SPONTANEOUS MAGNETIZATION AS A FUNCTION OF TEMPERATURE FOR MIXED CRYSTALS OF FERRITES WITH SEVERAL CURIE TEMPERATURES

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Summary
For mixed crystals of ferrites with more than one Curie temperature it is shown by an example how the spontaneous magnetization can be calculated as a function of temperature.

Résumé
Un exemple montre comment il est possible de calculer l’aimantation spontanée en fonction de la température pour des cristaux mixtes de ferrites avec plusieurs températures de Curie.

Zusammenfassung
Mit einem Beispiel wird gezeigt, wie der Verlauf der spontanen Magnetisierung für Ferrit-Mischkrystalle mit mehreren Curie-Temperaturen, berechnet werden kann.

1. Introduction

Yafet and Kittel 1) have predicted the existence of more than one Curie temperature for a spinel structure containing only one kind of magnetic ions. They expressed these Curie temperatures in some basic coefficients which play a role in Néel’s 2) theory of antiferromagnetism. The possibility of more than one Curie temperature was a consequence of the lattice of (tetrahedral) $A$ sites and that of (octahedral) $B$ sites each being composed of two sublattices ($A_I$, $A_{II}$ and $B_I$, $B_{II}$ respectively). Between these sublattices $A_I$ and $A_{II}$ and also between $B_I$ and $B_{II}$ the same kind of antiferromagnetic interaction exists as between an $A$ and a $B$ sublattice. When calculating the molecular magnetic fields the $AB$ interaction is taken into account by means of a term containing the interaction coefficient $n$ whereas the $A_I A_{II}$ and the $B_I B_{II}$ antiferromagnetic interactions are accounted for by a term containing $|\alpha_z|n$ and $|\gamma_z|n$ respectively. The coefficient $n$ is taken positive (owing to a later choice for positive directions for partial magnetizations) and $|\alpha_z|$ and $|\gamma_z|$ are the absolute values of negative coefficients $\alpha_z$ and $\gamma_z$ which in some respects may be called demagnetization coefficients.

The coefficient $|\alpha_z|$ is to be distinguished from an analogous coefficient $|\alpha_1|$ which is used in the expression for the $A_I A_I$ interaction and also for the $A_{II} A_{II}$ interaction. In the same manner $|\gamma_z|$ is different from the coefficient $|\gamma_1|$ which must be introduced for the $B_I B_{II}$ and the $B_{II} B_{II}$
interactions. Therefore $a_1$ and $\gamma_1$ resemble demagnetization coefficients still better than $a_2$ and $\gamma_2$.

To show the use of all these coefficients we will calculate the molecular field $h_{AI}$ for an ion of the sublattice $A_I$. Besides $n$, $a_1$, $a_2$, $\gamma_1$ and $\gamma_2$ we still need the number $(\lambda N)$ of magnetic ions on $A$ sites and the number $(\mu N)$ of the same kind of magnetic ions on $B$ sites in one “grammole”, $N$ being Avogadro’s number. These ions are assumed to be distributed equally over the sublattices $(\frac{1}{2} \lambda N$ on both $A_I$ and $A_{II}$ and $\frac{1}{2} \mu N$ on both $B_I$ and $B_{II}$).

The spontaneous magnetization brought about by $N$ magnetic ions of the $A_I(A_{II})$ sublattice is called $I_{asI}(I_{asII})$ and that originating from $N$ ions in $B_I(B_{II})$ will be called $I_{bsI}(I_{bsII})$.

If $I_{asI}$ and $I_{asII}$ are parallel we assume them to be directed toward the left and $I_{bsI}$ and $I_{bsII}$ (if parallel) directed toward the right. Analogous assumptions will be made for the molecular fields $h_{asI}$, $h_{asII}$, $h_{bsI}$, $h_{bsII}$ at an ion of $A_I$, $A_{II}$, $B_I$, $B_{II}$ respectively.

