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SOME RECENT ADVANCES IN THE STUDY OF MAGNETIC COMPOUNDS

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Résumé. — On rend compte des études expérimentales et théoriques effectuées récemment au Japon sur des composés magnétiques. Ces études sont relatives à des monocristaux artificiels de NiO, FeS, Fe₇S₈, à des monocristaux naturels et des polycristaux artificiels des solutions d’ilmé-nite-hématite, à des solutions de ferrite-chromite, ainsi qu’aux théories de FeO, CoO, FeCl₂, CoCl₂, NiCl₂, MnBr₂, à la surstructure des spins dans un cristal du type rutile, a CoF₂, etc... et à quelques considérations sur le super-échange.

Abstract. — Experimental and theoretical studies on magnetic compounds done in recent years in Japan are reviewed. They include measurements on artificial single crystals of NiO, FeS, Fe₇S₈, natural single crystals of ilmenite-hematite solutions, artificial polycrystals of ilmenite-hematite solutions, ferrite-chromite solutions, theories on FeO, CoO, FeCl₂, CoCl₂, NiCl₂, MnBr₂, spin superstructure of the rutile type crystal, CoF₂, etc..., and some super-exchange considerations.

I. Introduction. — In this communication the writer would like to bring forward some of the recent advances in Japan in the study of magnetic compounds, both theoretical and experimental, and mostly unpublished or partly published at the time of the preparation of this manuscript. It will intentionally be confined to compounds, which are increasingly attracting interest of the various investigators in university and industrial laboratories. However, no complete review is attempted. Only those investigations which would reveal some fundamental phenomenon of the magnetism of compounds will be included. (Abbreviations ferro and antiferro will be often used in the text for ferromagnetic and antiferromagnetic.)

II. Experimental studies. — (1) MONOXIDES OF THE IRON GROUP ELEMENTS. — Good single crystals of NiO and CoO have been grown by the flame fusion method of Verneuil by Dr. Nakazumi at Tochigi Chemical Industrial Company (Osaka), where he grows a large quantity of TiO₂ single crystals for artificial jewels. Cubes of about 1 cm size can be cleaved from the bullet-shaped virgin crystals and they were studied by Uchida and Kondoh (University of Osaka Prefecture). Cr₂O₃ and MnO also have been grown but so far not much studied. Since the measurements on CoO have not reached the stage of definite conclusion (though the antiferromagnetic structure with spin axis parallel to one of the [100] axes conforms with the experimental results), I will confine myself to NiO. They made precise torque measurements on this crystal in order to find out the spin arrangement. First I will briefly summarize the hitherto known facts and also a theoretical consideration made in connection with their measurements.

The spin arrangement in NiO suggested by Néel [1] and observed by neutron diffraction experiments [2] [3], is such that a particular set of (111) net planes is alternately occupied by plus spins and minus spins. The crystal contracts along this particular [111] axis by 10⁻³ below its Néel point (523 °K) as observed by X-rays [4] [5], presumably because the spins of the same sign repel and the spins of the opposite sign attract one another. The direction of the spin axis seems to be in the (111) plane [3], as expected theoretically: the electronic state of Ni⁺⁺ in the cubic crystalline electric field of NiO has no orbital moment, to the first approximation of taking account of the spin-orbit interaction energy, and therefore the magnetic dipolar interaction would make (111) the easy plane of magnetization. The easy axes may be either [110], [011] and [101] or [112], [211] and [121] from symmetry considerations. It might be supposed that in most actual crystals there are antiferro domains with axis of magnetization distributed at random over these three directions. Furthermore, the crystals may consist of small crystalline domains whose rhombohedral axes are distributed more or less at random over the four [111] axes of the original cubes. The latter was confirmed experimentally, as will be mentioned below.

Let the direction cosines of one of the axes of magnetization in the crystalline domain with rhombohedral axis [111] be χ, β, γ, which may be either 1/√2, -1/√2, 0 or 1/√6, 1/√6, -1/√6, and let the direction cosines of the external field be a, b, c. Then the free energy of the whole crystal will be given by

\[ F = -\sum \left( \frac{1}{2} \chi_n H_n^2 + \frac{1}{2} \chi_\perp H_\perp^2 \right) \]

\[ = \frac{1}{2} (\chi_\perp - \chi_n) \sum H_n^2 - \frac{1}{2} \chi_\perp H_\perp^2 V \]

\[ = \frac{1}{2} (\chi_\perp - \chi_n) H^2 \Sigma (a^2 + b^2 + c^2) - \frac{1}{2} \chi_\perp H_\perp^2 V, \] (1)
where $\chi_{II}$ and $\chi_{L}$ are, as usually, the susceptibilities parallel and perpendicular to the axis of magnetization, $\Sigma$ indicates the summation over all the magnetic and crystalline domains, and $V$ is the volume of the crystal. We simplify (1) by assuming that a fraction, $p$, of the total number of crystalline domains corresponds to domains with rhombohedral axis [111] and the remaining fraction, $1 - p$, to those whose rhombohedral axes are distributed at random over the four directions, [111], [111], [111], [111]. Furthermore, the random distribution of the magnetic axis over each crystalline domains will be assumed. Then, interchanging $x$, $\beta$, $\gamma$ cyclically in (1) and neglecting isotropic terms, one obtains

$$F = -\frac{1}{2} (\chi_{L} - \chi_{II}) H^2 (\beta \gamma + \gamma \alpha + \alpha \beta) (bc + ca + ab) pV.$$  (2)

The magnitude of the torque which acts on the crystal is given by $-\frac{\partial F}{\partial \theta}$, where $\theta$ is the angle of rotation. Since this differentiation operates on $(bc + ca + ab)$, which is a quadratic function of $\sin \theta$ and $\cos \theta$ if the axis of rotation is specified, it can be seen that the torque varies as

$$C \cos (20 + \varepsilon).$$

Constants $C$ and $\varepsilon$ corresponding to the specified axis of rotation can be easily calculated, and $C$ is proportional to $H^2$.

