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Magnetic heat capacity and electrical resistivity of RCoC (R=Dy, Ho, Er, Y)

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Abstract

The heat capacity and electrical resistivity was measured on the carbides RCoC (R=Dy, Ho, Er, Y). YCoC has a rather high electronic heat capacity of 14.0 mJ/K^2mol, suggesting the presence of narrow conduction bands. The magnetic transition temperatures were determined by the λ-type anomalies of the heat capacity for DyCoC: T_N=6.8 K, HoCoC: T_N=7.5 K and for ErCoC: T_N=4.0 K, respectively. All the compounds show metallic temperature dependence of the resistivity. Contrary to the metallic behavior of RCoC, T_N of DyCoC is lower than that of HoCoC. The physical properties of DyCoC under a magnetic field suggest the presence of a quadrupolar ordering above T_N, which can suppress the magnetic ordering temperature.

Keywords: Inorganic compounds; Magnetic properties; Phase transition; Quadrupolar ordering

1. Introduction

Rare earth metal cobalt carbide RCoC (R=Gd–Lu) is known to have a simple tetragonal structure (YCoC-type) with the lattice parameter a~3.6 Å and c~6.8 Å [1]. The cobalt and carbon atoms form infinite linear chains, which extend parallel to the a direction at $z=0$ and parallel to the b direction at $z=1/2$. The band calculation of the CoC^{3-} chain [2] indicates the presence of the half-filled π band. The magnetic R atoms locate at $z=1/4$ and $3/4$, surrounded by eight Co atoms and four C atoms. Thus, RCoC can be a model compound having the π–f magnetic interaction and orbital ordering (such as quadrupolar ordering) due to its simple crystal structure. The magnetic transitions have been found in the compounds with R=Gd–Er with the transition temperature ranging between 4 and 22 K [3]. In order to know the electronic properties of this system, details of the magnetic ordering of R, and the crystal–field effect, we measured the magentization, heat capacity, and electrical resistivity under magnetic field on RCoC with R=Dy, Ho, Er and Y.

2. Experimental

Polycrystalline samples of RCoC (R=Gd to Tm, Y) were prepared by arc melting using a water-cooled copper hearth in argon atmosphere. The samples were remelted several times for homogenization. Obtained samples were characterized by X-ray power diffraction. Within our synthesis, the Dy, Ho, Er and Y compounds could be isolated as single phase, but could not for TmCoC due to comparatively higher vapor pressure of Tm on arc-melting. It may be considered that large rare earth atoms are not stabilized in the tetrahedron of the carbon atoms, because the strongly covalent-bonded CoC chains cannot be elongated.

The magnetic susceptibility was measured with a SQUID magnetometer in the temperature range between 2 and 300 K with a magnetic field up to 5 T. The resistivity was measured by a usual four-probe method between 1.3 and 300 K and up to 5 T. The heat capacity was measured by an adiabatic method between 1.5 and 30 K and by an AC method between 4 and 20 K. The AC system was equipped to a superconducting magnet of a SQUID system in order to measure the heat capacity under magnetic fields of up to 5 T.

3. Result and discussion

3.1. Electrical resistivity

The temperature dependence of the electrical resistivity of RCoC is shown in Fig. 1. All the compounds show metallic temperature dependence with convex curvature.

