of the specific heat anomaly and the effect on the electrical resistivity of magnets are being examined.

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Theory of the Magnetic Scattering of Neutrons by CoO

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1. INTRODUCTION

THE spin arrangement in the antiferromagnetic state of cubic crystals MnO, FeO, CoO, and NiO has been a subject of active interest during the past several years. The first neutron diffraction study by Shull, Strauser, and Wollan[1] indicated that the spin superstructure in these oxides is such that a sheet of plus spins and a sheet of minus spins alternate along one of the [111] directions (a structure suggested by Néel[2]) and that the direction of the spins is one of the [100] axes, except in FeO in which it was found to be perpendicular to those sheets, i.e., parallel to [111]. The electronic state of a free Mn^{++} is $(5d)^5\ ^6S$ and so one expects the magnetic anisotropy energy in MnO to arise principally from the magnetic dipole-dipole interactions among the manganous ions, as the electronic state ^6S would suffer little change in the crystal. A simple elementary consideration, as well as an exact calculation due to Kaplan,[3] of these interactions shows that the stable spin direction should lie in the (111) plane, in contradiction to the experiment. A similar situation is encountered with NiO, since the orbital moment of Ni^{++}, whose electronic state is $(3d)^8\ ^3F$, is to be quenched in the cubic crystalline electric field of the oxide. A new neutron diffraction study carried out by Roth[4] has revealed features which are in favor of the theory. His results indicate that the spin direction in MnO is either $[\bar{1}11]$ or $[\bar{1}10]$, the latter in the (111) plane, and that in NiO $[\bar{1}10]$. Both experiments, new and earlier, conclude that the spin direction in FeO is perpendicular to the (111) sheets, as reflections from these planes vanish. This could be expected from a theory cited below. In CoO, Roth's preliminary interpretation of his results was that the spin direction might be either $[11\bar{2}]$ or $[0\bar{1}1]$, both being in the (111) plane, which, however, contradicts the theory. The situations with FeO and CoO are somewhat complicated due to the existence of a residual orbital moment of the ions in the crystal. This was already conceived by Shull *et al.*[1] in connection with larger observed intensities of diffraction lines than expected on the basis of the spin only theory.

The electronic states of a free Fe^{++} and a free Co^{++} are, respectively, $(3d)^6\ ^5D$ and $(3d)^7\ ^4F$. In the cubic crystalline field of the oxides, their orbital degeneracy is lifted only partially leaving the ground-state triply degenerate in both cases. This ground state is described in terms of an angular momentum operator $\mathbf{l}$ of magnitude one, i.e., the total angular momentum operator $\mathbf{L}$ of the free ion can be replaced by $-\mathbf{l}$ in FeO and $-\frac{3}{2}\mathbf{l}$ in CoO. This small $\mathbf{l}$ is coupled with the spin angular momentum, $\mathbf{S}$, to form a total angular momentum $\mathbf{l}+\mathbf{S}$, and the eigenstates of the ions are characterized by the eigenvalues of $(\mathbf{l}+\mathbf{S})^2=j(j+1)$, with $j=1, 2, 3$ in the case of FeO and $j=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ in the case of CoO, if no exchange couplings exist among the ions. Actually they do exist, and when taken into account in the approximation of the Weiss molecular field, states with different j but with the same l_z+S_z couple where z is the direction of the molecular field. Kanamori[5] has shown that the state of Co^{++} in CoO at absolute zero is described by the wave function

$$\psi=a\psi_{\frac{1}{2},-1}+b\psi_{\frac{1}{2},0}+c\psi_{-\frac{1}{2},1} \tag{1}$$

with

$$a=0.900, \quad b=-0.401, \quad c=0.169, \tag{2}$$

[1] Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951).
[2] L. Néel, Ann. phys. (12) 3, 137 (1948).
[3] J. I. Kaplan, J. Chem. Phys. 22, 1709 (1954).
[4] W. L. Roth, Annual Meeting, American Crystallographic Association, June, 1956.
[5] J. Kanamori, Progr. Theoret. Phys. (Kyoto) 17, 177, 197 (1956).

where the first indices of ψ represent values of S_z and the second indices those of l_z, z being in this case one of the [001] axes of the crystal. The wave function (1) represents a nonspherical spin distribution and a certain oriented current distribution, both of which should interact with neutron waves. The numerical values of (2) have been obtained by adjusting a parameter in his theory in such a way that the theoretical value of the Néel point agrees with its observed value; a slight perturbing effect of an excited state ^4P on the ground state and the influence of a small contraction along the [001] axis have been also taken into account.