Now coming back to experiment, I will first note that every crystal examined by Uchida and Kondoh showed the torque predicted from formula (1). They found on close examination by X-rays that the apparently cubic single crystals of NiO were composed of many small rhombohedral crystals twinned along (100) planes. In order to get more definite information by removing this composite structure, they applied a pressure along a particular [111] direction during the process of slow cooling from above the Néel point. A pressure of 30 to 40 kg/cm² was found to be the most effective. Also, mechanical shocks, such as the application of supersonic oscillations, combined with a small pressure applied at room temperature was found effective. Crystals so treated became uniaxial, i.e., felt practically no torque when they were suspended with that [111] axis vertical. Furthermore a few experiments were done to find out the effect of a strong magnetic field. However, up to 10 000 Oe, no definite effect was found. The results of the torque measurements strictly followed the theoretical prediction from (2), as seen in Table 1 for one particular case.

### Table 1

<table>
<thead>
<tr>
<th>Torque measurements by Uchida and Kondoh</th>
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<tr>
<td><strong>Axis of rotation</strong></td>
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<tr>
<td>Relative torque</td>
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<tr>
<td>Amplitude</td>
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<tr>
<td>Position of maximum torque</td>
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<td>(theor.)</td>
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</table>

(1) Angles are measured from [001] for the first three axes and from [111] for the fifth axis.

From the magnitude of the measured torque amplitude the value of $p(\beta \gamma + \gamma \alpha + \alpha \beta)$ was determined. In the best case attainable, this value was 0.38, from which we obtain $p = 0.76$ (76% aligned) assuming $\beta \gamma + \gamma \alpha + \alpha \beta = -1/2$, i.e., that the axis of magnetization lies in the (111) plane. At least it can be concluded that $\beta \gamma + \gamma \alpha + \alpha \gamma$ cannot be smaller than 0.38 since $p$ cannot exceed one, in other words, the axis of magnetization cannot deviate from the (111) plane by more than $16^\circ$. (A better sample with $p = 0.80$ was obtained later.)

Uchida and Kondoh are measuring the antiferromagnetic resonance absorption in NiO using a far infrared spectrometer recently built in Oaka University by Prof. Yoshinaga, which works in the range of 20 to 1 000 microns. A small peak of absorption was observed at 295 $\mu$ with no magnetic field, which might correspond to the mode of oscillation in which the antiparallel sublattice magnetizations oscillate principally perpendicular to the (111) plane and for which a theoretical calculation, based on the dipolar interaction only, predicts 275 $\mu$. The formation of antiferromagnetic domains might have broadened the absorption peak but better results are hoped to be obtained.

(2) Pyrrhotite, FeS. — Prof. Hirahara at Hiroshima University (moved recently to Tohoku University) prepared single crystals of nearly stoichiometric FeS, several millimeters in size. The susceptibility, thermal expansion, and electrical conductivity were measured for different crystallographic directions in the range from liquid air temperature to 600 °C [6].

The naturel pyrrhotite, mostly Fe$_7$S$_8$, is a well-known ferro (rather, ferri-) magnet which possesses a large anisotropy energy stabilizing the magnetization in the c-plane. Bertaut [7] reported a
superstructure of iron vacancies in it, which will be discussed later in connection with Fe₇S₈. The magnetism of the natural pyrrhotite is not yet fully understood, and the study of the stoichiometric FeS might shed light on it.

The stoichiometric FeS is antiferro and has a Néel point at 320 °C and another transformation point (α-point) at 138 °C. The anomalous specific heats associated with these points are 600 cal/mol and 550 cal/mol, respectively [8], the corresponding entropy changes being 1.0 and 1.3 cal/deg.mol, the total entropy change of 2.3 cal/deg.mol being comparable to $R \ln 4 = 2.8$ of the spin entropy of Fe⁺⁺. Hirahara observed that the α-point somewhat lowered with increasing sulphur content and the α-anomaly disappeared at FeS₁₀₉, the Néel point remaining unchanged. The most interesting feature observed is that the susceptibilities parallel and perpendicular to the c-axis, $\chi_c$ and $\chi_a$, of the stoichiometric FeS abruptly change at the α-point as shown in Fig. 1. $\chi_a$ is always isotropic in the c-plane. Above $T_N$, the molar susceptibility is given approximately by

$$\chi = 3.38/(T + 917° K),$$

in which the Curie constant 3.38 is comparable to, but greater than the spin-only value 2.96. Another interesting feature is an abrupt decrease in electrical conductivity parallel to the c-axis below $T_a$, which will, however, not be reproduced here.

Before going over to the interpretation of the above results, I might add two experiments. Ueda [9] observed by X-rays the variation of the lengths of the c- and a-axes of Fe₁₋ₓS with varying temperature. An abrupt change of the c-axis is seen in Fig. 3. Hirahara also observed the change of the c-axis by a dilatometric method. He observed further that the expansion of the c-axis on
cooling occurred at a temperature somewhat lower than the α-point at heating — all the measurements refer to heating unless otherwise stated.

