In terms of the level splitting of the electronic state $4f^1(2F_5/2)$ due to the crystalline and exchange field, the magnetic susceptibility and specific heat of cubic cerium are calculated theoretically and compared with experiments. The intensity of the crystalline field is also estimated using a simplified model of the metallic state. The agreement between theory and observation is fairly good.

§ 1. Introduction

Since the mass separation of rare earth metals has become possible by means of the ion exchange technique, the magnetic properties of these metals have been extensively studied experimentally. It is now known that many of these elements are ferro- or antiferromagnetic and their magnetic behaviors are quite different from those of the iron group. The carriers of the magnetic moment in rare earth metals are the electrons occupying $4f$ orbitals incompletely, which seem to localize almost as if they were in the free atomic state, and hence keep their orbital magnetic moments without much interference from the electric crystalline field. The mechanism of exchange coupling between magnetic moments in rare earth metals is therefore expected to be somewhat different from the case of ordinary magnetic metals in that conduction electrons would play an important role in aligning the spin magnetic moments of the ion core, each of which is strongly coupled to the orbital moment through the spin-orbit interaction. This is Zener's picture of exchange. A similar idea was applied by Pauling to Gd and more recently investigated in detail by Kasuya in connection with the electric and magnetic properties of transition metals. As was pointed out by Kasuya, the strange feature of magnetism in rare earth metals is believed to come from the fact that, beside the extraordinary exchange mechanism mentioned above, there exist interactions between an orbital moment and crystalline field or between an orbital moment and other orbital moments, which will give rise to complicated effects, varying with the number of $4f$ electrons and with the temperature.

The object of this paper is to present an atomistic theory of the thermal and magnetic properties of metallic cerium. This element is the simplest one in the sense

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that the incomplete shell has only one 4\textit{f}-electron, and therefore provides a good starting point for theoretical study.

The cerium metal has a cubic close-packed and hexagonal close-packed structure, but here we restrict our interest only to the former and the latter is reserved to a later paper. For the cubic close-packed cerium metal, the measurements on the specific heat, magnetic susceptibility, electrical resistivity, Hall effect and dilatometry reveal that there exists a kind of phase change accompanied with large temperature hysteresis extending over about 50–200 K, and from the remarkable contraction observed on cooling Pauling suggested that this phase change is caused by the promotion of 4\textit{f}-electrons to the 5\textit{d} valence band. According to the specific heat measurement there appears another anomaly at about 12 K and Lock showed in his recent experiments on susceptibility that this temperature corresponds to an antiferromagnetic Néel point. He also showed that the transition to the contracted phase, called the \( \alpha \)-phase, depends largely on the history of the sample: repeating the measurements more than one hundred times the transition did not take place, but in the first cycle half of the 4\textit{f}-electrons seemed to be promoted to the valence band. For the older observations we must therefore consider the cycle of experiment when we compare them with theoretical results.

§ 2. The state of the 4\textit{f}-electrons in metals with cubic close-packed structure

The same kind of problem has already been considered by Penney and Schlapp for paramagnetic rare earth salts in which there was no exchange field. We here treat the exchange field in the molecular field approximation, and hence the problem can be reduced to the one ion problem. In a cubic crystal the Hamiltonian has the form

\[ \mathcal{H} = D (x^4 + y^4 + z^4 - \frac{3}{2} r^4) + H_0 J_z, \]  

(1)

where \( D \) is a constant which expresses the intensity of the crystalline field and \( H_0 = g \mu \cdot (H_{ex} + H_s) \). \( g \) is the Lande \( g \)-factor, \( \mu \) Bohr magneton and \( H_{ex} \) and \( H_s \) mean respectively the effective exchange field which acts on each 4\textit{f}-electron and the applied external magnetic field. As the spin-orbit coupling is strong, the energy separation between the ground state, \( ^2F_{5/2} \), and the next excited state, \( ^2F_{7/2} \), is about 2200 cm\(^{-1}\) and we can regard \( J^2 = \text{constant} \). In the subspace of \( J = \frac{5}{2} \) the Hamiltonian (1) can be expressed in terms of equivalent operators:

\[ \mathcal{H} = q J_z^2 \left( 7 J_z^4 - \frac{190}{4} \right) + \frac{q}{2} (J_z^4 + J_z^2) - H_0 J_z, \]  

(2)

where \( q = D \beta \bar{r}^4 / 4 \), and the notations \( \beta \) and \( \bar{r}^4 \) are due to Stevens. Here we have dropped constant terms.