In the case $I_{asI}/I_{asII}$ and $I_{bsI}/I_{bsII}$ the role of the coefficients is shown in

$$
\begin{align*}
    h_{asI} &= n_1^\lambda a_1 I_{bsI} + n_2^\lambda a_2 I_{bsII} - |a_2| n_1^\lambda \gamma_1 I_{asII} - |a_1| n_2^\lambda \gamma_2 I_{asI}, \\
    h_{bsI} &= n_1^\lambda \gamma_1 I_{asI} + n_2^\lambda \gamma_2 I_{asII} - |a_1| n_1^\lambda a_2 I_{bsII} - |a_2| n_2^\lambda a_1 I_{bsI}.
\end{align*}
$$

We did not use different symbols to distinguish the vectors $I_{asI}$, $I_{bsI}$, $h_{asI}$, etc., from their absolute values, the latter being meant in the above equations. In equations these symbols will always mean absolute values. The first two terms in the right-hand members originate from the antiferromagnetic $AB$ interaction, the last two from the “demagnetizing” action in the $A$ lattice or $B$ lattice.

According to Yafet and Kittel the spin directions in $A_I$ and $A_{II}$ may be the same but they may also differ from one another (the angle between $I_{asI}$ and $I_{asII}$ then being called $2\phi$). The spin directions in $B_I$ and $B_{II}$ need not always be the same either: there may also be an angle $2\psi$ between $I_{bsI}$ and $I_{bsII}$.*). Since $I_{asI}$, of course, always points into the direction of $h_{asI}$ and $I_{asII}$ into that of $h_{asII}$ (the same holding for $I_{bsI}$ and $h_{bsI}$ and for $I_{bsII}$ and $h_{bsII}$), the same angles $2\phi$ and $2\psi$ will exist between the directions of $h_{asI}$ and $h_{asII}$ and between $h_{bsI}$ and $h_{bsII}$ respectively, as has been indicated separately in fig. 1. The relations between the molecular fields and the partial magnetizations in the case $\phi > 0$, $\psi > 0$ will be more complicated than the equations (1) holding for the case $\phi = \psi = 0$. Since the magnetic contribution (if antiferromagnetic) of a partial magnetization to some molecular field is always antiparallel to this partial magnetization we have in fig. 1 where $\phi > 0$, $\psi > 0$:

*) The angles here called $\phi$ and $\psi$ are not the same as those indicated by $\varphi$ and $\psi$ by Yafet and Kittel 1).
\[ h_{\text{AI}} = n_2 \mu I_{bsI} \cos (\psi + \varphi) + n_2 \mu I_{bsII} \cos (\psi - \varphi) - \left| a_1 \right| n_2 \lambda I_{asI} \cos 2\psi - \left| a_2 \right| n_2 \lambda I_{asII}, \]
\[ h_{\text{BI}} = n_2 \lambda I_{asI} \cos (\psi + \varphi) + n_2 \lambda I_{asII} \cos (\psi - \varphi) - \left| \gamma_1 \right| n_2 \mu I_{bsI} \cos 2\psi - \left| \gamma_2 \right| n_2 \mu I_{bsII}. \]

It may also occur that for instance the sublattices \( A_I \) and \( A_{II} \) are spontaneously magnetized but the sublattices \( B_I \) and \( B_{II} \) not yet \((I_{bsI} = I_{bsII} = 0)\) or vice versa. In this way, according to Yafet and Kittel, several Curie points may be found where some ordering effect or some change in the ordering of spins occurs. These authors for instance considered a very interesting but complicated case where the highest Curie temperature \((T_1)\) was given by the first occurrence of the spontaneous magnetization of the ions on \( A_I \) and \( A_{II} \) (with \( \varphi = \pi/2 \)), the spins of the ions on \( B_I \) and \( B_{II} \) remaining still unordered. For this temperature they found

\[ T_1 = C n_2 \lambda \left( |a_2| - |a_1| \right), \]

where \( C \) is a constant defined by

\[ C = N g^2 \mu_B^2 j(j + 1)/3k, \]

\( \mu_B \) being the Bohr magneton, \( k \) the Boltzmann constant and \( g \) and \( j \) the gyromagnetic ratio and the inner quantum number of the magnetic ion.

