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Magnetic properties of the new rare earth carbide fluoride layered compound: Ho_2CF_2

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We present magnetic susceptibility, specific heat and neutron diffraction data of the new layered rare earth carbide fluoride Ho_2CF_2. The susceptibility displays a rounded maximum centered around 4.6 K and a Curie–Weiss law at higher temperatures with a paramagnetic Curie temperature of −4.9(2) K. The specific heat shows a sharp anomaly at 3.61(5) K indicating the onset of long range ordering but also a considerable high temperature tail pointing to low dimensional magnetic behaviour. Low temperature neutron powder diffraction reveals additional magnetic Bragg peaks with significant critical scattering remaining well above the long range ordering temperature.

We are currently investigating the physical and in particular the magnetic properties of metal-rich halides of the rare earth elements [1]. Until recently, this class of compounds only comprised chlorides, bromides and iodides. Now, the first fluorides, namely Gd_2CF_2 and Ho_2CF_2 are available [2]. Here, we present a brief summary of our neutron diffraction, magnetic susceptibility and specific heat investigations of the magnetic properties of Ho_2CF_2. The particular interest in the magnetic properties of the metal-rich halides of the rare earth elements arises from the fact that their crystal structures are largely determined by the occurrence of low dimensional building units and the associated anisotropic chemical bonding relationship [3].

Ho_2CF_2, for example, has a layer type crystal structure in which a close packed metal atom bilayer that is sandwiched between F atom layers can be identified as the elementary structural unit (fig. 1). Such F–Ho–Ho–F sheets stack along [001] and are held together via van der Waals forces. The C atoms are located within the octahedral voids of the metal atom bilayer [2]. Ho_2CF_2 is non-metallic [4].

Fig. 2 presents the results of the neutron diffraction, magnetic susceptibility and specific heat experiments on Ho_2CF_2. Experimental details and full results will be given elsewhere [4].

The experimental results consistently prove long range antiferromagnetic (afm) ordering with a Néel temperature of $T_N = 3.61(5)$ K (specific heat result): At 1.6 K the neutron powder diffraction pattern contains very strong additional magnetic Bragg reflections which can readily be indexed after doubling the nuclear cell along a. The intensity of the magnetic reflections decreases on heating as exemplified in fig. 2a for the $\frac{1}{2}00$ and the $\frac{1}{2}01 + \frac{1}{2}0\bar{1}$ reflections. The critical temperature is determined from the turning point in the intensity vs T curves as 3.7(1) K. Above 4 K the intensity vs T curve ends in a long tail due to substantial critical magnetic scattering well above T_N.

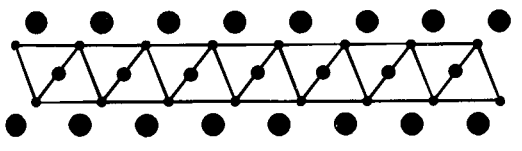

Fig. 1. Projection along [100] of one F–Ho–C–Ho–F sheet cut out of the crystal structure of the Ho_2CF_2. Small circles: Ho; medium circles: C; larger circles: F. The c-axis is perpendicular to the sheet.

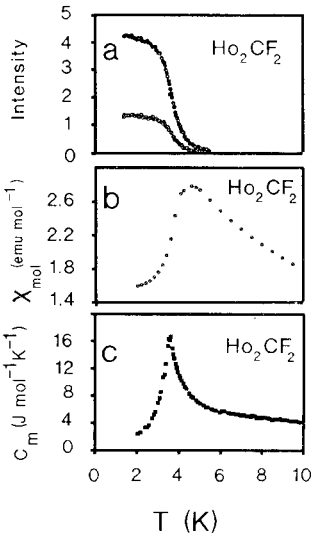

Fig. 2. (a) Integrated neutron intensities of the magnetic Bragg reflections $\frac{1}{2}00$ (upper) and $\frac{1}{2}01 + \frac{1}{2}0\bar{1}$ (lower), (diffraction patterns obtained on slow heating a powder sample on instrument D1B at ILL with $\lambda = 2.52$ Å); (b) powder molar susceptibility χ_{mol} and (c) magnetic contribution C_m (per g-atom Ho) in the heat capacity of Ho_2CF_2.