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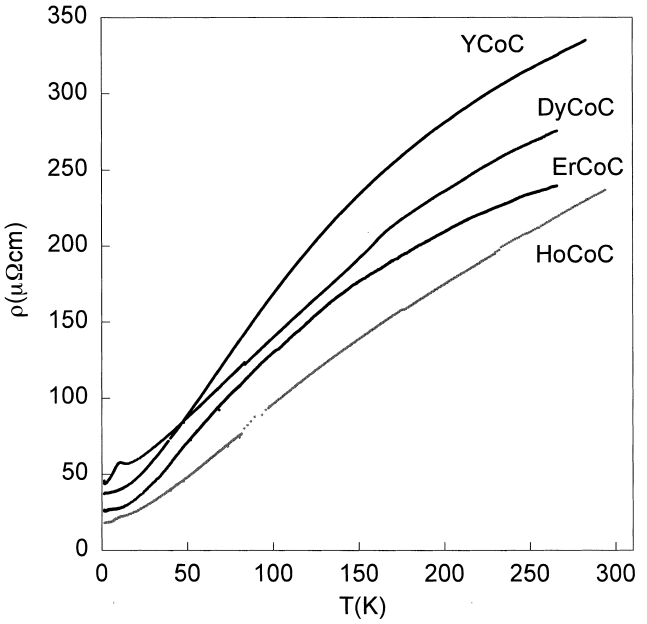

Fig. 1. Temperature dependence of the electrical resistivity of RCoC.

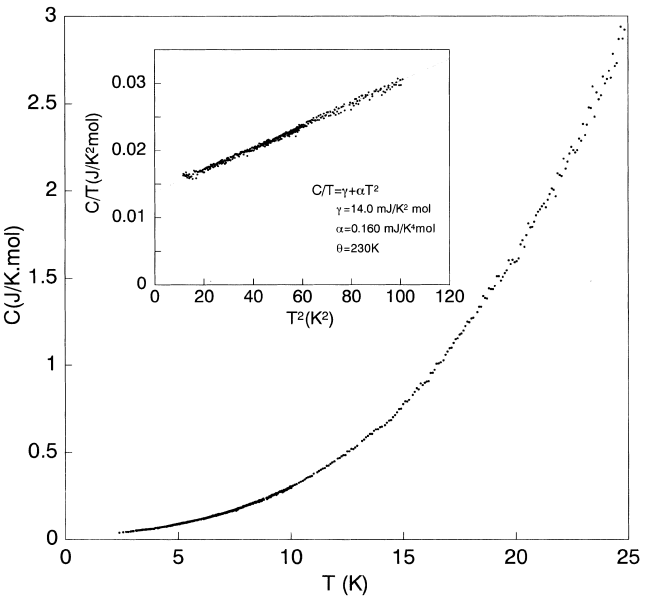

Fig. 2. Temperature dependence of the heat capacity of YCoC. The inset shows the $C/T-T^2$ plot at lower temperatures.

The room temperature resistivity and the residual resistivity are 275 and 42 μΩcm for DyCoC, 240 and 18 μΩcm for HoCoC Ho, 250 and 26 μΩcm for ErCoC, and 340 and 37 μΩcm for YCoC, respectively. A relatively high resistivity of non-magnetic YCoC and less sensitive resistivity to the magnitude of the magnetic moment of R atoms may suggest that the carrier scattering from grain boundaries is significant in the resistivity of polycrystalline RCoC. With decreasing temperature, the resistivity of DyCoC shows a shallow minimum at 15 K and a small hump at 13 K, then a change of the temperature gradient at 7 K. This feature suggests the presence of successive phase transitions, so we will discuss this in different sections with the magnetic field dependence of the physical properties. The change in the slope of the resistivity was also found in HoCoC and ErCoC at 7.5 K and 4.0 K, respectively, which are in good agreement with the antiferromagnetic transition temperatures found by magnetic susceptibility measurements [3].

3.2. Heat capacity

The temperature dependence of the heat capacity of YCoC is shown in Fig. 2 and the temperature dependence of the magnetic heat capacity and magnetic entropy of RCoC are shown in Fig. 3. As shown in the inset of Fig. 2, the heat capacity of the non-magnetic compound YCoC can be well expressed by the sum of the electronic and phonon contribution, $C = C_e + C_{ph} = \gamma T + \alpha T^3$, where γ and α are estimated at 14.0 mJ/K^{2}mol and 0.160 mJ/K^{4}mol, respectively. Applying the free electron model, the coefficient of the electronic specific heat γ gives the density of state at the Fermi level, $D(\varepsilon_F)=5.9$ states/eV, which value is comparable to 4.3 states/eV for yttrium metal. This considerably large value of $D(\varepsilon_F)$ in YCoC suggests the Fermi energy is located at the narrow conduction band consisting of strongly hybridized 4d orbital and 3d–π orbitals of the CoC chains.

