mathcal{H}=-2J_1z_1\langle S\rangle\cdot S_z+\lambda'\boldsymbol{l}\cdot\boldsymbol{S}, \tag{48}$$

neglecting smaller terms.* In the case of CoO, we must take account of the effect of ^4P on λ'. $\langle S\rangle$ is the average value of the spin which we assume to point in the positive z-direction. The state given by $S_z=S$ and $l_z=-1$, which corresponds to the classical ground state, is connected with the states given by $S_z=S-1$, $l_z=0$ and $S_z=S-2$, $l_z=1$ through the x, y components of $\lambda'\boldsymbol{l}\cdot\boldsymbol{S}$. Therefore we must solve a secular equation of the third order and determine $\langle S\rangle$ self-consistently. Adopting the value of $2J_1z_1$ obtained from the Néel temperature and the spectroscopic data of λ', we calculate the wave function of the ground state to

$$\psi_g=0.909\ \psi_{2,-1}-0.395\ \psi_{1,0}+0.135\ \psi_{0,1}\quad \text{for}\quad \text{FeO}, \tag{49}$$

$$\psi_g=0.875\ \psi_{3/2,-1}-0.446\ \psi_{1/2,0}+0.188\ \psi_{-1/2,1}\quad \text{for}\quad \text{CoO}. \tag{50}$$

Here $\psi_{2,-1}$ etc., mean the wave functions of the states $S_z=2$ and $l_z=-1$, etc..

In (48) the deformation of the crystal in antiferromagnetic state is not considered. Actually we must consider the influence of the deformation on the crystalline field and thus on the wave function. We shall develop the theory of the deformation in the next paper. Here, using the results of it in advance, we assume that, in the case of CoO, the effect is taken into account by adding a term $-cl_z^2$ to (48), where the constant c has the magnitude of about $100\ \text{cm}^{-1}$. Then the wave function for CoO becomes

$$\psi_g'=0.900\ \psi_{3/2,-1}-0.401\ \psi_{1/2,0}+0.169\ \psi_{-1/2,1}. \tag{50'}$$

From the data of the forward scattering of neutrons by the ions we can deduce the magnitude of the magnetic moment of the ions. Using the wave functions obtained above, we can calculate this quantity, m_0, theoretically. For CoO, using (50′), we have

$$m_0'=\mu_B\langle 2S_z-(3/2)\,(1-(5/3)\,\beta^2)\,l_z\rangle_{\text{Av.}}=3.69\,\mu_B.$$

More exactly, considering the small correction due to (19), we have

$$\begin{aligned} m_0&=\mu_B\langle 2S-(3/2)\,(1-(5/3)\beta^2)\,l_z+(15/4)\,(|\lambda|/\Delta E)\,\{4S_zl_z^2-l_z(\boldsymbol{l}\cdot\boldsymbol{S})-(\boldsymbol{l}\cdot\boldsymbol{S})\,l_z\}\rangle_{\text{Av.}}\\ &=3.83\,\mu_B. \end{aligned} \tag{51}$$

If we use (50) instead of (50′), we obtain $m_0=3.68\,\mu_B$. From the experimental data obtained by Shull et al[2]. we have $m_0\simeq 3.7\,\mu_B$. The agreement is therefore very good.

* The validity of neglecting the orbit-orbit interaction will be discussed in the next paper.

For FeO, experimental data are not available. Assuming the value of ΔE obtained from the point charge model and using (49) we calculate to $m_0=4.44\,\mu_B$.

§ 7. Discussion of the origins of the crystalline field

We have hitherto developed our theory with the assumption that, except for the spin-dependent exchange energy, the influence of the surrounding ions could be represented by an electrostatic potential included in the one-ion Hamiltonian. Though this assumption seems to be generally acceptable, we have yet no conclusive theory of the origins of the crystalline field. It may, therefore, be worth while to discuss here the probable origins in some detail and thereby investigate the validity of our theory.

Our estimation of the crystalline field, (43) or (44), was made with the assumption of the point charge model. However, this model is far from the reality, since it disregards the overlap of the electron clouds between neighbouring ions. In the first place, the overlap effect makes $D(r)$ of (40) depend on r, since the potential no longer satisfies Laplace's equation, but it satisfies Poisson's equation. Attempts to calculate this 'classical' effect of the overlap were made by several authors.[12),25)] In the case of cubic symmetry, it reduces or reverses the level splitting of the orbital states obtained from the point charge model because of an imperfect screening of the attractive potential arising from the nuclei of the neighbouring negative ions. In particular, Kleiner[25)] has shown in his calculation of Cr alum that the potential obtained from such an improved calculation gives the wrong sign to the level splitting, whereas the point charge model can give the correct sign and a correct order of the magnitude of the splitting. Recently, Tanabe and Sugano[26)] pointed out that the non-orthogonality of the electron orbits belonging to neighbouring ions has an important effect to the level splitting of the orbital state. To the first approximation this effect could be understood as the Heisenberg exchange interaction between the non-orthogonal orbits. Since the sign of this exchange integral is negative because of the attractive potential between the electron and the nucleus of the neighbouring ion, it works as a repulsive potential between the negative ion and the electron. These authors assert that in Cr alum the exchange part of the interaction of the electrons with the surrounding ions exceeds the coulomb part so that the level scheme originally obtained from the point charge model comes nearer to the truth. The corresponding exchange integral in our oxides is presumably of the order of $1000\,\mathrm{cm}^{-1}$, and therefore the exchange effect will in any case have an appreciable contribution to the level splitting.

