Magnetic properties of rare earth metals

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MAGNETIC PROPERTIES OF RARE EARTH METALS

by

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INTRODUCTION

The rare earths form an especially interesting group of elements in the periodic table. For the most part they have three electrons in the valence shell or conduction band, and as the atomic number increases the inner 4f shell is gradually filled up. The existence of an unfilled 4f shell leads to many interesting features in the electric and magnetic properties of these metals. In particular there is a smooth dependence of these properties on the number of electrons in this shell.

Most of these metals are paramagnetic at room temperature. Gadolinium and terbium become ferromagnetic below 289° K and 230° K respectively. Dysprosium, holmium, erbium and thulium also exhibit a transition to an ordered magnetic state when the temperature is lowered. This state is known to be antiferromagnetic and to have a very complicated structure. At still lower temperatures they undergo another transition and become ferromagnetic. Cerium, neodymium, samarium become antiferromagnetic at about 10° K (Lock, 1957). No ordered state has been observed in other elements of the group. A collection of pertinent data is found in the review article of Spedding et al. (1957).

The magnetic properties of these metals are due primarily to the electrons in the incomplete shell. In fact the magnetic moment per atom is determined by the number of electrons in the 4f shell according to the Russell-Saunders coupling scheme. However, one needs to consider other effects in order to understand the ferromagnetic or antiferromagnetic coupling in Gd etc. In these metals the 4f shell of each ion is completely surrounded by the 5s and 5p shells. As a result the
Direct exchange effect between neighboring ions must be very small because their magnetic shells have very little chance to overlap each other. Therefore the strong coupling in Gd etc. must be due to other mechanisms. One such mechanism which is believed to be the most important is the indirect exchange coupling via conduction electrons. This interaction can roughly be described as follows. A conduction electron first interacts with the 4f shell electrons of an ion through the electrostatic Coulomb exchange effect. This tends to line up the spin of the conduction electron parallel or antiparallel to the spin of the ion. As the electron travels in the crystal it also interacts with other ions and thus gives rise to a force which tends to line up all the ions in the crystal. Therefore a long range type of coupling results.

The interaction between the conduction electrons and the 4f shell electrons (s-f interaction) is believed to be responsible for many other properties of rare earths as well. Considerable success has been achieved in interpreting the anomalous resistivity of some rare earths and the reduction of superconductive transition temperature of dilute solutions of rare earths in lanthanum by this interaction.

Most of the rare earth metals have the hexagonal closed packed structure. Neutron diffraction experiments on holmium and erbium have revealed their very complicated magnetic structures when they are antiferromagnetic*1. In holmium it is found that the best fit to the experimental data is given by a spiral structure. The ion spins in

each basal plane are parallel and are perpendicular to the c axis. The resultant magnetic moments of adjacent planes make a certain angle such that a staircase structure is formed along the c axis of the crystal. The angle between adjacent planes is about 38° at 45° K and increases linearly with temperature up to 48.5° at 119° K, the Néel temperature being 132° K. Dysprosium, erbium and thulium may have similar structures when antiferromagnetic. The origin of the spiral structure as well as that of the ferromagnetic to antiferromagnetic transition has been the theme of many discussions.

The present work consists of two parts. The first part contains a detailed derivation of the first order s-f interaction Hamiltonian using basic principles. Some of the consequences of this interaction are also discussed. The second part is a phenomenological interpretation of the magnetic properties of dysprosium single crystals. Detailed agreement for the magnetization curves in the ferromagnetic and antiferromagnetic regions is obtained.
REVIEW OF EXISTING THEORIES

The model for rare earth metals one usually employs consists of a lattice of trivalent ions in a sea of conduction electrons. This model describes all members of the group except the following: cerium has four conduction electrons at low temperatures; europium is divalent; and ytterbium is divalent and has a filled \( 4f \) shell. The element promethium is radioactive, so very little is known about its physical properties. The present discussion of rare earth metals will exclude these exceptional cases.

The angular momentum and the magnetic moment of a trivalent rare earth ion are entirely determined by the structure of the \( 4f \) shell. It has been established that the electrons in this shell couple their orbital and spin angular momenta together according to the Russell-Saunders LS-coupling scheme. (Van Vleck 1932). The orbital angular momenta of the electrons couple into \( \hat{L} \) and the spin angular momenta into \( \hat{S} \) by the electrostatic interaction. Then \( \hat{L} \) and \( \hat{S} \) couple into the total angular momentum \( \hat{J} \) by the spin-orbit coupling. For a free ion \( J_z \) and \( \hat{J}_z \) are constants of motion of the dynamic system. In a metal the crystalline field splits levels of different \( J_z \), however for most members of the group this effect is quite small compared with the multiplet splitting, the splitting of levels of the same \( L, S \) but different \( J \). In a first order theory the ions are usually treated as free. The crystalline field splitting may give rise to magnetic anisotropy (Niira, 1960).
In the presence of a magnetic field $\vec{H}$, the Hamiltonian of the interaction between the $\ell f$ shell of an ion and the field is given by, in the units of $C = \hbar = 1$,

$$
H' = - \sum_i \left( \frac{e}{2m} \vec{H} \cdot (\vec{r}_i \times \vec{p}_i) - \frac{e}{m} \vec{H} \cdot \vec{s}_i \right),
$$  \hspace{1cm} (1)

where $e$ is the charge of an electron, $\vec{r}_i$, $\vec{p}_i$ and $\vec{s}_i$ are the position, momentum, and spin vectors of the $i$-th electron, and the summation is taken over all electrons in the shell. By definition of $\vec{L}$ and $\vec{S}$ operators, $H'$ can be written as

$$
H' = \frac{|e|}{2m} \vec{H} \cdot (\vec{L} + 2\vec{S}).
$$  \hspace{1cm} (2)

Taking $\vec{H}$ in the $z$-direction, one obtains

$$
H' = \frac{|e|}{2m} (L_z + 2S_z) = \frac{|e|}{2m} (J_z + S_z). \hspace{1cm} (2)
$$

The matrix element of the interaction is, to the first order,

$$
\langle J_{J_z} | H' | JJ_z \rangle = \frac{|e|H}{2m} \langle JJ_z | J_z + S_z | JJ_z \rangle.
$$
By the projection theorem of angular momentum, this is equal to

\[
\langle JJ_z | H' | JJ_z \rangle = \frac{|e|H}{2m} \langle JJ_z | (1 + \frac{S\cdot J}{2J(J+1)}) J_z | JJ_z \rangle
\]

\[
= \frac{|e|H}{2m} \left[ 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right] \times J_z \cdot J_z
\]

(3)

The quantity in the square bracket is called the Landé g-factor and is denoted by \(g\). The quantity \(\frac{|e|H}{2m}\) is the Bohr magneton \(\mu_B\). Therefore the degeneracy in \(J_z\) is completely split and the energy levels are equally spaced,

\[
E_{J_z} = \mu_B g H J_z
\]

(4)

The magnetic moment operator is defined by

\[
H' = - \mu \cdot \vec{H}
\]

(5)

Therefore, with \(\vec{H}\) in z-direction
\[ \mathcal{M}_z = -\frac{|e|}{2m} (I_z + 2S_z) \]
\[ = -\frac{|e|}{2m} (J_z + S_z). \tag{6} \]

The expectation value of \( \mathcal{M}_z \) in the state \( |J_J_z> \) is therefore

\[ \langle \mathcal{M}_z \rangle = -\frac{|e|}{2m} \langle J_J_z | J_z + S_z | J_J_z \rangle \]
\[ = -\mathcal{M}_B g J_z. \tag{7} \]

For a system of \( N \) free ions per unit volume in thermal equilibrium, the energy levels of different \( J_z \) are occupied according to the Boltzmann distribution. The total magnetic moment of the system is therefore

\[ \mathcal{M} = \frac{N \sum J_z \langle \mathcal{M}_z \rangle \exp(-\alpha J_z)}{\sum J_z \exp(-\alpha J_z)} \]
\[ = \mathcal{M}_B N J_B(\alpha) \tag{8} \]

where
\[ \alpha = \frac{\mathcal{M}_B G H}{kT}, \]

\[ B(\alpha) = \frac{J}{J} \coth \left[ \alpha (J + 1/2) \right] - \frac{1}{2J} \coth \frac{\alpha}{2} \tag{9} \]

is the Brillouin function. This gives the magnetic moment of a collection of free ions as a function of temperature and applied field.

In many rare earth metals the spins of the ions are coupled together by ferromagnetic or antiferromagnetic coupling. The simplest model for a ferromagnetic crystal is one where the coupling between spins is represented by the Hamiltonian
\[ H_{\text{ex}} = -2 \sum_{i \neq j} A_{ij} \vec{J}_i \cdot \vec{J}_j. \]  

(10)

A_{ij} represents the exchange energy between the \( i \)-th and the \( j \)-th ions. This Hamiltonian can be written alternatively as

\[ H_{\text{ex}} = -\sum_i \left( \sum_j A_{ij} J_j \right) \cdot \vec{J}_i. \]

Therefore the coupling can be represented by an effective field acting on the ions. For the \( i \)-th ion, the effective molecular field is

\[ \vec{H}_m = \frac{1}{\mu_B g} \sum_j A_{ij} J_j = \frac{1}{\mu_B g} \sum_j A_{ij} \left< \vec{J} \right> \]

where \( \left< \vec{J} \right> \) denotes the average spin over a certain number of nearest neighbors of the \( i \)-th ion. In the molecular field approximation, one approximates

\[ \left< \vec{J} \right> = \frac{\vec{M}}{\mu_B g N}. \]

So the molecular field acting on the \( i \)-th ion is

\[ \vec{H}_m = \frac{\sum A_{ij}}{\mu_B^2 g^2 N} \vec{M} = \lambda \vec{M}. \]

(12)

with

\[ \lambda = \frac{\sum A_{ij}}{\mu_B^2 g^2 N}. \]

(13)

\( \lambda \) is called the molecular field constant. Hence for a ferromagnetic crystal, the total effective field is the sum of the external field and
the molecular field,

\[ H = H_0 + H_m = H_0 + \lambda M. \]  

Substituting Equation (14) into Equation (8), one obtains an implicit dependence of the magnetic moment \( M \) as a function of the external field and temperature.

