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Novel magnetic phases in holmium

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The new magnetic phases, involving spin-slip and helifan structures, which have recently been identified in Ho, are described. The genesis of these structures and the cone in the competing magnetic interactions, and their possible significance for other rare-earth systems, are discussed.

1. Introduction

Through their classic neutron-diffraction studies of Ho, Koehler and his colleagues established the essential features of the magnetic structure as a function of temperature [1] and magnetic field applied in the basal plane [2]. Their work solved many problems but also left behind a number of questions about, for example, the competition between the exchange and the strong hexagonal anisotropy in the helical structure, the stability of the cone structure at low temperatures, and the nature of the phases observed at higher temperatures in intermediate fields.

In recent years, there has been a resurgence of interest in the magnetic phases of Ho, and a number of these questions have been answered through new insights into the role of the different magnetic interactions, and the discovery of two new classes of magnetic structures, the spin-slip phases and the helifans. In this paper, we shall briefly review the salient features of these novel structures, indicating their significance for the future development in our understanding of rare-earth magnetism.

2. Zero-field structures

The interplay of the various magnetic interactions that are of importance in the rare earths is comprehensively demonstrated in the structures of Ho [3]. The strong peak in the two-ion coupling $\mathcal{J}(\boldsymbol{q})$, at a wave-vector $\boldsymbol{Q}$ that varies with temperature, stabilizes periodic magnetic structures over the whole range from the Néel temperature to absolute zero. The positive value of the axial-anisotropy coefficient B_2^0 gives rise to a helix at the higher temperatures, but B_6^0 is negative and the rapid increase of the thermal expectation value $\langle O_6^0 \rangle$ compared to $\langle O_2^0 \rangle$, as the temperature is reduced, causes the moments to tilt towards the c-axis below about 20 K. If the only two-ion coupling were the isotropic exchange, this would give rise to a continuous transition to a tilted helix, which reduces the exchange energy more effectively than the cone [4]. However, the dipolar-interaction energy associated with a longitudinal wave is high compared to the ferromagnetic orientation of the c-axis moments. The dipolar contribution is so large that it shifts the position of the maximum in $\mathcal{J}_{cc}(\boldsymbol{q})$ from $\boldsymbol{q} = \boldsymbol{Q}$ to $\boldsymbol{q} = \boldsymbol{0}$ [5] and the vanishing of the total axial anisotropy leads to a second-order transition at T_C to the cone phase. We therefore have an unusually complete understanding of the origins and nature of this particular transition; it is the temperature dependence of $B_6^0 \langle O_6^0 \rangle$ that drives the helix into instability, but the dipolar interaction chooses the cone, rather than the tilted helix, as the stable low-temperature phase. This continuous transition is accompanied by a soft mode [5]. The dipolar interaction, which varies extremely rapidly near $\boldsymbol{q} = \boldsymbol{0}$, reduces the energy of a spin-wave mode at the origin below that at $\boldsymbol{Q}$, and it is the former that goes soft at T_C.

The hexagonal anisotropy in Ho is the largest in the rare earths and distorts the helix drastically when the temperature is reduced, as revealed by the appearance of higher harmonics in neutron diffraction [1]. The helical component in the cone structure is commensurable with the lattice, with an average turn angle of 30°, but the moments are strongly bunched around the easy b-axes, as shown in fig. 1(a). At 4 K, the constant angle ϕ in the plane between any moment and the nearest b-axis is only 5.8°, compared with the value of 15° which corresponds to a uniform helix. As the temperature is increased the expectation value, $\langle O_6^6 \rangle$, decreases rapidly with the relative magnetization σ, roughly as σ^{21}, and ϕ increases correspondingly. Simultaneously $\boldsymbol{Q}$ tends to increase, reflecting a change in the position of the maximum in $\mathcal{J}(\boldsymbol{q})$. As shown by Gibbs et al. [6], however, $\boldsymbol{Q}$ does not increase uniformly with temperature, but rather a series of commensurable wave-vectors is traversed with apparently discontinuous jumps between them. By 25 K, the helical structure has thus reduced its periodicity to 11 layers by introducing a regularly-spaced series of spin slips [6], at which one plane of a bunched doublet is omitted while the remaining member orients its moments along the adjacent easy axis. This configuration, illustrated in fig. 1(b), in which one spin slip is introduced for each repeat distance of the perfect commensurable structure, is the primordial spin-slip structure.

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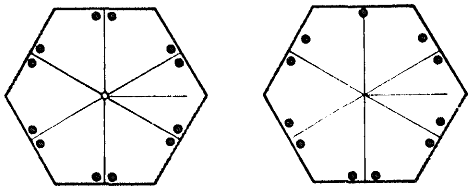

Fig. 1. Self-consistent mean-field calculations of periodic structures in Ho. Each circle represents the magnitude and direction of the ordered moment in a specific plane, relative to the size of the moment at absolute zero ($10\mu_B$), indicated by the length of the horizontal lines. The orientation of moments in adjacent planes is depicted by the positions of the neighbouring circles. (a) The 12-layer zero-spin-slip structure at 4 K. The open circle in the centre indicates the ferromagnetic component in the cone structure. (b) The 11-layer one-spin-slip structure at 25 K. The bunched pairs of moments are disposed unsymmetrically with respect to the easy axis in the vicinity of the spin slip.