The theory described above predicts a spin direction parallel to one of the cubic principal axes for CoO and a simultaneous contraction of the crystal along the same direction. The latter comes about principally as a result of the coupling between the residual orbital momentum of Co^{++} and a deformation of the crystal, and the calculated value is of a right order of magnitude. Applied to FeO the theory predicts, though with less certainty, that the spin direction is [111] and a small elongation of the crystal along the same direction should take place, in agreement with observations. These successes leave little doubt of the validity of the theory, and it is therefore desirable to calculate the neutron diffraction intensities on this basis and to compare with observations.

2. FORMULA FOR THE SCATTERED WAVE

The amplitude of the neutron wave elastically scattered by the spin and orbital current of an atom is, according to Halpern and Johnson,[6] Kleiner,[7] and Trammell,[8] proportional to

$$-(g_n e^2h^2/2\pi M_n mc^2)\sum_{n'}\times[(\langle n'|\mathbf{s}_n|n\rangle\cdot\mathbf{e})(\mathbf{P}_s\cdot\mathbf{e})-\langle n'|\mathbf{s}_n|n\rangle\cdot\mathbf{P}_s]-i(g_n e^2h/M_n mc^2\kappa)\sum_{n'}\langle n'|\mathbf{s}_n|n\rangle\cdot\mathbf{e}\times\mathbf{P}_L, \quad (3)$$

where M_n is the neutron mass, $g_n=-3.83$ the g factor of neutron, $\hbar\mathbf{s}_n$ the neutron spin angular momentum, n and n' denote the initial and final spin states of the neutron, respectively, $\mathbf{e}=\boldsymbol{\kappa}/\kappa$, κ being the scattering vector, i.e., the difference between the incident and scattered wave vectors, and

$$\mathbf{P}_s=(\psi^*,\sum_j \mathbf{s}_j\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)\psi), \quad (4)$$

$$\mathbf{P}_L=(\psi^*,\sum_j \exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)\mathbf{p}_j\psi), \quad \mathbf{p}_j=(\hbar/i)\,\mathrm{grad}_j \quad (5)$$

are the expectation values, with respect to the atomic state, of quantities related to electron spins $\mathbf{s}_j$ and momenta $\mathbf{p}_j$, respectively, the sum over j being extended over all the electrons in the atom. The wave function (1) is to be used for (4) and (5).

The differential cross section for an unpolarized incident neutron beam is given by

$$d\sigma\equiv\phi^2 d\Omega=\left(\frac{e^2}{mc^2}\frac{-g_n}{2}\right)^2|\mathbf{R}|^2 d\Omega, \quad (6)$$

where

$$\mathbf{R}=\mathbf{e}(\mathbf{P}_s\cdot\mathbf{e})-\mathbf{P}_s+\mathbf{e}\times\mathrm{Im}(-\mathbf{P}_L/\kappa\hbar). \quad (7)$$

The real part of $\mathbf{P}_L$ contributes nothing to the cross section, since $\psi^*\mathbf{p}_j\psi$ in (5) is originally the current density, $(\psi^*\mathbf{p}_j\psi-\psi\mathbf{p}_j\psi^*)/2$, and the latter changes sign with inversion of space coordinates of the electrons.

