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Interplay between 3d and 4f magnetism in CeCoPO

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ABSTRACT

The ground state properties of CeCoPO, a homologue of the new high temperature superconductors $LnFePnO_{1-x}F_x$, were studied by means of susceptibility, specific heat, and resistivity measurements on polycrystals. The observation of a well defined Curie–Weiss behavior above 230 K with $\mu_{eff} = 2.9\mu_B$ and a ferromagnetic ordering below $T_C = 75$ K is similar to what was observed in LaCoPO and points to magnetism of the Co-3d electrons. However, the Ce-ions are on the border to magnetism with a Kondo scale of $T_K \sim 40$ K and show an enhanced Sommerfeld coefficient of $\gamma \sim 200\,mJ/mol\,K^2$.

1. Introduction

The compound series LnTPnO (Ln: lanthanides, T: transition metal, Pn: P or As) have started to attract considerable attention because of the recent discovery of superconductivity with a transition temperature T_c exceeding 50 K in the $LnFeAsO_{1-x}F_x$ series of compounds [1–3], being the highest T_c except for cuprate systems. While the recent reports focus on the importance of electronic correlation effects due to 3d-electrons close to a magnetic state, the homologous compounds with Ln = Ce are attractive candidates for strong correlation effects induced by the 4f-electrons. Thus, last year we presented a detailed study of the properties of CeRuPO and CeOsPO [4–6] and demonstrated that the former one is a rare example for a ferromagnetic (FM) Kondo lattice system with a FM ordering temperature $T_C = 15$ K and a Kondo temperature $T_K \sim 10$ K, while the latter one shows antiferromagnetic order of stable trivalent Ce-ions below $T_N = 4.5$ K. More recently, we have shown that CeFePO is a heavy fermion metal close to a FM instability, dominated by the magnetism of the 4f-electrons [7]. Therefore, it was natural to look also for the physical properties of the related compound with T = Co.

In this report, we present a first study of the basic physical properties of CeCoPO using susceptibility $\chi(T)$, specific heat $C(T)$, and resistivity $\rho(T)$ measurements as well as X-ray absorption near-edge spectroscopy structure (XANES) at the Ce L_{III} edge. The results reveal a FM ordering of the Co-ions at $T_C = 75$ K in analogy to the FM order at 43 K in LaCoPO [8]. An enhanced Sommerfeld coefficient of $\gamma \sim 200\,mJ/mol\,K^2$ and the temperature dependence of the resistivity reveal a finite Kondo scale of the 4f-moments of order $T_K \sim 40$ K. In addition, we confirm the reported data of the magnetic properties of polycrystalline LaCoPO.

2. Experiment

Polycrystalline samples of CeCoPO and LaCoPO were synthesized using a Sn-flux method in evacuated quartz tubes as described elsewhere [4,9]. Several powder X-ray diffraction patterns recorded on a Stoe diffractometer in transmission mode using monochromated $Cu-K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) confirmed the formation of LnCoPO with ZrCuSiAs structure type (space group: P4/nmm; $Z = 2$). The lattice parameters refined by simple least square fitting for CeCoPO $a = 3.924(3)$ Å, $c = 8.223(5)$ Å and LaCoPO $a = 3.968(3)$ Å, $c = 8.379(5)$ Å were found to be in good agreement with the reported structure data [8,10]. In addition, energy dispersive X-ray spectra of CeCoPO and LaCoPO performed on a scanning electron microscope (Philips XL30) with Si(Li)-X-ray detector show similar strong intensities of the oxygen line which confirm a substantial oxygen content of both phases. However, they revealed diamagnetic CoP_2 [11] as impurity phase and some oxide phases which are present only with small concentration, so that they could not be observed in the X-ray diffraction patterns. $\chi(T)$ measurements were performed in the temperature range 2–350 K in a commercial Quantum Design (QD) magnetic property measurement system (MPMS), the T-dependent measurements were performed after zero-field cooling the sample. The resistivity was determined down to 0.4 K using a standard AC four-probe geometry in a QD physical property measurement system (PPMS). The PPMS was also used to measure $C(T)$ with a standard heat-pulse relaxation technique.