In this example the spontaneous magnetization of the ions on \( B_I \) and \( B_{II} \) took place at a lower temperature

\[ T_2 = C n \mu (|a_2| - |\beta|) < T_1 \]

with the abbreviation

\[ |\beta| = \frac{1}{2}(|\gamma_1| + |\gamma_2|), \]

and the partial magnetizations \( I_{bsI} \) and \( I_{bsII} \) (born at \( T = T_2 \) and increasing with decreasing temperature) were parallel \((\psi = 0)\). Their antiferromagnetic action on the \( A \) lattice caused the vectors \( I_{asI} \) and \( I_{asII} \) to
turn more and more to the left ($\varphi$ became $< \pi/2$) and at a temperature $T_3$ which could be found only in a graphical way the value $\varphi = 0$ was attained. In the whole interval $T_2 > T > T_3$ $\varphi$ remained zero. These values, $\varphi = \psi = 0$, for the first time occurring together at $T_3$, remained undisturbed for somewhat lower temperatures but not for very low temperatures since Yafet and Kittel assumed the basic coefficients (including $\lambda$ and $\mu$) to make $\varphi = 0$ but $\psi > 0$ at $T = 0$. The lowest temperature ($T_4$) at which both $\varphi$ and $\psi$ were still zero could be found from the basic coefficients only by means of a graphical solution. In the last interval $T_4 > T > 0$ the angle $\varphi$ remained zero whereas $\psi$ increased from 0 to $\arccos (\lambda/|\gamma_2|)$ at $T = 0$.

This example of Yafet and Kittel considered mathematically for the case of one kind of magnetic ions only will be extended in the present paper to the case of two kinds of magnetic ions (M and M') of which one kind (M) can occupy A sites as well as B sites whereas the other kind (M') occupies B sites only. This kind of mixed ferrites occurs often and may be important enough for a study in detail. Not only $T_2$, $T_3$ and $T_4$ but also the course of the spontaneous magnetization between these temperatures can be determined (graphically). Only the change in $T_2$ caused by the presence of the M' ions can be given by a simple formula.

2. Mixed ferrites, determination of $T_1$

We extend the case considered by Yafet and Kittel by assuming that one “grammole” contains $\lambda N$ magnetic ions M on A sites and $\mu N$ ions M together with $\mu' N$ magnetic ions M' on B sites. Thus this extension disappears for $\mu' = 0$.

The introduction of a second kind of magnetic ions in the B lattice implies the necessity to distinguish between the molecular magnetic field $h'_{b1}$ at an M' ion in $B_1$ and that ($h_{b1}$) at an M ion in $B_1$ and also between $h'_{b11}$ and $h_{b11}$ (at M' and M ions in $B_{11}$).

The molecular magnetic field at each M ion is brought about now not only by M ions (contribution proportional to $n$) but also by M' ions (contribution proportional to $n'$). On the other hand the molecular field at each M' ion now consists of contributions (proportional to $n'$) from M ions but also of contributions (proportional to $n''$) from M' ions. Just as in earlier papers they will be made. Properly we should have to introduce more than one factor $\gamma_1$, and more than one factor $\gamma_2$ for the antiferromagnetic action in the B lattice since several combinations in the B lattice would be possible owing to the presence of two kinds of magnetic ions. This, however, will not be done. The spontaneous magnetization ($I'_{bs1}$) of $N$ M' ions on $B_1$
is to be distinguished from the spontaneous magnetization \((I_{bs1})\) of \(N\) \(M\) ions on \(B_1\) and analogously \(I'_{bs1}\) from \(I_{bsII}\) in the sublattice \(B_{II}\).

The highest Curie temperature may be similar to that in the paper by Yafet and Kittel with only \(M\) ions:

\[
T_1 = Cn\frac{1}{2}\lambda(|a_2| - |a_1|),
\]

at which the spontaneous magnetizations of \(A_1\) and \(A_{II}\) are born (being directed antiparallel to one another, \(\varphi = \pi/2\)) whereas all spins in the \(B\) lattice remain still unordered.

3. Determination of \(T_2\)

The presence of \(M'\) ions can influence only the calculation of the lower Curie temperature \(T_2\) at which also the ions on \(B_1\) and \(B_{II}\) will be magnetized spontaneously. Here, however, one should know whether one kind of magnetic ions occupying \(B\) will be magnetized earlier, i.e. at a higher temperature than the other kind of occupants of \(B\). To answer this question we choose the temperature low enough to have to consider the situation given in fig. 2. The \(M\) an \(M'\) ions are assumed to be distributed equally over \(B_1\) and \(B_{II}\). Therefore we have in fig. 2