The heat capacity of the magnetic RCoC (Fig. 3) exhibits a λ-type anomaly at the magnetic transition temperatures (T_N), which can be precisely determined in this work for DyCoC: $T_N=6.8$ K, HoCoC: $T_N=7.5$ K and for ErCoC: $T_N=4.0$ K, respectively. The heat capacity of the magnetic compounds can be analyzed as the sum of the electronic, phonon and magnetic (C_m) contributions. The magnetic heat capacity C_m was evaluated by subtraction of the heat capacity of YCoC with a mass correction of the Debye temperature as $\theta_{D,R} = (\sqrt{M_Y}/\sqrt{M_R})\theta_{D,Y}$. The magnetic entropy can be derived by the integration of C_m/T by temperature. The entropy change associated with the magnetic transition is nearly R*ln*2 below T_N for all the compounds. In DyCoC and ErCoC, Dy^{3+} and Er^{3+} are the Kramers ions so that in the tetragonal crystal electric field, the ground state of the 4f level is a doublet, consistent with the entropy change below T_N. In case of HoCoC, the 4f states with the total angular momentum $J=8$ is split into nine singlets and four doublets in the tetragonal crystal–field. A smaller entropy than R*ln*2 below T_N found in HoCoC suggests that the ground state is not a doublet but a pseudo-doublet consisting of two singlets. Due to the presence of other excited 4f states, the Schottky-type anomalies appear in the heat capacity above T_N, which is apparent for ErCoC in Fig. 3.

In DyCoC, a hump of the heat capacity appears just above T_N with the peak at 10 K. The entropy change between T_N and 15 K (at the temperature where the

