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Magnetic Ordering in the Ferromagnetic Rare-Earth Metals

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The effect of the anisotropy energy on the screw structure is investigated concerning the magnetic structure of heavy rare-earth metals. In the high temperature region near the Néel temperature the free energy of the spin system is calculated and it is shown that if the preferred direction of the spin is in the c plane, a usual screw structure appears, whereas if the anisotropy energy makes the preferred direction of the spin parallel to the c axis, only the z-component oscillation first appears and then the oscillation of x or y component appears at a lower temperature. The change of the period of the screw and the various magnetic transitions observed in dysprosium, holmium and erbium are also discussed.

According to the neutron diffraction experiments on single crystals of dysprosium, holmium and erbium made by Koehler, Wilkinson, Wollan and Cable[1], these rare-earth metals have various types of spin ordering. Since these spin structures can be regarded as screw structures modified by the anisotropy energy, we investigate the effect of the anisotropy on a simple screw structure.

In the rare-earth metals, the orbital moment of each ion is not quenched. Therefore, the anisotropy energy is expected to be quite large compared with that in the iron-group metals. The one-ion anisotropy energy of a rare-earth ion in a crystal of hexagonal close packed structure, which is regarded as a predominant part of the anisotropy energy, can be described by the following four spherical harmonics:

$$H_a = V_2 + V_4 + V_6 + V_6^6 , \qquad (1)$$

$$V_2 = D\frac{1}{2}(3S_z^2 - S^2) = DS^2 P_2(\cos\theta) , \qquad (2)$$

$$V_4 = E\frac{1}{8}(35S_z^4 - 30S^2S_z^2 + 3S^4)$$
$$= ES^4 P_4(\cos\theta) , \qquad (3)$$

$$V_6 = F\frac{1}{16}(231S_z^6 - 315S^2S_z^4 + 105S^4S_z^2 - 5S^6)$$
$$= FS^6 P_6(\cos\theta) , \qquad (4)$$

$$V_6^6 = G\frac{1}{2}(S_+^6 + S_-^6) , \qquad (5)$$

where the z axis is taken along the hexagonal axis, θ represents the polar angle and P_n is the Legendre polynomial of the n-th order. The spin moment is treated as a classical quantity because the magnetic moment of the atom is large for the rare-earth metals under consideration.

The exchange interaction is given by

$$H_{ex} = -\sum_i \sum_j J(\boldsymbol{R}_j - \boldsymbol{R}_i)\, \boldsymbol{S}_j \cdot \boldsymbol{S}_i , \qquad (6)$$

and we assume that the Fourier transform of the exchange integral

$$J(\boldsymbol{q}) = \sum_j J(\boldsymbol{R}_j - \boldsymbol{R}_i) \exp[i\boldsymbol{q}\cdot(\boldsymbol{R}_j - \boldsymbol{R}_i)] \qquad (7)$$

has its maximum at $\boldsymbol{q} = \boldsymbol{Q}_0 \neq 0$ along the c axis so that a simple screw structure characterized by $\boldsymbol{Q}_0$ may be stable in the absence of the anisotropy energy.

In order to investigate the situation near the Néel temperature, we shall calculate the free energy of the spin system whose Hamiltonian consists of Eqs. (1) and (6) in a power series with respect to the ordered spin moment. According to the Weiss approximation we divide $\boldsymbol{S}_i$ into the following two parts in the expression (6) for the exchange interaction:

$$\boldsymbol{S}_i = \boldsymbol{\sigma}_i + (\boldsymbol{S}_i - \boldsymbol{\sigma}_i) , \qquad (8)$$

where $\boldsymbol{\sigma}_i$ is introduced as a measure of the thermal average of the i-th spin and the second term represents its deviation from $\boldsymbol{\sigma}_i$. Then the free energy of the system can be calculated as

$$F = \sum_i \sum_j J(\boldsymbol{R}_j - \boldsymbol{R}_i)\boldsymbol{\sigma}_j \cdot \boldsymbol{\sigma}_i - kT \sum_i \log$$
$$\int \exp\left[\frac{\{2\sum_j J(\boldsymbol{R}_j - \boldsymbol{R}_i)\boldsymbol{\sigma}_j \cdot \boldsymbol{S}_i - H_{ai}\}}{kT}\right] d\Omega_i , \qquad (9)$$