The bunching angle ϕ is still rather small and, in contrast to other observed spin-slip structures, it possesses a net moment in the basal plane, which has apparently been observed in magnetization measurements by Snigirev et al. [7]. Although the angle of 2ϕ between two bunched planes is almost constant, the exchange interaction distorts the structure near the spin slips so that the moments are not symmetrically disposed around the easy axis. The spin-slip structures of Ho have been subjected to a careful and extensive neutron-diffraction study by Cowley and Bates [8]. Their results generally agree well with mean-field calculations [9], both with respect to the bunching angle and the distortion due to the spin slips, although a number of the spin-slip structures are observed to be more distorted than they are calculated to be, indicating that the long-range periodicity in the position of the spin-slip planes may be somewhat irregular.

At higher temperatures, the bunching decreases, the concept of spin slips becomes less useful, and it becomes more difficult to identify commensurable structures in the data. In the vicinity of 96 K, however, at which temperature the hexagonal anisotropy is very small, a commensurable structure with an interlayer turn angle of 45° is stabilized by a magnetic field in the c-direction [10]. A similar phenomenon has been observed, but at much lower temperatures, in the cone phase of Er [11]. Such a structure can in principle be stabilized by the hexagonal anisotropy in second order, but this effect is extremely small, since the bunching is calculated to be only ±0.14°. However, a two-ion coupling with trigonal symmetry about the c-axis [3] may strongly enhance the tendency towards commensurability. This trigonal coupling leads to a modulated c-axis moment, with a wave-vector which just coincides with that of the basal-plane moment when the turn angle is 45°, so that the structure becomes a tilted helix. Such a c-axis moment allows a coupling between the transverse long-wavelength phonons propagating along the c-axis and the lowest-energy spin waves, which may explain the softening of c_{44} observed by Bates et al. [12] in this temperature range. The role of the magnetic field along the c-axis in stabilizing this phase in Ho is not yet clear.

3. Magnetic-field effects

As mentioned above, commensurable spin-slip structures rapidly become less stable as the temperature is increased, on account of the renormalization of the hexagonal anisotropy. The series of structures that results from the shift in the peak in $\mathcal{J}(\boldsymbol{q})$, and consequently of $\boldsymbol{Q}$, with temperature can therefore be difficult to detect. On the other hand, if $\mathcal{J}(\boldsymbol{q})$ can be modified by other means at low temperatures, where $\langle O_6^6 \rangle$ is large, many well-defined and highly-bunched structures may be observed. This could in principle be accomplished by, for example, uniaxial pressure, but in practice a magnetic field in the c-direction is more convenient. By applying such a field in the cone phase at 10 K, Cowley et al. [13] were able to increase $\boldsymbol{Q}$, and hence observe a number of spin-slip structures. The mechanism for the alteration of $\boldsymbol{Q}$ is presumably analogous to that which operates in the helical phase; the increase in the c-axis moment decreases the amplitude of the helical component, thus affecting the electronic structure and hence $\mathcal{J}(\boldsymbol{q})$ through the superzone energy gaps [3]. It is noteworthy that corresponding reductions in the helical planar magnetization by either temperature or a field give roughly the same change in $\boldsymbol{Q}$.

The effect of applying a field in the plane of a helix was first considered by Herpin and Mériel [14], Enz [15] and, in most detail, by Nagamiya et al. [16]. As the field is increased, the helix first distorts, giving rise to a moment along $\boldsymbol{H}$, and then undergoes a first-order transition to a fan structure, in which the moments oscillate about the field direction. A further increase in the field reduces the opening angle of the fan which, in the absence of magnetic anisotropy, goes continuously to zero, establishing a ferromagnetic phase at a second-order transition. Hexagonal anisotropy may modify this process by inducing a first-order transition or, if it is large enough, eliminate the fan phase entirely.

The magnetic structures of Ho in a planar field were investigated with neutron diffraction by Koehler et al. [2], who identified two intermediate phases which they called fans and characterized these by the intensity distribution of the Bragg peaks. A number of investigations of other properties helped to establish that there must be an extra phase, or phases, between the helix and the fan, and the nature of these phases was elucidated by Jensen and Mackintosh [17] through mean-field calculations of the effect of a magnetic field on commensurable periodic structures. Above about 40 K, when the hexagonal anisotropy has declined substantially, stable phases indeed appear between the helix and the fan. If the helix is considered as blocks of moments with components alternately parallel and antiparallel to the field, written schematically as (+ − + − + −), and the fan structure is described as (+ + + + + +), the new structures, the helifans, correspond to intermediate patterns. For example, the helifan (3/2), illustrated in fig. 2, which has a relatively short period and is calculated to be the most stable structure over a range of fields [17], may be depicted as (+ + − + + −). It is clear that these helifan structures represent compromises between the demands of the exchange for a periodic structure, and the field for a complete alignment of the moments. They are not due to the hexagonal anisotropy which, on the contrary,