There is another mechanism which will cause the splitting of the orbital levels. Owen[27)] has pointed out that the weak covalent bond between the anion and the cation can explain the discrepancy between the optical data and the magnetic data concerning the level splitting of the cation orbital state of some hydrated salts. Also in our case, as is well known, there exists a partial covalency between the anion and the cation which is an essential origin of the superexchange mechanism.[28)] Since its degree depends on the orbital state of the cation, the energy arising from this effect will contribute to the level splitting.

Its qualitative nature is the same as that of the point charge interaction and also that of the exchange effect mentioned above, because this effect lowers the energy of the state of the cation with the least overlap, since then there are vacant orbits which have large overlaps and available for electron jumps from the anions. As we shall show later, this energy amounts in our case to several thousands inverse centimeters.

Therefore, the value of $\Delta E'$ given by (37') should be interpreted as the combined result of these complicated effects. It will be questionable whether we can treat these effects in the form of an electrostatic potential in the one-ion Hamiltonian as in the case we have calculated the effect of ^4P. In other words, we have to ask whether we can adopt the one-electron approximation for the effective Hamiltonian of these effects. If we can do it, we can write the effective Hamiltonian in the form (40) and determine the coefficient D so as to get the actual level splitting of the d-orbits.

The effect of the non-orthogonality relates only to the energy of each d-orbit within the approximation of the Heisenberg model. On the other hand, the effect of the covalency can be treated in the scheme of the perturbation theory which will give the relevant energy in the second order. The degree of the covalency depends both on the transition probability of the electron from the p-orbit of the neighbouring oxygen ion to one of the five d-orbits and on the excitation energy required for this transition. We assume here that the potential field which causes the transition is well approximated by the Hartree field which does not depend on the orbital state of the cation, or in other words, the multipole part of the potential arising from the cation electron cloud is negligible. Then, as we shall show explicitly later, the transition probability is related only to the availability of a specific d-orbit into which an oxygen electron can jump. So assuming that we can neglect the effect of the electron correlation on the excitation energy of this jump, it can be concluded that the effect of the covalency is represented by an effective one-electron Hamiltonian. The mentioned assumption is valid, if the excitation energy is large compared with the internal coulomb energy among the electrons belonging to that cation, which has the magnitude of about 1 ev.. On the other hand, the excitation energy is given approximately by the following formula:[29]

$$\Delta W = (4\alpha - 1)e^2/a + E - I, \tag{52}$$

where α is the Madelung constant for the lattice of the NaCl type, a the distance between the anion and the cation, E the electron affinity of O^{--}, I the second ionization energy of the metal atom. Adopting the value of -9 ev. for E[30], we obtain from (52)

$$\Delta W = 14.3 \text{ ev.} \quad \text{for both oxides.}$$

The actual value of ΔW would be smaller, since polarisation effects are not considered in (52). According to soft X-ray emission data[31], ΔW for MgO is estimated to be 10∼15 ev.. Considering that the second ionization energy of Mg is smaller by about 1.5 ev. or 2.3 ev. than those of Fe or Co, it may reasonably be concluded that ΔW of our oxides is about 10 ev.. Thus the difference in excitation energy due to the internal coulomb energy and other effects for different orbital states of the cation may approximately be neglected.

An idea of the magnitude of the exchange and covalent effects can be got by making use of the theory of superexchange. Since the d-shells of Fe^{++} and Co^{++} are 'more-than-half' full, the mechanism originally proposed by Anderson[28] works here most effectively, i. e., the exchange integral J_1 between the next-nearest neighbours is given by

$$J_1=(t/\varDelta W)^2 J'/(2S+1), \tag{53}$$

where $(t/\varDelta W)^2$ is the degree of covalency, t the transfer integral, J' the average exchange integral between the p-orbit of the oxygen ion and the d-orbits of the cation. If we make an approximate estimation of J' by a relatation,

$$J'=ts/S,$$

where s means the overlap integral, we can obtain a rough estimate of t and thus of J' and $t^2/\varDelta W$ (depression of energy due to the covalent bond formation) with the use of the experimental value of J_1 given in § 5, the value of $\varDelta W$ estimated above and a reasonable value of s. Assuming thus $s=0.1$ and $\varDelta W=10$ ev., we obtain

$$t^2/\varDelta W=\begin{matrix}3000\ \mathrm{cm}^{-1} & \text{for} & \text{FeO}, \\ 4100\ \mathrm{cm}^{-1} & \text{for} & \text{CoO},\end{matrix} \qquad J'=\begin{matrix}780\ \mathrm{cm}^{-1} & \text{for} & \text{FeO}, \\ 1200\ \mathrm{cm}^{-1} & \text{for} & \text{CoO}.\end{matrix} \tag{54}$$