In the usual Weiss approximation, $\boldsymbol{\sigma}_i$ is determined by the self-consistency condition, but in our case this condition becomes hard to deal with because $\boldsymbol{\sigma}_i$ generally depends on i. Therefore, we assume the i-dependence

of σ_i in an appropriate form with several variational parameters and determine these parameters by the minimum condition for the free energy. The simplest form of σ_i which will be a good approximation at least at high temperatures is

$$\sigma_{ix}=\sigma_x \cos \boldsymbol{Q}\cdot\boldsymbol{R}_i\ , \qquad \sigma_{iy}=\sigma_y \sin \boldsymbol{Q}\cdot\boldsymbol{R}_i\ ,$$
$$\sigma_{iz}=\sigma_z \cos \boldsymbol{Q}\cdot\boldsymbol{R}_i\ . \tag{10}$$

The hodograph of the average spin moment for this form of σ_i is an ellipse. Inserting the expressions (10) into Eq. (9) and expanding this in a power series with respect to σ_x, σ_y and σ_z, we obtain the following expression for the free energy up to the fourth power of σ_i:

$$\frac{F}{N}=f$$
$$=J(Q)\Bigg[\left\{1-\frac{2J(Q)}{kT}\frac{1}{2}(S^2-\langle S_z^2\rangle)\right\}\frac{1}{2}(\sigma_x^2+\sigma_y^2)$$
$$+\left\{1-\frac{2J(Q)}{kT}\langle S_z^2\rangle\right\}\frac{1}{2}\sigma_z^2$$
$$+\frac{1}{32}\left(\frac{2J(Q)}{kT}\right)^3\left\{\frac{3}{8}(S^4-2S^2\langle S_z^2\rangle\right.$$
$$+2\langle S_z^2\rangle^2-\langle S_z^4\rangle)\left(\sigma_x^4+\frac{2}{3}\sigma_x^2\sigma_y^2+\sigma_y^4\right)$$
$$+(3\langle S_z^2\rangle^2-\langle S_z^4\rangle)\sigma_z^4+(\langle S_z^4\rangle$$
$$\left.-\langle S_z^2\rangle^2)\sigma_z^2(\sigma_y^2+3\sigma_x^2)\right\}\Bigg]\ , \tag{11}$$

where $\langle S_z^n\rangle$ means the thermal average of S_z^n in the presence of only the anisotropy energy, namely,

$$\langle S_z^n\rangle=S^n\frac{\int d\Omega \cos^n\theta \exp(-H_a/kT)}{\int d\Omega \exp(-H_a/kT)}\ . \tag{12}$$

At high temperatures, all the coefficients in Eq. (11) are positive and therefore the values of σ's which minimize the free energy are all zero. As the temperature is lowered, the coefficient of σ_z^2 or that of σ_x^2 becomes negative. Then, σ_z or σ_x and σ_y will take a non-zero value.

If the preferred direction of the spin lies in the c plane ($D>0$), the coefficient of σ_x^2 and σ_y^2 first becomes zero at the temperature which is determined, in the first order of the anisotropy energy, by

$$1-\frac{2J(Q)S^2}{3kT}\left(1+\frac{1}{5}\frac{DS^2}{kT}\right)=0\ . \tag{13}$$

