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Structure and ma
fluoride, Ho_2CF_2*

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(FRG)

(Received July 1, 1991; a

Abstract

The preparation of a ne
trigonal, space group $P\bar{3}$
temperature. On cooling
antiferromagnet with ma
magnetic to antiferroma
$P\bar{1}$ due to magnetoelastic
determined from high re
50 K. Evidence for critic
susceptibility and temper
tivity measurements show
dimensionality of the str
discussed.

1. Introduction

The chemistry o
characterized by a la
compounds have been
a review of the chemi
of the rare earths). In
atoms or C_2 units are
metal atoms. These G
may be condensed t
structures. In all the c
edges of the Gd_6 octa

So far, only one c
[3], in addition to the
reports on the prepa
properties of holmiu

*Dedicated to Professo
60th birthdays.

†Also at Institut Laue–

0925-8388/92/$5.00

gely characterized by the presence of extended bilayers and the highly sotropic chemical bonding associated with them, implying interesting gnetic and electrical properties.

Experimental details

. *Sample preparation and characterization*

The starting materials, holmium, HoF_3 and carbon, were prepared as lows. Sublimed holmium metal lumps (99.99%, Universal Matthey, Karls- ıe) were heated in a molybdenum crucible under hydrogen for 2 h at 900 to produce holmium hydride. This was ground and then dehydrogenated 1100 K for 5 h under high vacuum to yield powdered holmium metal. F_3 was prepared from Ho_2O_3 (99.99%, Universal Matthey) and HF following nethod described by Greis and Petzel [4]. Carbon, in the form of activated ırcoal (high purity, Merck, Darmstadt), was degassed at 1450 K in high :uum for 24 h and stored in a pure argon atmosphere.

Of the rare earth carbide fluorides, the holmium derivative was thought be easy to prepare owing to the fact that HoF_3 exhibits one of the lowest lting points of all the rare earth trifluorides. Ho_2CF_2 was synthesized from starting materials holmium, HoF_3 and carbon in the molar ratio 4:2:3 tal mass approximately 2.5 g) sealed under 1 bar of argon in a tantalum poule, which was then sealed under vacuum in a quartz glass tube and ıted to 1450 K for 8 days, resulting in the formation of a single-phase :rocrystalline dark brown Ho_2CF_2 powder. Ho_2CF_2 slowly decomposes in and is readily dissolved by dilute mineral acids at ambient temperature.

. *X-ray investigations*

Powdered samples of Ho_2CF_2 were characterized at room temperature the modified Guinier technique [5] with silicon ($a=5.430\,35$ Å) as an ernal standard using Cu $K\alpha_1$ ($\lambda=1.540\,56$ Å). The diffraction patterns, ich index as trigonal, matched those of the isostructural gadolinium npound Gd_2CF_2 [3] with space group $P\bar{3}m1$–D^3_{3d} (no. 164). The lattice ıstants, determined from coincidence measurements of 13 reflections in range $4°<\theta<30°$ ($\Delta\theta=\pm0.005°$) refined [6] to $a=3.6567(2)$ Å and 6.3171(5) Å. The 20 largest d spacings (Å) are (with relative intensities) 17(10), 3.167(60), 2.831(100), 2.236(70), 2.106(5), 1.828(60), 1.754(50), 83(10), 1.582(40), 1.579(5), 1.536(30), 1.416(20), 1.413(10), 1.381(10), 66(20), 1.263(5), 1.197(10), 1.195(10), 1.176(40) and 1.119(20).

. *Specific heat*

The specific heat was measured in an adiabatic calorimeter designed the examination of small samples [7]. Powder samples with typical masses about 500 mg were put in Duran glass ampoules and sealed under helium to ensure good thermal contact.