High-resolution neutron powder patterns taken at 1.5 K on the instrument D1A (ILL) reveal a broadening or a small splitting of some of the nuclear reflections pointing to a tiny distortion of the nuclear cell at this temperature. Rietveld refinement of the low temperature data set shows that the nuclear structure at 1.5 K is best described in the space group $P\bar{1}$, however with differences between the a and b-lattice constant of less than 0.02%. The distortions of the angles compared to the high temperature structure (50 K data set) are of the order of 0.2°.

The powder magnetic susceptibility (fig. 2b) undergoes a maximum at 4.6 K, typical for afm ordering, and a steep decrease below. Calculating $d/dT(T\chi)$, (Fisher's heat capacity, [5]) from our data we find a spike indicating the onset of long range ordering at 3.7(1) K, considerably lower than the maximum temperature. A Curie–Weiss law, $\chi_{mol} = C/(T - \Theta)$ is observed for high temperatures ($T > 100$ K), with a paramagnetic Curie temperature Θ of $-4.9(2)$ K proving predominant antiferromagnetic exchange interactions.

The specific heat (fig. 2c) shows a large magnetic anomaly with a singularity at 3.61(5) K and a long tail towards higher temperatures with sizable contributions up to 25 K.

The entropy S_m involved in the magnetic anomaly is obtained by numerically integrating C_m/T and amounts to $S_m(\infty) = 14.4$ J mol^{-1} K^{-1} $= 1.73R$ (R = gas constant). About 2/3 of the entropy is gained above T_N. Ho_2CF_2 is the first non metallic layered metal-rich carbide halide of the rare earth and the first metal-rich fluoride at all, the magnetic properties of which were investigated in more detail. The order of magnitude of T_N observed for Ho_2CF_2 is in line with what has been found for other insulating layered metal-rich halides containing H atoms as the interstitials in the metal atom bilayer, e.g. RXH_2 (R = Gd, Tb; X = Cl, Br, I) [1] whereas the ordering temperatures for layered carbides, e.g. $R_2C_2Br_2$ (R = Gd, Tb) which are metals and contain a dicarbide unit in the octahedral voids of the metal atom bilayer are about one order of magnitude larger [6].

The absence of conduction electrons in Ho_2CF_2 leaves the superexchange via the anions and dipolar coupling as the sources of interaction between the Ho ions. This results in ordering temperatures of a few kelvin typical for rare earth halides.

The magnetic moment depends on the actual crystalline electric field splitting. Ho^{3+} (configuration $4f^{10}$, ground term $^5I_8$) has C_{3v} site symmetry in Ho_2CF_2 (high temperature structure) in principle allowing a nonmagnetic singlet as the ground state. The entropy associated with the magnetic transition is found to be $1.73R$ being close to R ln 6 and indicates the ordering of a 6-level system. Such a large degeneracy for the crystal field ground state seems unlikely in view of the low site symmetry. We suggest that a substantial part of the entropy originates from the structural phase transition evidenced by the high resolution neutron investigation. Although the high resolution patterns are available only for 1.5 and 50 K, it is reasonable to assume that the afm ordering is directly accompanied by the lattice distortion. Such a behaviour was observed for HoSb and explained as due to the magnetoelastic coupling that comes about through the large orbital momentum of $L = 6$ in the Ho^{3+} ground term [7].

Finally, we want to address the issue of two dimensional magnetic behaviour. The special structural conditions are in favour of the necessary very anisotropic magnetic coupling situation and Ho_2CF_2 is a possible candidate for an interesting two dimensional *triangular* magnetic system. In fact, as is indicated by the critical magnetic scattering and the short range order "tail" in the specific heat above T_N, low dimensional behaviour is apparently a feature of the magnetic properties of Ho_2CF_2. However, as stressed before, since superexchange and dipolar interactions are of equal magnitude the interlayer interaction is by no means negligible compared to the intralayer coupling such that a sufficient decoupling of the layers necessary for an ideal behaviour is unlikely to the present.

Therefore, it seems unlikely, that Ho_2CF_2 has the properties prerequisite for a *model* low dimensional magnetic system. Moreover, the combination of a magnetic and a structural phase transition renders additional complexity to the magnetic ordering behaviour of Ho_2CF_2.

References

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