If there is no external field applied, \( M \) as a function of temperature is given by

\[ M = N \mu_B gJ_B \left( \frac{\lambda \mu_B gM}{kT} \right). \]  

Equation (15) has a non-zero solution for \( M \) as long as the temperature is less than a critical value \( T_c \), known as the Curie temperature, given by

\[ T_c = \frac{\lambda \mu_B g2N(J+1)}{3k}. \]  

From Equation (13), one obtains

\[ T_c = \frac{J(J+1)}{3k} \sum A_{ij}, \]  

which gives the relationship between the ferromagnetic-paramagnetic order-disorder transition temperature and the strength of coupling between ions.

At a temperature \( T > T_c \), the system has no net magnetization unless an external field is applied. The relationship between \( M \) and \( H_0 \) is given by Equation (8) with \( H = H_0 + \lambda M \). At high enough temperatures the Brillouin function can be approximated by
Thus one obtains

\[ M \left[ 1 - N \frac{\lambda \mu_B^2 g^2 J(J+1)}{3kT} \right] = \frac{N \mu'_B g^2 J(J+1)}{3kT} H_0. \]

Hence the crystal is paramagnetic with the paramagnetic susceptibility

\[ \chi = \frac{M}{H} = \frac{C}{T - T_c} \]

(18)

where

\[ C = \frac{N \mu'_B g^2 J(J+1)}{3k} \]

(19)

is the Curie constant.

For large enough \( J \), the Brillouin function can be approximated by the classical Langevin function

\[ \mathcal{L}(x) = \cot x - \frac{1}{x} \]

(20)

It can be shown that

\[ B \left( \frac{\mu g B}{kT} \right) \rightarrow \mathcal{L} \left( \frac{\mu B}{kT} \right) \]

where

\[ \mu' = \mu_B g \sqrt{J(J+1)}. \]

(21)

The quantity \( g \sqrt{J(J+1)} \) is usually called the equivalent number of Bohr magnetons of the ion.
An analogous theory of antiferromagnetism was derived by Néel (1932, 1936). In this theory one considers two identical sublattices A and B with self and mutual interactions. To illustrate the content of the theory a special model will be considered. Assuming that the sublattices have ferromagnetic interaction within the sublattices and antiferromagnetic interaction between them, one may write the effective fields acting on the sublattices as

\[ H_A = H_0 + \lambda M_A - \lambda' M_B, \]

\[ H_B = H_0 - \lambda' M_A + \lambda M_B. \quad (22) \]

The applied field is assumed to be in line with \( M_A, M_B \). Therefore \( M_A, M_B \) are solved from

\[ M_A = \frac{1}{2} \mu_B gNJ_B \left( \frac{\mu_B gH_A}{kT} \right), \]

\[ M_B = \frac{1}{2} \mu_B gNJ_B \left( \frac{\mu_B gH_B}{kT} \right). \quad (23) \]

With no external field applied, one can find non-zero solutions for \( M_A, M_B \) provided that the temperature is lower than \( T_N \), the Néel temperature, given by

\[ T_N = \frac{(\lambda + \lambda') N\mu^2}{6k} \quad (24) \]

where \( \mu' \) is defined by Equation (21). At high enough temperatures the crystal becomes paramagnetic with the susceptibility.
\[ X = \frac{C}{T - T_N'} \]  \hspace{1cm} (25)

where

\[ T_N' = \frac{(\lambda + \lambda') N \mu^2}{6k} \]  \hspace{1cm} (26)

and \( C \) is the Curie constant in Equation (19). The susceptibility in Equation (25) is usually called the parallel susceptibility. When the field is perpendicular to the magnetic moments one needs to consider other effects in order to study the behavior of the crystal.

Along the same line as the molecular field approximation, Néel (1956 a,b) gave an explanation to the ferromagnetic to antiferromagnetic transition of dysprosium. He assumed the material to consist of two sublattices with strong ferromagnetic exchange forces within each sublattice and weak interactions between them. The intralattice exchange forces are so strong that they are the only significant terms in the effective field expressions (22). Therefore to the first approximation \( M_A, M_B \) are regarded as independent of the applied field as well as their relative orientation. The interlattice interactions are important in determining the ordering of the sublattices. When a field is applied, one writes the total energy \( E \) as a sum of the interaction with the applied field

\[ E_h = -\mathbf{H} \cdot (\mathbf{M}_A + \mathbf{M}_B) \]

an exchange energy between the sublattices.
\[ E_W = + \frac{1}{2 nM^2} \cos (\theta_A - \theta_B), \]

and a magnetocrystalline energy

\[ E_C = - \frac{1}{2} K_0 (\cos^2 \theta_A + \cos^2 \theta_B) - K_1 \cos \theta_A \cos \theta_B. \quad (27) \]

\( \theta_A, \theta_B \) are the orientations of the sublattice magnetic moments with respect to the axis of magnetization and \( 1/2 M = |\vec{M}_A| = |\vec{M}_B| \). The magnetocrystalline energy is the energy associated with the axis of magnetization. The equilibrium configuration, and thus the magnetization curve, is found by minimizing the total energy with respect to \( \theta_A \) and \( \theta_B \).

The properties of the system depend on the relative sizes of the parameters as discussed in detail by Néel. With no external field applied, the equilibrium state of the system is antiferromagnetic \( (\theta_A = 0, \theta_B = \pi) \), if \( K_0 - K_1 > 0, K_1 < 1/lnM^2 \) and is ferromagnetic \( (\theta_A = \theta_B = 0) \) if \( K_0 - K_1 > 0, K_1 > 1/4 \, nM^2 \). Therefore, a transition from ferromagnetic state to antiferromagnetic state is possible if \( K_1 \) and \( nM^2 \) have different temperature dependences. It is also of interest to study the magnetization curve when the system is antiferromagnetic.

When the field is in the direction of the axis of magnetization, one finds that if \( K_0 \geq 1/lnM^2 \) the system remains antiferromagnetic as long as \( H \) is less than a critical value \( H_S \) given by

\[ H_S = \frac{1}{2 nM} \left[ 1 - \frac{4K_1}{nM^2} \right]. \]

When \( H \) becomes greater than \( H_S \) the system goes into the ferromagnetic
state with a magnetic moment \( M \). There is a discontinuity in the magnetization curve at \( H = H_s \). This resembles roughly the observed magnetization curves for dysprosium in the temperature range from 85° K to 179° K.

The origin of the ferromagnetic coupling in rare earth metals is also a problem of great interest. It is apparent that the strong ferromagnetic coupling is not a result of the direct exchange interaction of Heisenberg because there is a lack of overlap between neighboring \( \text{hf} \) shells. Kasuya (1956a) was the first to point out that this paradox could be resolved by the Zener’s model of ferromagnetism (Zener, 1951; Zener and Heikes, 1953), namely the indirect exchange coupling via conduction electrons. In his paper, Kasuya studied in some detail the exchange interaction between a conduction electron and the magnetic shell electrons of an ion, and the indirect exchange coupling between different ions resulting from this \( s-f \) interaction. For gadolinium where there is no spin-orbit coupling, he showed that the scattering of a conduction electron by an ion through the \( s-f \) interaction can be represented by an operator

\[
H' = -\frac{1}{2} \Delta (\vec{k}, \vec{k}') \left[ (a_{k'}^+ a_{k}^* - a_{k'} a_{k}^*) S_z^+ + a_{k'}^+ a_{k}^* S_- + a_{k'}^+ a_{k}^* S_z \right] \exp \left[ i(\vec{k} - \vec{k}') \cdot \vec{R} \right]
\]

where \( a_{k}^* \) creates an electron with momentum \( \vec{k} \) and spin up, \( a_{k} \) destroys an electron with momentum \( \vec{k} \) and spin down etc; \( \vec{k}, \vec{k}' \) are the initial and final momenta of the conduction electron; \( \vec{R} \) is the position and \( \vec{S} \) is the spin of the ion, \( S_z^+ = S_z^+ iSy \), \( \Delta (\vec{k}, \vec{k}') \) is the strength of interaction.
In terms of spin operators, it can be written simply as

\[ H' = -\Delta(k,k') \vec{s} \cdot \vec{S} \exp \left[ i(k-k') \cdot \vec{R} \right], \]  

(28)

where \( \vec{s} \) is the spin operator of the conduction electron. In gadolinium \( \vec{S} \) is equal to the total angular momentum \( \vec{J} \), but for other rare earth metals the spin-orbit coupling complicates the problem.