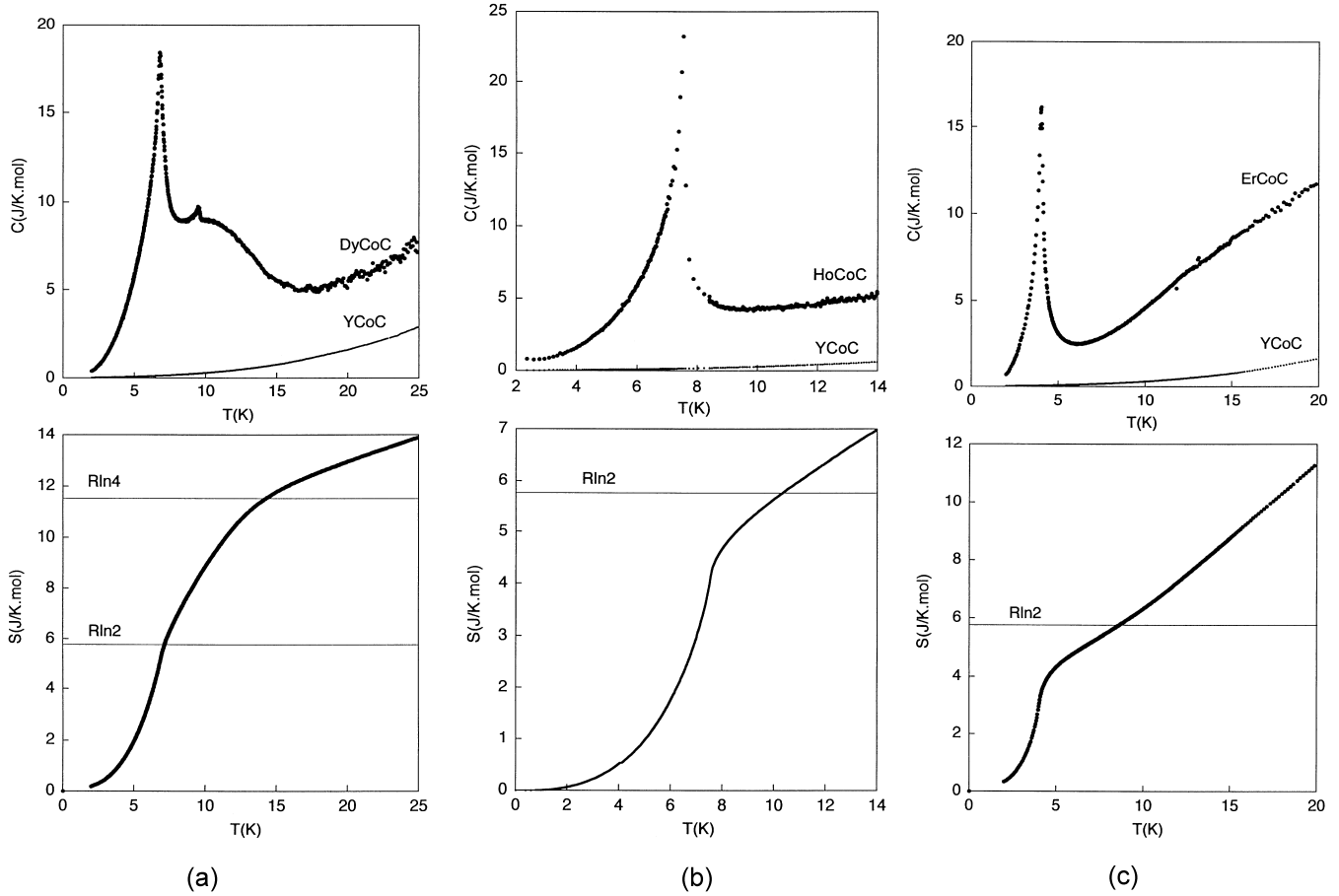

Fig. 3. Temperature dependence of the magnetic heat capacity and the entropy change of DyCoC (a), HoCoC (b) and ErCoC (c). A small anomaly at around 9 K in (a) is due to the second phase $DyCoC_2$. The contribution of this phase to the total entropy change is less than 0.1%.

anomaly vanishes) is close to R*ln*2, thus the anomaly is related to the first exited doublet. This hump looks like the Schottky anomaly but the temperature dependence cannot be fit to the two-level Schottky-type heat capacity.

3.3. Properties of DyCoC under magnetic field

The dominant magnetic interaction in metallic RCoC is considered as the RKKY (Ruderman–Kittel–Kasuya–Yoshida) interaction, therefore the magnetic transition temperature should be proportional to the de Gennes parameter, $(g_J - 1)^2 J(J+1)$ where g_J is the Lande's g-factor. In contrast to this fact, the antiferromagnetic transition temperature of DyCoC is lower than that of HoCoC. This experimental finding suggests a mechanism that suppresses the magnetic transition in DyCoC. To clarify the anomalous nature of DyCoC, we measured the temperature dependence of the electrical resistivity, heat capacity, and magnetic susceptibility under several magnetic fields. Fig. 4 reveals the temperature dependence of the heat capacity of DyCoC under magnetic field measured by the AC method. The anomaly at T_N shifts to lower temperatures and is suppressed by applying magnetic fields, which is a usual behavior of an antiferromagnet. The broad hump of the heat capacity at 10 K seems to consist of two peaks in the magnetic field below 1 T. The low temperature-side peak becomes well defined and shifts to higher temperature to 13.8 K with increasing magnetic field up to 5 T. On the other hand, the high temperature-side peak is still unclear. This result indicates the presence of a field-induced magnetic transition. As shown in Fig. 5, the zero-field resistivity shows a maximum at 13 K and a steep decrease at 7 K, corresponding to the heat capacity anomalies. With increasing magnetic field, the resistivity in the whole temperature region shown in Fig. 5 is lowered due to the decrease of the carrier scattering by disordered spins (spin-disorder resistivity). The hump of the resistivity is suppressed and the maximum of the resistivity shifts to higher temperature. Fig. 6 shows the temperature dependence of the magnetic susceptibility defined by M/H. In addition to a steep decrease of the susceptibility at T_N, a small anomaly in the shoulder of the peak of the susceptibility can be seen at H = 0.1 T. By applying the magnetic field, DyCoC exhibits a metamagnetic transition at H = 0.2 T [3] below T_N. Above T_N, the small anomaly can be seen clearly as a kink, which also shifts to higher temperatures.

