References


Abstract

The preparation of a new trigonal, space group $P\bar{3}$ structure. On cooling antiferromagnet with ma magnetic to antiferromagnetic $P1$ due to magnetoelastic determined from high re 50 K. Evidence for crit susceptibility and temperu measurements show dimensionality of the str discussed.

1. Introduction

The chemistry of characterized by a la compounds have been a review of the chem of the rare earths). In atoms or $C_2$ units are metal atoms. These $Gd$ may be condensed to structures. In all the edges of the $Gd_6$ octa

So far, only one [3], in addition to the reports on the prepau properties of holmium

* Dedicated to Professo 60th birthdays.
† Also at Institut Laue-
gely characterized by the presence of extended bilayers and the highly
otropic chemical bonding associated with them, implying interesting
gnetic and electrical properties.

Experimental details

Sample preparation and characterization

The starting materials, holmium, HoF3, and carbon, were prepared as
lows. Sublimed holmium metal lumps (99.99%, Universal Matthey, Karls-
) 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.
F3 was prepared from Ho2O3 (99.99%, Universal Matthey) and HP following
method described by Greis and Petzel [4]. Carbon, in the form of activated
arcoal (high purity, Merck, Darmstadt), was degassed at 1450 K in high
vacuum for 24 h and stored in a pure argon atmosphere.

Of the rare earth carbide fluorides, the holmium derivative was thought
easy to prepare owing to the fact that HoF3 exhibits one of the lowest
lings points of all the rare earth trifluorides. Ho2CF3 was synthesized from
starting materials holmium, HoF3 and carbon in the molar ratio 4:2:3
al mass approximately 2.5 g) sealed under 1 bar of argon in a tantalum
oule, which was then sealed under vacuum in a quartz glass tube and
ed to 1450 K for 8 days, resulting in the formation of a single-phase
ocrystalline dark brown Ho2CF3 powder. Ho2CF3 slowly decomposes in
and is readily dissolved by dilute mineral acids at ambient temperature.

X-ray investigations

Powdered samples of Ho2CF3 were characterized at room temperature
the modified Guinier technique [5] with silicon (a=5.430 35 Å) as an
rnal standard using Cu Kα1 (λ=1.540 56 Å). The diffraction patterns,
index as trigonal, matched those of the isostructural gadolinium
pound Gd2CF3 [3] with space group P3m1–D3d (no. 164). The lattice
stants, determined from coincidence measurements of 13 reflections in
ge 4°<θ<30° (Δθ=±0.005°) refined [6] to a=3.6567(2) Å and
3.6171(5) Å. The 20 largest d spacings (Å) are (with relative intensities)
, 1.317(10), 1.367(60), 1.281(100), 2.236(70), 2.106(5), 1.828(60), 1.754(50),
, 1.582(40), 1.579(5), 1.536(30), 1.416(20), 1.413(10), 1.381(10),
, 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 Cm to the heat capacity was obtained by
tracting a lattice contribution Cl which was estimated according to the
following procedure. A temperature derived from the specific heat

\[ C_p = gR \left( \frac{T}{\Theta_B} \right)^3 \int_0^{\Theta_B/T} \frac{e^{\alpha/\Theta_B}}{(e^{\alpha/\Theta_B} - 1)^2} \, d\alpha \]

At high temperature a peak was extrapolated to low temperature part of the heat capacity, Cl, numerically integrating Cm/T capacity, Cm = Cp - Cl, followed by

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

2.4. Magnetic susceptibility

The susceptibility of powdered samples was determined with a Quanti
were contained in dried gelatin in separate runs and corrected

2.5. Electrical conductivity

The resistance was determined using a two-point electrometer method
and steel pistons and cooled

2.6. Neutron diffraction

For the neutron diffraction study, samples were sealed under helium gas in diameter which was then submitted to a 400-wire 3He–Xe gas mixture. The temperature was scanned from 0 to 150 K in steps

3. Results and discussion

The structure of Ho2CF3, P3m1, was refined 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 Å².

Figure 2 shows a projection of the structure along [110]. The structure may be described in terms of Ho₃ octahedra filled with carbon atoms which are connected via their edges to form infinite [Ho₂C] layers. The coordination of the remaining edges by fluorine atoms results in [Ho₂C] layers sandwiched between fluorine layers and stacked along [001] according to the sequence \( \cdots \text{Ab'yAb} \ cdots ( \cdots \text{FHoCHOoF} \ cdots ) \). Such FHoCHOoF 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 is well known from a great number of different compounds such as Gd₂Er₃C [10], CaAl₂Si₂ [11], Ta₂SnC [12], Ce₂O₂S [13] and Ln₂O₃ [14], which have structural subunits [CGd₂], [CaSi₂], [CTa₂], [SCE₂] and [OLn₂] respectively based on the C₁₂₂ structure [15]. The remaining atoms fill the tetrahedral holes between the metal or silicon double layers.

Conductivity experiments show that Ho₂CF₂ is non-metallic as predicted by the simple ionic description (Ho⁺)₂C⁴⁻(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 filled with hydrogen intercalated in the rare earth halide dications formulated as (RE⁢⁺)₂(C⁴⁻) as the covalent interaction of the states.