De Gennes (1958) however suggested that the Hamiltonian in Equation (28) should be applicable to all rare earths if \( \vec{S} \) is taken as the spin angular momentum of the ion. Since \( J \) is the exact quantum number of the ion, one may consider only the interaction within the manifold of ground state \( J \). Then \( \vec{S} \) can be replaced by its projection on \( \vec{J} \) and

\[ H' = -\Delta(k,k') (g-1) \vec{s} \cdot \vec{J} \exp \left[ i(k-k') \cdot \vec{R} \right], \]  

(29)

where \( g \) is the Lande factor. A fundamental derivation of the Hamiltonian (29) will be given in the text of the present work. It will be shown that under certain approximations the Coulomb exchange interaction between a conduction electron and an ion can indeed be represented by this Hamiltonian. Furthermore the strength of interaction \( \Delta(k,k') \) depends on the conduction band structure of the metal and is independent of the directions of \( k, k' \).

Following Ruderman and Kittel's (1954) model of indirect exchange, one can show that the interaction in Equation (29) leads to an interaction Hamiltonian between ions of the form in Equation (10). It is assumed that the interaction between the spins \( \vec{J}_i \) and \( \vec{J}_j \) located at \( \vec{R}_i \) and \( \vec{R}_j \) arises from a double scattering of a conduction electron. By the
second order perturbation theory the energy of interaction is

\[ H_{ij} = -\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{J}}_i \rangle \langle \hat{\mathbf{S}} \cdot \hat{\mathbf{J}}_j \rangle \]

\[ x \int_0^{k_m} \int_0^{\infty} \int_0^{\infty} \frac{(g-1)^2 |\Delta(\mathbf{k},\mathbf{k}^*)|^2 \exp[i(\mathbf{k} - \mathbf{k}^*) \cdot (\mathbf{R}_i - \mathbf{R}_j)]}{E(k^*) - E(k)} \]

+ complex conjugate \hspace{1cm} (30)

The first term represents the coupling which arises when the electron is first scattered by the \( i \)-th ion and then by the \( j \)-th ion, the second term, which is the complex conjugate of the first, arises from a scattering process of the reversed order. \( k_m \) denotes the wave number corresponding to the Fermi energy. The second integral extends between the limits \( k_m \) and infinity because all levels below \( k_m \) are filled, so by the Pauli principle \( k^* \) must take on some value greater than \( k_m \). The largest contribution to the integrals comes from values of \( k, k^* \) near the Fermi energy, so one may approximate \( |\Delta(\mathbf{k},\mathbf{k}^*)|^2 \) by \( |\Delta(k_m,k_m)|^2 \) and take it outside the integral signs. Summing over the spins of the electron, one reduces Equation (30) to

\[ H_{ij} = -|\Delta(k_m,k_m)|^2 (g-1)^2 \hat{\mathbf{J}}_i \cdot \hat{\mathbf{J}}_j \]

\[ x \int_0^{k_m} \int_0^{\infty} \int_0^{\infty} \frac{dk^*}{(2\pi)^3} \frac{dk}{(2\pi)^3} \frac{dk}{(2\pi)^3} \frac{\exp[i(\mathbf{k} - \mathbf{k}^*) \cdot (\mathbf{R}_i - \mathbf{R}_j)]}{E(k) - E(k^*)} \]

+ complex conjugate \hspace{1cm} (31)

Here \( \mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j \). If one assumes an isotropic energy band structure for
the conduction electron such that

\[ E(\vec{k}) = \hbar^2 k^2 / 2m^* , \]

then the integral in Equation (31) can be readily evaluated. The final result as given by Ruderman and Kittel is

\[ H_{ij} = -2A_{ij} \vec{j}_i \cdot \vec{j}_j , \]  \hspace{1cm} (32)

where

\[ A_{ij} = -\frac{m^* |\Delta(k_m, k_m)|^2 (g-1)^2}{(4\pi)^3 R^2} \]

\[ \times \left( \frac{1}{R_{ij}} \right)^3 \left[ 2k_m R_{ij} \cos(2k_m R_{ij}) - \sin(2k_m R_{ij}) \right] . \]  \hspace{1cm} (33)

Therefore, one obtains Equation (10) if one sums \( H_{ij} \) in Equation (32) over all ions. The strength of the indirect exchange coupling \( A_{ij} \) is an oscillatory function of the distance between ions and is of much longer range than the direct exchange coupling.

Most rare earths have very similar physical properties. Accordingly de Gennes (1958) assumed that the strength of s-f interaction \( \Delta(k_m, k_m) \) is the same for all members of the group. If the metals have similar conduction band structures, then the free electrons should have the same effective mass \( m^* \). Hence one may conclude that

\[ A_{ij} \propto (g-1)^2 \]. \hspace{1cm} (34)

Substituting this into the expression for the Curie temperature
Equation (16), one obtains

\[ T_c \propto (g-1)^2 J(J+1) \]  \hspace{1cm} (35)

This is the de Gennes formula for paramagnetic Curie temperatures of rare earth metals. The same result was also obtained by Brout and Suhl (1959). For the elements gadolinium to lutetium there is the relationship \( J = L + S \), so

\[ T_c \propto S^2(J+1)/J \]  \hspace{1cm} (36)

which is the Néel formula. This result is in agreement with the observed paramagnetic Curie temperatures of these elements. For the elements lanthanum to samarium \( J = L - S \) applies, so

\[ T_c \propto S^2 J/(J+1) \]  \hspace{1cm} (37)

This however does not agree with the experiments.

The long range nature of the indirect exchange coupling may give rise to the peculiar magnetic structure of some of the rare earths. For the study of this effect Villain (1959) proposed a very interesting way of investigating the relative stability of various magnetic structures. Under certain conditions the most stable configuration may be a spiral structure.

From Equation (11) the molecular field at the \( i \)-th ion is

\[ \vec{H}_{mi} = \sum_j A_{ij} \vec{J}_j / \mu_B \] 

The average value of \( \vec{J}_i \) is given by the equation
where \( \vec{u}_1 \) is the unit vector in the direction of the molecular field.  

Near the critical (or Néel) temperature one has \( |\vec{J}_1| \ll J \).  The Brillouin function can be expanded to the first order, so

\[
\vec{J}_1 = J(J + 1) \sum_j A_{ij} \vec{J}_j / 3kT .
\]  

(39)

If one defines the following Fourier transforms

\[
T(k) = \sum_j \vec{J}_j \exp(ik \cdot \vec{R}_j) ,
\]

\[
\zeta(k) = \sum_j A_{ij} \exp \left( ik \cdot (\vec{R}_i - \vec{R}_j) \right) ,
\]

Equation (39) can then be written as

\[
\vec{T}(k) = \frac{J(J + 1)}{3kT} \zeta(k) \vec{T}(k) .
\]

Thus one obtains the Néel temperature \( T_N \) as

\[
T_N = \frac{J(J + 1)}{3kT} \zeta(\vec{k}_0) .
\]  

(40)

where \( \vec{k}_0 \) is the \( k \) which gives a maximum value to \( \zeta(k) \). In this way the critical temperature is obtained by a study of the reciprocal lattice structure instead of the various possible sublattice structures. In the reciprocal lattice space the possible points \( \vec{k}_0 \) form a set which is invariant under translation, inversion at the origin and the symmetry operations of the reciprocal lattice.

Assuming for simplicity that there exist only two vectors \( \vec{k}_0 \) which
are symmetric with respect to the center of the lattice, one can show by direct substitution that Equation (39) has solutions of the form

$$J_i^\alpha = \lambda_\alpha \cos(k_0 \cdot \vec{R}_i - \phi_\alpha)$$  \((41)\)

where \(\alpha = x, y, z\). This is seen to be a spiral structure along the \(k_0\) direction. In a hexagonal lattice it is possible to find such a pair of \(k_0\) directions only along the c axis. Therefore, if such spiral structure exists in a crystal with hexagonal lattice, it must have its spiral axis along the c direction. This has been verified experimentally in holmium and erbium*. Villain also proved that a spiral structure of this kind is stable below the Néel temperature by showing that any small deviation from this arrangement tends to raise the free energy of the system. The magnetostriction effect is neglected in this analysis.

According to this theory the spiral angle is determined completely by the strength of coupling \(A_{ij}\) and the structure of the reciprocal lattice. Consequently the spiral angle should be insensitive to temperature. This conclusion, however, is not in agreement with the observation in holmium. There it was found that the spiral angle is 48.5° at 110° K and decreases linearly with temperature until at 45° K it becomes 38°.

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THE S-F INTERACTION

In this section Kasuya's work (1956 b) is extended to other rare earth metals where the spin orbit coupling must be taken into account. It will be proved that the Coulomb exchange interaction Hamiltonian can be put in the form of Equation (28) under certain approximations. This gives a fundamental proof of de Gennes' proposal (1958).