In this recent experiment he observed an anomalous hysteresis effect in the susceptibility on heating and cooling as shown in Fig. 2. It will further be noted in connection with Ueda's experiment that a value 1.66 of the axial ratio $c/a$ appears to play a certain role in the magnetism of pyrrhotite: in the measurements at room temperature samples with axial ratio greater than 1.66, corresponding to sulphur concentration greater than 52%, are antiferro, while samples with axial ratio less than 1.66, corresponding to sulphur concentration less than 52%, are ferro; also in Fig. 4 the axial ratio passes through 1.66 at the α-point. However, the axial ratio corresponding to the close-packed hexagonal structure is 1.63.

The mechanism underlying the facts observed for the stoichiometric FeS may be as follows. Between $T_N$ and $T_a$ the spins may lie in the c-plane and below $T_a$ they may point along the c-axis. Then, between $T_N$ and $T_a$, $\chi_c$ will be the usual perpendicular susceptibility which is independent of temperature, and the actually observed variation with temperature may be attributed to the variation of the $g$-factor, which is expected from the more specific model to be mentioned below. The fact that $\chi_a$ is isotropic in the c-plane suggests that there exist random antiferromagnetic domains and that $\chi_a$ is $(\chi_{\|} + \chi_L)/2$ which decreases with decreasing temperature. Below $T_a$, $\chi_a$ will be $\chi_{\|}$ and $\chi_a$ will be $\chi_L$. The observed sudden decreases of these susceptibilities may be attributed to the sudden expansion of the c-axis and the consequent changes (increases) of the exchange constants.

A more specific model could be the following: the triply degenerate orbital state of Fe$^{++}$(3d)$^5$(3d$e$) in the cubic crystalline electric field is split into two in such a way that the ground state is singlet above $T_a$ and doublet below, the singlet-doublet separation varying with temperature and eventually vanishing at a certain value of $c/a$ (say, 1.66) which is realized in the neighbourhood of $T_a$. This singlet-doublet separation should be a function of $c$ and $a$, principally of $c/a$, and should behave qualitatively so if $c/a$ increases with decreasing temperature, although its vanishing at $T_a$ cannot easily be deduced from theory. Anyway, the change of the anisotropy energy at $T_a$ is accounted for by this model, supposing (as is legitimate) that the anisotropy energy arises mainly from the crystalline field and spin-orbit coupling. Furthermore, the anomalous change of $c/a$ can be accounted for by the same model: in the singlet state the 3d$e$ electron cloud is more dense in the c-direction and thus it repels the surrounding sulphur ions sideways, while in the doublet state it is less dense in that direction and so repels the sulphur ions along the c-axis. At present we know little about the nature of the (super-) exchange interactions operating among the ferrous ions in FeS, but they surely are functions of atomic distances and depend on the form of the electron cloud. Such dependences may account for the changes of $\chi_{\|}$ and $\chi_L$ at $T_a$. The anomalous behaviours of the susceptibilities on cooling (Fig. 2) can be understood on the same basis if one assumes that just below $T_a$ change of the anisotropy energy takes place but expansion of the c-axis is delayed by several degrees for some reason.

(3) IRON Selenide. — Hirakawa and Okazaki at Kyushu University are studying the magnetic properties and crystalline structure of Fe$_{1-x}$Se, particularly Fe$_7$Se$_8$ and Fe$_3$Se$_4$, with single crystals which they prepared. The stoichiometric com-
pound in this case cannot be obtained [10]. Here I shall confine myself to Fe$_7$Se$_8$. The crystalline structure of it which they previously reported [11] is very similar to that found by Bertaut [7] for Fe$_7$Se$_8$ but the unit c-axis of the superstructure is three times the unit c-axis of the original NiAs structure, while Bertaut’s structure has that four times. In recent measurements Hirakawa and Okazaki observed the Bertaut type structure, too. Fig. 5 gives a basal plane which contains Fe ions and vacancies in a regular way. Such a plane and a plane consisting of Fe ions only are alternately piled up in both the structures; in going to the next plane having vacancies, the vacancies are shifted as shown by arrows in Fig. 5, and when the successive shifts terminate after three steps, the structure is that reported earlier, while when they terminate after four steps, the structure is that given by Bertaut. Hirakawa and Okazaki found that these two structures are stable in different temperature ranges:

- **Structure with \( C = 4c \)**
  - mono-(or tri-)clinic, stable below 317 ± 3 °C.
- **Structure with \( C = 3c \)**
  - hexagonal, stable between 317° and 375 ± 3 °C.

The transition temperature of 317 °C is not definite, depending on the materials from which the sample is made, and in some cases the structure with \( 4c \) cannot be obtained. Above 375 °C the vacancies are distributed at random. The hexagonal and random structures can be quenched to room temperature, but the quenched random structure changes to the hexagonal structure in one or two hours.