It should be noted that E and F do not take part in this expression. Since $\sigma_x=\sigma_y\neq 0$ and $\sigma_z=0$ below this temperature, the spin system takes a simple screw structure. This corresponds to the cases of dysprosium and holmium. If the anisotropy energy makes the preferred direction of the spin parallel to the c axis ($D<0$) as is the case for erbium and thulium, the coefficient of σ_z^2 first comes to zero. This temperature is determined by

$$1-\frac{2J(Q)S^2}{3kT}\left(1-\frac{2}{5}\frac{DS^2}{kT}\right)=0\ . \tag{14}$$

Since $\sigma_z\neq 0$ and $\sigma_x=\sigma_y=0$ in this case, only the z component of the spin oscillates. As the temperature is further lowered, the coefficient of σ_y^2 next becomes negative. The temperature at which this coefficient passes through zero is determined in the present approximation by

$$1-\frac{2J(Q)}{kT}\frac{1}{2}(S^2-\langle S_z^2\rangle)$$
$$+\frac{1}{16}\left(\frac{2J(Q)}{kT}\right)^3(\langle S_z^4\rangle-\langle S_z^2\rangle^2)\sigma_z^2=0\ . \tag{15}$$

This temperature corresponds to 52°K for erbium. Below this temperature the hodograph of the spin moment becomes an ellipse with its major axis along the c axis. When the coefficient of σ_x^2 reaches zero, this ellipse begins to tilt. This would occur only when E and F have appropriate values. At such low temperatures, however, the present expansion of the free energy would no longer be valid.

In Eq. (11), Q which characterizes the screw structure appears only through $J(Q)$. Therefore, the pitch of the screw does not vary with temperature in the present approximation. As a matter of fact, the assumed form for σ_i does not satisfy the self-consistency condition. This means that the higher harmonics appear superposed on the fundamental tone. For the case in which only the z component of the spin is oscillatory, higher harmonics with odd multiples of the fundamental frequency are superposed. The amplitude of the lowest higher harmonics can be calculated in a similar way by putting

$$\sigma_{iz}=\sigma_z \cos \boldsymbol{Q}\cdot\boldsymbol{R}_i+\sigma' \cos 3\,\boldsymbol{Q}\cdot\boldsymbol{R}_i\ ,$$
$$\sigma_{ix}=\sigma_{iy}=0\ . \tag{16}$$

The result is given by

$$\sigma'=-\frac{1}{24}\left(\frac{2J(Q)}{kT}\right)^3\frac{{\sigma_z}^3}{1-\frac{2J(3Q)}{kT}\langle {S_z}^2\rangle}(3\langle {S_z}^2\rangle^2-\langle {S_z}^4\rangle)\,. \quad (17)$$

It can be seen from this result that this component tends to square the fundamental sinusoidal modulation because of its negative sign. For the screw structures, the G-term also contributes the 5-th and the 7-th higher harmonics. These higher harmonics have an effect of changing the period of the spin modulation, but this change of the period is small.

The quadrupole interaction between nearest-neighbor atoms can also change a pitch of the screw. If we take into account this quadrupole interaction, the following terms are added to the expression for the free energy (11),

$$\frac{81}{400}A\left(\frac{T_s}{T}\right)^4\left(1+\frac{1}{2}\cos 2Qc'\right)\{8{\sigma_z}^4+3({\sigma_x}^4+{\sigma_y}^4)+2{\sigma_x}^2{\sigma_y}^2-8{\sigma_z}^2({\sigma_y}^2+3{\sigma_x}^2)\}\,, \quad (18)$$

$$A=\alpha^2\langle r^2\rangle^2\frac{e^2}{R^5}\frac{1}{8}(35{n_3}^4-30{n_3}^2+3)\,, \quad (19)$$

$$T_s=2J(Q)S^2/3k\,, \quad (20)$$

where α is a constant determined by L, S and J of the rare-earth ion and was calculated by Stevens, $\langle r^2\rangle$ the average of r^2 over the $4f$ radial wave function, R the distance between neighboring atoms on two adjacent layers, n_3 the cosine of the angle between the c axis and the direction joining these two nearest neighbors and c' a half of the lattice parameter c. In deriving (18) we neglected the anisotropy energy.