Basic Model and Wave Functions

In this analysis one is interested in the electrostatic Coulomb forces between a conduction electron and the core electrons of an ion. Since the filled shells of the ion do not contribute to any angular momentum, it is sufficient to consider only the 4f shell electrons of the ion. The interaction Hamiltonian may be written as

\[ H_I = \sum_{i=1}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_{N+1}|} \]

where

\[ \vec{r}_{N+1} = \text{coordinates of the conduction electron}, \]
\[ \vec{r}_i = \text{coordinates of the i-th magnetic shell electron}. \]

The summation is taken over all electrons in the shell. The perturbation method will be used to calculate the interaction matrix elements. The appropriate wave function for the conduction electron is of the form

\[ \psi(\vec{r},s) = u_g(\vec{r})\exp(ik\cdot\vec{r})\chi \]
which is the Pauli wave function for a Bloch wave normalized in a large volume. \( \chi \) is the Pauli spinor. The wave function for the magnetic shell has a rather complicated structure. In absence of spin-orbit coupling and electrostatic interactions each electron in the \( lf \) shell would have a wave function of the form

\[
\psi_{l \mu}(r) \chi = R(r) Y_{l \mu}(\theta, \phi) \chi
\]

The residual interactions couple the electrons together according to the Russell-Saunders scheme, i.e., the orbital angular momenta of the electrons couple into \( \vec{L} \), spin angular momenta couple into \( \vec{S} \), and then \( \vec{L} \) and \( \vec{S} \) couple into \( \vec{J} \). So

\[
\vec{J} = \vec{L} + \vec{S}
\]

\[
\vec{L} = \sum_i \vec{l}_i
\]

\[
\vec{S} = \sum_i \vec{s}_i
\]

The wave function of the shell will be of the form

\[
\psi_{JM}(1,2,\ldots,i,\ldots,N) = \sum_m C(\{LSC\}; m, M - m) \psi_{lm}(1,2,\ldots,N)
\]

\[
\times \psi_{SM-m}(1,2,\ldots,N).
\]

The wave function \( \psi_{lm} \) and \( \psi_{SM-m} \) are eigen functions of the operators \( \vec{L}^2, L_z \) and \( \vec{S}^2, S_z \) respectively, and are constructed according to the Pauli principle and Hund's rule of maximum multiplicity. Two cases will be discussed separately.

When the magnetic shell is less than half or half filled \((N \leq 2 l + 1)\), \( \psi_{SM-m} \) is completely symmetrical and \( \psi_{lm} \) is completely
antisymmetrical with respect to exchange of particles. The electrons must be in different eigenstates of the operator $l_z$. According to Hund's rule

$$S = N/2,$$
$$L = Nl - N(N - 1)/2,$$
$$J = L - S = Nl - N^2/2$$

for $0 \leq N \leq 2l$,

$$= L + S = l + 1/2$$

for $N = 2l + 1$.

Therefore the spin function $\psi_{S, M-M}$ has the form of a symmetrized product

$$\psi_{S, M-M}(1, 2, \ldots, N) = \frac{1}{A} \mathcal{J}[\alpha(1) \alpha(2) \cdots \alpha(p)$$

$$\times \beta(p + 1) \cdots \beta(N)]$$

(46)

where $\mathcal{J}$ is the symmetrization operator defined by

$$\mathcal{J} = \sum P,$$

$P$ is a permutation operator of the $N$ particles and the sum is taken over all possible permutations. $\alpha, \beta$ are the spin up and spin down eigenfunctions; $A$ is the normalization factor which is equal to $\sqrt{N!p!(N-p)!}$; and $p = S + M - m$. The space function contains a linear combination of products of single particle wave function $\psi_{i\mu}(\vec{r})$, and is completely antisymmetrical with respect to all $N$ particles. It is convenient for later calculations to group the terms together according to different quantum states of the $i$-th particle, i.e.
\[ \psi_{Lm}(1,2,\ldots,N) = \sum_{\mu} \Phi_{\mu}(1,2,\ldots,i-1,i+1,\ldots,N) \]
\[ \times \psi_{L\mu}(r_{i}^{2}) . \] 

The normalization property of \( \psi_{Lm} \) assures that
\[ \sum_{\mu} \langle \Phi_{\mu}, \Phi_{\mu} \rangle = \sum_{\mu} \int \Phi_{\mu}^{*}(1,2,\ldots,N) \Phi_{\mu}(1,2,\ldots,N) \]
\[ dr_{1} \ldots dr_{i-1} dr_{i+1} \ldots dr_{N} = 1 \] 

Putting (46) and (47) into (45), one obtains the wave function for the magnetic shell.

When the magnetic shell is more than half filled \( (N > 2 \ell + 1) \), the space and spin wave functions have more complicated symmetries. It is most convenient to express the symmetries by Young diagrams shown in Figure 1 (Landau and Lifshitz, 1956, pp. 210-215). One symmetrizes with respect to all particles in the same row and then antisymmetrizes with respect to all particles in the same column of the diagrams. Let there be \( 2q \) electrons that are paired off and \( n \) electrons that are unpaired; then Hund's rule gives

\[ S = n/2, \]
\[ L = n \ell - n(n-1)/2, \]
\[ J = L + S = n \ell - n(n-2)/2 . \]

If one labels the electrons by 1, 2, \ldots, \( N \) and arranges them in the Young diagrams such that the first \( (2 \ell + 1) \) electrons are in the long column of the space diagram and in the long row of the spin
Figure 1. The Young diagrams for space and spin symmetries of a more than half filled lf shell.
diagram, one can carry out the symmetrization and antisymmetrization and obtain the wave functions

\[ \psi_{LM,t}^{(1,2,\cdots,N)} \text{ and } \psi_{S,M-m,t}^{(1,2,\cdots,N)} \]

where \( t \) denotes the complementary tableaux obtained by this arrangement of the particles in the frames. Similar terms can be formed by arranging the particles in different ways in the same frames. The completely antisymmetric eigenfunction of the operators \( \hat{L}^2 \), \( L_z \), \( \hat{S}^2 \) and \( S_z \) can then be expressed by a sum of the form

\[ \sum_t A_{mt} \psi_{LM,t}^{(1,2,\cdots,N)} \psi_{S,M-m,t}^{(1,2,\cdots,N)} \] (49)

where the summation is taken over all possible tableaux with the same frame. One should note that since the terms in the above sum are not linearly independent, the coefficients \( A_{mt} \) are not uniquely defined even though the sum is. Therefore the required eigenfunction of \( J^2 \) and \( J_z \) is

\[ \psi_{J\mu} = \sum_{m,t} C(LSJM;m-m)A_{mt} \psi_{LM,t} \psi_{S,M-m,t} \] (50)

Matrix Elements of Interaction

Now one can calculate the exchange part of the matrix elements of the interaction Hamiltonian (42), using a wave function constructed
from (43) and (45). The wave function of the system of one conduction electron and one magnetic shell is, with no regard to symmetry,

$$\Psi = \psi_J M(1, 2, \ldots, N) \psi(N+1)$$

where \( \psi(N+1) \) denotes \( \psi(\vec{r}_N+1, s_{N+1}) \) of the conduction electron. In general this wave function should be antisymmetrized with respect to all \((N+1)\) electrons. However, one may avoid this tedious procedure by making the following observations. The Hamiltonian \((4.2)\) contains a sum of two particle operators and is completely symmetrical with respect to the magnetic shell electrons. It can be proved that one obtains the correct energy if one calculates the contribution of each term of Equation \((4.2)\) separately using a wave function which is antisymmetrized only with respect to the two particles involved. As an example, for the term \( -\frac{e^2}{|r_1 - r_{N+1}|} \), the proper wave function may be taken as

$$\Psi = \frac{1}{\sqrt{2}} [\psi_J M(1, 2, \ldots, i, \ldots, N) \psi(N+1)$$

$$- \psi_J M(1, 2, \ldots, N+1, \ldots, N) \psi(1)] .$$

Assuming the following initial and final states (unsymmetrized)

$$\Psi_i = \psi_J M(1, 2, \ldots, N) \psi(N+1),$$

$$\Psi_f = \psi_J M(1, 2, \ldots, N) \psi'(N+1),$$

where

$$\psi(N+1) = u^\dagger_N(\vec{r}_{N+1}) \exp(i \vec{k} \cdot \vec{r}_{N+1}) \chi_{N+1} ,$$
\[ \psi'((N+1) = u_{K_l}^{*}(r_{N+1}) \exp(ik^{l}\cdot r_{N+1}) \chi_{N+1}^{l} \]

element to be \begin{align*}
\mu_{l} &= \int \psi_{J^{l}}^{*}(1,2,\cdots i,\cdots N) \psi'((N+1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \\
&\times \psi_{J^{l}}(1,2,\cdots i,\cdots N) \psi'(N+1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \\
&\times \psi_{J^{l}}(1,2,\cdots N+1,\cdots N) \psi(1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \\
&\times \psi_{J^{l}}(1,2,\cdots N+1,\cdots N) \psi(1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \end{align*}

after some simple manipulations. The second term is the exchange part one is interested in. For the entire shell the exchange part of the matrix element is

\[ M_{\text{ex}} = -\sum \int \psi_{J^{l}}^{*}(1,2,\cdots i,\cdots N) \psi'((N+1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \\
&\times \psi_{J^{l}}(1,2,\cdots N+1,\cdots N) \psi(1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \end{align*}

This will be calculated separately for \( N \leq 2 \ell + 1 \) and \( N > 2 \ell + 1 \).

In the case of \( N \leq 2 \ell + 1 \), each term of (54) contributes the same amount because of the symmetry of the space functions. So

\[ M_{\text{ex}} = -N \int \psi_{J^{l}}^{*}(1,2,\cdots i,\cdots N) \psi'((N+1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \\
&\times \psi_{J^{l}}(1,2,\cdots N+1,\cdots N) \psi(1) \frac{e^{2}}{|r_{1} - r_{N+1}|} \end{align*}
Putting in the wave function (1.5), one obtains

\[ M_{\text{ex}} = -N \sum \text{C}(L;J; m, m') \text{C}(L;J; m', m') \]

\[ \times \int_{\text{int}} \psi_{L;J} (1, 2, \ldots, i, \ldots, N) \psi_{S, M', m'} (1, 2, \ldots, i, \ldots, N) \]

\[ \times \psi^*_{S, M, m} (1, 2, \ldots, N+1, \ldots, N) \psi^*_{L;J} (i) d\vec{r}_1 \cdots d\vec{r}_{N+1} \]  \hspace{1cm} (55)

In each term of (55) the spin functions are multiplied together to form a sum of products of Pauli spinors for all the particles. A typical term in the sum is of the form

\[ \chi_1^* (1) \chi_2^* (2) \cdots \chi_i^* (i) \chi_N^* (N) \chi_{N+1}^* (N+1) \]

\[ \times \chi_1 (1) \chi_2 (2) \cdots \chi_{N+1} (i) \chi_N (N) \chi_i (N+1) , \]

which is zero unless

\[ \chi_j^* = \chi_j \quad \text{for} \quad j \neq i \text{ or } N+1 \]

and

\[ \chi_i^* = \chi_{N+1} , \quad \chi_{N+1}^* = \chi_i . \]  \hspace{1cm} (56)

If these are satisfied the product equals unity. The following four cases will be examined.

