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Magnetic properties of the dipole-coupled singlet--singlet system HoF_3

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Abstract

Experimental investigations of HoF_3 have revealed that it is a unique magnetic system. The electronic properties of the Ho-ions are dominated by two singlet states well separated from the remaining 4f-levels. The classical dipole coupling is an order of magnitude larger than any other two-ion interaction between the Ho-moments. The hyperfine-coupled electronic and nuclear moments on the Ho-ions order co-operatively in a ferrimagnetic structure at $T_C = 0.53$ K. A theory has been developed for describing this system, and it is found that the leading-order corrections to the mean-field behaviour, obtained from the high-density $1/z$-expansion, are significant. The magnetic heat capacity between 90 mK and 7–8 K is accounted for accurately by the theory, as is the paramagnetic excitation spectrum. The only discrepancy of importance is that the calculated moment in the zero-temperature limit is about 9% smaller than the neutron diffraction result of $5.7\mu_B$.

The magnetic properties of HoF_3 have recently been the subject of a series of papers [1–3], which are summarized here. Bleaney et al. [4] performed magnetization measurements and determined the heat capacity down to 0.45 K, and they concluded that the holmium moments in HoF_3 order at 0.53 K. The structure and the magnitude of the ordered moments were determined from neutron diffraction experiments by Brown et al. [5]. The experimental work was continued by a study of the excitations in the paramagnetic and in the ordered phase by inelastic neutron-scattering [1], and measurements of the heat capacity down to 0.1 K, well below the transition temperature [2]. The experimental results have been analysed, first in terms of a mean-field (MF) model [1], and subsequently in terms of a theory which includes the corrections to the MF-approximation to leading order in the high-density $1/z$-expansion [3].

HoF_3 is orthorhombic with 4 Ho^{3+} and 12 F^-ions per unit cell. The low symmetry of the crystalline electric field at the Ho sites causes a splitting of the $J = 8$ multiplet-ground-state into singlets, and the local electronic properties are dominated by two singlet states lying well below the remaining 4f-levels. In the paramagnetic phase the energy gap between the two singlets is 0.69 meV and the dipole matrix element is about $0.82J$. At low temperatures the system is close to being an Ising system, with the only modification that there are two easy directions. Both easy directions lie in the a–c plane, making angles $+\theta$ and $-\theta$ with the a-axis, where $|\theta|$ has been established to be 25° ± 1°. Except for the slight complication that there are two non-equivalent ions per unit cell (which are, however, locally identical), the electronic system is to a good approximation a simple singlet–singlet system at low temperatures.

The classical dipole coupling between the Ho-moments, which may be calculated accurately from first principles, is weak but is an order of magnitude stronger than any other interaction between the dipoles. The ratio between the two-ion coupling and the threshold value required for inducing magnetic ordering of the electronic system is found to be less than 1, about 0.86, and the phase transition occurs only because of the hyperfine interaction between the nuclear spin and the angular moment on the Ho-ions. The hyperfine interaction enhances the static susceptibility and induces a cooperative ferrimagnetic ordering of the two systems at T_C, with the moments ordered along the two easy directions.

The expansion of the Matsubara Green function has been considered [3] to first order in the high-density

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$1/z$-expansion. In this approximation, all the single sites are assumed to be placed in equivalent surroundings, and the fluctuations in this effective medium are determined self-consistently from the single-site susceptibility [3,6]. Due to the fluctuations, the non-interacting susceptibility is effectively reduced by the renormalization factor $1 + \sigma(\omega)$, where $\sigma(\omega)$ has been calculated as a function of temperature and field. The effective mean field H_{MF} acting on the angular moments along the (local) easy x-axis is determined self-consistently by

$$g\mu_B H_{MF} = \mathcal{J}_{xx}(\mathbf{0})\langle J_x\rangle - A\langle I_x\rangle - g\mu_B \delta H, \qquad (1a)$$

at zero applied field, with

$$\delta H = \int_0^{H_{MF}} \sigma(0; H)\, dH. \qquad (1b)$$

$\langle I_x\rangle$ is derived from the effective hyperfine Hamiltonian and $\langle J_x\rangle$ is equal to the effective-mean-field expectation value of J_x. The relative reduction of the mean field $\delta H/H_{MF}$ due to the fluctuations is found to be of the order of 10% at low temperatures when the moments are small. The single-site renormalization leads to small adjustments of the model parameters. The exchange interaction has to be slightly larger in order to compensate for the smaller value of the effective non-interacting susceptibility, which is reduced by up to 12% at the lowest temperature compared with the MF-value.