The magnetic contribution C_m to the heat capacity was obtained by ɔtracting a lattice contribution C_l which was estimated according to the following procedure. A tempe derived from the specific hea

$$C_p = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x-1)^2}\,dx$$

At high temperature a pc was extrapolated to low temp part of the heat capacity, C_l. numerically integrating C_m/T capacity, $C_m=C_p-C_l$, followi

$$S_m(T) = \int_0^T \frac{C_m(T')}{T'}\,dT'$$

2.4. *Magnetic susceptibility*

The susceptibility of pow was determined with a Quantu were contained in dried gelatin in separate runs and correcte

2.5. *Electrical conductivity*

The resistance was deter a two-point electrometer metho and steel pistons and cooled

2.6. *Neutron diffraction*

For the neutron diffractio was sealed under helium gas in diameter which was then su 6 mm in diameter. Diffracti Laue–Langevin, Grenoble on tl a 400-wire ^{3}He–Xe gas multi temperature was scanned at 0 data were stored at approxima reasons). In addition, quick sca the absence of further phase resolution patterns of Ho_2CF_2 the 2θ range 6°–156° in steps

3. Results and discussion

The structure of Ho_2CF_2 $P\bar{3}m1$ by the Rietveld method

D1A data collected on the sample at 50 K. From the 2900 data points containing 48 contributing reflections, a total of 13 parameters (of which six are structural) were refined. The final parameters, which are uncorrected for the effects of absorption, are shown in Table 1, with the best fit to the data displayed in Fig. 1. The correction to the temperature factors due to the effect of absorption is estimated at about 0.2 Å^2.

Figure 2 shows a projection of the structure along [110]. The structure may be described in terms of Ho_6 octahedra filled with carbon atoms which are connected via their edges to form infinite $[Ho_2C]$ layers. The coordination of the remaining edges by fluorine atoms results in $[Ho_2C]$ layers sandwiched between fluorine layers and stacked along [001] according to the sequence $\cdots$AbγaB$\cdots$ ($\cdots$FHoCHoF$\cdots$). Such FHoCHoF layers are held together by van der Waals forces. Owing to the trigonal symmetry, only two short metal–metal distances are found: the shortest (3.41 Å) is between the planes of the metal bilayers and the second, within the plane, is equal to the lattice constant a (3.65 Å).

The structure type is well known from a great number of different compounds such as Gd_2Br_2C [10], $CaAl_2Si_2$ [11], Ta_2S_2C [12], Ce_2O_2S [13] and Ln_2O_3 [14], which have structural subunits $[CGd_2]$, $[CaSi_2]$, $[CTa_2]$, $[SCe_2]$ and $[OLn_2]$ respectively based on the CdI_2 structure [15]. The remaining atoms fill the tetrahedral holes between the metal or silicon double layers.

Conductivity experiments show that Ho_2CF_2 is non-metallic as predicted by the simple ionic description $(Ho^{3+})_2C^{4-}(F^-)_2$. The resistance of the measured pellet is of the order of several megaohms at room temperature and increases by three orders of magnitude on cooling to liquid helium temperature. The result is similar to that observed for the layered metal-rich rare earth halides in which all voids in the metal atom bilayer are fully

TABLE 1

Final parameters, R factors and interionic distances for Ho_2CF_2 at 50 K. R factors are defined as in ref. 8 with y_i(obs) referring only to the Bragg intensity, *i.e.* y_i(obs)=y_i(total) − y_i(background). Weights are given by $1/\sigma_{y(\text{obs})}^2$. Scattering lengths Ho=8.37 fm, C=5.65 fm, F=6.65 fm [22]. λ=1.911 Å. Space group $P\bar{3}m1$. a=3.653 73(1) Å, c=6.3098(2) Å. V=72.949(2) Å^3, ρ_{calc}=8.646 g cm^{-3}

Atom	Site symmetry		X	Y	Z	B (Å^2)	N
Ho	2d	$3m$	$\frac{2}{3}$	$\frac{1}{3}$	0.7876(6)	−0.16(7)	2
C	1a	$\bar{3}m$	0	0	0	0.07(14)	1
F	2d	$3m$	$\frac{2}{3}$	$\frac{1}{3}$	0.3882(6)	0.51(10)	2

U, V, W (deg^2): 0.172(5), −0.423(13), 0.365(7)