The magnetic properties observed by torque measurements are as follows: — The crystal of the hexagonal structure, obtained by quenching from 317 ~ 375 °C is magnetized perpendicularly to the c-axis above — 150 °C, showing no measurable anisotropy within the c-plane, but below — 150 °C it is magnetized parallel to the c-axis (Fig. 6). On the other hand, the crystal of the Bertaut type structure (probably monoclinic, the c-axis being tilted a little), which can be obtained by slow cooling, shows a strong six-fold anisotropy in the c-plane over the whole range of temperature covered by the experiment (above liquid air temperature), the easy axis of magnetization being [1010] or its equivalent. A strange fact found is that the axis of easy magnetization turns towards the c-axis in the plane containing [1010] and c-axis in a gradual manner when the temperature is lowered below — 130 °C (Fig. 6), as already reported [12]. The six-fold anisotropy within the c-plane seems to be the consequence of twinning structure in which the monoclinic axes are distributed in a six-fold manner, each crystalline domain having its own unique easy axis of magnetization. Some magnetic domain patterns have been photographed and indicated such a structure.

The Curie point was observed at 150 °C and the saturation magnetization was measured against temperature. When the latter was extrapolated to absolute zero, a value of 70 gauss, or 3.8 Bohr magnetons per 2Fe$_7$Se$_8$, was obtained for both the structures. If all the ferric ions are on the planes with vacancies, one would obtain 4 Bohr magneton per 2Fe$_7$Se$_8$, assuming antiparallel spins on alternate layers. It is noted that in the case of pyrrhotite a value of 5.5 Bohr magnetons per 2Fe$_7$S$_8$ is reported.

(4) ferrite-chromite series. — Studies on ferrites and related compounds are being carried out in Japan in various laboratories, but only one
of them will be reported here. Miyahara at Hokkaido University previously described the properties of the Cu ferrite-chromite series [13]:

\[
\text{[Cu}_x\text{Fe}_{1-x} \text{] } [\text{Cu}_{1-x}\text{Fe}_1 + x\text{[Cr]} \text{]} \text{O}_4,
\]

where ( ) and [ ] refer to the tetrahedral and octahedral sites, respectively, and it is assumed that the Cr ions are on the octahedral sites. The copper concentration on the tetrahedral sites, \( x \), was measured by X-rays. For samples quenched from 900 °C, \( x \) varied from 0.18 to 0.9 when \( t \) was varied from 0 to 2, and for slowly cooled samples \( x \) varied from 0.05 to 0.9. Thus the spinel type structure of Cu ferrite-chromite is inverse on the ferrite side and normal on the chromite side. This disappeared, and reappeared with the opposite sign beyond \( t = 1.4 \) (tetragonal expansion on the ferrite side and tetragonal contraction on the chromite side). These tetragonalties disappeared above 400 °C. The Curie temperature varied linearly with \( t \). The saturation magnetization extrapolated to absolute zero decreased with increasing \( t \), first slowly and then more rapidly. Néel's theory of ferrimagnetism applied directly to this series would predict a quite different variation of the saturation magnetization.

More recently he extended his study to the Ni, Co and Mg ferrite-chromite series. The results obtained for the Mg series are reproduced in Fig. 7 and Fig. 8. The structure is inverse for \( t < 0.6 \), normal for \( 1.2 < t \), and a gradual transition occurs in the intermediate region. The saturation magnetization increases approximately as Néel's theory predicts in the inverse region but decreases in the normal region towards the antiferromagnetic Mg-chromite. In the Ni and Co series observations were made on the variations of the lattice constant and saturation magnetization. The variation of the lattice constant in the Ni series indicated that the inverse type persisted up to \( t \sim 1.0 \), in which region the monotonically decreasing saturation magnetization approximately followed Néel's theory, but beyond \( t \sim 1.0 \) the structure changed gradually to normal. In the Co series, a gradual change to the normal type below \( t \sim 0.4 \) and persistance of the normal type beyond it were observed but the monotically decreasing saturation magnetization, similar to that in the Ni series, did not obey Néel's theory. At the moment no definite conclusion can be drawn for the spin arrangement in these ferrite-chromite series, but a certain anti-parallel spin arrangement on the octahedral sites must arise as Cr concentration increases.

(5) The hematite-ilmenite series, \( x\text{Fe}_2\text{Ti}_0\text{O}_5\) \((1 - x)\text{Fe}_2\text{O}_3\). — As known well, alpha hematite is an antiferromagnetic crystal showing a weak parasitic ferromagnetism. Its structure is such that the nearly even honey-comb net planes of ferric ions are imbedded in a nearly close-packed hexagonal stacking of oxygen ions, the ferric ions being accomodated in the positions octahedrally surrounded by the oxygen ions; the ferric spins point one way on one honey-comb net plane and the other way on the next plane, pointing perpendicularly to the c-axis above \(-15\) °C and parallel below it. Ilmenite, FeTiO_3, has a similar crystalline structure but layers of Fe and Ti alternate along the c-direction. The spins of Fe point parallel to the c-axis and form an antiferromagnetic layer structure according to neutron diffraction measurements [14], and the Néel point is at \( 68 \) °K [15].

The study of the solid solutions of hematite and
Ilmenite has been undertaken by Ishikawa and Akimoto [16] at Tokyo University and by Kawai and Kume at Kyoto University. The former authors prepared artificial samples over the whole concentration range and the samples were quenched from 1200 °C after having been left at this temperature for more than 12 hours or only for six hours; the samples obtained by the latter treatment, when re-annealed properly, showed nearly the same characteristic as the samples obtained by the former treatment. The latter authors used natural samples with \( x \geq 1/2 \) and artificial samples with \( x < 1/2 \); the natural samples are believed to have been produced under a high pressure and at low temperatures. The results obtained by these two pairs of authors are somewhat contradictory.