1. \[ \chi_{N+1} = \chi_{N+1}^* = \alpha \]. In this case \[ \chi_j^* = \chi_j \] for \[ 1 \leq j \leq N \]. Hence \[ M-m = M'-m' \]. The total number of non-zero terms
in the product of spin function can be found to be \( p \cdot p! (N-1)! (N-p)! \).

The product of the spin functions is this quantity divided by the product of the normalization factors. Thus it is found to be \( p/N \) and

\[
(M_{\text{ex}})_1 = - \sum_{mm'} C(\text{LSJ}m,M-m)C(\text{LSJ}m',\text{M'}-m')(S+M-m)
\]

\[
\times \int \psi^*_{Jm}(1,2,\ldots i,\ldots N)u_{K'}(\vec{r}_{i+1}) \exp(-i\vec{k}' \cdot \vec{r}_{i+1})
\]

\[
\times \frac{e^2}{|\vec{r}_i - \vec{r}_{i+1}|} \psi_{Jm}(1,2,\ldots N+1,\ldots N)u_K(\vec{r}_i)
\]

\[
\times \exp(ik \cdot \vec{r}_i) \, d\vec{r}_i \ldots \, d\vec{r}_{i+1} \, \delta_{M-m,M'-m'} \quad (57.1)
\]

after putting \( p = S + M - m \).

2. \( \chi_{N+1} = \chi'_{N+1} = \beta \). In this case the condition \( M-m = M'-m' \) still holds. The product of the spin functions comes out to be

\( (N-p)/N = (S-M+m) \), so

\[
(M_{\text{ex}})_2 = - \sum_{mm'} C(\text{LSJ}m,M-m)C(\text{LSJ}m',\text{M'}-m')(S+M+m)
\]

\[
\times \text{(same integral)} \, \delta_{M-m,M'-m'} \quad (57.2)
\]

3. \( \chi_{N+1} = \beta', \chi'_{N+1} = \alpha \). In this case \( \chi'_{i} = \beta', \chi_{i} = \alpha \), so \( M-m = M'-m'+1 \). The product is
\[ \psi_{S, M'}^* \chi_{N+1}^* \psi_{S, M} \chi_{N+1} = \frac{1}{N} \sqrt{p(N+p+1)} \delta_{M-M', M'-m+1} \]

\[ = \frac{1}{N} \sqrt{(S+M-m)(S-M+m+1)} \]

\[ \times \delta_{M-m,M'-m'+1}. \]

Hence one finds

\[ (M_{\text{ex}})_3 = - \sum_{mm'} C(LSJ;m,M-m)C(LSJ;m',M'-m') \]

\[ \times \sqrt{(S+M-m)(S-M+m+1)} \delta_{M-m,M'-m'+1} \]

\[ \times \text{(same integral)}. \quad (57.3) \]

4. \( \chi_{N+1} = \alpha, \chi_{N+1} = \beta \). A similar calculation gives that

\[ (M_{\text{ex}})_4 = - \sum_{mm'} C(LSJ;m,M-m)C(LSJ;m',M'-m') \]

\[ \times \sqrt{(S+M+m)(S+M+m+1)} \delta_{M-m,M'-m'-1} \]

\[ \times \text{(same integral)}. \quad (57.4) \]

The integral involved in Equation (57) will be approximated as follows. The conduction electrons are the 6s and 5d electrons, of which only the s electrons penetrate appreciably into the ion core. So one may neglect the effect of the 5d electrons and take \( u_k^*(\mathbf{r}) \) of the Bloch wave to be spherically symmetrical, i.e., \( u_k^*(\mathbf{r}) = u_k(\mathbf{r}) \). The phase factor \( \exp(ik \cdot \mathbf{r}_1) \) can be expanded into a multipole expansion

\[ \exp(ik \cdot \mathbf{r}_1) = 4\pi \sum_{\lambda m} j_{\lambda}(kr_1)Y_{\lambda m}(\hat{r}_1) \]
If the radius of the $hf$ shell is small compared with the wave length of the conduction electron, only the leading term will be of significance. If one is concerned with the effect of the leading term only, the integral reduces to

$$
\int \psi^*_{Lm}(l,2,\cdots N) u^*_{k}(r_{iN+1}) J_0(k'r_{iN+1}) \frac{e^2}{r_1 - r_{iN+1}} \\
\times \psi_{Lm}(l,2,\cdots N+1,\cdots N) u_k(kr_1) dr_1 \cdots dr_{iN+1}
$$

The orbital wave functions may be expanded according to Equation (17),

$$
\psi_{Lm'} = \sum_{\mu'} \bar{\phi}_{\mu'}(l,2,\cdots i-1,i+1,\cdots N) \psi_{\mu'}(r_1^*)
$$

$$
\psi_{Lm} = \sum_{\mu} \bar{\phi}_{\mu}(l,2,\cdots i-1,i+1,\cdots N) \psi_{\mu}(r_{iN+1})
$$

Then the integral can be written as

$$
\sum_{\mu',\mu} \langle \bar{\phi}_{\mu'}, \bar{\phi}_{\mu} \rangle \int \psi^*_{Lm'}(r_1^*) u^*_{k}(r_{iN+1}) J_0(k'r_{iN+1}) \frac{e^2}{r_1 - r_{iN+1}} \\
\times \psi_{Lm}(r_{iN+1}) u_k(kr_1) dr_1 \cdots dr_{iN+1}
$$

$$
= \sum_{\mu',\mu} \langle \bar{\phi}_{\mu'}, \bar{\phi}_{\mu} \rangle \delta_{\mu'\mu} I(k,k')
$$

The last integral is evaluated by standard techniques and the result is

$$
I(k,k') = \frac{1}{2l+1} \int R^*(r_2) R(r_{N+1}) u^*_{k}(r_{iN+1}) u_k(r_1) \\
\times J_0(k'r_{iN+1}) J_0(kr_1) \frac{r_i^l}{(2\pi)^{3/2}} \frac{r_{iN+1}^l}{(2\pi)^{3/2}} dr_i \cdots dr_{iN+1}
$$

(58)

Thus the orbital integral in (57) becomes

$$\sum_{\mu} \langle \Phi_{\mu}', \Phi_{\mu}\rangle I(k,k') = \delta_{M'M'} I(k,k').$$

The last result follows from the orthogonality properties of $\psi_{Im}$ and $\psi_{Im'}$. Substituting this result into (57), one obtains

$$(M_{ex})_1 = -\sum_m c^2 (LSJ;m,M-m)(S+M-m)I(k,k') \delta_{MM'},$$

$$(M_{ex})_2 = -\sum_m c^2 (LSJ;m,M-m)(S-M+m)I(k,k') \delta_{MM'},$$

$$(M_{ex})_3 = -\sum_m C(LSJ;m,M-m)C(LSJ;m,M-m-1)$$

$$\times \sqrt{(S+M-m)(S+M+m+1)}I(k,k') \delta_{M'M'+1},$$

$$(M_{ex})_4 = -\sum_m C(LSJ;m,M-m)C(LSJ;m,M-m+1)$$

$$\times \sqrt{(S-M+m)(S+M+m+1)}I(k,k') \delta_{M'M'-1}. \quad (59)$$

By using the wave function (45) it is easy to verify that

$$S_z \psi_{JM} = \sum_m C(LSJ;m,M-m)(M-m)\psi_{Im} \psi_{S_z M-m}.$$

Therefore

$$\langle JM' | S_z |JM \rangle = \sum_m c^2 (LSJ;m,M-m)(M-m) \delta_{MM'}.$$

Similarly
\[ \langle JM' | S_- | JM \rangle = \sum_{m} C(\text{LSJ};m,M-m)C(\text{LSJ};m,M-m+1) \]
\[ \times \sqrt{(S+M-m)(S-M+m+1)} \delta_{M,M'-1} \]
\[ \langle JM' | S_+ | JM \rangle = \sum_{m} C(\text{LSJ};m,M-m)C(\text{LSJ};m,M-m+1) \]
\[ \times \sqrt{(S-M+m)(S+M+m+1)} \delta_{M,M'-1} \].

Hence the matrix elements in (59) can be written as

\[ (M_{\text{ex}})_{1} = -\langle JM' | S+ S_z | JM \rangle I(k,k') \]
\[ (M_{\text{ex}})_{2} = -\langle JM' | S- S_z | JM \rangle I(k,k') \]
\[ (M_{\text{ex}})_{3} = -\langle JM' | S_- | JM \rangle I(k,k') \]
\[ (M_{\text{ex}})_{4} = -\langle JM' | S_+ | JM \rangle I(k,k') \].

In terms of the spin operator \( \vec{s} \) of the conduction electron the above expressions can be put in a compact form

\[ M_{\text{ex}} = -\langle JM' \chi' | \mathbf{S} + 2\vec{s} \cdot \mathbf{S} | JM \chi \rangle I(k,k') \].