The energy eigenvalues and their eigenfunctions are easily obtained: Putting \( x = H_0 / q \), the eigenvalues are

\[ W_1 = \frac{q}{32} \left\{ -1518 + 16x - (1327104 + 98304x + 4096x^2)^{1/2} \right\}, \]
On the Magnetic Properties of Cubic Cerium

\[ W_2 = \frac{q}{32} \left\{ -1518 - 16x - (1327104 - 98304x + 4096x^2)^{1/2} \right\}, \]

\[ W_3 = \frac{q}{32} \left\{ -1518 + 16x + (1327104 + 98304x + 4096x^2)^{1/2} \right\}, \]

\[ W_4 = \frac{q}{32} \left\{ -1518 - 16x + (1327104 - 98304x + 4096x^2)^{1/2} \right\}, \]

\[ W_5 = q \left\{ \frac{-183 + x}{16} \right\}, \]

\[ W_6 = q \left\{ \frac{-183 - x}{16} \right\}, \]

and their corresponding eigenfunctions are

\[ \Psi_1 = N_1 (\phi_{-3/2} + c_1 \phi_{-5/2}), \quad \Psi_2 = N_1 (\phi_{-5/2} + c_2 \phi_{-3/2}), \]

\[ \Psi_3 = N_3 (\phi_{-3/2} + c_3 \phi_{-5/2}), \quad \Psi_4 = N_3 (\phi_{-5/2} + c_4 \phi_{-3/2}), \]

\[ \Psi_5 = \phi_{1/2}, \quad \Psi_6 = \phi_{-1/2}, \]

where

\[ c_1 = \frac{1}{384 \sqrt{5}} \left( 768 \pm 64x - (1327104 \pm 98304x + 4096x^2)^{1/2} \right), \]

\[ c_3 = \frac{1}{384 \sqrt{5}} \left( 768 \pm 64x + (1327104 \pm 98304x + 4096x^2)^{1/2} \right). \]

In eqs. (5), plus signs are taken for \( c_1 \) and \( c_3 \) and minus signs for \( c_2 \) and \( c_4 \). \( N_1 \) in eqs. (4) are normalization constants, namely \((1 + |c_1|^2)^{-1/2}\), and \( \phi_{1/2} \) is the normalized eigenfunction of \( J_2 \).

For \( x = 0 \) they group into a doublet (1 and 2) and a quartet (3, 4, 5 and 6), and their energy separation \( \Delta \) equals \( 72q \). In § 5, where we calculate the magnitude and sign of \( D \), it is shown that \( q > 0 \), and therefore the doublet is lower. When \( x \neq 0 \), all of the degeneracies are removed completely and the ground level is the state 1. This is illustrated in Fig. 1. In terms of these energy levels, we can calculate the magnetic susceptibility and the specific heat, from which the parameter \( q \) can be determined.

At sufficiently low temperature, \( T \ll \Delta/k \), where the lower levels play a dominant role in determining the physical properties, the quasi-angular momentum defined for the lower levels is expected to be replaced by an effective spin, \( s \), which will have the magnitude
1/2 in the present instance, for the ground state is a doublet and must be symmetrical with respect to the \( x \), \( y \) and \( z \) directions. The wave functions for these two levels are given by

\[
\Phi_1 = \sqrt{\frac{5}{6}} \left( \psi_{3/2} - \frac{1}{\sqrt{3}} \psi_{1/2} \right), \quad \Phi_2 = \sqrt{\frac{5}{6}} \left( \psi_{-3/2} - \frac{1}{\sqrt{3}} \psi_{-1/2} \right).
\]

Taking \( \Phi_1 \) and \( \Phi_2 \) as a basis, the matrix elements of \( J \) may be calculated and expressed as

\[
J = -\frac{s}{3},
\]

where \( s \) is the usual spin operator with \( s=1/2 \). This means that the problem can be reduced to the case in which the magnitude of the spin is 1/2 but the Lande \( g \)-factor is modified to \( g' = -(5/3)g \).