Since both effects depend largely on the different degrees of overlap between different d-orbits of the cation and the oxygen orbit, the values of (54) themselves represent also the order of magnitude of their contributions to the level splitting. Thus we see that these effects are as large as those of the classical electrostatic field of the point charges and the finite spread of the oxygen electron clouds. In the following, we shall discuss in detail the different degrees of overlaps and the consequent contribution of the covalency to the level splitting.

We define the five d-orbits, $\phi_i(i=1, \cdots, 5)$, by the following symmetry properties:

$$\phi_1 \sim zx,\ \phi_2 \sim xy,\ \phi_3 \sim yz,\ \phi_4 \sim (3z^2-r^2),\ \phi_5 \sim (x^2-y^2). \tag{55}$$

ϕ_i have the same symmetry properties as ψ_i of the ferrous ion. We consider a cation at the origin and an oxygen ion situated on the positive z-axis and denote its $2p$ and $2s$ orbits by p_x, p_y, p_z and s. There are three kinds of the electron transition involved in covalency: from p_z to ϕ_4, from p_x or p_y to ϕ_1 or ϕ_3, and from s to ϕ_4. Other transitions are small owing to their symmetry properties. We define t_1, t_2 and t_3 by

$$t_1=(p_z|\mathcal{H}|\phi_4),\ t_2=(p_x|\mathcal{H}|\phi_1)=(p_y|\mathcal{H}|\phi_3),\ t_3=(s|\mathcal{H}|\phi_4). \tag{56}$$

If a relevant d-orbit is vacant, the energy of the covalency effect in the second order perturbation is given respectively by

$$-t_1^2/\varDelta W,\ -t_2^2/\varDelta W,\ -t_3^2/\varDelta W'.$$

Here we distinguish the excitation energy $\varDelta W'$ for the $2s$-electron transition from that of the $2p$-electron transition, ΔW. Since the promotion energy of the $2s$-electron to one of the $2p$-orbits is about 15 ev.[13] in the neutral oxygen atom, $\Delta W'$ is larger by a factor of 2 or more than ΔW, given by (52).

For the covalent effect with an oxygen ion on the x-axis, we notice that

$$\phi_4=(1/2)\phi_4'+(\sqrt{3}/2)\phi_5', \qquad \phi_5=(\sqrt{3}/2)\phi_4'-(1/2)\phi_5', \tag{57}$$

where the primed orbits are those which can be obtained from the unprimed orbits by replacing the z-axis with the x-axis and therefore ϕ_4' and ϕ_5' are given by

$$\phi_4'\sim(3x^2-r^2), \qquad \phi_5'\sim(y^2-z^2).$$

From (57) we easily see that the availability of ϕ_4 for the electron jump from the oxygen ion on the x-axis is $1/4$ of that from the oxygen on the z-axis, since only ϕ_4' is available for this jump. Similarly, the availability of ϕ_5 for the electron jump from the oxygen ion on the x-axis is $3/4$. Therefore, if ϕ_4 is vacant, the relevant total energy of the covalency effect with six oxygen ions surrounding the cation is given by

$$\begin{aligned}E(\phi_4)&=-\frac{2t_1^2}{\Delta W}-(1/4)\times\frac{4t_1^2}{\Delta W}-\frac{2t_3^2}{\Delta W'}-(1/4)\times\frac{4t_3^2}{\Delta W'}\\&=-3t_1^2/\Delta W-3t_3^2/\Delta W'.\end{aligned} \tag{58}$$

If ϕ_5 is vacant, the corresponding energy is

$$E(\phi_5)=-(3/4)\times\frac{4t_1^2}{\Delta W}-(3/4)\times\frac{4t_3^2}{\Delta W'}=-\frac{3t_1^2}{\Delta W}-\frac{3t_3^2}{\Delta W'}. \tag{58'}$$