Ishikawa and Akimoto observed that the unit cell volume changes linearly with hematite (or ilmenite) concentration, while Kawai and Kume found a certain deviation from linearity. They both found that the hematite-rich samples (\( x < 1/2 \)) are weakly ferromagnetic and the ilmenite-rich samples (\( x > 1/2 \)) strongly ferromagnetic. I and A observed that the saturation magnetization extrapolated to absolute zero of the ilmenite-rich samples shows a maximum at about \( x = 3/4 \), the maximum value being about 2.5 Bohr magnetons per mole (for well annealed samples) and falls on both sides, while K and K observed the same quantity to follow approximately

\[
4 \mu_B x - 5 \mu_B 2(1 - x),
\]

which varies linearly with \( x \) and vanishes at \( x = 10/14 \). This law is, however, dubious as the authors refer only to a few different concentrations, and it is not improbable that the saturation magnetization of the natural samples does not vanish between \( x = 1 \) and \( x = 1/2 \). The main difference between the artificial samples and the natural samples seems to lie in that the latter show higher values of the saturation magnetization on the ilmenite side. In adding hematite to ilmenite, a fraction of \( Ti^{4+} \) (valency 4 being assumed in accordance with no spin moment, as neutron diffraction experiment indicates) is replaced by \( Fe^{3+} \) and the same fraction of \( Fe^{2+} \) by \( Fe^{3+} \). If the titanium ions and ferrous ions are on alternate layers and the ferric ions on both layers, and if furthermore the spins of all these ions form the antiferromagnetically arranged ferromagnetic layers, the saturation moment would result only from the ferrous ions and it would be \( 4\mu_B \) for the pure ilmenite and would decrease linearly with the hematite concentration, vanishing at the pure hematite. A partial disorder of the titanium ions may be possible in the artificial samples when the concentration of ilmenite is large, and this might account for the decreasing saturation magnetization of the artificial samples towards the ilmenite side.

I and A found that the Curie temperature of the quenched samples varied linearly with \( x \) over the whole range of the latter, from 950 °K at \( x = 0 \) to 55 °K at \( x = 1 \); the pure ilmenite was found to be antiferromagnetic with a Néel point at 55 °K. On the other hand, I and A with well-annealed samples and K and K with natural and artificial samples observed that the Curie point falls to the ilmenite side but not linearly (see Fig. 11); K and K further found a Néel point-like anomaly above the Curie point (Figs. 11, 12 and 13). They observed a change in electrical conductivity at the latter...
temperature, and when this temperature was extrapolated to $x = 1$ a value of 70 oK was obtained, which is close to the Néel point of ilmenite, 68 oK, observed by Bizette and Tsaï [15]. The existence of the Néel point in homogeneous samples is hard to believe, however.

![Fig. 11](image1)

**Fig. 11.** — Curie temperature and Néel temperature of the ilmenite-hematite series; black circles: natural samples white circles: artificial samples (Kawai and Kame).

![Fig. 12](image2)

**Fig. 12.** — Saturation magnetization versus temperature of an ilmenite-hematite solid solution.

An illuminating experiment done by I and A is the observation of the transition temperature of the order-disorder of Ti and Fe (Fig. 9). It falls towards the hematite side, so that the samples on the hematite side obtained artificially would have more or less random distribution of all the cations. In natural samples the distribution may be more ordered. Such a difference may account at least for a part of the different results.

I and A extended their study to the series of $x\text{MnTiO}_3(1-x)\text{Fe}_2\text{O}_3$, with $M =$ Ni, Co, Mn and Mg. In all these series, solid solutions cannot be formed in a certain range of mixing ratio which includes 1:1. The solid solutions on the ilmenite side have an $R3$ structure and are ferromagnetic at low temperatures, except for $M =$ Mg, and the saturation magnetization in the three series $M =$ Fe, Ni, Co behaves similarly with varying mixing ratio. The magnetization in the Mn series is small and appears to indicate that the spin superstructure of the antiferromagnetic $\text{MnTiO}_3$ is different. The hematite side has a $R3c$ structure and is always parasitically ferro whose intensity is independent of the kind of $M$. The essential part of these experimental results is shown in Fig. 10.

(6) **Other investigations.** — An extensive study of the 1:1 and 2:1 compounds of the iron group elements with O, S, Se, Te, Sb, As and P is being done by the group headed by Prof. Hirone at Tohoku University, which I expect will be reported by Hirone himself. Dr. Iida at Tokyo University has been engaged in the field cooling effect of Co-ferrite diluted in magnetite [17], and he believes that a certain directional configuration of cation vacancies and Co ions is set up by field cooling and it introduces an additional anisotropy energy. He recently looked for the effect of $V^{3+}$ but negative result was obtained. He started the study of the $\text{Ni}^{2+}-\text{Fe}^{3+}-M-O$ series with $M =$ alkali metals, alkaline earth metals and several polyvalent metals.