To perform the calculation, the actual forms of the wave functions appearing in the right-hand side of (1) are needed. They are mixtures of the F function, ζ, and the P function, ζ', of the free cobaltous ion in the following way:

$$\psi_{\frac{1}{2},-1}=-\alpha\frac{1}{2\sqrt{2}}[5^{\frac{1}{2}}\zeta_{\frac{1}{2},3}+(3)^{\frac{1}{2}}\zeta_{\frac{1}{2},-1}]+(1-\alpha^2)^{\frac{1}{2}}\zeta_{\frac{1}{2},-1}', \quad (8)$$

$$\psi_{\frac{1}{2},0}=\alpha\zeta_{\frac{1}{2},0}+(1-\alpha^2)^{\frac{1}{2}}\zeta_{\frac{1}{2},0}', \quad (9)$$

$$\psi_{-\frac{1}{2},1}=\alpha\frac{1}{2\sqrt{2}}[5^{\frac{1}{2}}\zeta_{-\frac{1}{2},-3}+(3)^{\frac{1}{2}}\zeta_{-\frac{1}{2},1}]-(1-\alpha^2)^{\frac{1}{2}}\zeta_{-\frac{1}{2},1}', \quad (10)$$

where α takes the following numerical value after Kanamori[5]:

$$\alpha=0.983, \text{ and therefore } (1-\alpha^2)^{\frac{1}{2}}=0.185. \quad (11)$$

The functions ζ and ζ' are constructed in the usual way as linear combinations of products of one-electron wave function of the three holes of Co^{++}. A calculation shows that the quantity $\mathbf{P}_s$ is expressed in the form

$$\begin{aligned}\mathbf{P}_s=\mathbf{k}[&c_0{}^0I_0+c_2{}^0P_2{}^0(\cos\theta)I_2+\{c_4{}^0P_4{}^0(\cos\theta)\\&+c_4{}^4P_4{}^4(\cos\theta)\cos4\varphi\}I_4]+\mathbf{i}[c_2{}^1P_2{}^1(\cos\theta)\cos\varphi I_2\\&+\{c_4{}^1P_4{}^1(\cos\theta)\cos\varphi+c_4{}^3P_4{}^3(\cos\theta)\cos3\varphi\}I_4]\\&+\mathbf{j}[c_2{}^1P_2{}^1(\cos\theta)\sin\varphi I_2+\{c_4{}^1P_4{}^1(\cos\theta)\sin\varphi\\&-c_4{}^3P_4{}^3(\cos\theta)\sin3\varphi\}I_4], \quad (12)\end{aligned}$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors along the cubic principal axes, the spin direction being along $\mathbf{k}$, c's are certain numerical factors, θ and φ the polar and azimuthal angles of vector $\boldsymbol{\kappa}$, and I's the following integral:

$$I_l=\int_0^\infty \zeta_d(r)\left(\frac{1}{\kappa r}\right)^{\frac{1}{2}}J_{l+\frac{1}{2}}(\kappa r)\zeta_d(r)r^2dr, \quad (13)$$

$\zeta_d(r)$ being the radial $3d$ function. For a spherical atom with only spin, other terms than the first term, $kc_0{}^0I$, drop from (12), and the coefficient $c_0{}^0$ becomes equal to

[6] O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).
[7] W. H. Kleiner, Phys. Rev. **90**, 168 (1953).
[8] G. T. Trammell, Phys. Rev. **92**, 1387 (1953).

$(\frac{3}{2})(\pi/2)^{\frac{1}{2}}$. The imaginary part of $\mathbf{P}_L$ is of the form

$$\mathrm{Im}(\mathbf{P}_L) = \mathbf{i}[d_1 P_1^1(\cos\theta)\sin\varphi I_1 + d_3 P_3^1(\cos\theta)\sin\varphi I_3] - \mathbf{j}[d_1 P_1^1(\cos\theta)\cos\varphi I_1 + d_3 P_3^1(\cos\theta)\cos\varphi I_3], \quad (14)$$

where d's are again certain numerical factors.