R_{wp}=6.3%, R_{exp}=3.6%, R_I=3.8%

Interatomic distances (Å)

Ho–Ho	3.411(4), 3.653(1)	Ho–C	2.499(2)	Ho–F	2.520(5), 2.383(3)
F–F	2.538(3)	F–C	3.233(3)		

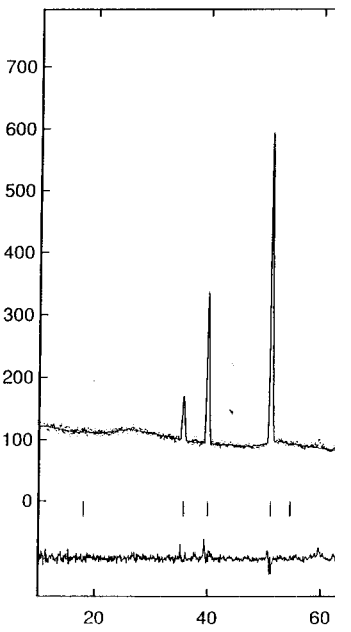


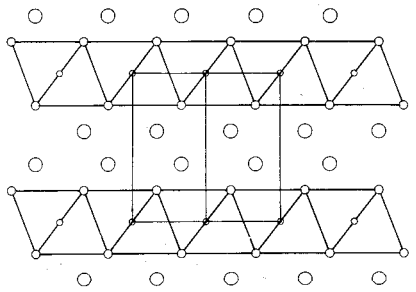
Fig. 1. Observed, calculated and with λ=1.911 Å. Vertical tick ma estimated by graphical methods, decreases as the holmium form f the background are due to diffu

filled with hydrogen inters the rare earth halide dicar formulated as $(RE^{3+})_2(C^4$ covalent interaction of th states.

The specific heat (Fig 3.61(5) K and a long tail tov up to 25 K. The specific h to be of antiferromagnetic ments (Fig. 4). The latter e below. The derivative $d(\chi T$ at 3.7(1) K in agreement v susceptibility follows a Cu

$$\chi_{mol} = \frac{C}{T-\Theta}$$

with a paramagnetic Curie predominantly antiferroma



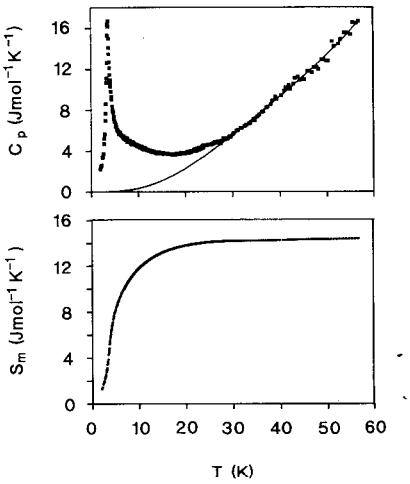


Fig. 2. Projection of the structure as seen down [110]. Holmium, carbon and fluorine are represented by medium, small and large circles respectively.

Fig. 3. (a) Specific heat C_p and estimated lattice heat capacity C_l (full curve) of Ho_2CF_2. (b) Magnetic part S_m of the entropy according to eqn. (2). (All data are per one formula unit of $HoC_{0.5}F$.)

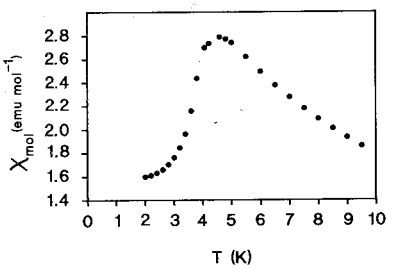


Fig. 4. Molar magnetic susceptibility χ_{mol} of Ho_2CF_2 at low temperatures.

C corresponds to an effective magnetic moment of 9.4 μ_B, which is slightly lower than the expected free-ion value of 10.6 μ_B.