### III. Theoretical studies.

(1) **The monoxides of Fe and Co.** — Among the monoxides of Mn, Fe, Co and Ni, FeO and CoO are peculiar in their magnetic properties and crystalline deformations below the Néel point. While in MnO and NiO the spin direction appears to be in one of the $(111)$ planes and the corresponding $[111]$ axis contracts by $10^{-3}$ below the Néel point, the spins in FeO align along the $[111]$ axis and an expansion of
about 1% occurs along this axis, and the spins in CoO appear to align along one of the [100] axis and this axis contracts by about 1%. Kanamori [18] at Osaka University explained these peculiarities by considering the orbital moments of Fe\(^{++}\) and Co\(^{++}\) which partly remain in the cubic crystalline electric field. The orbital state of Fe\(^{++}\) in the cubic crystalline field is triply degenerate corresponding to the three wave functions, of the forms \(yz, zx\) and \(xy\), of the extra one d\(\varepsilon\) electron. That of Co\(^{++}\) is also triply degenerate corresponding to the same wave function of one d\(\varepsilon\) hole (approximately). The spin-orbit coupling energy makes the spin and orbital moments align parallel. The resulting form of the cloud of the extra electron or hole, which is flat perpendicularly to the direction of the spin, deforms the crystal in the observed way. The anisotropy energy, which determines the direction of the spins was shown to arise mainly from two origins: the interaction between spin and deformation, and the interaction between neighbouring spins through the electric interaction between their non-spherical charge distribution, both combined with the spin-orbit interaction. The former dominates in CoO and orients the spins along one the cubic axes, and the latter dominates in FeO orienting the spins along one of the cube diagonals. In FeO the rhombohedral spin arrangement adds another anisotropy energy which makes the unique rhombohedral [111] axis the easy axis of magnetization. In CoO, the same kind of anisotropy energy tilts the axis of magnetization a little from the cubic axis, away from the rhombohedral axis. The interpretation of the neutron diffraction line intensities of CoO in terms of this picture was underkaten by Nagamiya and Motizuki [19]. They predict that the angle of deviation is about 10\(^{\circ}\).

Spin waves in CoO are being studied by Tachiki (Osaka University) and by Kitano (University of Osaka Prefecture). The existence of the residual orbital moment makes the treatment intricate but interesting theoretically. Tachiki roughly estimated the antiferromagnetic resonance wave lengths in CoO to be 40 and 20 microns, which do not significantly vary with the applied magnetic field. The corresponding experiment is being planned by Uchida and Kondoh.

(2) FeCl\(_2\), CoCl\(_2\), NiCl\(_2\), and MnBr\(_2\). — In all these hexagonal layer crystals, spins on one cation layer point parallel and spins on the adjacent layer antiparallel, according to neutron diffraction studies. The crystal structure of the three chlorides (and also of MnCl\(_2\)) can be derived from the NaCl structure by removing alternate (111) layers of cation, and that of MnBr\(_2\) from the NiAs structure by removing alternate (0001) layers of cation. Within the same layer a strong ferromagnetic coupling seems to operate, except for the Mn halides, and a weak antiferro coupling between adjacent layers. Kanamori theoretically considered the intra-layer superexchange coupling (and several other types of superexchange mechanisms applicable to other compounds) and furthermore studied the anisotropy energies and metamagnetic behaviours of these halides. His treatment of the superexchange mechanism will be given first.

(2a) Intra-layer superexchange mechanism. — Each cation in these halides is surrounded octahedrally by halogen ions, so the cation finds itself in a cubic crystalline field with an additional small trigonal field. The three principal axes of the octahedron will be taken as \(x, y, z\)-axes. The trigonal field is along [111]. Now, two superexchange mechanisms are conceivable. One is such that one outer p electron of Cl\(^{−}\) (or Br\(^{−}\)) in orbit \(p_z\) (wave function proportional to \(x\)) is transferred to the d orbit of the cation which neighbours the Cl\(^{−}\) (or Br\(^{−}\)) in the \(x\)-direction, another outer p electron in orbit \(p_y\) is simultaneously transferred to another cation neighbouring in the \(y\)-direction, and the two unpaired electrons left on the anion couple each other to align their spins parallel, since \(p_z\) and \(p_y\) have orthogonal wave functions and so the exchange integral between them is positive. This superexchange coupling gives rise to ferromagnetic coupling. The second mechanism, which is probably more important, is similar to that proposed by Anderson [20]. Only one p electron, say in orbit \(p_x\), is transferred at a time and the spin of the unpaired electron left on the anion couples with the spin of the other cation by the ordinary exchange interaction. This mechanism gives either ferro or antiferro coupling depending on the sign of the latter exchange integral. In Ni\(^{++}\), there are two unpaired d\(\varepsilon\) electrons, with wave functions of the forms

\[
3z^2 - r^2 - p^2 \quad \text{and} \quad x^2 - y^2,
\]

and since these wave functions are orthogonal to the \(p_x\) wave function, owing to different symmetries, the exchange integral is positive, hence the coupling is ferro. In Co\(^{++}\), there is another unpaired d electron in d\(\varepsilon\) orbit, and since one of the three d\(\varepsilon\) wave functions, \(xy\), which mostly overlaps with the \(p_x\) function, is non-orthogonal to the latter, the d\(\varepsilon\) electron contributes a negative exchange integral. Going over to Fe\(^{++}\) and Mn\(^{++}\), the negative contribution from the d\(\varepsilon\) electrons will increase. Therefore the Neél point will lower in this order. Table 2 gives some data of these halides.

