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MAGNETISM IN THE LIGHT RARE EARTH METALS

A. R. MACKINTOSH

H. C. Ørsted Institute, University of Copenhagen

Abstract. — The magnetic properties of the light rare earth metals are reviewed with special emphasis on crystal field effects, which may be comparable in magnitude to the effective exchange interaction. The discussion is illustrated by recent magnetization and neutron diffraction measurements on single crystals of Eu, Nd and Pr. The theoretical and experimental methods by which the magnetic interactions in the light rare earths may be further elucidated are considered.

1. Introduction. — Because of the extensive experimental and theoretical studies of their properties which have been carried out over the last decade, the magnetism of the heavy rare earth metals is now rather well understood. The magnetic and transport properties of single crystals have been measured, the magnetic structures have been elucidated by neutron diffraction, and inelastic neutron scattering studies of the spin waves have led to a rather detailed understanding of the magnetic interactions. On the other hand, the light rare earths have received substantially less attention, partly because of the technical difficulty of producing good single crystals and partly on account of the forbidding complexity of their structural and magnetic properties.

The most important distinction between the heavy and light rare earths lies in the relative magnitudes of the exchange and crystal field energies. Beyond Gd, Hund’s rules ensure that the spin is parallel to the orbital momentum so that the projection \( (g-1) J \) of the spin on the total angular momentum is large, and hence so is the indirect exchange. The magnitude and long range of this exchange dominates the magnetic properties, although the crystal fields give rise to a magnetic anisotropy which is frequently large and acts as an important perturbation in modifying the magnetic structures and excitations. The \( 4f \) charge clouds in the light rare earths extend further into the crystal, so that crystal field effects tend to be stronger, but a more important distinction is that \( (g-1) J \) and hence the effective exchange is frequently small, as may be seen in Table I. Under such circumstances, the exchange and the crystal fields must be treated on an equal footing and, as we shall see, in the case of Pr it is the latter which dominate the magnetic properties.

In this paper, we will attempt to review briefly the available information on the magnetic properties of the light rare earths, with special emphasis on the results which have recently been obtained in Denmark on single crystals, of Pr, Nd and Eu. We will begin by reviewing the spectroscopic properties of the ions, and the crystal and electronic structures which determine the magnetic interactions in the metal. We will then discuss the magnetic structures and properties of the individual metals, beginning with Eu, in which crystal field effects are not very important, and proceeding towards the beginning of the series, where they play a vital role. The extent to which the magnetic properties can be understood in terms of the magnetic interactions will be considered. Finally the deficiencies in our understanding of the magnetism of the light rare earths will be emphasized, and experimental and theoretical possibilities for further elucidation of their properties will be suggested.

2. Ionic properties. — The \( 4f \) electrons in the light rare earth metals are sufficiently well protected from their environment by the filled \( 5s \) and \( 5p \) shells that they behave very much as in the free ions. Their ionic ground states are therefore determined by Hund’s rules; \( S \) is maximized, \( L \) is maximized subject to maximum \( S \) and, since the subshell is less than half-filled, \( J \) is minimized. The resulting configurations are shown in Table I. The spin-orbit coupling is sufficiently large that, with the exception of Sm and to a lesser extent Nd, the first excited \( J \)-multiplet is negligibly populated at ordinary temperatures. With the exception of Eu, which is divalent and unlike the other metals, \( L \) and \( J \) are both quite large, as \( g \) is small so that the theoretical paramagnetic moment \( g/\mu_B[J(J+1)]^{1/2} \) is generally smaller than in the heavy rare earths. This is in accord with the experimentally measured values.