\[
\begin{align*}
h_{b1} &= n\frac{1}{2}\lambda I_{as1} \cos \varphi + n\frac{1}{2}\lambda I_{asII} \cos \varphi - |\gamma_2|n\frac{1}{2}\mu I_{bs1} - |\gamma_1|n\frac{1}{2}\mu' I_{bs1}, \\
h'_{b1} &= n'\frac{1}{2}\lambda I_{as1} \cos \varphi + n'\frac{1}{2}\lambda I_{asII} \cos \varphi - |\gamma_2|n'\frac{1}{2}\mu I_{bs1} - |\gamma_1|n'\frac{1}{2}\mu' I_{bs1}.
\end{align*}
\]

Application of (4) here gives

\[
h'_{b1} = (n'/n)\ h_{b1}
\]

\[\begin{align*}
\frac{1}{2}\lambda I_{as1} & \quad \frac{1}{2}\lambda I_{asII} \\
\frac{1}{2}\mu I_{bs1} + \frac{1}{2}\mu' I'_{bs1} & \quad \frac{1}{2}\mu I_{bsII} + \frac{1}{2}\mu' I'_{bsII}
\end{align*}\]

\[
\begin{align*}
h_{af} & \quad h_{bf} \\
h_{asI} & \quad h'_{bf} \\
h_{asII} & \quad h'_{bII}
\end{align*}
\]

Fig. 2. Partial magnetizations and molecular fields for \(T_2 > T > T_3\).
and analogously one can derive

\[ h'_{b11} = (n'/n) h_{b11}. \]

The assumption (4) therefore implies the simultaneous appearance or disappearance of the molecular fields at both kinds of ions (M, M') in B. The simultaneous appearance may take place at some temperature \( T_2 \) which now will be calculated. The values

\[ \eta = I_{bs1}/Ng\mu_B \text{ and } \eta' = I'_{bs1}/Ng'\mu_B \]

are still small for \( T \) just below \( T_2 \). The general formulae

\[
\begin{align*}
\eta &= (j + \frac{1}{2}) \coth (j + \frac{1}{2}) Q - \frac{1}{2} \coth \frac{1}{2} Q, \\
\eta' &= (j' + \frac{1}{2}) \coth (j' + \frac{1}{2}) Q' - \frac{1}{2} \coth \frac{1}{2} Q' = \\
&= (j' + \frac{1}{2}) \coth (j' + \frac{1}{2}) (n'g'/ng) Q - \frac{1}{2} \coth \frac{1}{2} (n'g'/ng) Q,
\end{align*}
\]

with \( Q = g\mu_B h_{bt}/kT \) and \( Q' = g'\mu_B h'_{bt}/kT \)

may be approximated giving

\[ h_{b1} = (T/C)I_{bs1} \text{ and } h'_{b1} = (T/C')I'_{bs1}. \]

Here \( C \) is defined by (3) and \( C' \) by

\[ C' = Ng'^2\mu_B^2j'(j' + 1)/3k, \]

where \( g' \) and \( j' \) are the gyromagnetic ratio and the inner quantum number for the M' ion. If the equations (6) and (7) are taken for \( T \) just below \( T_2 \), \( h_{b1} \) may be replaced by (11) and if further all symbols with index II are replaced by the corresponding ones with index I (on account of the symmetry in fig. 2) we obtain

\[
\begin{align*}
(T/C)I_{bs1} &= n\lambda I_{as1} \cos \varphi - |\beta|n\mu I_{bs1} - |\beta|n'\mu'I'_{bs1}, \\
(T/C')I'_{bs1} &= n'\lambda I_{as1} \cos \varphi - |\beta|n'\mu I_{bs1} - |\beta|n''\mu'I'_{bs1},
\end{align*}
\]

valid for \( T_2 - T \ll T_2 \).

Application of (4) gives with the same restriction

\[ I'_{bs1} = (n'C'/nC)I_{bs1} \text{ (} T_2 - T \ll T_2 \text{).} \]

An equation for \( h_{a1} \) analogous to (11) could not be given for \( T \) below \( T_2 \), the temperature then being too far from \( T_1 \) where \( h_{a1} \) was small. Instead of the value of \( h_{a1} \) we have, however, to consider the direction of \( h_{a1} \). Since \( I_{as1} \) as a matter of fact will point in the same direction as \( h_{a1} \), the contributions to \( h_{a1} \) originating from the several partial magnetizations must have components perpendicular to \( I_{as1} \) which compensate one another. This gives in fig. 2 the equation
n\frac{1}{2}\mu (I_{bst} + I_{bsII}) + n'\frac{1}{2}\mu'(I'_{bst} + I'_{bsII}) \sin \varphi = |a_2| n\frac{1}{2}\lambda I_{asII} \sin 2\varphi.

