Antiferromagnetic ordering in RE$_2$C$_2$I$_2$ (RE = Ce, Nd, Tb)

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The non-magnetic layered rare earth (RE = Y, La) metal carbide halides RE$_2$C$_2$X$_2$ (X = Cl, Br, I) form two-dimensional metals and show superconductivity, e.g., Y$_2$C$_2$I$_2$ at 10 K. So far, a maximum $T_c$ of 11.6 K has been reached in the phase Y$_2$C$_2$Br$_{0.5}$I$_{1.5}$. Recently, by applying hydrostatic pressure to Y$_2$C$_2$I$_2$ we demonstrated that $T_c$ can be increased to 11.7 K. In several preceding annual reports (e.g., the annual reports of 1994, 1995, and 1997) we have described the superconducting properties of the RE$_2$C$_2$X$_2$ (RE = Y, La; X = Cl, Br, I) in more detail. With magnetic RE atoms the phases RE$_2$C$_2$X$_2$ undergo antiferromagnetic (afm) ordering at temperatures up to $T \approx 2.5 T_N$ which we ascribe to the pronounced layer character and to magnetic frustration due to the competing exchange interaction in the RE triangular layers. The large Tb magnetic moment of about 9µB and application of the new D20 high intensity medium-resolution powder diffractometer at the Institute Laue-Langevin in Grenoble allows us to observe and to analyze the diffuse scattering in Tb$_2$C$_2$I$_2$. In addition, long-range afm ordering was also investigated with the diffractometer DMC at the Paul-Scherrer Institute in Villingen.

The phases RE$_2$C$_2$X$_2$ crystallize in structures which contain doublelayers of close-packed metal atoms with C$_2$ units occupying the RE octahedral voids. These doublelayers are sandwiched by layers of halogen atoms to form X–RE–C$_2$–RE–X slabs which connect via van der Waals forces in stacks along the crystallographic c-axis (Fig. 1). Two stacking variants (1s- and 3s-type) have been discerned, which differ in the number of such slabs within the unit cell.

Figure 1: Perspective view of the the crystal structures of RE$_2$C$_2$X$_2$, (X = I); 1s stacking variant left and 3s stacking variant right.
Figure 2 displays the diffraction patterns of 3s-Ce$_2$C$_2$I$_2$ at 30 K (in the paramagnetic regime) and at 2 K in the afm ordered state. The diffraction pattern at 30 K was analyzed and fitted with Fullprof powder profile fitting programs and the refined lattice and atomic parameters are consistent with results obtained from room temperature X-ray diffraction investigations.

At 2 K weak additional Bragg reflections are observed which can be attributed to magnetic scattering from an ordered afm arrangement of the Ce moments. These magnetic Bragg reflections are clearly seen in a difference pattern (lower panel in Fig. 2). The magnetic reflections can be indexed on the basis of a $\tau = [0,0,1/2]$ propagation vector to give a magnetic unit cell of $a = 7.4848(3)$ Å, $b = 4.0736(2)$ Å, $c = 21.5254(7)$ Å, and $\beta = 100.69(1)^\circ$. The final results of the full magnetic Rietveld refinement ($R_{\text{mag}} = 8.8\%$) indicate a magnetic moment of $1.3(1)\mu_B$ which is significantly reduced from the maximum possible moment of $2.14\mu_B$ for the $^2F_{5/2}$ crystal field ground state of the Ce$^{3+}$ ions. The Ce moments lie within the $ac$-plane and enclose an angle of $\approx 30^\circ$ with the $c$-axis and alternate antiferromagnetically along the $a$-axis. The magnetic structure is depicted for one magnetic unit cell in Fig. 3.

A rather similar picture is observed for the arrangement of the magnetic moments in a single Nd–C$_2$–Nd slab in 3s-Nd$_2$C$_2$I$_2$. The magnetic structure was refined from high-resolution neutron powder patterns collected at the diffractometer = D1A (ILL, Grenoble). At $T = 2$ K, sev-
eral additional peaks are observed in the diffraction patterns (not shown here) due to coherent magnetic scattering from the Nd\(^{3+}\) moments. Unlike for 3\(s\)-Ce\(_2\)C\(_2\)I\(_2\), these peaks can now be indexed assuming identical crystallographic and magnetic unit cells (propagation vector \(\tau = [0,0,0]\)). The final Rietveld refinements reveal that the Nd magnetic moments – as in Ce\(_2\)C\(_2\)I\(_2\) – lie entirely within the \(ac\)-plane with a magnitude of 3.4(1)\(\mu\)\(_{\text{eff}}\), and are arranged with parallel orientation across the C–C dimers. Compared to 3\(s\)-Ce\(_2\)C\(_2\)I\(_2\) the Nd moments, however, are significantly more rotated towards the \(ab\)-plane.

The broad maximum in the susceptibility is a typical signature of short-range magnetic ordering effects preceding the long-range ordering transition at 65 K. The paramagnetic Curie temperature \(\theta_P\) is found to be negative indicating predominant afm exchange interaction. However, the magnitude of \(\theta_P\) is significantly reduced as compared to these ordering temperatures. This reduction points to competing exchange interactions most likely due to geometrical frustration in the metal atom triangles present in the metal atom doublelayers but also due to possible cancellations of the long-range oscillatory RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction. The long-range ordering transition at 65 K is also visible in the electrical resistivity as a local maximum while the effect of the preceding magnetic short-range ordering on the resistivity is less prominent (Fig. 4(b)).