From the diffraction patterns collected on D1B (Fig. 5) it is evident that between 1.5 K and room temperature Ho_2CF_2 exhibits only one phase transition at about 4 K, in agreement with the specific heat (Fig. 3) and magnetic susceptibility (Fig. 4) measurements. The extra peaks that appear at low temperature in Fig. 5 are attributed to antiferromagnetic ordering of the magnetic spins of the Ho^{3+} ions and may be indexed in terms of a doubling of the trigonal unit cell along a with consequent loss of threefold symmetry. Several magnetic space groups are possible and the correct structure was determined by trial and error to have the magnetic space group symmetry $P_a\bar{1}'$.

The complete magnetic structure was refined by the Rietveld method from the D1A data of Ho_2CF_2 at 1.5 K (Fig. 6) using the program MPROF

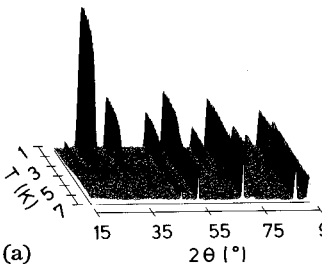


Fig. 5. (a) Diffraction patterns obtained on heating on D1B wit artefact due to a bad wire of t reflections ½00 (upper) and ½01

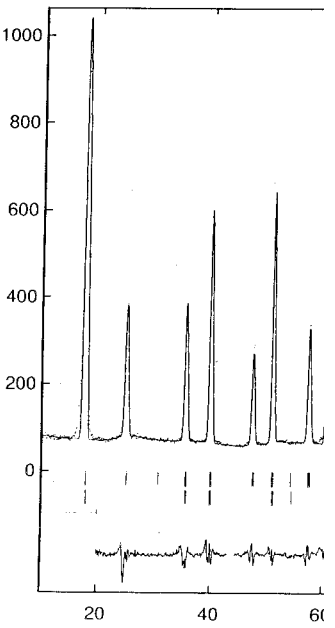


Fig. 6. Observed, calculated an with $\lambda = 1.911$ Å. Upper and lowe and nuclear reflections respecti Rietveld least-squares refinemen background is considerably redu

[18] with the reflection c and $\gamma \approx 120°$. The magneti Brown [19]. During the in for the cell constants were refinement converged to R

of the D1A data shows that the nuclear peaks are split at high angle and this is readily seen for the peak at 98.7° in Fig. 6 where the diffractometer has its best resolution. Removal of the symmetry conditions applied to the cell constants gave a significantly better fit to the data with $R_{wp} = 11.4\%$. However, it was apparent from the difference profile that the magnetic peaks were slightly broadened with respect to the nuclear peaks and a multiphase fit to the data was carried out with separate U, V and W parameters to describe the peak widths as a function of 2θ for the nuclear and magnetic peaks. The best fit to the data, shown in Fig. 6, with $R_{wp} = 9.0\%$, was achieved with 23 parameters (of which nine are structural) in which the x, y coordinates of Ho and F were fixed at 0.6667, 0.3333 as in the trigonal structure and with the intense magnetic peak at 17.9° excluded from the refinement owing to instrumental asymmetry effects. The final parameters and R factors are listed in Table 2.

The arrangement of the magnetic moments corresponds to an antiferromagnetic collinear structure with the propagation vector along [100]. In the ab plane the components of the magnetic moments lie 17° off the [010] direction and are tilted out of the ab plane by 24° as illustrated in Fig. 7. The total magnetic moment refined to 7.63(5) μ_B.

An interesting result of the high resolution D1A data analysis is the observation of lattice deformation due to magnetoelastic effects. The magnitude of this distortion is very small and is generally not observable in the low resolution diffraction patterns commonly used to determine magnetic structures on D1B. The difference between the a and b lattice constants is of the order of 0.02% and the angles deviate from those of the trigonal lattice by only 0.2%. The reduction in symmetry from $P\bar{3}m1$ to $P\bar{1}$ on transforming to the low temperature antiferromagnetic phase is consistent in terms of subgroup–supergroup relationships with the observation of the colour space