Therefore if one is interested only in the spin dependent part, the Coulomb exchange interaction can be represented by the operator

\[ H = -2I(k,k')\vec{s} \cdot \mathbf{S} \]

which is just the de Gennes Hamiltonian (28) for an ion at \( \vec{R} = 0 \). The strength of interaction \( \Delta(k,k') \) is equal to \( 2I(k,k') \) and is a function
of the sizes of $k$, $k'$ only.

In the case of $N > 2 \ell + 1$ one needs to break up the sum in
Equation (54) into two parts,

$$M_{\text{ex}} = M_{\text{ex}}^{(1)} + M_{\text{ex}}^{(2)}$$

where $M_{\text{ex}}^{(1)}$ represents the interaction with the paired electrons and $M_{\text{ex}}^{(2)}$ is the interaction with the unpaired electrons. Since each paired
electron has equal probabilities to be in the spin up and spin down
state, it can be readily verified that the part $M_{\text{ex}}^{(1)}$ is independent of
the spin state of the conduction electron. The calculation of $M_{\text{ex}}^{(2)}$ is
exactly in parallel with the case of $N \leq 2 \ell + 1$. To avoid repetitions
the final results are given here without proof

$$M_{\text{ex}} = - \langle \hat{J} M' X' | N/2 \pm 2 \hat{s} \cdot \hat{s} | \hat{J} M X \rangle I(k,k') .$$

(62)

The spin dependent part of the interaction is given by the same
Hamiltonian (28).

Within the manifold of constant $J$ value, one may apply the pro-
jection theorem and replace $\hat{s}$ by its projection along $\hat{J}$, so

$$H = - 2 I(k,k') \frac{\hat{s} \cdot \hat{j}}{J(J+1)} \hat{s} \cdot \hat{j}$$

$$= - 2 I(k,k')(g-1)\hat{s} \cdot \hat{j}$$

(63)

where $g$ is the Landé $g$-factor. If transitions between states of different
$J$ values are considered, the operator in (28) should apply.
Discussion

The s-f interaction is believed to be responsible for the following phenomena in rare earth metals:

1. The ferromagnetic or antiferromagnetic coupling between ions.
2. The anomalous resistivity.
3. The reduction in superconductive transition temperature of dilute solutions of rare earths in lanthanum.

The first effect is observable in the elements between gadolinium and thulium. The paramagnetic Curie temperatures of these metals satisfy the Néel formula (36). That the elements cerium, praseodymium, neodymium, and samarium are paramagnetic or very weakly antiferromagnetic seems to be an inconsistency in this model. However, it is known that these elements have peculiar crystal structures instead of the hexagonal closed packed structure of other elements (Spedding et al. 1957). As a result their conduction band structure may be so different that the same exchange integral $I(k,k')$ no longer applies to them. The results of Hall measurements on rare earths seem to give some support to this speculation (Anderson and Legvold, 1958 a; Kevane et al. 1953). It was found that cerium, praseodymium and neodymium have positive Hall constants; gadolinium, dysprosium, erbium, and thulium have negative Hall constants in the paramagnetic temperature region; and samarium has a very peculiar dependence of its Hall constant on temperature. The Hall constants for terbium and holmium have not been measured.

The anomalous resistivity in gadolinium was explained by Kasuya.
(1956 a) and by de Gennes and Friedel (1958) on the basis of s-f interaction. This effect is also observable in other rare earths having more 4f electrons than gadolinium. The dependence of the anomalous resistivity in the paramagnetic temperature region on the number of 4f electrons of these metals was discussed by Anderson and Legvold (1958 b) and by Brout and Suhl (1959). The experimental dependence is in good accord with the assumption of s-f interaction. Again this effect is not observed in cerium, phraseodymium, neodymium and samarium. This also shows that the interaction does not exist or is very weak in these pure elements.

The negative value of the Hall constant of lanthanum (Kevane et al. 1953) indicates that it has a normal conduction band. When small amounts of rare earths atoms are dissolved in lanthanum, one expects the s-f interaction to exist between the free electrons and the solute ions. This effect manifests itself as a reduction of superconductive transition temperature compared with pure lanthanum. The theory of Suhl and Matthias (1959) is in satisfactory agreement with the experiment for almost all rare earth solutions.

One may therefore conclude that a large number of electric and magnetic properties of rare earths can be understood by a simple s-f interaction. A detailed study of the conduction band structure of these elements may give explanation to the exceptional cases as well.
INTERPRETATION OF THE MAGNETIC PROPERTIES
OF DYSPROSIUM

This work was done in collaboration with D. R. Behrendt and S. Legvold.

The magnetic properties of polycrystalline dysprosium were measured by Trombe (1945, 1951, 1953), and by Elliott et al. (1954); they found it to be ferromagnetic below 85° K, antiferromagnetic between 85° K and 179° K, and paramagnetic above 179° K. Behrendt et al. (1958) succeeded in growing a single crystal and measuring the magnetic properties as a function of direction in the crystal in all three temperature regions. They found the material to be highly anisotropic, such that the spontaneous moments lie always in the basal plane. Above 110° K the dysprosium is isotropic in the basal plane but below that temperature it has a sixfold anisotropy with <11̅20> direction easy. (This is the direction along the line joining two next nearest neighbors in the basal plane.) In their paper they gave the experimental results for the magnetization as a function of temperature, applied field, and direction in the basal plane for both the ferromagnetic and antiferromagnetic regions.

Néel (1956 a, b) proposed a very interesting, partly phenomenological, theory to explain the properties in the ferromagnetic and antiferromagnetic regions. The content of this theory has been reviewed earlier in this work. However, Néel's original calculations do not apply for dysprosium because the single crystals showed properties inconsistent
with his initial assumptions. In fact, between 110° K and 179° K a unique axis of magnetization does not exist because all directions in the basal plane are equivalent magnetically.

Above 110° K the isotropy in the basal plane suggests that the interaction between the sublattices depends only on the angle between their magnetic moment vectors. Thus instead of Néel's magnetocrystalline energy terms, one may assume a two term Fourier expansion for the interaction energy $E = a \cos(\phi_A - \phi_B) + b \cos 2(\phi_A - \phi_B)$. The second term is necessary to explain the antiferromagnetic transition. This assignment, though not unique, does give a consistent fit with the experimental magnetization curves at all temperatures and orientations.

**Basic Equations**

The following expression is postulated for the angular dependence of the magnetic interaction energy per unit volume of the material:

$$E = -\frac{1}{2}MH\cos\phi_A - \frac{1}{2}MH\cos\phi_B + a \cos(\phi_A - \phi_B) + b \cos(2\phi_A - 2\phi_B) + \frac{1}{2}k \cos(\phi_A + (1/2)k \cos \phi_B).$$

Here the subscripts $A$, $B$ refer to the two sublattices; $(1/2)M$ is the magnetic moment per unit volume of each sublattice; $H$ is the internal magnetic field in either the $\langle 10\bar{1}0 \rangle$ or $\langle 11\bar{2}0 \rangle$ direction; $\phi_A$ and $\phi_B$ are the angles between the sublattice magnetizations and the magnetic field, $a$, $b$ are the interlattice interaction constants; $k$ is the anisotropy constant; and the plus sign applies when $H$ is in the $\langle 10\bar{1}0 \rangle$ direction and the minus when $H$ is in the $\langle 11\bar{2}0 \rangle$ direction.
For most purposes the dependence of \( M \) on \( H \) may be ignored. An estimate of this dependence can be made from the Weiss formula

\[
M = M_s \chi \left[ (\mu / kT)(H + \lambda M) \right],
\]

(65)

where \( M_s \) is the saturation magnetization, \( \chi \) is the Langevin function, \( \mu \) is the magnetic moment per ion, and \( \lambda \) is the molecular field constant. From the paramagnetic susceptibility data, Behrendt et al. (1958) one estimates \( \mu \) to be 10.6 Bohr magnetons and \( \lambda \) to be 470. The dependence of \( M \) on \( H \) is found to be negligible except at temperatures higher than \( 130^\circ \text{K} \). The Weiss formula is used below to give \( M(H) \) at these higher temperatures when the magnetization is parallel to the field and otherwise the dependence of \( M \) on \( H \) is ignored.

The parameters \( M, a, b, k \) (and \( M_s \) at temperatures above \( 130^\circ \text{K} \)) are to be chosen to give agreement with the experimental data at each temperature.

