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LETTER TO THE EDITOR

The nuclear heat capacity of HoF₃

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Abstract. The hyperfine-coupled electronic and nuclear moments on the Ho ions in HoF₃ order in a ferrimagnetic structure at $T_c = 0.53$ K. The heat capacity has been measured from above T_c down to 0.09 K. The electronic contributions are vanishingly small below T_c , whereas the nuclear heat capacity increases rapidly with decreasing temperature in the ordered phase, reaching a maximum of about $9 \text{ J K}^{-1} \text{ mol}^{-1}$ near 0.2 K. The polarization of the nuclear spins and the heat capacity have been calculated. The theory, which includes the modification of the hyperfine field due to the single-site fluctuations of the electronic moments, leads to a very satisfactory account of the heat capacity measurements.

Experimental investigations of HoF₃ have revealed that it is a unique magnetic system. Bleaney *et al* [1] performed magnetization measurements and determined the heat capacity down to 0.45 K, and they concluded that the holmium moments in HoF₃ order at 0.53 K. The structure and the magnitude of the ordered moments was determined from neutron diffraction experiments by Brown *et al* [2]. The excitations, in the paramagnetic and in the ordered phase, were studied by Leask *et al* [3] by inelastic neutron scattering experiments. One important property, which was not determined in these experiments, is the behaviour of the heat capacity down to temperatures well below the transition temperature. Here we report such a study.

The experimental results obtained previously to this work have been analysed, first in terms of a mean-field model [3], and subsequently in terms of a theory that includes the corrections to the mean-field approximation to leading order in the high-density $1/z$ -expansion [4]. The introduction of the renormalization effects due to the single-site fluctuations systematically improved the comparison between theory and experiment, most pronouncedly in the case of the paramagnetic heat capacity. This theory, without any adjustment of the model parameters, is used here for calculating the heat capacity in the ordered phase.

HoF₃ is orthorhombic with the lattice parameters $a = 6.404 \text{ \AA}$, $b = 6.875 \text{ \AA}$ and $c = 4.379 \text{ \AA}$, and there are four Ho³⁺ and twelve F⁻ ions per unit cell. The magnetic Hamiltonian for the Ho ions at the four different sites in the unit cell is the same when referred to one local coordinate system for one pair of ions and another—which is rotated 180° around the a -axis compared with the first coordinate system—for the other pair. 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 Δ between the two singlets is 0.69 meV and the dipole matrix element M 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 planes, making angles $+\theta$ and $-\theta$ with the a -axis, where $|\theta|$ has been established to be $25^\circ \pm 1^\circ$. Except for the slight complication of the 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 is weak but is an order of magnitude stronger than any other interaction between the dipoles. The classical coupling may be calculated accurately from first principles, and the magnetic properties of the electronic system at low temperature are determined by a small number of parameters: Δ , M and θ plus two to three very small exchange-coupling parameters. Δ is determined by the position of the Schottky anomaly in the paramagnetic heat capacity, M and θ are derived from the magnetization curves, and the exchange parameters are used for an adjustment of T_c and the excitation energies.

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

$$\mathcal{H}_{\text{hf}} = A \mathbf{I} \cdot \mathbf{J}$$

between the nuclear spin \mathbf{I} and the angular momentum \mathbf{J} on the Ho ions. \mathcal{H}_{hf} may lift the $(2I + 1)$ -fold degeneracy of the ground-state manifold, and second-order perturbation theory [5, 6] shows that the splitting of these levels is described by the effective hyperfine Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{hf}}(\text{eff}) = & A \langle \mathbf{I} \rangle \cdot (\mathbf{J} - \frac{1}{2} \langle \mathbf{J} \rangle) + A \langle \mathbf{J} \rangle \cdot (\mathbf{I} - \frac{1}{2} \langle \mathbf{I} \rangle) \\ & - \frac{1}{2} A^2 (\mathbf{I} - \langle \mathbf{I} \rangle) \cdot \left[\frac{1}{N} \sum_{\mathbf{q}} \overline{\overline{\chi}}(\mathbf{q}) \right] \cdot (\mathbf{I} - \langle \mathbf{I} \rangle) \end{aligned} \quad (1)$$

where $\overline{\overline{\chi}}(\mathbf{q})$ is the \mathbf{q} -dependent static susceptibility divided by $(g\mu_B)^2$, and N is the number of Ho ions. $I = 7/2$ and $A = 3.36 \mu\text{eV}$ [7], and the intrinsic quadrupole term is neglected, as it is only a factor of about -0.2 times the quadrupole term induced by the hyperfine coupling near T_c . 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, applicable to this system, has been considered [4] to first order in the high-density $1/z$ -expansion (neglecting the $1/z$ -correction of the nuclear response which is of the order A^4). 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, as discussed in [4, 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. It may then be shown [4] that the effective mean field H_{MF} acting on the angular moments along the (local) easy x -axis is determined self-consistently by

$$g\mu_B H_{\text{MF}} = \mathcal{J}_{xx}(\mathbf{0}) \langle J_x \rangle - A \langle I_x \rangle - g\mu_B \delta H \quad (2a)$$

at zero applied field, with

$$\delta H = \int_0^{H_{MF}} \sigma(0; H) dH. \quad (2b)$$

$\langle I_x \rangle$ is derived from $\mathcal{H}_{MF}(\text{eff})$ and $\langle J_x \rangle$ is equal to the effective-mean-field expectation value of J_x . The temperature dependence of the two parameters is shown in figure 1, where the calculated $\langle J_x \rangle$ is compared with the neutron diffraction result [2]. The relative reduction of the mean field $\delta H/H_{MF}$ due to the fluctuations is here of the order of 10%. The entropy of the electronic system is calculated to vanish just above T_c , and the heat capacity in the ferrimagnetic phase is determined by the variation in the population of the nuclear levels alone.