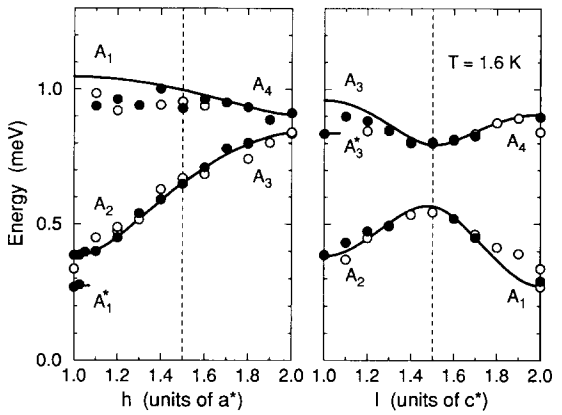

Fig. 1. Dispersion relations of the paramagnetic singlet–singlet excitations along a^* and c^* in HoF_3 at 1.6 K. Closed circles are the experimental results obtained with the neutron-scattering vector along $(h00)$ and $(00l)$ open circles those along $(h01)$ and $10l)$, with h and l between 0 and 1. Solid lines are the theoretical predictions including the single-site fluctuations. The ferromagnetic modes in the long-wavelength limit A_1 and A_3 behave in a singular way because of the rapid variation of the dipole forces. The short solid lines marked A_1^* and A_3^* show the energies of the two ferromagnetic modes in this limit, when the direction of the wave-vector is perpendicular to respectively $(h00)$ and $(00l)$. In combination with the non-zero experimental resolution width, the A_1^* mode in particular contributes much more strongly to the scattering cross-section than the A_1 mode close to (100). Similar effects may also be important for explaining the difference between theory and experiment for the upper A_1 mode.

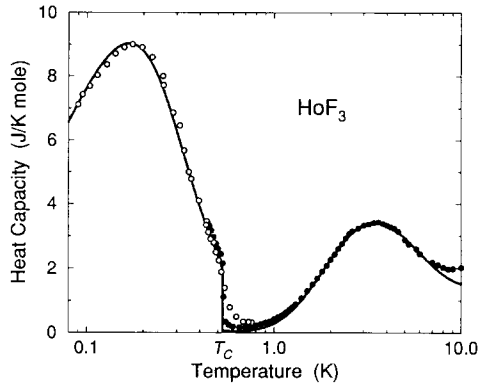

Fig. 2. Low temperature specific heat of HoF_3. Open and closed circles are respectively the experimental results from Refs. [2] and [4] (results of [2] scaled by a factor with an uncertainty of about 10%). The solid line is the result derived when the renormalization effects due to be single-site fluctuations are included. Above 7–8 K the phonons start to contribute, as do the higher lying 4f-levels on the Ho-ions.

The two theories predicts almost the same excitation spectrum shown in Fig. 1, however, the correction to the MF-behaviour of the heat capacity and of the magnetization due to the single-site fluctuations is rather substantial. In Fig. 2 is shown the specific heat of HoF_3 between 0.1 and 10 K. The agreement between the heat capacity calculated to first order in the $1/z$-expansion and the experiments is very convincing. The only discrepancy left (below ~ 7 K) is that occurring in the critical regime just above T_C. The ordered moment in the zero-temperature limit is calculated to be $5.16\mu_B$, which is about 9% smaller than the result $(5.7 \pm 0.2)\mu_B$ obtained from the neutron diffraction experiments [5]. This discrepancy is surprisingly large, considering how well the heat capacity is described by the theory and deserves further analysis, both theoretically and experimentally.

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