The temperature dependence of the neutron powder diffraction of Tb\(_2\)C\(_2\)I\(_2\) as measured using the diffractometer D20 (ILL, Grenoble) is shown in Fig. 5. This thermodiffractogram also reveals two magnetic transitions at about 85 K and at 65 K. Below 65 K sharp additional magnetic Bragg reflections are observed. Between 85 K and 65 K these reflections broaden beyond experimental resolution and become incommensurate with the underlying nuclear lattice. Above 85 K the magnetic reflections form a diffuse but structured magnetic background which decays with increasing temperature. We ascribe this diffuse part to incommensurate magnetic scattering from short-range ordered areas in the Tb metal atom layers. A detailed quantitative analysis of the diffuse part of the magnetic scattering is currently underway. Figure 4(c) displays the integrated intensity around the magnetic Bragg reflection 100 which is the most intense magnetic peak observed. A sharp increase from the magnetic and electrical bulk properties. Tb\(_2\)C\(_2\)I\(_2\) shows afm ordering with two transition temperatures. A first transition at \(\approx 90\) K is characterized by a broad maximum in the magnetic susceptibility followed by a second sharp transition at 65 K (Fig. 4(a)).

Figure 4: (a) Magnetic susceptibility of powder sample of Tb\(_2\)C\(_2\)I\(_2\), (b) temperature dependence of the electrical resistivity of a sintered pellet (c) temperature dependence of the integrated magnetic intensity in the vicinity of the magnetic Bragg reflection 100, taken from powder diffraction data collected at D20 (ILL, Grenoble).

In contrast to Ce\(_2\)C\(_2\)I\(_2\) and Nd\(_2\)C\(_2\)I\(_2\), the magnetic ordering behavior of 1\(s\)-Tb\(_2\)C\(_2\)I\(_2\) is much more complex. This finding is already indicated
of the intensity at about 60 K and a broader intensity increase around 90 K parallels the two transitions seen in the bulk properties.

Figure 5: Thermodiffractogram (false color representation) of $1s$-Tb$_2$C$_2$I$_2$ taken at the high intensity medium-resolution powder diffractometer D20 (ILL, Grenoble). Yellow and red colors mark zones of high intensity (coherent nuclear and magnetic Bragg reflections). Light blue color indicates weak diffuse magnetic scattering above $\approx 85$ K. A wavelength of $\lambda = 2.56$ Å was used in all measurements.

In a first approach to analyze the afm ordering processes of Tb$_2$C$_2$I$_2$ we determined the magnetic structure at 10 K by profile refinements of neutron powder diffraction patterns collected at the diffractometer DMC (PSI, Villingen). All magnetic Bragg reflections can be indexed based on the commensurate propagation vector $\tau = [0,0,0]$. The Shubnikov group is $P2/m$. The final results of the Rietveld refinement of the pattern at 10 K are shown in Fig. 6. The magnetic moment amounts to $8.0(1) \mu_B$ which is somewhat smaller than the possible maximum moment ($J = 6$, $g_J = 3/2$) of a Tb$^{3+}$ ion ($9 \mu_B$). The Tb moments were found to be aligned in the $ac$-plane with a collinear antiferromagnetic arrangement as shown in Fig. 6. The moments point along the direction of the C–C dumbbell in antiparallel orientations.

Figure 6: Magnetic structure of Tb$_2$C$_2$I$_2$ as refined from a diffraction data set collected at 10 K at DMC (PSI Villigen). Only the magnetic atoms (Tb) are shown.

In summary, the antiferromagnetic ordering behavior of the layered rare earth (RE = Ce, Nd, Tb) metal carbide halides RE$_2$C$_2$X$_2$ (X = Br, I) has been investigated, and the magnetic structures have been established from neutron powder diffraction (Tab. 1).

Table 1: Compilation of magnetic parameters of the investigated RE$_2$C$_2$X$_2$. For $3s$-Ce$_2$C$_2$Br$_2$ magnetic Bragg reflections could not be observed in the diffraction patterns.

<table>
<thead>
<tr>
<th></th>
<th>$T_N$ [K]</th>
<th>$\theta_P$ [K]</th>
<th>$\mu^{\text{sat}}$ [$\mu_B$]</th>
<th>$\mu^{\text{eff}}$ [$\mu_B$]</th>
<th>$g_J \sqrt{J(J+1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3s$-Ce$_2$C$_2$I$_2$</td>
<td>15(1)</td>
<td>$-54(1)$</td>
<td>$1.3(1)$</td>
<td>$2.6(1)$</td>
<td>$2.53$</td>
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<tr>
<td>$3s$-Ce$_2$C$_2$I$_2$</td>
<td>32(1)</td>
<td>$-32(1)$</td>
<td>$3.4(1)$</td>
<td>$3.57(5)$</td>
<td>$3.62$</td>
</tr>
<tr>
<td>$1s$-Tb$_2$C$_2$I$_2$</td>
<td>65+85</td>
<td>$-32(3)$</td>
<td>$8.0(1)$</td>
<td>$9.6(1)$</td>
<td>$9.72$</td>
</tr>
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While Ce$_2$C$_2$X$_2$ and Nd$_2$C$_2$X$_2$ undergo rather standard transitions to long-range ordered collinear afm phases, magnetic ordering in Tb$_2$C$_2$I$_2$ takes place in two consecutive steps from a short-range ordered phase via an incommensurate intermediate phase to a long-range ordered phase, the properties of which are similar to those of the afm phase seen for Ce$_2$C$_2$I$_2$ and Nd$_2$C$_2$I$_2$. Due to the exceptional magnitude of the Tb moments the short-range order shows up as sizeable diffuse scattering. The analysis of the diffuse scattering should allow us to study in detail the character of the unusual short-range ordering process in Tb$_2$C$_2$I$_2$.