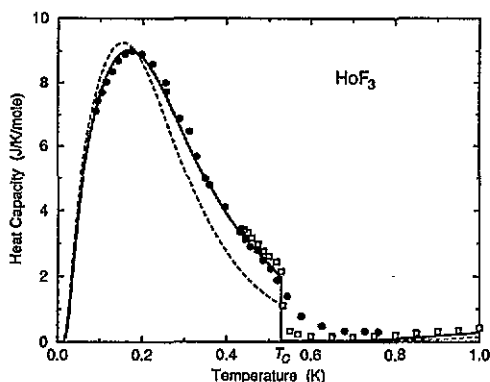


Figure 1. The solid lines show the calculated values of the angular momentum $\langle J_x \rangle$ and the nuclear spin $\langle I_x \rangle$ of a Ho ion as a function of temperature below T_c . The dashed lines are the corresponding results derived in the mean-field approximation. The filled circles are the experimental values of $\langle J_x \rangle$ determined from the variation of the magnetic scattering intensities at (1 0 0) obtained by Brown *et al* [2]. Their results have been scaled to agree with the magnetic moment of $5.7 \mu_B$, which they obtained from structure refinements at 70 mK.

The specific heat $C(T)$ was measured using a standard semi-adiabatic heat pulse technique in a top-loading dilution refrigerator. Initial experiments with the sample epoxied onto the sapphire substrate showed internal equilibration times of the order of half an hour at $T \simeq 0.3$ K. To alleviate this problem, the surface area of the sample was increased by powdering it, mixing it with Ag powder for enhanced thermal conduction, and pressing it into a hard pill. The pill was then affixed to the calorimeter using Stycast 1266 epoxy. Corrections due to the substrate and Ag are negligible, due to the very large specific heat of HoF₃ in the temperature range studied.

The mass of the HoF₃ was less than 2 mg and, due to the powdering procedure, could not be accurately determined. We therefore considered the possibility of scaling the magnitude of $C(T)$ to the previous specific heat results of Bleaney *et al* [1] in the region of overlap, 0.45–0.75 K. Reasonable agreement between the two data sets is found, except that the present results display a rounded transition. This is perhaps a result of the powdering; at least the value of T_c is sensitive to any change of the two-ion coupling, and as the dipole coupling is of very long range, it is influenced by all fluctuations in the density. The difference between the variations of $C(T)$ near T_c in the two experiments makes the

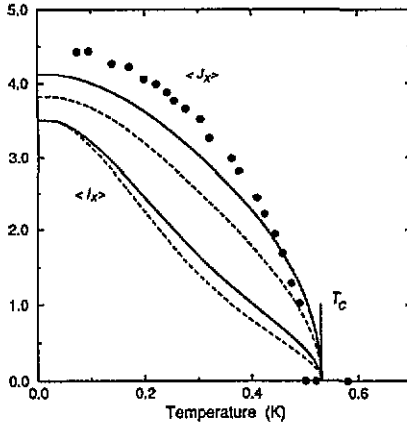


Figure 2. The low-temperature specific heat of HoF_3 . The solid circles are the experimental results and the open squares are the results obtained previously by Bleaney *et al* [1]. The dashed line is the magnetic contribution predicted by the mean-field theory and the solid line is the result derived when the renormalization effects due to the single-site fluctuations are included. The experimental results are scaled as explained in the text, by a factor with an uncertainty of about 10%.

scaling procedure somewhat uncertain. If we scale the results with respect to an integrated quantity, like the change of entropy between 0.45 and 0.75 K, we end up with a scale factor that is about 16% smaller than the one obtained if our specific heat results are adjusted so to coincide with the previous ones near 0.45 K. Besides these two possibilities, we may utilize the knowledge that the nuclear and thus the total entropy change, between about 0.6 K and the zero-temperature limit, should be $R \ln 8$. Combining the experimental result for the entropy change between 0.09 K and 0.6 K with the theoretical value $0.284 R \ln 8$ for the entropy at 0.09 K, we obtain a scale factor 9% smaller than the upper of the two other estimates, i.e. close to their average value, and this is the scale factor applied in figure 2. If the theoretical value of the entropy at 0.09 K is correct, the uncertainty of the estimate is about 1%, but without reference to theory we may only claim that the scale factor is determined to within 10%.

The agreement between the calculated heat capacity in the ordered phase and the experiment is very convincing; even the uncertainty of the order of 10% in the scale factor of the experimental results is considered. Figure 2 also shows that the correction to the mean-field behaviour of the heat capacity due to the single-site fluctuations is rather substantial in the ordered phase, which is also the case [4] in the paramagnetic phase. The only discrepancy left between the theoretical and experimental heat capacity below ~ 7 K, where the phonons cease to contribute, is the one occurring just above T_C . The results of Bleaney *et al* [1], which must be considered to be the most trustworthy at these temperatures, do not approach zero as closely as the theoretical predictions. This may indicate that the long-range critical fluctuations are of importance, or possibly that effects of the order of $(1/z)^2$ should be included at these low temperatures.

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 [2]. 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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