Replacing II by I and dividing by \sin \varphi we have

n\mu I_{bst} + n'\mu'I_{bst} = |a_2| n\lambda I_{asII} \cos \varphi. \quad (14)

Using this equation together with (13) in order to express all partial magnetizations occurring in (12) in \(I_{bst}\), we then obtain after dividing by \(I_{bst}\)

\[ T_2 = \left[ Cn\mu + C'n\mu' \right] (1/|a_2| - |\beta|). \quad (15) \]

If for a spinel containing M' and M ions in the ratio \(\mu'_1: (\lambda + \mu)\) the temperature \(T_2\) is determined experimentally and if this is done also for a spinel containing these ions in the ratio \(\mu'_2: (\lambda + \mu)\) the quotient of these temperatures will lead to the value of \(n'/n\), i.e. of \((n'/n)^2\). The value of \(T_2\) can be found from the experimental course of the spontaneous magnetization. For \(T_1 > T > T_2\) we have \(\varphi = \pi/2\) and \(I_{bst} = I_{bsII} = I_{bst} = I_{bsII} = 0\). Since \(I_{as} = I_{asII}\) and \(\varphi = \pi/2\) the total spontaneous magnetization is zero in this interval of temperature. At \(T_2\) it begins to appear and its course for lower temperatures will be studied below.

4. Molecular spontaneous magnetization for \(T_2 > T > T_3\)

In a following interval \(T_2 > T > T_3\) the angle \(\varphi\) will decrease from \(\pi/2\) to zero under the influence of increasing partial magnetizations in the \(B\) lattice which remain parallel \((\varphi = 0)\). A method for the determination of \(T_3\) will be given afterwards.

The spontaneous magnetization \(m_s\), calculated per "molecule" and expressed in \(\mu_B\) is

\[ m_s = \frac{1}{2}\lambda (I_{asI} + I_{asII}) \cos \varphi - \frac{1}{2}\mu (I_{bst} + I_{bsII}) - \frac{1}{2}\mu' (I'_{bst} + I'_{bsII})/|N\mu_B|. \]

Introducing as an analogue of (8) and (9)

\[ \xi = I_{as}/N\mu_B = (j + \frac{1}{2}) \coth (j + \frac{1}{2}) P - \frac{1}{2} \coth \frac{1}{2} P \] with \(P = g\mu_B h_{ai}/kT\), (16)

and replacing the index II by I (on account of symmetry) we have

\[ m_s = g |\lambda \xi \cos \varphi - \mu \eta - \mu' \eta' g'/g| \]

in which according to (14)

\[ \lambda \xi \cos \varphi = (1/|a_2|) [\mu \eta + (n'g'/ng) \mu' \eta']. \quad (17) \]

So in order to know \(m_s\) as a function of \(T\) it is sufficient to determine \(\eta\) and \(\eta'\) as functions of \(T\) and to substitute in

\[ m_s = g |\mu (1/|a_2| - 1) \eta + (g'/g) (n'/n |a_2| - 1) \mu' \eta'|. \]

An expression for \(\eta\) follows here from (8) and (10), where \(h_{bi}\) is given by the right-hand member of (6). Expressing here the first term by means of (14) in \(I_{bst}\) and \(I'_{bst}\) one obtains
\[ Q = (g\mu_B/kT) [n\mu I_{b1} + n'\mu'I_{b1}'] (1/|\alpha_2| - |\beta|). \]

By using the expression (15) for \( T_2 \), this equation can be written in the form

\[ a(T/T_2)Q = \mu \eta + (n'\mu'/n) \mu' \eta' \]

with the abbreviation

\[ a = [j(j+1) (2-f) + j'(j'+1) (n'\mu'/n)^2 f]/\beta. \]

With (8) and (9) the right-hand member of (18) can be drawn as a function of \( Q \) and the left-hand member is represented as a function of \( Q \) by means of a straight line through the origin, the inclination depending on \( T/T_2 \). Thus the abscissa \( Q \) of the common point is found as a function of \( T/T_2 \) and consequently also \( \eta \) and \( \eta' \) by (8) and (9), and with these the spontaneous magnetization \( m_s \) as a function of \( T/T_2 \) (at least in the interval \( T_2 < T < T_3 \)).