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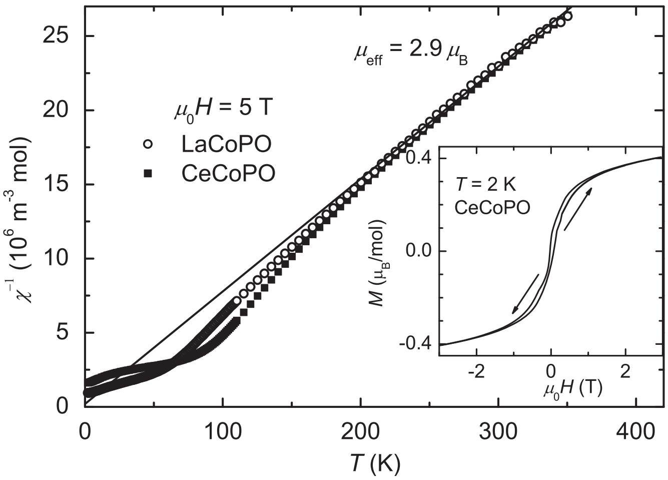

Fig. 1. Inverse susceptibility as a function of temperature for CeCoPO (squares) and LaCoPO (circles) measured in a magnetic field of $\mu_0H = 5\,T$. Both compounds show similar Curie–Weiss behavior above 230 K with $\mu_{eff} = 2.9\mu_B$ and $\Theta_W = -3\,K$ (straight line). Inset: the magnetization of CeCoPO presents a small hysteresis at small magnetic fields and a nearly saturated moment at higher fields.

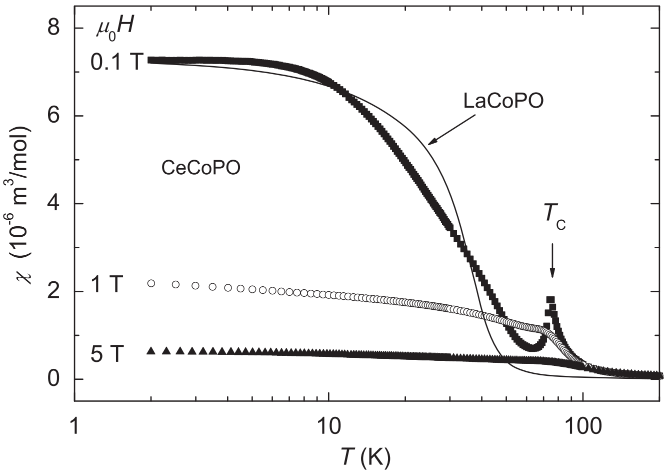

Fig. 2. $\chi(T)$ of CeCoPO at various magnetic fields. The magnetic transition into a FM ordered state is visible at $T_C = 75\,K$. For comparison, $\chi(T)$ for LaCoPO at $\mu_0H = 0.1\,T$ is presented as well (straight line).

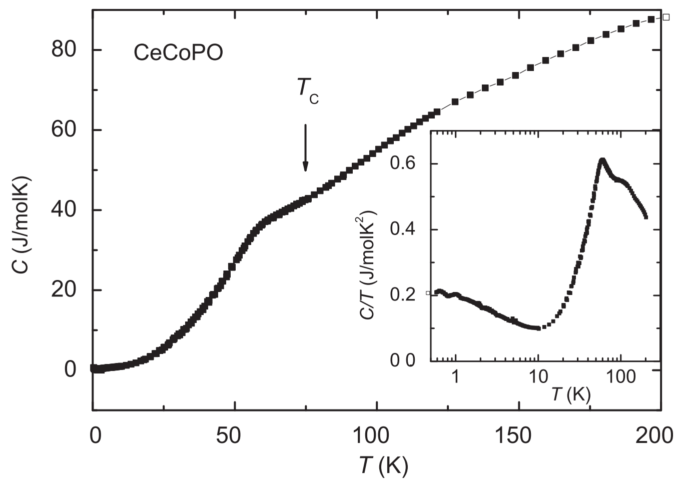

Fig. 3. Temperature dependence of the specific heat of CeCoPO. The phonon contribution is not subtracted in this representation. A broad anomaly is visible below T_C due to the FM order of CeCoPO. The inset shows the specific heat plotted as C/T on a logarithmic temperature scale. Below $T = 10\,K$, C/T of CeCoPO increases logarithmically down to lower T, presenting an enhanced $\gamma \sim 200\,J/mol\,K^2$ at 0.35 K.