First the temperature range \( 110^\circ \text{K} \) to \( 179^\circ \text{K} \) will be considered. The material is isotropic in the basal plane so one can put \( k \) equal to zero. Equation (65) can be written as

\[
E = -MH \cos(1/2)(\phi_A + \phi_B)\cos(1/2)(\phi_A - \phi_B) + a \cos(\phi_A - \phi_B) + b \cos2(\phi_A - \phi_B),
\]

(66)

and then the minimization is easily carried out by regarding \( \phi_A + \phi_B \) and \( \phi_A - \phi_B \) as the independent variables. Physically it is clear that only \( 0 \leq \phi_A \leq (1/2)\pi \) and \( -(1/2)\pi \leq \phi_B \leq 0 \) need be considered. From the dependence on \( \phi_A + \phi_B \) one sees that, at the minimum,
so the problem reduces to finding the minimum of

\[ E = -MH\cos\phi_A + a\cos2\phi_A + b\cosh\phi_A. \]  

Depending on the size of \( H \), \( E \) as a function of \( \phi_A \) may have either of the dependences shown in Figure 2. For small field \( H \), case \( \alpha \) applies and \( \phi_A \) at the minimum of \( E \) is near \( \pi/2 \); for large field, case \( \beta \) applies and \( \phi_A \) at minimum energy is zero. There is a discontinuity in the equilibrium value of \( \phi_A \) as a function of \( H \) at the point where the two minima are at equal values of \( E \). As long as the minimum is so near \( \phi_A = \pi/2 \) that an expansion for small \( \cos\phi_A \) applies, one finds that at weak fields the equilibrium value of \( \phi_A \) is given by

\[ \cos\phi_A = \frac{MH}{(4a-16b)}, \]

and that the discontinuity takes place at the field value given by

\[ M^2H^2 - 8(a-hb)MH + 16a(a-hb) = 0. \]

The net magnetization of the material \( \sigma \) is given by

\[ \sigma = (1/2)M \cos\phi_A + (1/2)M \cos\phi_B, \]

where \( \phi_A, \phi_B \) are the angles at which \( E \) is a minimum. Equations for the magnetization curves are then

\[ \sigma = \frac{M^2H}{(4a-16b)} \]

for weak fields, Equation (65) for strong fields, and with a
Figure 2. Typical dependences of $E$ on $\phi_A$, as given by Equation (68).
discontinuous jump between at a field value given by Equation (70).

In Figures 3 and 4 the values of $M$, $a$, and $b$ which give the best agreement between theoretical and experimental magnetization curves are plotted and the actual agreement for three of the magnetization curves is shown in Figure 6(A). The solid lines are the theoretical curves and the marked points show the experimental results from Behrendt et al. (1958).

Next the temperature range $85^\circ K$ to $110^\circ K$ will be considered. The problem is now more complicated because of the anisotropy. When the magnetic field is in the $\langle 10\overline{1}0 \rangle$ direction, Equation (64) can be rewritten as

$$E = -MH\cos(1/2)(\phi_A + \phi_B) \cos(1/2)(\phi_A - \phi_B)$$

$$+ a \cos(\phi_A - \phi_B) + b \cos2(\phi_A - \phi_B)$$

$$+ k \cos3(\phi_A + \phi_B) \cos3(\phi_A - \phi_B) \cdot$$

There are several qualitatively different types of minimum energy configurations possible, depending on the relative sizes of the parameters. The one that leads to agreement with the experimental data has the sublattices oriented antiparallel before the transition and parallel after. An analysis similar to that of the previous paragraph gives the following equations for the net magnetization:

$$\sigma = \frac{M^2H}{(4a-16b+36k)} ,$$  \hspace{1cm} (74a)

$$MH = 36k \left[ (\sigma/M) - (16/3)(\sigma/M)^3 + (16/3)(\sigma/M)^5 \right] ,$$  \hspace{1cm} (74b)
\[ \sigma = \mu \quad , \quad (7\text{a}) \]

where the first equation applies for weak fields, the second for intermediate fields, the third for strong fields. An analytical formula for the field at the transition from Equation (7\text{a}) to Equation (7\text{b}) would be complicated: the actual values were found numerically in each case. The transition from Equation (7\text{b}) to Equation (7\text{c}) takes place at \( MH = 36k \). Figures 3, 4, and 5 exhibit the values of the parameters chosen and Figure 6(B) shows the agreement with the experimental data at 100° K.

The next consideration is the temperature range 85° K to 110° K, with the field in the \( \langle 11\bar{2}0 \rangle \) direction. Equation (6\text{b}) applies with the minus signs. One can see that the simple relationship

\[ \phi_A = -\phi_B \]

does not hold because it would imply that at small field the magnetic moments are perpendicular to the field in the hard direction of magnetization \( \langle 10\bar{1}0 \rangle \). In the absence of an external field, the spontaneous moments lie in \( \langle 11\bar{2}0 \rangle \) directions so that the equilibrium conditions are

\[ \phi_A - \phi_B = \pi , \quad \phi_A = 0 , \quad \pm (1/3)\pi , \quad \pm (2/3)\pi , \quad \pi . \]

The first condition gives the minimum exchange energy and the second the minimum of anisotropy energy. When \( k \) is large enough the system is at

\[ \phi_A \approx (1/3)\pi , \quad \phi_B \approx -(2/3)\pi \] (or a physically equivalent orientation) for small \( H \), and then there is a discontinuous jump to
Figure 3. Empirical values of sublattice magnetization at zero external magnetic field.
Figure 4. Empirical values of interaction energy parameters $a$ and $b$, as introduced in Equations (66) and (73).
Figure 5. Empirical values of the anisotropy constant for the sixfold anisotropy of a sublattice in the basal plane.
Figure 6. Comparison of typical theoretical and experimental magnetization curves.
Figure 6. (Continued).
Figure 6. (Continued).
\( \phi_A = 0, \phi_B = 0 \) when \( H \) exceeds a certain value. One can discuss the magnetization curves by making expansions about these configurations. In terms of the angles \( \delta \) and \( \epsilon \), defined by

\[
\phi_A + \phi_B = -\frac{1}{3} \pi + \delta, \phi_A - \phi_B = \pi + \epsilon,
\]

the energy before the jump is

\[
E = -a + b - k + \frac{1}{2} \sqrt{3M} H + \frac{1}{2} (a - 4b + 9k) \epsilon^2 + \frac{1}{8} M S \delta + \frac{1}{8} k \delta^2
\]

where higher powers of \( \delta \) and \( \epsilon \) have been disregarded. Treating \( \delta \) and \( \epsilon \) as independent variables, one finds that at minimum energy

\[
\epsilon = -\sqrt{3M} H / [a - 4b + 9k],
\]

\[
\delta = +\sqrt{3(MH)^2 / 288k (a - 4b + 9k)}.
\]

The net magnetization is

\[
\mathcal{M} = (1/2) M \cos \phi_A + (1/2) M \cos \phi_B
\]

\[
= M \sin(\epsilon/2) (1/2) \sqrt{3} \cos(\delta/2) + (1/2) \sin(\delta/2/2).\]

To the first order in \( H \) one finds

\[
\mathcal{M} = \frac{3M^2 H}{16 (a - 4b + 9k)},
\]

and this gives the initial slope of the magnetization curve. Similarly for high fields, one finds that the first order solutions for the equilibrium position are
\[ \phi_A = \phi_B = 0, \quad \sigma = M \]  \hspace{1cm} (77)

The transition takes place at the field

\[ H = 2a/M \]  \hspace{1cm} (78)

Figure 6(B) shows the comparison of the theory with the experimental data.

In the ferromagnetic temperature range, \( T < 85^\circ K \), the constant \( a \) in the leading term of interlattice interaction energy is negative. The total energy is a minimum when

\[ \phi_A = \phi_B \]

and Equation (64) becomes

\[ E = -MH \cos \phi_A + a + b + k \cos \theta \]  \hspace{1cm} (79)

where the proper sign of the anisotropy energy should be chosen according to the direction of the magnetic field as explained under Equation (64). Equation (71) becomes

\[ \sigma = M \cos \phi_A \]

If the field is applied in the easy direction, the material simply remains magnetized and \( \sigma = M \). In fact, a finite field is required to magnetize the sample; this is probably an effect of domain structure. If the field is applied in the \( \langle 10\bar{1}0 \rangle \) direction, the plus sign in Equation (79) is to be used. The resulting magnetization curve is
\[
MH = 36k \left[ (\sigma/M) - (16/3)(\sigma/M)^3 + (16/3)(\sigma/M)^5 \right] \quad (80a)
\]
\[
\sigma = M, \quad (80b)
\]

the saturation taking place at
\[
MH = 36k \quad (81)
\]

Figures 3 and 5 show the choice of \( M \) and \( k \) which gives best agreement with the data and a comparison of magnetization curves is given in Figure 6(C).

In addition to the magnetization curves, this model can be used to discuss the large anisotropy relative to the \( c \) axis. Assuming the field \( H \) is applied in the \( c \) direction and considering the antiferromagnetic region, one may take the energy to be
\[
E = (1/2)MH \cos \theta_A - (1/2)MH \cos \theta_B + a \cos (\theta_A + \theta_B)
+ b \cos 2(\theta_A + \theta_B) + (1/2)k' \cos 2 \theta_A + (1/2)k' \cos^2 \theta_B, \quad (82)
\]

where \( \theta_A, \theta_B \) are the angles between the magnetization vectors of the sublattices and the \( c \) axis, and \( k' \) is the anisotropy constant for this direction. Minimization of this energy for \( \theta_A, \theta_B \) near \( \pi/2 \) leads to the susceptibility
\[
\chi = M^2/4(k' + a + \lambda b) \quad . \quad (83)
\]

The value of \( k' \) can be determined from the previously established values of \( M, a, b \) and the measured susceptibility. The same formula with \( a, b = 0 \)
applies in the ferromagnetic region. The results are displayed in Figure 7.

Discussion

The curve of the sublattice magnetization when plotted as a function of temperature (Figure 3) resembles that obtained from the conventional molecular field theory. That the curve goes smoothly through the ferromagnetic to antiferromagnetic transition temperature \( T_c \) gives support to the basic assumptions that the sublattices are ferromagnetic, but their interaction may create ferromagnetism or antiferromagnetism. The antiferromagnetic to paramagnetic transition temperature is the Curie temperature of a sublattice.

Figure 4 shows the temperature dependence of the interlattice interaction energy constants \( a \) and \( b \). The strong temperature dependence of these parameters shows that the interaction is different in nature from the ordinarily assumed exchange energy,

\[
\lambda' \mathbf{M}_A \cdot \mathbf{M}_B,
\]

where \( \lambda' \) is almost temperature independent.