3. INTENSITIES OF REFLECTIONS AT ABSOLUTE ZERO

With the use of ϕ defined by (6), the structure amplitude factor for reflection hkl can be written

$$F(hkl) = \phi \sum \pm \exp 2\pi i(hx/a + ky/b + lz/c) \quad (15)$$

where the sum is extended over the magnetic atoms in the magnetic unit cell, the plus and minus signs are for the plus and minus spins, respectively, and a, b, c are the edge lengths of the magnetic unit cell. We use the values [9]

$$a = b = 8.5104 \text{ A}, \quad c = 8.4116 \text{ A}. \quad (\text{CoO at } -180°\text{C})$$

The Debye-Waller factor is omitted, since it should be

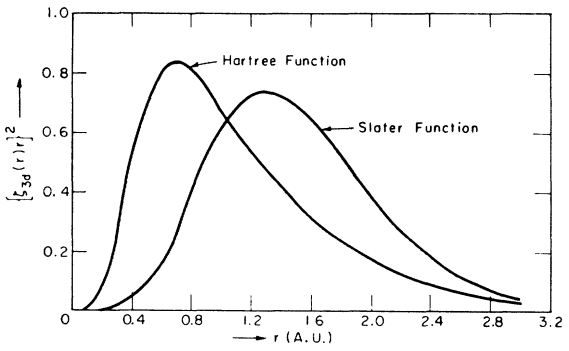

FIG. 1.

ineffective below, say, 100°K for scattering angles less than 45°.

In the numerical caluclations, we assumed either of the two forms of the radial $3d$ function of Co^{++}. One is the hydrogenic function given by Slater[10]:

$$\zeta_{3d}(r) = \left(\frac{\lambda^7}{6!}\right)^{\frac{1}{2}} r^2 e^{-(\lambda/2)r}, \quad \lambda = 4.6 \text{ in atomic units.} \quad (16)$$

The other is the self-consistent Hartree function recently obtained by Ariyama, Kayama, and Sugimoto[11] (see Fig. 1). Table I shows the results obtained for $|\mathbf{R}|^2$ using these Hartree and Slater functions. The figures in the column "spin and orbit" are due to the present theory.

We assume that the sample is a powder made in a cylindrical form. Then the diffracted power is proportional to[12]

$$\sum F(hkl)^2/\sin\theta \sin 2\theta, \quad (17)$$

the $\sum$ being extended over cooperating planes. The absorption factor is here assumed to be independent of the scattering angle, which should be true to a good approximation. Table II summarizes the calculated intensities for a wavelength of 1.024 A, together with intensities measured by Roth.[13] The 111 intensity is here normalized to 1000, but the relative values of this intensity calculated for different models are also given in parentheses. The observed 111 intensity originally given by Roth[13] is 835 if the diffuse scattering in the vicinity of this line is included, and 635 if the sharp Bragg portion only is taken into account; in Table II the latter value is adopted and all the values given by Roth are multiplied by 1000/635. The calculated nuclear line intensities which correspond to the figures in the first column of Table II are 177 for the 222 line, 815 for the 400 line, and 847 for the 440 line, if the Debye-Waller factor is ignored; however, the zero-point vibration of the oxygen ions should contribute a factor somewhat smaller than one. The corresponding measured values by Roth are 132, 480, and 460, respectively, which are obviously too small.

The tables show that the calculated intensities of the magnetic lines depend very much on the assumed form of the $3l$ wave function. With the Slater function the intensities for higher indices fall off more rapidly than with the Hartree function. The 311 intensity with the Hartree function is somewhat too large compared with its measured intensity, while the intensities of the

TABLE I. Values of $|\mathbf{R}|^2$.

Direction of κ[a]	$\lvert\kappa\rvert$[a]	Spin and orbit Hartree	Spin and orbit Slater	Spin only Hartree	Spin only Slater
111	0.679	1.790	1.550	1.164	0.998
$\bar{3}11, 1\bar{3}1$	1.297	1.517	0.899	0.892	0.447
$11\bar{3}$	1.297	0.276	0.132	0.178	0.089
331	1.704	1.028	0.341	0.560	0.144
$3\bar{1}3, \bar{1}33$	1.704	0.494	0.133	0.311	0.080
511, 151	2.031	0.774	0.240	0.359	0.038
115	2.031	0.035	0.003	0.028	0.003
333	2.031	0.433	0.057	0.249	0.026

[a] $|\kappa|$ is measured in units of (Bohr radius)$^{-1}$.