TABLE 2

Final parameters and R factors for Ho_2CF_2 at 1.5 K. $\lambda = 1.911$ Å. Nuclear space group $Pa\bar{1}$, magnetic space group $P_a\bar{1}'$. $a = 3.6517(2)$ Å, $b = 3.6510(2)$ Å, $c = 6.3085(2)$ Å, $\alpha = 90.121(5)°$, $\beta = 89.808(3)°$, $\lambda = 119.893(3)°$. $V = 72.918(4)$ Å^3, $\rho_{calc} = 8.642$ g cm^{-3}

Atom	Site	symmetry	X	Y	Z	B (Å^2)	N
Ho	2i	1	0.6667	0.3333	0.7859(6)	−0.14(5)	2
C	1a	$\bar{1}$	0	0	0	−0.01(10)	1
F	2i	1	0.6667	0.3333	0.3858(6)	0.36(9)	2

M (μ_B): 7.63(5)
k_x, k_y, k_z (μ_B): −2.34(13), 5.46(6), 3.19(9)
U, V, W (deg^2) (nuclear): 0.17(1), −0.37(2), 0.33(1)
U, V, W (deg^2) (magnetic): 0.38(2), −0.87(3), 0.65(1)
$R_{wp} = 9.0\%$, $R_{exp} = 6.4\%$, $R_I = 4.4\%$, R_I(nuclear) = 2.0%, R_I(magnetic) = 7.5%

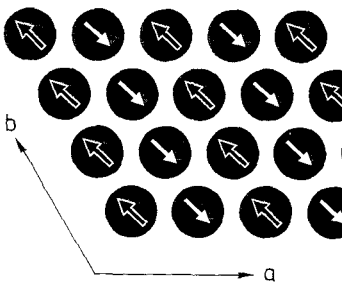


Fig. 7. View of the magnetic str
Black and white arrows indicate m

group $P_a\bar{1}'$ for the magneti
are only available for 1.5 a
of lattice distortion is direc
onset of long-range antife
uncommon for rare earth c

At 1.5 K the differenc
reflections is attributed to
structure. This is not so su
with very anisotropic magn
shown in the analysis of t
measured on D1B as a fu
shaped curve demonstrates
to short-range magnetic ord
corroborated by the broad
and the high temperature ta
of magnetic short-range o
entropy occurs above T_N (

The temperature depe
reflections obtained from t
around 3.7(1) K in good a
from specific heat and susc
of T_N observed for Ho_2CF_2 i
layered metal-rich rare eart
atoms, *e.g.* $REXH_2$ (RE≡G
temperatures for metallic l
are about one order of ma
electrons excludes RKKY i
range dipolar coupling via th
the Ho^{3+} magnetic momen
chemical bonding, the super
interactions are of equal im
be neglected, Ho_2CF_2 is no

Owing to crystal field
moment is lower than the

50

ır the $^5I_8$ ground term (Landé factor $g_J=\frac{5}{4}$) of Ho^{3+} with $4f^{10}$ electronic ɔnfiguration. In Ho_2CF_2 the degeneracy of the ground term is lifted by a ystal electric field of C_{3v} symmetry, in principle allowing that Ho_2CF_2 could *priori* be diamagnetic at low temperatures, with a singlet as the crystal ɛld ground state, which obviously is not the case for Ho_2CF_2. The magnetic ıtropy is found to be 14.4 J mol^{-1} K^{-1} or $R\times1.73$, being close to $R\ln6$ ig. 3), and indicates the ordering of a six-level system. Such a large ɛgeneracy for the crystal field ground state, on the other hand, seems ılikely in view of the low site symmetry. We suggest that a substantial part the entropy also originates from the structural phase transition.

Assuming as a first approximation that the magnetic ordering takes place a crystal field doublet as, for example, was observed for $Ho(OH)_3$ [21], ound state eigenfunctions composed primarily of $J_z=\pm6$ states could ɛcount for the experimentally detected magnetic moment of 7.63 μ_B. Inelastic ɛutron-scattering experiments should be carried out to establish the full ystal field level scheme of Ho^{3+} in Ho_2CF_2 in order to enable a detailed ɔmparison with the results reported here.

cknowledgments

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