The specific heat (Fig. 3.61(5) K and a long tail to up to 25 K. The specific heat to be of antiferromagnetic in Fig. 4). The latter is below. The derivative \( d(\chi)/dT \) at 3.7(1) K in agreement with the paramagnetic Curie susceptibility follows a Cu

\[ \chi_{mol} = \frac{C}{T - \Theta} \]

with a paramagnetic Curie constant predominately antiferromagnetic.
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$_2$CF$_3$. (b) Magnetic part $S_m$ of the entropy according to eqn. (2). (All data are per one formula unit of HoCF$_3$F$_3$.)

Fig. 4. Molar magnetic susceptibility $\chi_{mol}$ of Ho$_2$CF$_3$ at low temperatures.

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

From the diffraction patterns collected on D1B (Fig. 5) it is evident that between 1.5 K and room temperature Ho$_2$CF$_3$ 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 $\alpha$ 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 $P_\alpha\bar{1}$.

The complete magnetic structure was refined by the Rietveld method from the D1A data of Ho$_2$CF$_3$ at 1.5 K (Fig. 6) using the program MPREF. Fig. 6. Observed, calculated an with $\lambda=1.911$ Å. Upper and low and nuclear reflections respectively. Rietveld least-squares refinement background is considerably refined.
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 multipe phase 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) $\mu_B$.

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 P3m1 to P1 on transforming to the low temperature antiferromagnetic phase is consistent in terms of subgroup—supergroup relationships with the observation of the colour space

![Fig. 7. View of the magnetic str](Black and white arrows indicate m group $P_3\overline{1}$ for the magneti are only available for 1.5 a of lattice distortion is direct onset of long-range antif uncommon for rare earth c)

At 1.5 K the difference reflections is attributed to structure. This is not so with very anisotropic magn shown in the analysis of t measured on D1B as a flat shaped curve demonstrates to short-range magnetic ord corroborated by the broad a and the high temperature of magnetic short-range or entropy occurs above $T_N$ (2)

The temperature dependent reflections obtained from 3.7(1) K to 49(1) K from specific heat and susc of $T_N$ observed for Ho$_2$CF$_3$ is layered metal-rich rare earth atoms, e.g. REX$_2$ (RE=Gd) temperatures for metallic La are about one order of magnitude electrons excludes RKKY and range dipolar coupling via the Ho$^{3+}$ magnetic moment. Chemical bonding, the super exchanges are of equal importance and can be neglected, Ho$_2$CF$_3$ is nonmagnetic.

Owing to crystal field effects the magnetic moment is lower than the

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>symmetry</th>
<th>$X$</th>
<th>$Y$</th>
<th>$Z$</th>
<th>$B_i$ ($\mu_B$)</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>2i</td>
<td>1</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.7859(6)</td>
<td>-0.14(5)</td>
<td>2</td>
</tr>
<tr>
<td>O</td>
<td>1a</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.01(10)</td>
<td>1</td>
</tr>
<tr>
<td>F</td>
<td>2i</td>
<td>1</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.3686(6)</td>
<td>0.36(9)</td>
<td>2</td>
</tr>
</tbody>
</table>

$M$ ($\mu_B$): 7.63(5)

$k_r$, $k_r$, $k_y$ ($\mu_B$): -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)

$R_{wp}=9.0\%$, $R_{exp}=6.4\%$, $R_1=4.4\%$, $R_2$ (nuclear) = 2.0\%, $R_2$ (magnetic) = 7.5\%
or the \( ^5I_8 \) ground term (Landé factor \( g_J = \frac{2}{3} \)) of Ho\(^{3+} \) with 4f\(^{10} \) electronic configuration. In Ho\(_2\)CF\(_2\) the degeneracy of the ground term is lifted by a crystal electric field of \( C_{3v} \) symmetry, in principle allowing that Ho\(_2\)CF\(_2\) could \textit{a priori} be diamagnetic at low temperatures, with a singlet as the crystal field ground state, which obviously is not the case for Ho\(_2\)CF\(_2\). The magnetic entropy is found to be 14.4 J mol\(^{-1}\) K\(^{-1}\) or \( R \times 1.73 \), being close to \( R \ln 6 \) (Fig. 3), and indicates the ordering of a six-level system. Such a large degeneracy for the crystal field ground state, on the other hand, seems likely in view of the low site symmetry. We suggest that a substantial part of the entropy also originates from the structural phase transition.

Assuming as a first approximation that the magnetic ordering takes place in a crystal field doublet as, for example, was observed for Ho(OH)\(_3\) [21], ground state eigenfunctions composed primarily of \( J_z = \pm 6 \) states could account for the experimentally determined magnetic moment of 7.63 \( \mu_B \). Inelastic neutron-scattering experiments should be carried out to establish the full crystal field level scheme of Ho\(^{3+} \) in Ho\(_2\)CF\(_2\) in order to enable a detailed comparison with the results reported here.

\textbf{Acknowledgments}

We thank E. Brücher, H. Diem, R. Eger and W. Röthenbach for experimental help and E. Gmelin for very valuable discussions. N.P.R. gratefully acknowledges full financial support by the DAAD (German Academic Exchange Service).

\textbf{References}

A. Simon, \textit{J. Solid State Chem.}, 57 (1986) 2;