TABLE II. Relative intensities of magnetic reflections.

Magnetic lines	Spin and orbit Hartree	Spin and orbit Slater	Spin only Hartree	Spin only Slater	Exptl. (Roth)
111	1000 (1.0)	1000 (0.87)	1000 (0.65)	1000 (0.56)	1000
311	515	347	469	274	323
331	185	64	166	50	157
511, 333	132	41	100	12	165

[9] Nagamiya, Yosida, and Kubo, *Advances in Physics* (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.
[10] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[11] Ariyama, Kayama, and Sugimoto, J. Phys. Soc. Japan **12**, 285 (1957).
[12] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, New York, 1955), p. 93.
[13] W. L. Roth (private communication).

higher indices with the Slater function are too small compared with their observed values. In the case of MnO, the $3d$ function deduced by Shull *et al.*[1] from their measurements in the paramagnetic temperature region has a maximum which lies between the maximum of the Hartree function and that of the Slater function, and this function falls off more rapidly than the Hartree function for increasing radial distance. If such is also true with the $3d$ function in CoO, we might expect a better agreement between the calculated and measured intensities. We hope to try another series of calculations with such a function.

The diffuse magnetic scattering in the paramagnetic region would also give certain informations of the electronic state of Co^{++} in CoO; the theory in this case must take account of the spin and residual orbital moment as well as the exchange coupling among the ions.

4. MODIFICATION OF THE THEORY AND A CLOSER COMPARISON WITH EXPERIMENT

There exist thus two main discrepancies between theory and experiment. First, the calculated nuclear line intensities are too large compared with the observed ones, and, second, the calculated 311 magnetic line intensity relative to that of the 111 line is too large if the Hartree $3d$ function is assumed, or the higher order magnetic lines are relatively too weak if the Slater $3d$ function is assumed. We now investigate how far these discrepancies can be removed within the framework of Kanamori's theory. As it appears that the Slater function is too much spread out, we confine ourselves to the Hartree function.

First, Kanamori's theory predicts a spin orientation which does not exactly coincide with one of the cubic principal axes. The spin superstructure is trigonal, so that we have a trigonal anisotropy energy, besides a cubic anisotropy energy, which tilts the spin orientation away from the direction of the trigonal axis, [111], if we consider mainly the magnetic interactions. Kanamori estimated the angle of deviation from the [001] axis to be 2°, in the direction away from the [111] axis, assuming a value of 20 cm^{-1} per ion for the cubic anisotropy constant, K, and a value of 1 cm^{-1} per ion for the trigonal dipolar anisotropy constant, T, (coefficients of $\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2+\alpha_1^2\alpha_2^2$ and $\alpha_2\alpha_3+\alpha_3\alpha_1+\alpha_1\alpha_2$, respectively). It is quite possible, however, that the angle of deviation is actually larger, say, 10°, for the following reason. K consists mainly of two parts: one arises from the coupling between the deformation of the crystal and the orbital moment, the spin being coupled to the latter, the other from the electric multipolar interactions among the nonspherical ionic clouds to which the spins are coupled. Kanamori estimated the former to be 28 cm^{-1} per ion and the latter to be -8 to -15 cm^{-1} per ion, and the maximum total value of K to be $28-8=20$ cm^{-1} per ion. In estimating the first value, 28 cm^{-1}, the elastic constants of MgO were used, instead of those of CoO, which are not known, and, further, the Slater $3d$ function was used to obtain the coupling constant of the electric multipolar interactions. Thus K was very roughly estimated, and it is therefore possible that K is as low as 10 cm^{-1}. The trigonal anisotropy energy may arise, besides from magnetic dipolar interactions, also from anisotropic exchange interactions, electric multipolar interactions, etc., which he did not estimate. It is therefore not improbable that T is as large as 3 cm^{-1}. With $K=10$ cm^{-1} and $T=2.9$ cm^{-1}, we have 10° for the angle of deviation.