### § 3. Specific Heat

For the moment we shall forget the antiferromagnetism below \( T_N=12^\circ K \) in which case we can easily calculate the anomalous part of the specific heat due to Stark splitting, and by making comparison with observation it will be possible to determine the parameter \( q \). Without considering the lattice vibration and other small contributions, the specific heat is given by

\[
C = \frac{2Nk_\beta^4 e^{-\Delta}}{(1+2e^{-\Delta})^2},
\]

where \( \beta = 1/kT \) and \( N \) is the number of 4f-electrons. If we take

\[
\Delta/k = 240^\circ K,
\]

the maximum of the general trend of the calculated specific heat coincides with that part of the experimental curve which is believed to be due to the crystalline splitting. The experimental values are however far lower than the theoretical curve if we take \( N \) as one electron per atom. In Fig. 2 we show the observed and theoretical specific heat curves calculated for two typical cases: (a) one 4f-electron per atom and (b) 1/2 per atom on the average. From the figure we see that experimental values observed by Parkinson et al. corresponds nearly to the case (b).

Actually, this can be confirmed still further when we consider the specific heat below the Néel point. The entropy of the anomalous part below the Néel point estimated by Parkinson et al. is about 0.6, which is close to \( (R/2)\ln 2 \approx 0.688 \). Parkinson and Roberts\(^{15} \) made a more detailed experiment on the specific heat and found that the entropy under the highest peak up to \( 20^\circ K \) is only a little less than \( R \ln 2 \) for the 50th cycle of measurement in which case there should be almost no phase transition to \( \alpha \)-phase. But for the first cycle the anomalous part of specific heat is very nearly equal to half of that of the 50th cycle at every temperature they observed. On the other hand, the
magnetic entropy seems to tend to the value $R \ln(2J+1)$ at $300^\circ K$, and this leads us to consider the $\alpha$-phase as that half the atoms having a trivalent configuration and the other half a quadrivalent configuration are in some kind of ordered state. The magnetic moments of the former group are to have an antiferromagnetic arrangement below the Néel point.

![Fig. 2. Specific heat of cubic cerium observed by Parkinson, Simon and Spedding (Proc. Roy. Soc. A207 (1951), 137) (a) calculated assuming one $4f$-electron per atom (b) calculated assuming $1/2$ $4f$-electron per atom](https://academic.oup.com/ptp/article-abstract/18/3/215/1934789)

Using the molecular field approximation, the specific heat below the Néel point can be expressed as

$$C = -\frac{1}{2} NkT_N \cdot \partial \sigma^2 / \partial T,$$

where $\sigma$ is the reduced spontaneous magnetization of each sublattice. As was already mentioned in § 2, the reduced magnetization of spin $1/2$ can be used for $\sigma$. Taking $T_N=12^\circ K$, the calculated curves are shown in Fig. 2 as (a) and (b), corresponding to the two cases mentioned above. The tail immediately above the Néel point is thought to be due to short-range order.

§ 4. Magnetic susceptibility

The susceptibility was observed by La Blanchetais, for pure samples down to $80^\circ K$ and it was found that the susceptibility of the $\gamma$-phase, (high temperature phase of cubic close-packed structure) and of the hexagonal $\beta$-phase almost coincided with each other. Lock also observed the susceptibility in successive cycles of measurements and found
nearly the same result qualitatively, but he found that the Néel temperatures of each cycle were almost the same and that the successive cycles inhibited the transition to the α-phase. The phase obtained after many cycles seems to correspond to the γ-phase, although X-ray analysis shows traces of β-phase in addition to the γ-phase. On the other hand, the Curie constant estimated for the first cycle was nearly half of that of the γ-phase. This again confirms the supposition that half of the 4f-electrons are promoted to the valence band.

We now calculate the susceptibility with the same value of Δ as obtained in § 3. The value Δ/k=240°K is, however, thought to be due to 3.5 valence electrons per atom on the average in the α-phase. Hence we use Δ/k=240×(3/3.5)=206°K for the γ-phase, because in our approximation Δ is proportional to the valency (see § 5). The statistical mean value of the magnetic moment per atom, ⟨mz⟩, is generally given by

$$\langle m_z \rangle = \frac{1}{Z_0} \sum_{n} \sum_{n'} \frac{1-e^{-\Delta_{nn'}}}{\Delta_{nn'}} e^{-\beta E_n} |m_{zz}|^2 (H_{ez} + H_z),$$  \hspace{1cm} (11)

where E_n is the energy eigenvalue of the n-th state and Δ_{nn'}=E_n-E_{n'}, Z_0=∑_n exp(−βE_n), and m_{zz} is the matrix element of the operator gμJ_z between the state n and n'. The summation is performed over all states. Calculating the matrix elements by (4) and (5), we can express the magnetization M=N⟨m_z⟩ as

$$M = \frac{C}{T} F(T) (H_{ez} + H_z),$$  \hspace{1cm} (12)

where C=N(gμ)^2J(J+1)/3k is the Curie constant for sufficiently high temperatures and F(T) is a correction factor due to crystalline field given by

$$F(T) = \frac{4}{7} \left[ \frac{1}{2 + e^{\Delta/kT}} \right] \left[ \frac{1}{12} (26 + 5 e^{\Delta/kT}) + \frac{8 kT}{3} (e^{\Delta/kT} - 1) \right].$$  \hspace{1cm} (13)