As the entropy change below this anomaly is close to R*ln*4 as seen in Fig. 3, the two Kramers doublets take part

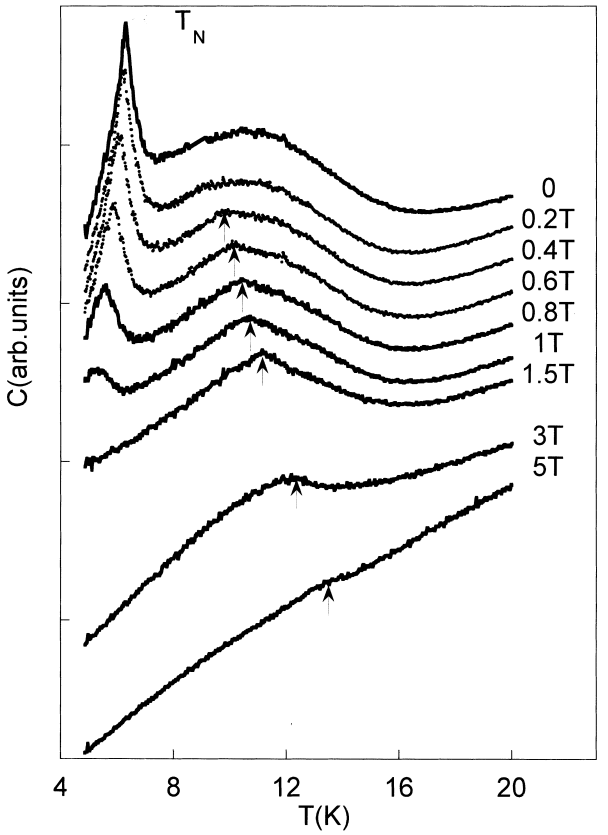

Fig. 4. Heat capacity of DyCoC under magnetic field. The arrows indicate lower temperature anomaly of the heat capacity.

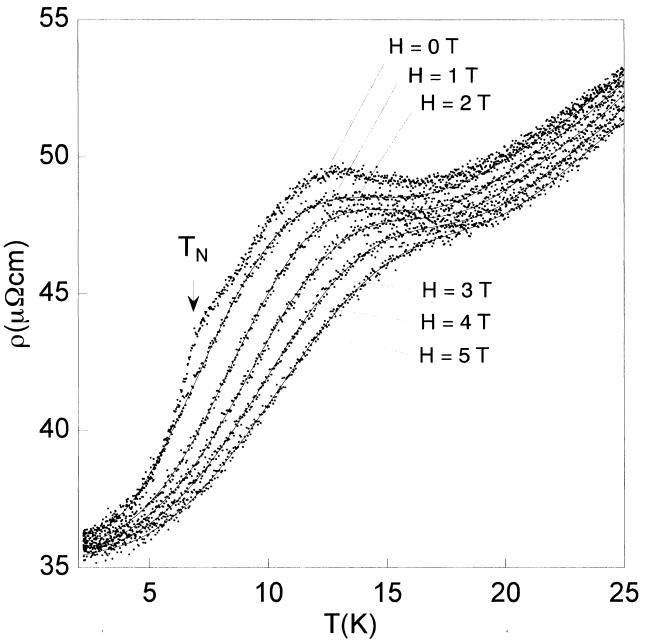

Fig. 5. Electrical resistivity of DyCoC under magnetic field.