Figures 5 and 7 give the sublattice anisotropy constants as functions of temperature. The solid curves show the dependence predicted by Zener's theory (Zener, 1954; see also Keffer, 1955; Pincus, 1959) for a ferromagnetic lattice. In this theory the anisotropy constant depends on the temperature through the relationship

\[
k(T) \propto \left| M(T) \right|^{(1/2)n(n+1)},
\]  

(8h)
Figure 7. Empirical values of the anisotropy constant for the twofold anisotropy of a sublattice relative to the c axis.
where \( n \) is an integer. The agreement is good if \( n = 6 \) for \( k \) and \( n = 2 \) for \( k' \). The \( M^{21} \) dependence of the sixfold anisotropy constant implies a spatial dependence of the anisotropy energy of the form \((1/2)k \cos^6 \theta \sin 6\phi\). This term does not appreciably affect the discussion of the magnetization curve when the external field is out of the basal plane because \( k \ll k' \). The agreement of \( k' \) with \( M^3 \) shows that the assumed spatial dependence of this anisotropy energy is correct. However, one cannot expect a very good agreement at low temperatures because \( k' \) is so strong that it can no longer be treated as a perturbation to the spin-wave system (Pincus, 1959). The application of \( a, b \) terms out of the basal plane also introduces some small corrections on \( k' \). However, the shape of the magnetization curves is too insensitive to the effect of the \( a, b \) terms to tell definitely whether the use of these terms out of the basal plane is sensible or not.

The specific heat of the dysprosium was measured by Griffel, Skochdopole, and Spedding (1956). The magnetic contribution to the specific heat can be found by subtracting the lattice and the electronic contributions from the experimental data as described in their paper. The resulting data are shown in Figure 8, together with the curve (in dashed lines)

\[
C_M = \alpha \left( \frac{1}{4} \right) \lambda \frac{M^2}{dT},
\]

as suggested by the molecular field theory and using magnetization values from Figure 3. As before, \( \lambda \) is taken to be \( 470 \). The effects of the interaction between sublattices, as estimated by the values of \( a \) and \( b \), are negligible. The agreement is fair.
Figure 8. Magnetic contribution to the specific heat.
The anomaly at the ferro-antiferromagnetic transition temperature can be understood by the following thermodynamic argument. The Gibbs free energy of the system is

\[ G = U - TS + PV - HI, \quad (86) \]

where \( I \) is the net magnetization. Hence

\[ dG = (dU - TdS + PdV - HdI) - SdT + VdP - IdH \]

\[ = - SdT + VdP - IdH. \quad (87) \]

The quantity in the parenthesis is zero by definition. In terms of quantities per mole

\[ dg = - sdT + vdP - idH. \quad (88) \]

At the transition the Gibbs function is continuous, so

\[ \varepsilon_f = \varepsilon_i \]

So

\[ dg_f = dg_i \quad (89) \]

along the equilibrium surface. The subscripts denote initial and final values. If the transition is of the first order, then \( s, v, i \) do not change continuously. But because of Equation (89), one has

\[ -s_fdT + v_fdP - i_fdH = -s_idT + v_idP - i_idH. \]

There is no apparent change in volume during the magnetic transition, one obtains
\[
S_f - S_i = (i_f - i_i) \frac{dH}{dT} |_P \quad (90)
\]

The initial state is ferromagnetic with \( i_i = M \); the final state is antiferromagnetic with no net magnetization \( i_f = 0 \), so

\[
\Delta s = \mu \frac{dH}{dT} |_P
\]

Experimentally (Behrendt et al., 1959) it was found that

\[
\frac{dH}{dT} |_P \cong 1.3 \times 10^2 \quad \text{gauss/°K},
\]

\[
\mu \cong 5.7 \times 10^4 \quad \text{cgs/mole},
\]

so

\[
\mu \frac{dH}{dT} |_P = 7.6 \times 10^6 \quad \text{ergs/°K mole}
\]

The latent heat of transition is then

\[
T_{cl} \Delta s = 15 \text{ cal/mole}
\]

This should correspond to the area under the first peak of the specific heat curve. The experimental value as estimated from Figure 1 of Griffel et al. (1956) is about 5 calories per mole.

Kittel (1960) suggested a possible origin of the interlattice exchange energy postulated in Equation (61). A more general theory was also proposed by Behrendt (1959). Kittel assumes that the strength of exchange coupling between the sublattices is a linear function of a lattice parameter \( \alpha \), and it crosses zero at \( \alpha = \alpha_C \). The exchange energy per unit volume is then

\[
\text{...}
\]
When writing the free energy of the system, the elastic energy must be taken into account since a variation in lattice parameter is accompanied by a change of elastic energy. Hence the free energy per volume is

\[ F = \frac{1}{2R}(\alpha - \alpha_T)^2 - \rho (\alpha - \alpha_c) \mathbf{m}_A \cdot \mathbf{m}_B \]  

(91)

where \( R \) is the appropriate stiffness constant and \( \alpha_T \) is the equilibrium value of \( \alpha \) at the temperature \( T \) when \( \mathbf{m}_A \perp \mathbf{m}_B \). The value of \( \alpha \) that minimizes \( F \) is found to be

\[ \alpha = \alpha_T + \frac{\rho}{R} \mathbf{m}_A \cdot \mathbf{m}_B \]  

(92)

If the crystal undergoes a ferro-antiferromagnetic transition, the change in \( \alpha \) will be

\[ \Delta \alpha = \frac{2\rho}{R} M^2 \]  

(93)

Experimentally no decisive discontinuous change in either \( a_0 \) or \( c_0 \) parameter was observed at the transition \( (\text{Banister et al. } 1954) \) due to the large uncertainty of the data.

The minimum value for \( F \) is

\[ F = -\frac{\rho^2}{2R} (\mathbf{m}_A \cdot \mathbf{m}_B)^2 - \rho (\alpha_T - \alpha_c) \mathbf{m}_A \cdot \mathbf{m}_B \]  

(94)

In terms of the angles, \( F \) can be put in the form
\[ F = \frac{\rho \mu_0^2}{4\pi} \cos 2(\phi_A - \phi_B) - \rho(\alpha_T - \alpha_c)\cos(\phi_A - \phi_B) + \text{constant} \] (95)

which is just the exchange energy expression postulated for dysprosium.

The effective sign of the exchange interaction is determined by \( \rho(\alpha_T - \alpha_c) \). A transition of magnetic state with temperature occurs when this quantity changes sign. The quantity \( b \) in the exchange energy expression in Equation (64) corresponds to

\[ b = -\frac{\rho \mu_0^2}{4\pi} \]

However, the quantity on the right-hand side of the above equation should not have the strong temperature dependence as shown in Figure 4.

Kittel also predicted a pressure dependence of the ferro-
antiferromagnetic transition temperature. By Clausius-Clapeyron equation

\[
\frac{dT_{cl}}{dP} = \frac{\Delta V}{\Delta S} = \frac{V}{-\Lambda} \frac{\Delta \alpha/\alpha}{(\partial G/\partial T)_P} .
\] (96)

Neglecting the effect of the atmospheric pressure

\[
\Delta \left( \frac{1}{V} \frac{\partial G}{\partial T} \right)_P \approx \Delta \left( \frac{\partial F}{\partial T} \right)_P = \left( \frac{\partial}{\partial T} \Delta F \right)_P .
\]

From Equation (94) one finds

\[
\Delta F = -2 \rho \mu_0^2(\alpha_T - \alpha_c) .
\]

Hence
\( \left( \frac{\partial}{\partial T} \Delta F \right)_P = -2 \rho M^2 \frac{\partial \alpha}{\partial T} \). 

Substituting this result and Equation (93) into Equation (96), one obtains

\[
\frac{dT_{cl}}{dP} = \frac{1}{\alpha R} \left( \frac{1}{\frac{d\alpha T}{dT}} \right) \tag{97}
\]

By the Gruneisen relation, the coefficient of thermal expansion

\[
\beta = \frac{1}{\alpha T} \frac{d\alpha T}{dT} = \gamma C_L
\]

where \( K \) is the compressibility, \( C_L \) is the lattice specific heat per volume and \( \gamma \) is the Gruneisen constant. \( K \) is related to \( R \) by

\[
K = \frac{1}{\alpha^2 R}.
\]

Therefore

\[
\alpha R \frac{d\alpha T}{dT} \cong \gamma C_L
\]

and

\[
\frac{dT_{cl}}{dP} \cong \frac{1}{\gamma C_L} \tag{98}
\]

Assuming a Debye temperature of 158° K one estimates

\[
C_v \cong 4.9 \text{ cal/mole °K}
\]

at the transition temperature of 85° K. This gives
Taking $\gamma = 2$, one obtains

$$\frac{dT_{c1}}{dP} = 2 \text{ cm}^3 \text{ } ^{6}K/\text{cal.} = 0.05 \text{ } ^{6}K/\text{atoms}.$$ 

Experimentally Swenson and Legvold* found this quantity to be $-0.0012 \pm 0.0003$ degree Kelvin per atmospheric pressure. This is in definite disagreement with the theoretical estimation.

Therefore, though the theory of Kittel gives the correct form of the exchange energy, it does not tell the whole story because some of the conclusions do not agree with the experiment.

It is difficult to see at the present how should one proceed to derive a fundamental theory of the ferro-antiferromagnetic transition in dysprosium. A detailed study of the magnetic structure in the antiferromagnetic temperature region should be very helpful.

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