For the case of $D>0$, namely, $\sigma_x=\sigma_y=\sigma$ and $\sigma_z=0$, the quadrupole contribution (18) gives Q the following temperature dependence:

$$\frac{(Q-Q_0)c'}{T_s-T}=\frac{27}{10}\frac{S^2}{T_s}\frac{Ac'^2}{(-d^2J(Q)/dQ^2)_{Q=Q_0}}\sin 2Q_0c'\,, \quad (21)$$

This change of Q is linear in temperature in accordance with experimental results for dysprosium and holmium. However, this change is too small in its magnitude compared with the experimental results. Therefore, the indirect quadrupole interaction might be considered to be a possible source of the observed change of Q for these metals. But this interaction will also change the period of the z-component oscillation as can be seen from Eq. (18). No change in the period was actually observed in the temperature region of the z-component oscillation for erbium. Therefore, the origin of the change of the pitch is not clear.

At low temperatures the higher-order terms of anisotropy, E-, F- and G-terms in Eq. (1) become large. These terms including D-term may be small compared with the exchange interaction itself, but they may have the same order of magnitude as the energy difference between ferromagnetic and screw states, namely, $S^2\{J(Q)-J(0)\}$. For such a case somewhat complicated spin orderings are expected.

We calculated the free energies for several ordered structures on the basis of the Weiss approximation up to the first order of the anisotropy energy and compared them with each other. Thus, it can be understood that the magnetic transitions observed at lower temperatures in dysprosium, holmium and erbium take place due to the growth of the higher-order anisotropy. Namely, in dysprosium, the axial anisotropy including higher-order terms tends to keep the spin moment in the c plane. Therefore, in this case the screw structure with the rotation axis of the spin parallel to the c axis will be stable. However, G-term which describes the anisotropy in the c plane will lower the energy of the ferromagnetic state in its first order, whereas this term stabilizes the screw state only in its second order. Therefore, if G-term is larger than the difference in exchange energy between these two states, the ferromagnetic state will be more stable than the screw state. As the temperature is raised, sixth-order G-term decreases more rapidly than the exchange energy. Therefore, the transition from the ferromagnetic state to the screw state takes place.

In the case of holmium, the second-order D-term of anisotropy makes the spin moment parallel to the c plane but the fourth-order E-term tends to make the moment point to a direction tilting to the c axis. Therefore, a combined action of these two together with the screw-like exchange interaction is considered to make a conical structure stable at low temperatures. With rising temperature, however, the fourth-order term becomes

smaller compared with the second-order term. Accordingly, the cone becomes gradually flat and it is transformed into a simple screw structure. This transition is of second kind.

In the case of erbium, both the second- and fourth-order terms make the preferred axis of the spin moment parallel to the c axis. The conical spin arrangement found below 20°K is, therefore, considered to be stabilized by the sixth-order axial term which makes the spin moment parallel to a direction between the c axis and the c plane. As the temperature rises, the higher-order terms of anisotropy energy decrease, and we can show that a cycloidal structure with the rotation axis of the moment perpendicular to the c axis or a screw structure with the rotation axis inclining to the c axis is more stable than the conical arrangement above a certain temperature. This transition will correspond to that found at 20°K.

References

1 W. C. Koehler, M. K. Wilkinson, E. O. Wollan and J. W. Cable: J. Appl. Phys. **32** (1961) 20S, 48S and 49S.

DISCUSSION

B. T. MATTHIAS: Can anyone of these authors predict the magnetic structure of the light rare earths from cerium to gadolinium? (Gadolinium has the same crystal structure as the elements discussed.)

R. J. ELLIOTT: The light rare earths La-Eu have different crystal structure and so both the exchange and anisotropies will be different and so one cannot extrapolate.