### TABLE 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>NiCl(_2)</th>
<th>CoCl(_2)</th>
<th>FeCl(_2)</th>
<th>MnBr(_2)</th>
<th>MnCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_N) (°K)</td>
<td>50</td>
<td>25</td>
<td>23.5</td>
<td>2.16</td>
<td>(\sim 2)</td>
</tr>
<tr>
<td>(\Theta) in (\chi = C(T - \Theta))</td>
<td>68</td>
<td>38</td>
<td>48</td>
<td>4.66</td>
<td>-3.3</td>
</tr>
<tr>
<td>Spin axis</td>
<td>(\perp c)</td>
<td>(\perp c)</td>
<td>(\parallel c)</td>
<td>(\perp c)</td>
<td>?</td>
</tr>
</tbody>
</table>
The anomalous behaviour of FeCl₂ is to be expected, as is discussed below. The ferromagnetism of CrCl₃ is understood by a similar argument as above.

(2b) The magnetic properties, particularly of FeCl₂. — The orbital state of the extra one d⁵ electron of Fe²⁺⁺, which is triply degenerate in the cubic field, is split into two by the additional trigonal field. The corresponding wave functions are

\[ yz + zx + xy \] for singlet

and

\[ yz + e^{2\pi i/3}zx + e^{4\pi i/3}xy \] for doublet

where the trigonal axis is [111] and mixing of the d’y orbitals is neglected. For the singlet the expectation value of the component of orbital angular momentum along the trigonal axis is zero and for the doublet it is either +1 or -1 in units of ℏ. The spin couples strongly with the orbital moment in the doublet and the spin and orbital magnetic moments point parallel in the lowest spin-orbit state. So, if the doublet lies lower than the singlet, the magnetization axis is parallel to the c-axis and it will be very difficult to turn it aside. Therefore, the susceptibilities parallel and perpendicular to the c-axis would be much different. Kanamori inferred, by analysing the susceptibility above the Néel point, that the first excited spin-orbit state is separated from the ground spin-orbit state by \( kT_r \). It appears that the doublet-singlet separation is several times larger than this. The calculation of the trigonal field was also undertaken, but it was found that the polarization of the chlorine ions critically affects the results and so no definite conclusion was obtained.

The above model for FeCl₂ has two consequences: the coupled spin and orbital moments can point either up or down along the c-axis, not sideways, so that the statistical assembly is just what is called the Ising model, for which one expects a higher Néel point than for a system of isotropic spins if the exchange integral is the same; another consequence is that the antiferromagnetic layers become ferromagnetic when the component of applied field along the c-axis exceeds a certain value (about 10 000 Oe) and that this occurs without any deviation of the sublattice magnetizations from the c-axis. The reason for it is that the external field overcomes the weak inter-layer coupling, as already suggested by Néel [21].

In the case of CoCl₂, there are, roughly speaking, two unpaired d⁵ electrons, or, one d⁵ hole in Co²⁺⁺. Therefore the singlet lies lower. In this case the second order perturbation energy of \( \lambda L S \) will make the c-plane the easy plane of magnetization, the upper doublet contributing a small component of \( L \) in the c-plane. Also in NiCl₂, in which case the ground orbital state of Ni²⁺⁺ in the cubic crystalline field is a singlet, the second order perturbation of \( \lambda L S \) as well as the magnetic dipolar coupling, will stabilize the magnetization in the c-plane. When a high field is applied in the c-plane in the case of these chlorides, the antiparallel spins will turn continuously with increasing field strength and they will finally coincide.

MnBr₂ is being studied by Nagamiya and Suzuki. The dipolar energy is not at all negligible compared with \( kT_r \) in this substance; assuming that the spins in each layer all are parallel (which is not true according to a recent neutron diffraction experiment), the dipolar energy associated with turning over a spin in the ordered antiferromagnetic arrangement is calculated to be 1.1 cm⁻¹ and the corresponding energy in the Weiss field approximation is \( 3\hbar kT_r/(S + 1) = 3.2 \) cm⁻¹ for \( S = 5/2 \) using the observed Néel temperature. The dipolar anisotropy energy constant is 1.6 cm⁻¹ per ion. The antiferromagnetic resonance is also studied.

Metamagnetic behaviours of antiferromagnetic bodies in high magnetic fields have been studied by various authors, notably by Gorter et al. [22]. Essentially the same, but a little more detailed, theoretical study was done by Kanamori, Motizuki and Yosida [23] prior to Gorter et al., but the content was not published in an European language. Motizuki recently extended her study to the interesting metamagnetism of chrome methyl amine alum (Cr(CH₃ NH₃)₂(SO₄)₂12H₂O) which has a very low Néel temperature of \( 0.02 \) °K. The details will be published in Journ. Phys. Soc. Japan, together with some points contained in her previous publication with Kanamori and Yosida.

(3) Crystals of the rutile type. — Many studies have been done on MnF₂, mostly in U. S. A., and we now know in detail the state of the ions in this substance. However, other crystals of the rutile type remain more or less obscure.