5. Determination of \( T_3 \)

For the graphical determination of \( T_3 \) (the highest temperature where \( \varphi = 0 \)) we should first determine \( \cos \varphi \) as a function of \( T/T_2 \) in the region \( T_2 > T > T_3 \) since \( T_3 \) is found by the condition \( \varphi = 0 \). The expression for \( \cos \varphi \) following from (14) contains \( \eta, \eta' \) and \( \xi \). In the preceding section we learned to find \( \eta \) and \( \eta' \) as functions of \( T/T_2 \), so that now also \( \xi \) is to be determined as a function of \( T/T_2 \). For \( \xi \) we need in (16)

\[ h_{al} = [n\frac{1}{2}\mu(I_{b1} + I_{b2}) + n'\frac{1}{2}\mu'(I_{b1}' + I_{b2}')] \cos \varphi - |\alpha_2| n\frac{1}{2} \alpha I_{ast} \cos 2\varphi - |\alpha_1| n\frac{1}{2} \lambda I_{ast} = \]

\[ = \cos \varphi [n\mu I_{b1} + n'\mu'I_{b1}' - |\alpha_2| n\lambda I_{ast} \cos \varphi] + (|\alpha_2| - |\alpha_1|) n\frac{1}{2} \lambda I_{ast}. \]

The first term disappears according to (14) and \( |\alpha_2| - |\alpha_1| \) can be expressed in \( T_1 \) by means of (5). Thus we have

\[ P = g\mu_B h_{al}/kT = [3/j(j+1)] (T_1/T) \xi. \]

Cutting the curve

\[ y = (j + \frac{1}{2}) \coth (j + \frac{1}{2})x - \frac{1}{2} \coth \frac{1}{2}x \]

by the straight line

\[ y = (1/3)j (j+1) (T/T_1)x \]

\( \xi \) is found as the ordinate of the common point, obviously as a function of \( T/T_1 \) and then easily as a function of \( T/T_2 \). The \( T/T_2 \)-dependence of \( \cos \varphi \) is now known, and where \( \cos \varphi \) becomes unity we find the value \( T_3/T_2 \).
6. Course of \( m_s \) in the region \( T_3 > T > T_4 \)

From \( T_3 \) to the temperature \( T_4 < T_3 \) which afterwards will be derived from the basic coefficients, the angles \( \varphi \) and \( \psi \) remain zero. In this rectilinear case the partial magnetizations \( \frac{1}{2} \lambda I_{ast} \) and \( \frac{1}{2} \lambda I_{asII} \) point to the left and \( \frac{1}{2} \mu I_{bsI} \), \( \frac{1}{2} \mu I_{bsII} \), \( \frac{1}{2} \mu' I_{bsI} \) and \( \frac{1}{2} \mu' I_{bsII} \) to the right and these vectors are equal in pairs (fig. 3). Per "molecule" the spontaneous magnetization, expressed in \( \mu_B \), amounts to

\[
m = g \left[ \lambda \xi - \mu \eta - (g'/g) \mu' \eta' \right].
\]

Fig. 3. Partial magnetizations and molecular fields for \( T_3 > T > T_4 \).

In the present region of \( T \) none of the three Brillouin functions for \( \xi, \eta \) and \( \eta' \) can be replaced by a simple approximation since \( T \) generally is far from both Curie temperatures \( T_1 \) and \( T_2 \). The three arguments of these functions are

\[
P = \left( g\mu_B / kT \right) \left[ n\mu I_{bsI} + n'\mu' I_{bsI} - |\alpha|n\lambda I_{ast} \right],
\]

where symbols with II have been replaced by those with I and \( |\alpha| \) has been introduced, defined by

\[
|\alpha| = \frac{1}{2}(|\alpha_1| + |\alpha_2|),
\]

\[
Q = \left( g\mu_B / kT \right) \left[ n\lambda I_{ast} - |\beta| n\mu I_{bsI} - |\beta| n'\mu' I_{bsI} \right],
\]

\[
Q' = (n'g'/ng)Q.
\]