If crystal field effects are neglected, the magnetic ordering temperature in the molecular field theory is given by

\[
kT_e = \frac{3(Q)}{3} (g-1)^2 J(J + 1)
\]

where \( Q \) is the wavevector of the ordered structure and \( 3(q) \) is the Fourier transform of the indirect exchange interaction, defined by

\[
3(q) = \sum_{k} 3(R_k) e^{i\mathbf{q} \cdot \mathbf{R}_k}.
\]

Again with the exception of Eu, the low values of \( (g-1)^2 J(J + 1) \) are reflected in low ordering temperatures.
3. Crystal and Electronic Structure. — The crystal structure of a metal at low temperatures is determined by the minimization of the sum of the Ewald energy of the ions and the conduction electron energy. The intra-ion exchange energy is an important feature in determining the valence. Thus Ce, in which this exchange is small, has a tendency to promote its 4f electron to the conduction band, forming a quadrivalent ion, while the gain in exchange energy associated with filling all states of a particular spin causes Eu and Yb to be divalent. These metals are therefore analogous to the alkaline earth metals and their structures are largely determined by the effect of the d-bands on the conduction electron energy [1], which favours the bcc structure in Eu. The other light rare earths reduce their Ewald energies by forming symmetrical, close-packed structures, but the exact nature of the packing is again apparently determined by the conduction electrons. At low temperatures, trivalent La, Ce, Pr, and Nd all form stable phases with the ABAC-dhcp structure, in which the ionic sites have local symmetry which is cubic or hexagonal according to the pattern chch. Under some circumstances, they also form the ABC-fcc structure. The unusual rhombohedral structure of Sm, in which the planes are stacked in the order ABABCBCAC is a generalization of the dhcp structure in which the local symmetry follows the pattern chhchchhchh. In all of the uniaxial structures the c/a ratio is less than the ideal value of 1.63.

The packing in the light rare earths is probably determined by the minimizing of the conduction electron energy through reducing the Fermi surface area. Some support is given to this hypothesis by qualitative arguments based on band structure calculations [2]. These show the importance of the d-electrons in the band structure, and the characteristics of Fermi surface associated with the d-bands, which are important in determining the magnetic structures. There is however virtually no explicit experimental evidence about the conduction electrons available at present, so it is difficult to draw more than qualitative conclusions about their influence on the properties of the light rare earths.

4. Magnetic Properties. — Recent studies on single crystals have resulted in substantial progress in our understanding of the magnetic properties of the light rare earths. In this section we will review the present state of knowledge of each metal in turn, emphasizing those features which seem to be of fundamental interest.

4.1 Europium. — Magnetization [3] and neutron diffraction [4] measurements have earlier revealed that Eu is antiferromagnetic, with an ordering temperature around 90 °K. The magnetic structure is a helix characterized by a Q vector along the [100] direction, which is slightly temperature dependent and corresponds to an incommensurable periodicity of about 3.6 lattice spacings. More recent magnetization and neutron diffraction studies [5] on single crystals have added further details to this picture.

Table I

<table>
<thead>
<tr>
<th>Properties of light rare earth metals</th>
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<tbody>
<tr>
<td>Structure</td>
</tr>
<tr>
<td>dhcp, fcc</td>
</tr>
<tr>
<td>Valence</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>J</td>
</tr>
<tr>
<td>g</td>
</tr>
<tr>
<td>g(dJ)</td>
</tr>
<tr>
<td>(g - 1)²J(J + 1)</td>
</tr>
<tr>
<td>T_s (°K)</td>
</tr>
<tr>
<td>12.5</td>
</tr>
</tbody>
</table>

where \( j(q) \) is the Fourier transform of the s-f exchange and \( \chi(q) \) is the wavevector-dependent susceptibility of the conduction electron gas. The peak in \( \chi(q) \) which gives rise to the periodic structure has been attributed by Krogh Andersen and Loucks [1] to a particular feature of the Fermi surface, and the low value of \( \chi(q) \), compared with that for the heavy rare earths, is due to the fact that the Fermi level falls near the bottom of the d-bands, where the density of states is low.

The magnetic structure of Eu is reminiscent of that of Cr, the other bcc antiferromagnetic metal, and this parallel is made more striking by the fact that they both undergo first-order transitions to the ordered state. For Eu, this was first deduced from Mössbauer studies on a very imperfect sample [6], but it may also be observed in the single-crystal magnetization curves [5] of figure 1, and accounts for the unusual temperature dependence of the neutron diffraction intensities [4]. The formation of a magnetic state in Cr, which has no local moments, requires a singularity in \( \chi(q) \), but the conduction electrons in Eu minimize their energy by taking advantage of the s-f interaction. This coupling between the conduction and localized electrons is also manifested in the paramagnetic moment which, because of conduction electron polarization, takes the value 8.48 μB/atom [5] compared...
with the theoretical 7.9 \( \mu_B/\text{atom} \). It is also largely responsible for the rapid change in the electrical resistivity [7] near \( T_N \), shown in figure 2. Unlike Cr, the resistance falls at the transition, indicating that the effect of new energy gaps in the conduction electron bands is more than compensated by the decrease in disorder scattering. There is a large amount of critical scattering of the conduction electrons above \( T_N \), as is also observed in Gd.