XANES spectra near the Ce L_{III} edge were taken at 300 K in transmission geometry at the EXAFS beamline A1 of HASYLAB at DESY, Germany. The wavelength selection was realized by means of Si(111) double crystal monochromator, which allowed an experimental resolution of approximately 2 eV (FWHM) at the Ce L_{III} threshold of 5723 eV.

In Fig. 1 the inverse susceptibility is shown for both CeCoPO and LaCoPO. Above 230 K both curves present similar Curie–Weiss behavior with an effective moment of $\mu_{eff} = 2.9\mu_B$ and a Weiss temperature of $\Theta_W = -3\,K$. Our results for LaCoPO are very similar to those of Ref. [8] but important to analyze the magnetism in CeCoPO. The identical behavior of CeCoPO and LaCoPO in $\chi^{-1}(T)$ evidences that in both compounds the main contribution to the magnetism results from the 3d-electrons of Co. However, in CeCoPO the Ce-ions are not completely unmagnetic as will be discussed later. In the inset of Fig. 1, the magnetization $M(H)$ of CeCoPO is shown. $M(H)$ presents a small hysteresis at low field and a saturated moment of $\mu_{sat} \sim 0.4\mu_B$ at $\mu_0H \sim 3\,T$, similar to what was observed in LaCoPO [8]. At higher fields, $M(H)$ increases further slightly which might be due to the paramagnetism of the Ce-ions.

In Fig. 2, we present $\chi(T)$ of CeCoPO as a function of temperature at three different magnetic fields. The transition into a FM ordered state is visible by a sharp increase at $T_C = 75\,K$ and a strong field dependence of χ at low T. However, the peak at T_C observed in low fields ($\mu_0H \leq 0.1\,T$) does not correspond to the expectation for a simple ferromagnet. Presently, it is not settled whether this is the result of measuring powder samples of a system with a complex anisotropic behavior or if it points to a more intricate magnetic structure with polarization effects on the Ce-ions by the internal magnetic fields of the Co-magnetism. The later scenario is more likely, because the T-dependence of χ for LaCoPO (line in Fig. 2), where no 4f-electrons are present, behaves as expected for a simple ferromagnet.

The temperature dependence of the specific heat of CeCoPO is shown in Fig. 3 without any subtraction of the phonons. Therefore, at high T, $C(T)$ converges to the classical limit of $4 \cdot 3R \sim 100\,J/mol\,K$. An anomaly is visible on top of the phonon excitations just below T_C. This anomaly is rather broad, possibly due to inhomogeneities in our polycrystalline sample. In the inset of Fig. 3 we have plotted the specific heat as C/T on a logarithmic temperature scale. In this representation the peak due to the onset of FM order is more pronounced. Below $T = 10\,K$, C/T increases logarithmically and tends to saturate below $T = 1\,K$ at $\gamma \sim 200\,mJ/mol\,K^2$. This value is strongly enhanced compared to the expectation for a normal FM Co-system. This enhancement can be attributed to 4f-correlation effects resulting in the formation of heavy fermions. The entropy at low T was calculated by integrating C/T over temperature. The entropy gain at 10 K corresponds to about 25% of $R\ln 2$, giving a rough estimation of the Kondo energy scale of order $T_K \sim 40\,K$. For the calculation, we have not subtracted any nonmagnetic contribution which for $T < 10\,K$ is negligible compared to the large value of C/T. As an example, the contribution of the nonmagnetic LaRuPO to the specific heat at $T = 1\,K$ would only correspond to 2% of the here measured specific heat [4].

In Fig. 4 we present the resistivity data on a pressed powder-pellet of CeCoPO which was subsequently annealed for 150 h at 700 °C, improving the conductivity of the sample by a factor of 20. However, the absolute value of $\rho_{300\,K} = 5\,m\Omega\,cm$ is still rather high; we believe that this is not intrinsic of CeCoPO but due to the remaining granularity of the polycrystalline sample. To compare