Fortunately \( Q \) can be expressed in \( P \) since from (20) and (21)

\[
|\beta|P + Q = (g\mu_B / kT) \left( 1 - |\alpha| |\beta| \right) n\lambda I_{ast}
\]

and therefore

\[
Q = (1 - |\alpha| |\beta|) \left[ (j + \frac{1}{2}) \coth (j + \frac{1}{2})P - \frac{1}{2} \coth \frac{1}{2}P \right] (\tau/T) - |\beta|P
\]

with

\[
\tau = 3Cn\lambda/j(j + 1).
\]

Thus all three values \( \xi, \eta \) and \( \eta' \) are expressible in \( P \) and in order to find \( m_s \) as a function of \( T \) we first should find \( P \) as a function of \( T \). This can be done by writing (20) in the form

\[
(T/\tau)P + |\alpha|\xi = (\mu/\lambda)\eta + (n'g'/ng) (\mu'/\lambda)\eta'
\]
and replacing \( \xi, \eta \) and \( \eta' \) by the functions of \( P \) mentioned above. \( P \) thus being found graphically as a function of \( T/\tau \) we finally know \( \xi, \eta, \) and \( \eta' \); thus \( m_s \) in the linear case, i.e. for \( T_3 > T > T_4 \), is found as a function of \( T/\tau \).

7. Determination of \( T_4 \)

In order to find \( T_4 \), the lowest temperature for the rectilinear case, we have to consider the situation illustrated in fig. 4 and holding for the next region \( T_4 > T > 0 \). Here \( \psi \) and \( \psi' \) are angles varying with \( T \) and indicating the directions of \( I_{bst} \) and \( I'_{bst} \) separately. However, it will be shown that \( \psi = \psi' \) on account of the introduction of only one factor \( |\gamma_2| \) and only one factor \( |\gamma_2| \) notwithstanding \( B_I \) and \( B_{II} \) are occupied by two different kinds of magnetic ions.

\[
\sin \psi + \sin \psi' = \sin \theta + \sin \theta' = 0.
\]

Since \( I_{bst} \) must have the direction of \( h_{bst} \), the contributions to \( h_{bst} \), made by the several partial magnetizations must have components perpendicular to \( I_{bst} \), the sum of which is zero, those on one side compensating those on the other side:

\[
n_{2}^{2} \lambda (I_{ast} + I_{ast II}) \sin \psi = |\gamma_2| n_{2}^{2} \mu I_{bst II} \sin 2\psi + |\gamma_2| n'_{2}^{2} \mu' I'_{bst} \sin (\psi + \psi') + |\gamma_2| n'_{2}^{2} \mu' I'_{bst} \sin (\psi - \psi').
\]

The same holds for the directions of \( I'_{bst} \) and \( h'_{bst} \), so that

\[
n_{2}^{2} \lambda (I_{ast} + I_{ast II}) \sin \psi' = |\gamma_1| n_{2}^{2} \mu I_{bst} \sin (\psi - \psi') = |\gamma_1| n'_{2}^{2} \mu' I'_{bst} \sin (\psi - \psi') = |\gamma_1| n'_{2}^{2} \mu' I'_{bst} \sin 2\psi'.
\]
These equations can be written in the form

\[ n\lambda I_{as1} \sin \varphi = |\gamma_2| n_{\frac{1}{2}} \mu I_{bs1} \sin 2\varphi + |\beta| n' \mu' I'_{bs1} \sin \psi \cos \varphi' + \frac{1}{2} (|\gamma_2| - |\gamma_1|) n' \mu' I'_{bs1} \sin \psi' \cos \varphi, \]

\[ n'\lambda I_{as1} \sin \psi' = \frac{1}{2} (|\gamma_2| - |\gamma_1|) n' \mu I_{bs1} \sin \psi \cos \varphi' + |\beta| n' \mu I_{bs1} \sin \psi' \cos \varphi + |\gamma_2| n' \frac{1}{2} \mu' I'_{bs1} \sin 2\psi'. \]