In Sec. 3, we tacitly omitted the effect of the excited orbital levels on the g value of the ion. Kanamori considered this and obtained for the expectation value of the magnetic moment of the ion along the [001] direction a value of 3.83 Bohr magnetons, instead of 3.69 Bohr magnetons without the effect of the excited levels. We have therefore to multiply our calculated magnetic line intensities by $(3.83/3.69)^2=1.077$, or divide the relative nuclear line intensities by this factor. Table III and Table IV, column a, give the results with an angle of deviation 10°, and with this correcting factor. The magnetic line intensities are now satisfactory compared with experiment but the nuclear line intensities are still somewhat too large. Here it is assumed that the magnetic form factor takes the same values as before, except for the coefficient $q^2(=1-(\mathbf{m}\cdot\boldsymbol{\kappa})^2/(m\kappa)^2$, $\mathbf{m}$ being the magnetization of each ion and $\boldsymbol{\kappa}$ the scattering vector, as before).

A further reduction of the nuclear line intensities is possible by assuming a reasonably larger magnetic moment of the ion. The numerical coefficients a, b, c in the wave function (1) are determined by $\lambda'(=-3\lambda/2$, $\lambda=-180$ cm^{-1} being the spin-orbit coupling constant for the free Co^{++}), $2J_1z_1$ (the exchange coupling constant which is effective in antiferromagnetic state), and a certain constant c which considers the effect of the crystal deformation on the orbital motion. In particular, b/a is given approximately by $\sqrt{6}\lambda'/[3(\lambda'+2J_1z_1)+2c]$. λ' can be smaller (and for smaller λ', the cubic anisotropy constant K becomes smaller), the value 180.5 cm^{-1} for $2J_1z_1$, which Kanamori estimated using an approximation of the type of the molecular field, can be larger (by a factor of at most 2), and Kanamori's value, 100 cm^{-1}, for c has to be replaced by 140 cm^{-1}, since his value is based on a tetragonal contraction of 1% while actually it is 1.2% (extrapolated

TABLE III.

Magnetic lines	Theoretical values	Exptl. (Roth)
111	1000	1000
311	376	323
331	156	157
511, 333	121	165

TABLE IV.

Nuclear lines	Theoretical values a	b	c	Exptl. (Roth)
222	137	115	108	132
400	631	530	488	480
440	655	550	466	460

to 0°K).* If we take arbitrarily 326 cm^{-1} for $2J_1z_1$ (1.8 times the original value) and assume the original value for λ', we have (with $c=140$ cm^{-1}) $\frac{3}{4}$ times the original value of b/a; alternatively, we may leave $2J_1z_1$ unchanged and reduce λ' by a factor of about $\frac{2}{3}$. Neglecting the third term of (1), the magnetic moment of Co^{++} now becomes 1.09 times larger (4.2 Bohr magnetons).

Table IV, column b, gives the results when the above modification is made. In column c, corrections for the Debye-Waller factor are made in such a way that the ratio of the 400 and 440 intensities agrees with the observed ratio, but errors in the observation will perhaps make such corrections meaningless.

A good agreement between theory and experiment can therefore be attained when suitable modifications are made which are allowed within Kanamori's theory. At least one can say that his picture of the magnetic structure of CoO is not necessarily subject to a radical change in order to explain the neutron diffraction data. If one assumes, instead of making the above modifications, that the magnetic moments of the Co ions lie in the (111) plane, the theoretical magnetic line intensities become definitely in disagreement with the experimental ones, the relative intensities of 111, 311, etc., calculated with the Hartree function, being 1000, 248, etc. It is hoped that other evidences for the features described in this section, for instance that the magnetization axis deviates by 10° from [001], can be found by some experimental method.

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