As for the covalent energy for ϕ_1, ϕ_2 and ϕ_3, we notice that

$$\phi_1=\phi_3', \qquad \phi_2=\phi_1', \qquad \phi_3=\phi_2'.$$

Therefore the total energy of the covalency effect of these orbits is given by

$$E(\phi_{1,2,3})=-4t_2^2/\Delta W. \tag{59}$$

In the case of FeO, only one of the five d-orbits is doubly occupied: in Γ_5, one of the three orbits ϕ_1, ϕ_2 and ϕ_3 is doubly occupied, and in Γ_3, ϕ_4 or ϕ_5 is doubly occupied. So the contribution of the covalency to the level separation between Γ_3 and Γ_5 is the difference between (59) and (58), that is,

$$\Delta E=(3t_1^2-4t_2^2)/\Delta W+3t_3^2/\Delta W'. \tag{60}$$

The case of CoO is a little more complicated because of the configuration mixing arising from the presence of ^4P. For example, the orbital wave function, ψ_2, is obtained by antisymmetrizing the product,

$$(2/\sqrt{5})\phi_1(\mathrm{I})\phi_3(\mathrm{II})+(1/\sqrt{5})\phi_2(\mathrm{I})\phi_5(\mathrm{II}), \tag{61}$$

and the corresponding product for ψ_5 is given by

$$\phi_2(\mathrm{I})\phi_4(\mathrm{II}). \tag{62}$$

Here we treat the case of Co^{++} as the two-electron case. Then the energy of the covalency effect with an oxygen on the z-axis is given by

$$-\frac{t_1^2}{\Delta W}-(2/5)\frac{t_2^2}{\Delta W}-\frac{t_3^2}{\Delta W'}, \quad \text{for the state given by } \psi_2, \tag{63}$$

and

$$-\frac{2t_2^2}{\Delta W} \quad \text{for} \quad \psi_5. \tag{64}$$

The corresponding energy arising from the covalency with an oxygen on the x-axit is, using the relation (57), obtained as

$$-(17/20)\frac{t_1^2}{\Delta W}-\frac{t_2^2}{\Delta W}-(17/20)\frac{t_3^2}{\Delta W'} \quad \text{for} \quad \psi_2. \tag{65}$$

and

$$-(3/4)\frac{t_1^2}{\Delta W}-\frac{t_2^2}{\Delta W}-(3/4)\frac{t_3^2}{\Delta W'} \quad \text{for} \quad \psi_5. \tag{66}$$

Using these relations, the total contribution of the covalency effect to the energy separation between Γ_5 and Γ_4 of ^4F is obtained as

$$\Delta E'=\frac{12t_1^2-16t_2^2}{5\Delta W}+\frac{12t_3^2}{5\Delta W'}.$$

Since the wave functions have the largest overlap for the transition given by t_1, t_1^2 is probably larger than t_2^2 by a factor of 2 or more. If the former is much larger than the latter and if the covalency effect with the $2s$ electrons, specified by t_3, is ineffective in the superexchange because of a large excitation energy, we can identify t_1 with t given in (53). Then we see that the level splitting arising from the covalency effect has an order of magnitude comparable with those from other effects.

Finally, one might question the validity of the fact that we disregarded in the calculation of § 3 the effect of the configuration mixing arising from our covalency effect. As Owen points out, this configuration mixing leads to a smaller absolute value of the coefficient of the spin-orbit coupling, especially for the non-diagonal part of the spin-orbit coupling with respect to the levels split by the crystalline field potential. The latter is due to the fact that the non-diagonal parts connect the orbital states of different degrees of covalency. On the other hand, however, Tanabe and Sugano[26] obtained by a rigorous treatment of non-orthogonality a larger coefficient of the spin-orbit coupling, the orthogonalization making the effective weight of the d-orbits larger than unity. It is therefore difficult to infer a plausible value of the coefficient of the $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling. We estimate that our ΔE and $\Delta E'$, which are affected by the non-diagonal parts of the $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling, have errors of about 10 percent.

Another question is whether the residual orbital angular momentum is partially quenched by the covalency effect. Since the orbits used by the predominant bond specified by t_1 are almost unoccupied by the electrons in the lowest sublevel of both Fe^{++} and Co^{++}, the three states can have an equal covalency with all the neighbouring oxygen ions. It can therefore be concluded that, even in the state in which an electron has jumped into one of these unoccupied orbits, the orbital momentum is still 'alive' and has approximately the same magnitude as in non-covalent states.

§ 8. Summary

In this paper we stressed the importance of the residual orbital angular momentum for the interpretation of the magnetic properties of FeO and CoO. In § 2 we derived the effective Hamiltonian of the Zeeman and $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling for degenerate orbital states. In § 3 and § 4 we discussed the paramagnetic susceptibility and obtained reasonable results especially for CoO. A difficulty pointed out by Smart in interpreting the relation between θ and T_N of CoO have been removed. In § 5 we discussed the Néel temperature and in § 6 we calculated the wave functions of the ground states of the cations at absolute zero. Using these wave functions, we calculated the magnetic moment of these ions and obtained a good agreement with experiment for cobalt ion. Finally, in § 7 we discussed the origins of the crystalline field.

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