As it should be, F(T) tends to unity as T→∞. In the molecular field approximation H_{ez} can be assumed proportional to M, and hence we may put

$$H_{ez} = -(\Theta/C) M.$$  \hspace{1cm} (14)

From (12) and (14) susceptibility $\chi=M/H$ is obtained as

$$\chi = \frac{CF(T)}{T + \Theta F(T)}.$$  \hspace{1cm} (15)

We calculate $\chi$ as a function of temperature by adjusting the parameter Θ in such a way that theoretical value coincides with observed one at T_N. The results are shown in Fig. 3 together with experimental values measured by Lock. The assumed values of Δ, Θ, etc., are as follows;

<table>
<thead>
<tr>
<th>cycle no. in Lock's exp.</th>
<th>Δ/k</th>
<th>Θ</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>curve (b)</td>
<td>1</td>
<td>240°K</td>
<td>10°K 1/2 4f-electron per atom</td>
</tr>
<tr>
<td>curve (a)</td>
<td>102</td>
<td>206°K</td>
<td>12°K one 4f-electron per atom</td>
</tr>
</tbody>
</table>
On the Magnetic Properties of Cubic Cerium

The susceptibility below the Néel point depends on the nature of magnetic superstructure and anisotropy energy, and since little is known experimentally about both properties we cannot go into the detailed discussion. As was seen in § 2, however, cerium at low temperatures can be regarded as an assembly of spin 1/2 with the Lande factor \( g' = -(5/3)g \), and magnetic anisotropy will be very small. Therefore the susceptibility below the Néel point is constant in the first approximation as shown in Fig. 3.

§ 5. The intensity of the crystalline field

In order to verify that the empirically derived crystalline field intensity used in the earlier sections is consistent, we calculate it using a reasonable model: The valence electrons are smeared out uniformly over the metal and the point (or spherical) charges of ion cores are located at each lattice site. The uniform minus charge does not contribute to the crystalline field except for the Madelung term and may be omitted here. The \( D \) in (1) is then given by

\[
D = -\frac{5}{3} \sum_n e^2 \nu / R_n^5
\]

where \( \nu \) is the valency and \( R_n \) means the distance of the n-th atom from the origin. We adopt the direct sum method, and actually the summation is performed within the cube of edge length \( 12a \) including the origin. Here \( 2a \) equals the lattice constant. The result is

\[
D = +0.680 (ve^2/a^4).
\]

Hence we get

\[
q = \frac{D \beta^2 \nu A}{4} = +170 \beta \frac{ve^2}{a} \frac{r^4}{a^4}.
\]

Taking \( a = 2.57 \times 10^{-8} \text{cm}, \quad \beta = 2/7.45, \quad q = 2.86k \) (§ 3, § 4) for the \( \gamma \)-phase, we obtain
If we use the Slater-function for the 4f-orbital to determine \( \bar{r}^2 \) in terms of \( Z^* \), the effective nuclear charge, \( v \) equals 2.5 for \( Z^* = 12 \). This value of \( Z^* \) is also obtained from the Slater-rule, although it is not very reliable for 4f-electrons. The result here obtained is nevertheless quite reasonable. That the value of \( v \) is smaller than 3 is thought to be due to the screening by conduction electrons.

§ 6. Conclusions

The anomalous behavior of cerium metal at low temperatures can be partly explained by taking account of the crystalline field as well as exchange field. The magnetic properties of the \( \alpha \)-phase are interpreted by assuming that half of the 4f-electrons are promoted to the valence band. The detailed structure of this phase can be revealed only by neutron diffraction experiments however. The order of magnitude of the exchange coupling between nearest neighbours can be given by \( k \theta \). If the exchange force affects more than nearest neighbours, as is the case of Zener's mechanism, the small value of the ratio \( \theta F(T_N)/T_N \), which is 0.264 for the \( \alpha \)-phase and 0.312 for the \( \gamma \)-phase, suggests that the exchange interaction changes its sign with distance.\(^{4,47}\)

Analysis of hexagonal rare earths is now in progress and will be discussed in another paper.

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