4.2 Samarium. — The difficulty of preparing pure single crystals and the unfavourable neutron properties of natural Sm have served to limit the amount of experimental information on this metal. Anomalies in the resistivity [7] (see Fig. 2) and the heat capacity [8] at about 106 \(^\circ\)K and 14 \(^\circ\)K may indicate magnetic transitions on the two different types of site. Mössbauer results [9] at 80 \(^\circ\)K show that at least one type of site is disordered at this temperature. Preliminary measurements on a single crystal [10] indicate that the \( c \)-axis is the easy direction.

An interesting feature of Sm is the low-lying \( J = 7/2 \) multiplet, which lies only about 0.1 eV above the \( J = 5/2 \) ground state. This has the consequence that Curie's law is not satisfied at high temperatures, where the magnetization varies relatively slowly with temperature [11, 12]. This behaviour is explained qualitatively by the theory of Van Vleck [13], but the quantitative agreement is not very good for the level scheme used [12]. The complete neglect of crystal field effects may contribute to this discrepancy.

4.3 Neodymium. — The relatively detailed measurements which have been made on monocristalline dhcp Nd have revealed that the magnetic ordering is substantially affected by the crystal fields. The magnetic structure was first investigated by Moon et al [14] by means of neutron diffraction, and the effect of a magnetic field studied by Johansson et al [15]. At 19.2 \(^\circ\)K the moments on the hexagonal sites form a periodic structure

\[
\mathbf{\mu}_B = - u_c = \mu_B \mathbf{b}_c \cos Q_a \mathbf{R}
\]

where B and C refer to layers of ions. The ordered moments lie along a [100] \( \mathbf{b}_4 \) direction, as does the temperature-dependent wavevector \( Q_a \). At 7.5 \(^\circ\)K the cubic sites order according to

\[
\mathbf{\mu}_A = - \mathbf{\mu}_A' = \mu_A \mathbf{b}_2 \cos Q_c \mathbf{R}
\]

where A and A' are neighbouring cubic layers. The moments lie along [110] while \( Q_c \), which is again temperature-dependent, is along [100]. These structures are illustrated in figure 3. Because of crystal field effects, the maximum moment in zero field does not approach the theoretical maximum \( g\mu_B J = 3.2 \mu_B \) at low temperatures, on either type of site. The occurrence of these periodic structures has been tentatively ascribed to peaks in \( \chi(\mathbf{q}) \) associated with specific features of the Fermi surface [2], and the ferromagnetism of the fcc phase [16] which has a Curie temperature of about 29 \(^\circ\)K has also been related to the band structure [17].

A magnetic field in the [110] direction at 4.2 \(^\circ\)K has a profound effect on these structures as is illustrated in figure 4. In low fields the moments on the hexagonal sites turn parallel to those on the cubic sites, and at the same time a ferromagnetic moment is developed on the cubic and hexagonal sites in the ratio of approximately 5/2. At about 23 kG, there

![Fig. 2. — The temperature dependence of the electrical resistivities of Eu, Sm and Pr, after Ref. [7].](image)

In the antiferromagnetic phase, there is a small magnetic anisotropy, as may be seen in figure 1, which does not change greatly with temperature. The moment developed when the field is in the [100] direction results from tilting the ordered spins out of the plane of the helix, which requires more energy than distorting the helix in its plane. The low field susceptibility in all directions increases very slowly with temperature up to 14.5 \(^\circ\)K, when it drops abruptly [5]. This behaviour, which is not at present understood, may be associated with magnetic anisotropy.
is an abrupt increase in both the ferromagnetic and periodic moments on the hexagonal sites, so that the greatest total moment at a hexagonal site approaches the theoretical maximum. This abrupt change may be due to the crossing of crystal field levels in the magnetic field. Above this field, the ferromagnetic moment on the hexagonal sites grows at the expense of the periodic moment. The periodic moment on the cubic sites decreases steadily with field and disappears at about 31 kG, with a corresponding increase in the ferromagnetic moment. A magnetic field in the [001] direction has considerably less effect.