Gd is the same and so should have a similar set of exchange parameters. It is surprising it has no spiral but there does seem to be a well defined trend towards ferromagnetism at this end of the heavy element sequence which is not understood. Tb for example is only spiral over a very narrow temperature range.

V. JACCARINO: Why does the momentum dependent exchange interaction have a maximum at $q \neq 0$?

K. YOSIDA: The Fourier transform of the exchange integral has its maximum at a non-zero value of q in heavier rare-earth metals. The main contribution to such an exchange interaction is considered to come from the indirect exchange through conduction electrons. However, since this exchange interaction depends on the details of the structure of the conduction bands, it would be hard to derive it by calculation.

J. S. JARRETT: Kittel has recently pointed out that a fourth order in magnetization is obtained by taking into account in the free energy both the elastic strain energy and the dependence of the exchange parameter on strain. By taking into account both first and second nearest neighbour exchange interactions to stabilize the helical arrangement of spins, as well as elastic energy, in a linear chain model, one obtains the result that the angle between neighbouring spins changes with lattice parameter. As I recall the calculation, a 0.1% change in lattice parameter gives a 5° change in angle between spins. This result assumes that the change of the exchange interaction per unit change in lattice parameter is the same for both first and second nearest neighbour interactions. These results seem to be in good agreement with observation of rare earth, since the change in lattice parameter, due to normal thermal contraction over the temperature range of the observation of the change in angle between spins, is probably of the order of 0.1%.

R. J. ELLIOTT: This could presumably be easily checked experimentally, but I shall be surprised if it is as large as suggested. It does not seem to me to account for the fact that only the spiral structures show a change of wave length with temperature—the longitudinal sine wave arrangements do not. Moreover the pitch of the spirals shows the same hysteresis effects as the magnetisation.

C. J. GORTER: The pitch of the screws and cones be influenced by the high terms of crystalline anisotropy like V_6. Should not this lead to some irregularity of the

pitch (and the susceptibility) as a function of the temperature in a second approximation?

R. J. ELLIOTT: Yes, the hexagonal anisotropy certainly distorts the spirals and is presumably the cause of the more complicated ordering patterns observed for example in Ho.

J. SMIT: When considering transitions from a spiral or a fanned structure to the ferromagnetic state, either induced by a field or not, I think it is of importance to take into account the magnetoelastic energy. For a spiral structure the strain is zero, whereas, for the completely aligned (ferromagnetic) structure the stress is zero. The difference in energy is of the order $\lambda^2 E$. For Dy the magnetostriction λ is found to exceed 10^{-3}, so that $\lambda^2 E$ is at least 10^6 erg/cm^3. Thus the energy of the ferromagnetic state is lowered by this amount. It causes the transition to become of the first kind, as is observed in Dy.

D. S. RODBELL: Gadolinium is supposed to be a well behaved rare-earth and usually accepted as such. I have recently found some rather interesting behavior that perhaps you might comment upon. I have been measuring the magnetocrystalline anisotropy of single crystals of gadolinium and find that the easy axis (c-direction) that is appropriate to temperatures just below the Curie point ($\sim$20°C) changes abruptly between that temperature and 77°K. Since these are preliminary experiments I have not yet determined the exact temperature of the transition but it occurs very sharply. Can you suggest a reason for this behavior within the theories you have been discussing?

R. J. ELLIOTT: The magnetic anisotropy in Gd, while it has the same symmetry as the crystal field I wrote down, is related to that field in a complicated way, because it is an S-state ion. The energy terms are exactly those that appear in the spin hamiltonian of Gd salts and extensively in paramagnetic resonance.

The terms like V_n^0 vary as M^n so that the high order terms come in very rapidly at low T and thus may account for your effect.

S. G. COHEN: I would like to ask to what extent in time one would expect these spin ordering patterns to be fixed in the lattice.

R. J. ELLIOTT: The spin orders incommensurate with the lattice are not fixed except by domain effects and imperfections. However the neutron observations indicate that any motion of this kind is too slow to be observable.