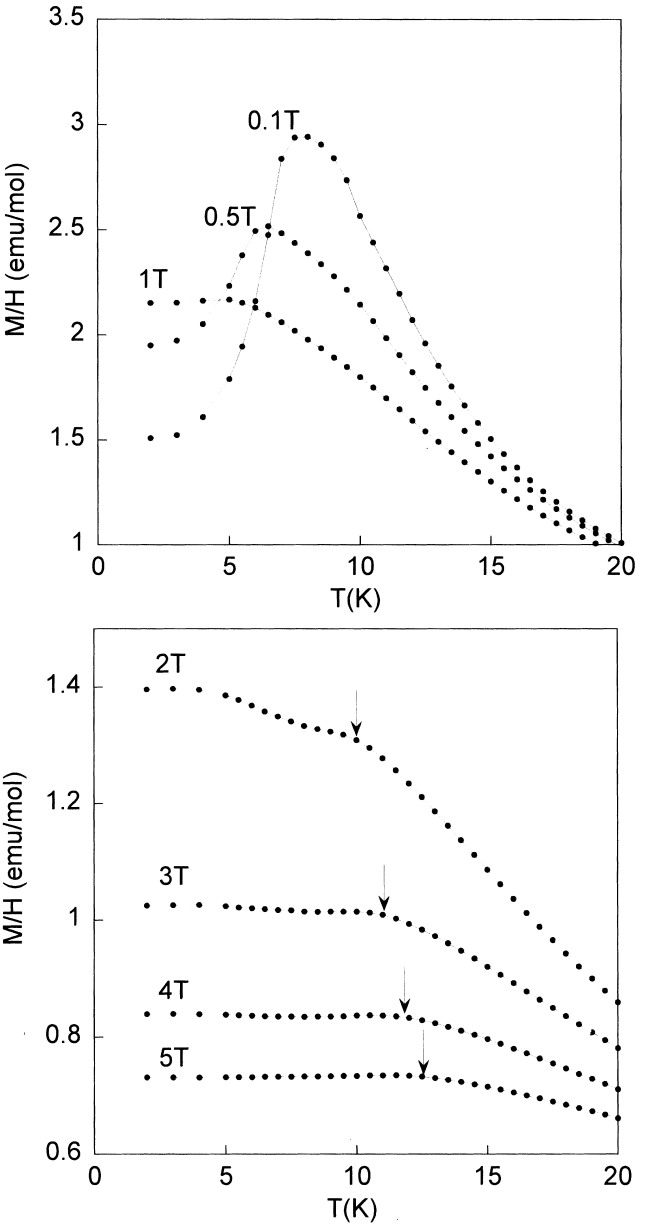

Fig. 6. Temperature dependence of the susceptibility MJH of DyCoC with H = 0.1–5 T. The arrows indicate anomalies of the susceptibility.

in these two phase transitions. If these two transitions are both of magnetic origin and are the successive transitions from one to another magnetic phase at zero field, then the entropy change does not seem to be so well separated by R*ln*2 for each transition. Moreover, these transitions show completely different behavior under a magnetic field. However, in the higher magnetic field region, it is clear that the anomaly observed in the magnetic susceptibility is due to a field-induced magnetic phase transition. All these behaviors are very reminiscent of the behaviors of the properties in CeB_6 [4], where the higher temperature phase transition corresponds to a quadrupolar ordering [5,6]. Quadrupolar ordering can occur when the ground state degeneracy of the 4f state is larger than a triplet, and the

ordering is such that the principle axis of the electric quadrupoles of the 4f orbital orders in parallel (ferroquadrupolar ordering, FQ) or in rectangular (antiferroquadrupolar ordering, AFQ). The fact that the magnetic transition temperature in DyCoC is lower than in HoCoC also supports the presence of a quadrupolar ordering since it can suppress the magnetic (dipole) ordering. Experimentally, the presence of the quadrupolar ordering can be proved by a structural change that can be found by very precise X-ray diffraction measurements or by confirming the lack of an ordered magnetic moment at zero field by neutron diffraction method. Hence neutron diffraction measurements are in progress.

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