There are no qualitative changes in the magnetic structure, but a substantial ferromagnetic moment develops, almost exclusively on the cubic sites. As may be seen in figure 5, the susceptibility suffers no abrupt changes, apart from that associated with domain formation at low fields, and the susceptibility is considerably smaller than that in the basal plane.

The excited $J = \frac{1}{2}$ multiplet is separated from the ground state multiplet by only about 0.2 eV and there are therefore relatively small but significant departures from Curie's law at high temperatures, which may be accounted for rather accurately by Van Vleck's theory.

4.4 PRASEODYMIUM. — Pr$^{3+}$, which has two f-electrons, is a non-Kramers ion so that, unlike for instance Nd, a crystal field may produce singlet states. In fact the ground states of the ions at both the cubic and hexagonal sites in the metal are singlets and so, as pointed out by Trammell [20], magnetic ordering cannot occur unless the exchange exceeds a critical value.

The crystal field levels of the ions in Pr metal were first discussed in detail by Bleaney [21]. A slight modification of his level scheme, due to Rainford [22], which takes account of the reduced c/a ratio, is shown in figure 6, together with a comparison between the heat capacity calculated on the basis of this model.
and the experimental results of Parkinson and al. [23]. Above 10°K the agreement is very good ; below this temperature collective effects make the simple independent-ion model inadequate.

The properties of systems with singlet ground states have been discussed by a number of authors, particularly by Cooper [24]. If magnetic ordering does not occur, the susceptibility at 0°K of a system consisting of ions with two singlet states, separated by an energy $\omega$, is given in the molecular field theory by

$$\chi = \frac{\omega}{g^2 \mu_B^2 \omega^2 - \lambda}$$

where $\omega$ is the matrix element of $J_x$ between the states. $\lambda$ is the molecular field constant, defined by

$$\lambda = \frac{4 \lambda(0)}{8 \lambda_{fB}}.$$ 

The condition for ferromagnetism is that $\chi$ should diverge, or

$$4 \lambda(0) \omega^2 / \lambda > 1.$$ 

More sophisticated treatments [24] modify this result slightly, but it remains true that ordering occurs only if the ratio of exchange to crystal field splitting exceeds a critical value.

It appears that the energy separation between the ground and excited states at the cubic sites in dhcp Pr is too great to allow magnetic ordering, although the fcc allotrope is ferromagnetic [16] with a Curie temperature of 8.7°K. Neutron diffraction measurements on a polycrystalline sample by Cable and al. [25] revealed antiferromagnetic reflections which were ascribed to the hexagonal sites. However, more recent measurements on single crystals [15] failed to detect any spontaneous ordering in zero field at 4.2°K. A magnetic field in the basal plane produces a large induced moment which shows a substantial tendency towards saturation at high fields, as illustrated in figures 4 and 5. This moment is divided between the hexagonal and cubic sites in the ratio 2/1. The molecular field constant required to fit these results is close to the critical value necessary for ferromagnetism. When the field is applied in the [001] direction, the susceptibility is more than an order of magnitude smaller, as illustrated in figure 5, and the moment on the hexagonal sites is extremely small. The [001] susceptibility has a maximum at about 30°K, so that the moment induced at this temperature is considerably greater than that at 4.2°K. Using an isotropic molecular field constant, Bleaney [21] showed that the susceptibility for the hexagonal sites should be about five times greater in the [001] direction than in the plane, while the cubic sites should have an isotropic susceptibility. The experimental results therefore require an extremely anisotropic temperature-dependent effective exchange, which results in a negative molecular field constant for the [001] direction. Such an anisotropic effective exchange is one of the features of the Wang and Cooper [24] pseudo-spin formulation of the singlet ground state problem. We may therefore suppose that the temperature dependence of the [001] susceptibility is the result of the development of this anisotropic effective exchange as the ions fall into their singlet ground states.