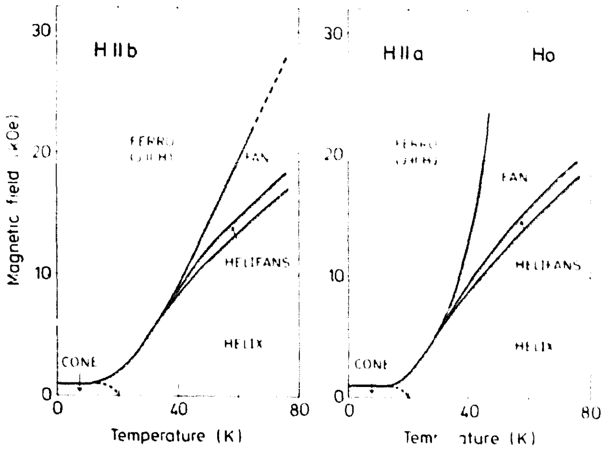

Fig. 3. Schematic phase diagrams for Ho for magnetic fields applied along the easy b-axis and the hard a-axis, deduced from mean-field calculations and a variety of experimental measurements. Full lines represent first-order and dashed lines second-order transitions.

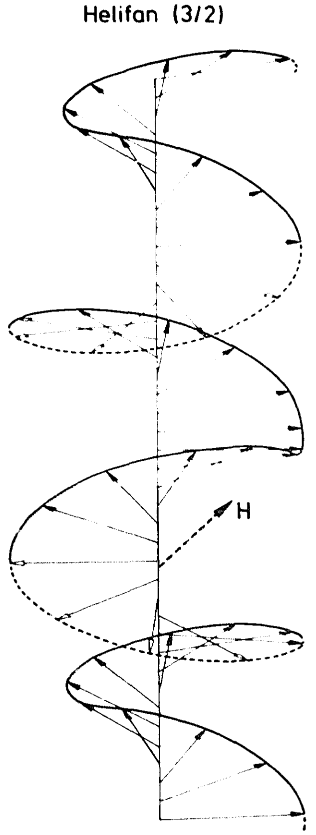

Fig. 2. The helifan (3/2) structure in Ho at 50 K. The moments lie in planes normal to the c-axis and their relative orientations are indicated by arrows. A magnetic field of 11 kOe is applied in the basal plane, and moments with components respectively parallel and antiparallel to the field are designated by filled and open arrowheads. This component of the moments has a periodicity which is 3/2 that of the corresponding helix, and the helicity of the structure changes regularly.

tends to suppress them, and occur both when the field is applied along the easy and hard directions in the plane. The helifan (3/2) accounts very well for the observed neutron-diffraction pattern, but other stable and metastable helifans have apparently also been observed, or could be observed under suitable conditions. For example, the calculations predict that other stable phases appear in the phase diagram of fig. 3 in a narrow interval between the helix and the helifan (3/2), e.g., the helifan (4′) (+ + − + + − + −), and similarly a sequence of helifans with m (+) blocks followed by a (−) ($m \geq 3$) occurs in the close neighbourhood of the fan phase.

4. Conclusions

The discovery of the spin-slip and helifan structures in Ho has led to a remarkable renaissance in the study of the magnetic structures of the heavy rare earths, which was previously considered to be an essentially closed chapter in magnetism research. A greatly improved insight has also been attained into the competition and cooperation of the various interactions in determining the details of the configurations of the moments. One of the most notable features of these structures is the large number of hexagonal layers involved in a single period, which implies that a great variety of new phases may await discovery, provided that crystals of sufficient purity and perfection can be fabricated.

Helifans, or analogous structures, may also occur in other rare-earth systems where periodic ordering is observed. For example, a recent study of the phase diagram of Dy by Andrianov et al. [18] shows evidence for an extra phase transition between the helix and the fan which might well be due to a helifan. As we have seen, the concept of blocks of spins with components parallel and antiparallel to an applied magnetic field may be very useful when considering the effect of such a field on periodic structures. A different but analogous example is provided by the modulated structures with wave-vectors in the basal plane observed in Nd. These may be described as (+ − + − + − + −), indicating blocks of moments with a component parallel or antiparallel to a magnetic field applied in the plane. A periodic reversal of (−) blocks will then generate subharmonics of the basic $\boldsymbol{Q}$-vector. Thus the sequence (+ + + − + − + −) generates $\boldsymbol{Q}/4$, and (+ + + − + + + −) gives $\boldsymbol{Q}/2$, both of which have been observed by neutron diffraction in a magnetic field [19]. It is tempting to suppose that some of the intermediate phases observed in Tm [19] may be ascribed to the periodic reversal of blocks of spins, although careful neutron-diffraction experiments will be required to distinguish such effects from the formation of domains. Interesting modifications of both spin-slip and helifan structures may be induced by alloying. A start has recently been made on the Ho–Er system [20]; this promises to be a long and fruitful project.

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