Dividing the first equation by \( n \sin \varphi \) and the second by \( n' \sin \psi' \) (replacing \( n''/n' \) by \( n'/n \)) and then subtracting, one obtains

\[ \frac{1}{2} (|\gamma_2| - |\gamma_1|) \sin (\psi' - \varphi) \left[ \frac{\mu I_{bs1} \sin \varphi'}{\sin \psi} + \frac{n' \mu I'_{bs1}}{\sin \psi} \right] = 0, \]

from which follows: \( \varphi = \psi' \). Therefore further on we will use fig. 5 instead of fig. 4. The two conditions, now being identical, give

\[ n\lambda I_{as1} = |\gamma_2| \left[ n\mu I_{bs1} + n' \mu' I'_{bs1} \right] \cos \psi. \quad (22) \]

\[ \text{Fig. 5. Approximate partial magnetizations and molecular fields for } T_4 > T > 0. \]

That temperature for which (22) gives \( \cos \psi = 1 \) is identical with the required temperature \( T_4 \). For the temperature dependence of \( I_{as1} \), needed in (22), we calculate the quantity \( P = g\mu_B h_{as1}/kT \) for the situation illustrated in fig. 5:

\[ P = (g\mu_B/kT) \left[ n\mu I_{bs1} \cos \psi + n' \mu' I'_{bs1} \cos \psi - |a| n\lambda I_{as1} \right] \]

which by means of (22) can be expressed in \( I_{as1} \), so that

\[ P = \left[ 3/j(j+1) \right] (\tau'/T)\xi \]
with \( \tau' = Cn\lambda(1/|\gamma_2| - |a|) \).

Cutting the curve (19) by the straight line
\[
y = (1/3) j(j + 1) (T/\tau') \ x,
\]
we obtain in the ordinate of the common point the value of \( \xi \) obviously as a function of \( T/\tau' \). The temperature dependence of \( I_{bst} \) and \( I'_{bst} \) also needed in (22), cannot be found in a similar manner since in the case of fig. 5 we have
\[
h_{bl} = n\lambda I_{asl} \cos \psi - \frac{1}{2} [n\mu I_{bst} + n'\mu' I'_{bst}] (|\gamma_2| \cos 2\psi + |\gamma_1|),
\]
so that expressing \( \cos 2\psi \) in \( \cos \psi \) and then applying (22) we obtain for
\[
Q = g\mu_B h_{bl}/kT
\]
which contains not only \( \eta \) but also \( \eta' \). This requires quite another method for the determination of \( \eta \) than we could use for \( \xi \). We will use (23) as an equation to determine \( Q \) as a function of \( T \), namely by substituting (8) and (9) for \( \eta' \) and \( \eta' \):
\[
(T/\tau')Q = A(\mu/\lambda) ((8)) + (\mu'/\lambda) (n'g'/ng) (\mu'\eta'),
\]
in which ((8)) and ((9)) represent the right-hand members of (8) and (9), whereas
\[
A = (3/2) (|\gamma_2| - |\gamma_1|) / (1/|\gamma_2| - |a|) j (j + 1).
\]

\( Q \) being found as a function of \( T/\tau' \), the quantities \( \eta \) and \( \eta' \) follow and these together with \( \xi \) give in
\[
\cos \psi = \lambda \xi/|\gamma_2| [\mu\eta + (n'g'/ng)\mu'\eta']
\]
cos \( \psi \) as a function of \( T/\tau' \). The abscissa where \( \cos \psi \) becomes unity is identical with \( T_4/\tau' \).

8. Course of \( m_s \) for \( T_4 > T > 0 \)

In the region \( T_4 > T > 0 \) the spontaneous magnetization per "molecule" amounts (in \( \mu_B \) to
\[
m_s = g|\lambda\xi - [\mu\eta + (g'/g)\mu'\eta'] \cos \psi|
\]
and its dependence on \( T/\tau' \) follows immediately from the preceding section, where \( \cos \psi \) is given by (24) and where \( \xi \), \( \eta \) and \( \eta' \) were found as functions of \( T/\tau' \). For \( T = 0 \) we have \( \xi = \eta = j \), \( \eta' = j' \) and
\[
\cos \psi = |\gamma_2|^{-1}[\mu/\lambda + (\mu'/\lambda) n'g'j'/ngj]^{-1}.
\]

Eindhoven, January 1954

REFERENCES