In the absence of exchange, the excitations of the singlet system are just the excitation of a single ion from the ground to excited state, created by

$$a_i^+ = c_i^+ c_i^-.$$ 

Exchange couples the ions together so that the excitations have the form of magnetic excitons, created by an operator of the form

$$a_q^+ = N^{-1/2} \sum_i c_i^+ c_i^- e^{i \mathbf{q} \cdot \mathbf{R}_i}.$$ 

with a low-temperature dispersion relation, in a simple approximation [20]

$$\varepsilon(q) = A \left[ 1 - 4 \frac{\chi(0)}{A} \right]^{1/2}.$$ 

The condition (8) for ferromagnetism then corresponds to the instability of the $q = 0$ mode. Again more sophisticated treatments [24] change this picture quantitatively, but not qualitatively. These excitations may be studied by inelastic neutron scattering, and their recent observation by Rainford and Houmman [22] opens the possibility for detailed measurements of the crystal field levels and exchange interactions.

### 4.5 Cerium.

Experimental studies of the magnetic properties of Ce are plagued by the difficulty of producing a pure phase to study. Available experimental data are therefore somewhat fragmentary and difficult to interpret. The high temperature paramagnetic susceptibility [11] corresponds to the $J = 5/2$ ground state, with small corrections due to the proximity of the $J = 7/2$ multiplet and conduction electron polarization [26]. Paramagnetic neutron scattering at room temperature is also consistent with the free-ion configuration [27]. Magnetic susceptibility [11] and heat capacity [23, 28] measurements have anomalies at 12.5°K, which powder neutron diffraction measurements [27] show to be due to an ordered state in the dhcp structure. The data are consistent with a periodic magnetic structure with the moments along the $c$-axis, and a maximum ordered moment of about 0.6 $\mu_B$/atom. This is considerably less than the free-
ion value of 2.14 μB/atom, presumably due to crystal field effects. These are also apparent in the heat capacity measurements [28], and have been studied in the trivalent fcc phase by inelastic neutron scattering [29]. The results are consistent with a crystal field splitting of about 10 meV and a rapid relaxation of the excited levels through interaction with the conduction electrons. More detailed information on the magnetic properties of Ce will probably have to await improved techniques for the production of single phases and single crystals. Recent progress in this direction is reported elsewhere in this Conference.

5. Conclusion. — In this review, we have emphasized the importance of the crystal field interactions with the 4 f electrons in understanding the magnetic properties of the light rare earths. Unfortunately the fundamental theory of crystal fields in metals is still at a fairly rudimentary level, but model calculations, using a few parameters and taking account of the crystal symmetry, can be very useful in interpreting the experimental data. The crystal field interactions and the indirect exchange together determine the magnetic properties, and it is therefore particularly important to understand the way in which they act together. In particular, the projection of Heisenberg exchange into a situation in which the ions are sizably the importance of the crystal field interactions are at present

The exchange interaction between the conduction electrons and the localized moments can be effectively studied through the transport properties. For instance, the resistivity measurements on Pr of figure 2 clearly contain substantial information on the scattering of the conduction electrons from the crystal field states of the ions, and studies of single crystals in a magnetic field would be even more informative. The performance of such experiments requires the preparation of relatively large, high-quality single crystals. Because of the absence of such samples, the experimental results on Sm and Ce are at present rather fragmentary. There seems no reason why single crystals of Sm with good neutron properties should not be made, but Ce presents a more formidable problem. In the cases of Pr and Nd, the way seems open for the production of large single crystals and a detailed study of their properties. Eu is a special case, since crystal field effects are relatively unimportant, but its magnetic behaviour has some surprising features which require further theoretical and experimental study. Fortunately large single crystals are already available.

Our understanding of the light rare earths has reached the level which was attained for the heavy rare earths approximately five years ago. The basic theoretical ingredients for explaining their magnetic properties are available, and we may hope that further experimental work, especially perhaps with inelastic neutron scattering, will take us to the point in another few years where we can claim to have a good understanding of the magnetic interactions and properties of all the rare earth metals.

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