R. KUBO: I saw some difference between the three papers on the rare earth magnetism. I wish I could hear discussions on those points where these authors differ essentially from one another.

R. J. ELLIOTT: The main difference between the papers lies in the approximate statistical mechanics used on the order-disorder problem. Yosida and Miwa and I both derived the same hamiltonian and Kaplan's is a little simplified. However I used the simplest order-disorder theory to get an answer at all temperatures and they used a more rigorous theory. There is also some difference of opinion about the origin of the temperature dependence of the spiral pitch.

T. A. KAPLAN: Two difference come to mind. Both Yosida-Miwa and myself considered the anisotropy to be small, whereas Elliott used the Ising model, i. e., a large anisotropy limit, for the high temperature behaviour in Er. Concerning the two-body anisotropy forces (which are important in connection with the thermal variation of wave length), Yosida-Miwa considered quadrupolar terms whereas I assumed dipolar terms. Both of these symmetries would be expected to arise in a way analogous to Van Vleck's "pseud" anisotropies. Since, however, in the present case the relative size of spin-orbit coupling and crystalline fields is the opposite of that considered by Van Vleck, the coefficients will be of a different form. This certainly should be calculated.

K. YOSIDA: One different point between Dr. Kaplan's treatment and ours is in the functional form of the anisotropy energy. Dr. Kaplan used the dipole-dipole type of anisotropy but we used the one-ion anisotropy which seems to be more realistic for rare-earth metals. If one uses the one-ion anisotropy, the temperature change in the period of the spin modulation becomes small compared with experimental results. On the other hand, according to Dr. Kaplan, if one uses the pseudodipolar anisotropy, the temperature dependence of the period can be explained for erbium because the ratio of the amplitude of the spin modulation along the c axis to that perpendicular to the c axis changes with temperature. However, this type of anisotropy can not explain the change of the pitch with temperature for dysprosium and holmium.

H. SUHL: May I ask the authors of the preceding three papers if they have considered the nature of elementary excitations above the state with the spins all aligned along the c-axis but varying sinusoidally in magnitude?

R. J. ELLIOTT: In the paper mentioned at the end of my preprint it is shown that when the sine wave is incommensurate with the lattice the elementary excitations cannot be conveniently described as waves. For example the ferromagnetic resonance will be very broad.

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Magnetization Process of a Spin Screw System

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1. Introduction

After the discovery of screw spin structure by Yoshimori[1] (first reported by Nagamiya[2] at the International Conference on Magnetism at Grenoble, 1958) and later by Villain[3] and Kaplan[4], a number of substances with this structure have been found by neutron diffraction experiment. Of particular interest are modifications of screw structure found in rare earth metals by Oak Ridge people[5] and theoretically interpreted by Elliott[6], Kaplan[7], Miwa and Yosida[8], and also by Kitano[9]. These modifications come about due to the effect of the anisotropy energy inherent in these metals. Another interesting phenomenon is the change of screw structure due to the action of an applied magnetic field, first observed by neutron diffraction experiment by Herpin and Mériel in $MnAu_2$[10]. They and also Enz[11] developed a theory for this phenomenon, but the present paper deals with it more generally and with more mathematical rigour*).

* Herpin and Mériel assume J_1 and J_2 only and further assume that the anisotropy energy is sufficiently large to confine the spin vectors in the plane of the layers. Enz treats the limiting case of $q_0 \to 0$. These restrictions are removed in the present paper. Furthermore, the particular cases of $q_0 = 180°$, 90°, 120°, which were not discussed by them, are studied in detail in the present paper. The merit of the present study lies in the calculation of the fourth order energy terms of Fourier amplitudes. For low fields, the fourth order term becomes infinite for $q_0 = 180°$ and 90° and vanishes for $q_0 = 120°$, which show that these cases have to be dealt with carefully. For high fields, the fourth order terms are essentially important when the second order terms become negative, namely when