Yoshimori (University of Osaka Prefecture) studied possible spin superstructures in the rutile crystal. Depending on the relative magnitudes of the three exchange integrals, \( J_1, J_2, J_3 \), where \( J_1 \) is the exchange integral between a corner cation and a neighbouring body-centre cation, \( J_2 \) that between corner cations neighbouring along the c-axis and \( J_3 \) that between those neighbouring along the a-axis, there appear three types of the spin superstructure. One is the MnF₂ type structure, in which the corner cations and body-centre cations point antiparallel, the second is the structure proposed by Bizette [24], Yosida [25] and Erickson [26] for MnO₂ which consists of uncorrelated antiferromagnetic simple tetragonal sublattices of corner atoms only and body-centre atoms
only, and the third is a new type in which positive spins on the corner sites and negative spins on the body-sites are spiralled along the c-axis. The stability boundaries are shown in Fig. 14 assuming that all the exchange interactions act in antiferromagnetic way. The pitch of the screw varies continuously depending on the value of $J_2/J_1$, even if there exists anisotropy energy; the boundary at $J_2/J_1 = 1$, near which the pitch tends to infinity, is shifted in MnO$_2$ to 1.19 if dipolar interactions are taken into consideration and the pitch corresponding to the new boundary is about 5c; between $J_2/J_1 = 1.19$ and 1.56 the spins spiral in a plane which contains the c-axis, and beyond 1.56 they are parallel to the c-plane and spiral about the c-axis, again taking dipolar interactions only into account. A screw structure of pitch 3.5c, which occurs at $J_2/J_1 = 1.60$, seems to account for the neutron diffraction lines by MnO$_2$ supplied privately by Dr. Erickson. The reciprocal lattice points are each split into two and displaced by plus and minus wave vectors of the spiral. A spin wave treatment has also been applied.

In conclusion, the writer would like to summarize a contribution by Toshima and Nakamura (Kyushu University) to the theory of CoF$_3$. Previously, Nakamura and Taketa [27] analyzed the experimental data given by Stout and came to the conclusion that the lowest Kramers doublet of Co$^{++}$ in this crystal is separated from the next doublet by 130 k. Stout and Catalano [28] measured the specific heat and found that the separation must be twice as large. Further experimental data have accumulated: Tinkham [29] measured the paramagnetic resonance of Co$^{++}$ dilute in ZnF$_2$, and Shulman and Jaccarino [30] as well as Baker and Hayes [31] measured the fluorine nuclear magnetic resonance. Toshima and Nakamura examined how far the previous theory accounts for the new data and in what way it is to be modified. First, the $g$-factor of the lowest Kramers doublet predicted by the previous theory is compared with that observed by Tinkham:

<table>
<thead>
<tr>
<th>Nakamura-Taketa</th>
<th>Tinkham</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_z$</td>
<td>1.92</td>
</tr>
<tr>
<td>$g_y$</td>
<td>6.24</td>
</tr>
<tr>
<td>$g_x$</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Here the value in ( ) was estimated by Tinkham on the basis of the crystalline field theory and Abragam and Pryce’s hyperfine structure theory; the $x$, $y$, $z$ axes are taken so that the $z$-axis coincides with the c-axis, the $x$-axis is along the line connecting the given Co ion to one of the two F ions neighbour in opposite sides in the [110] or [110] direction, and the $y$-axis perpendicular to the both. Next, for the hyperfine coupling constant of F nucleus the spin part of the above $g$-factor must be considered, since the main part of that coupling arises from the s-electron hole produced in the F atom and the spin of this hole is a part of the Co spin. Such spin part was calculated and it was found that the ratio $g_x$ (spin)/$g_y$ (spin) was 4.76/3.11 = 1.53, which is in close agreement with the observed ratio of the hyperfine coupling constants $A_x/A_z = 1.52$, indicating that the hyperfine coupling in F is isotropic. Tinkham himself also estimated this ratio and found it to be 4.42/3.25 = 1.36. However, the assumption of isotropic coupling may not strictly apply. Toshima and Nakamura further considered the paramagnetic shift in F nuclear resonance. This shift is proportional to the thermal average value of the spin angular momentum of Co$^{++}$ in the direction of the applied field and depends on temperature through thermal excitation to the next Kramers doublet and thermal motion of the spin. Toshima and Nakamura modified the previous theory by assuming the doublet-doublet separation to be 240 k, in conformity with Stout and Catalano’s observation, and showed that both the paramagnetic shift and the susceptibility plotted against temperature could well be represented by their theory.

The writer thanks all those Japanese colleagues whom he quoted in the text and who kindly supplied their recent data, particularly Profs. Uchida, Hirahara, Miyahara, and Drs. Hira-kawa, Nakamura, Ishikawa and Kawai. He also appreciates illuminating discussions with Dr. Kana-mori.

REFERENCES


**DISCUSSION**

**Mr. Jacobs.** — Do the torque measurements on NiO allow an estimate of the appropriate susceptibilities so as to estimate what magnetic field would be needed to cause irreversible movement of the antiferromagnetic domain walls?

**Mr. Nagamiya.** — Uchida and Kondoh applied a field up to 10 000 Oe and found some irreversible effects for some samples, but not always. The effects seem to depend on the preparation of the sample and we do not know well the determining factor.

**Mr. Van Vleck.** — Is the type of pyrrhotite studies by Prof. Hirahara the same as that for what gyromagnetic measurements made at Zurich some 30 years gave the surprising result $g = 0.6$? It would be very interesting to correlate the behavior with the Japanese magnetic measurements and theory. Since the result $g^2 = 0.6$ is rather unusual I would like to ask Prof. Sucksmith whether new measurements could not be made on the gyromagnetic ratio of pyrrhotite?

**Mr. Sucksmith.** — I think it would be quite easy to carry out this experiment for pyrrhotites of different constitution, and investigate the relationship between the apparent $g$ value and the constitution of pyrrhotites of different intensities of magnetization. I hope someone will investigate this important point.

**Mr. Casimir.** — As far as I remember the Zurich experiments of Dr. Goeterier were carried out with natural crystals and I do not think that the composition was accurately analyzed; also there were some experimental difficulties so it might will be worth while to repeat the measurements.