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Localization of magnetic moments of cerium in single crystalline $CePt_4In$

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Single crystals of $CePt_4In$ were studied by means of magnetic susceptibility and Seebeck coefficient measurements. Moreover, Ce-L_{III} edge x-ray absorption near-edge structure experiments were performed on polycrystalline samples. The results show that the $4f$ electrons in this compound have fairly localized character, with rather stable $4f^1$ configuration. These findings supplement previous literature reports on $CePt_4In$ being a valence fluctuation system.

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I. INTRODUCTION

A large number of intermetallics based on cerium is known to be materials, in which the electrons of the unfilled $4f$ shell strongly interact (hybridize) with conduction-band and/or valence-band electrons ($k=s$, p, and d). The overall low-temperature behavior of these strongly correlated electron systems (SCES) is determined mainly by the strength of this hybridization, measured by the exchange integral J_{kf}.[1] For low values of J_{kf}, the Ruderman-Kittel-Kasuya-Yosida interaction dominates and thus long-range magnetic order occurs. With increasing J_{kf}, the Kondo interaction leads to the suppression of long-range magnetic order. Finally, for large values of J_{kf}, an intermediate-valence state forms. In the latter one, the f electrons are only partly localized even at room temperature.

Several intermetallics from the ternary Ce-Pt-In system, in particular: CePtIn, Ce_2Pt_2In, $Ce_3Pt_4In_{13}$, and $Ce_6Pt_{11}In_{14}$, were reported as being examples of SCES.[2–8] In all these phases the magnetic moments of Ce ions are rather well localized yielding a paramagnetic (Curie-Weiss) behavior above 100–150 K. At low temperatures the Kondo-type scattering of conduction electrons on the magnetic moments results in the formation of heavy quasiparticles, which manifest themselves, e.g., in an enhancement of the electronic specific heat. The C/T ratio attains values from $0.25\ \mathrm{J\,mol_{Ce}^{-1}\,K^{-2}}$ in Ce_2Pt_2In (Ref. 6) to over $1\ \mathrm{J\,mol_{Ce}^{-1}\,K^{-2}}$ in CePtIn (Ref. 3).

Another compound from the Ce-Pt-In system, namely cubic $CePt_4In$, was also reported to be a heavy-fermion system. Its C/T coefficient reaches a value of $1.75\ \mathrm{J\,mol_{Ce}^{-1}\,K^{-2}}$ at 100 mK and can be extrapolated to about $2.5\ \mathrm{J\,mol_{Ce}^{-1}\,K^{-2}}$ at 0 K (Ref. 9). Interestingly and physically questionable, the temperature variation of the magnetic susceptibility of this particular compound, measured on polycrystalline samples, was interpreted in terms of a model treating valence fluctuations in the presence of a crystalline electric field (CEF).[9]

In order to shed more light on the intriguing ground state of cerium in $CePt_4In$ we have undertaken comprehensive investigations of its physical properties, performed in wide ranges of temperature and magnetic field, using single crystalline specimens. In the present paper we briefly report on the results of magnetic susceptibility and Seebeck-coefficient measurements, carried out on non-oriented crystals, as well as data of x-ray absorption at the Ce-L_{III} threshold [x-ray absorption near-edge structure (XANES)], obtained from powdered polycrystalline samples. The main aim of this paper is to show that, as in the other phases from the ternary Ce-Pt-In system, the f electrons have rather localized character in $CePt_4In$ also.

II. EXPERIMENTAL DETAILS

A polycrystalline sample of $CePt_4In$ was synthesized by arc melting the constituents (Pt foil, Ce and In pieces; purity 99.9%) under protective purified-argon atmosphere and subsequent heat treatment at 900 °C for 1 month. The product was examined by x-ray powder diffraction [Stoe diffractometer, Cu $K\alpha$ radiation, $\lambda=1.540\,56$ Å, $a=7.6112(2)$ Å] and energy dispersive x-ray spectrometry (EDXS; EDAX PV9800 microprobe attached to a Philips 515 scanning electron microscope). The x-ray pattern was fully indexed within cubic symmetry yielding the lattice parameter $a=7.611(1)$ Å, in fairly good agreement with the literature data ($a=7.602$ Å; Ref. 10). The EDXS examination revealed the presence of a small amount ($\sim 5\%$) of a few different binary Pt-In alloys. Nevertheless, because none of the detected secondary phases contains cerium, they should have a negligible influence on the results of the XANES experiments, performed on a powdered piece of this sample.

High-quality single crystals of $CePt_4In$ were grown from Pb flux. The starting materials were Pt foil, Ce, In, and Pb pieces, all with nominal purity at least 99.9%. The constituents were weighed in the atomic ratio of 1:4:1:20 and loaded into an alumina crucible, which was then sealed in a silica tube under argon gas pressure of 0.3 atm. The ampoule was subsequently heated up to 1030 °C, held at this temperature for 2 h followed by a slow cooling at a rate of 1–2 °C/h down to 400 °C, and finally fast cooled to room temperature. The Pb flux was etched away from the crystals in a solution of acetic acid and hydrogen peroxide. The obtained single crystals had a shape of well-faceted polyhedra with dimensions up to 0.6 mm. The cubic lattice parameter refined from the x-ray data collected on a four-circle diffractometer (Xcalibur CCD Oxford Diffraction using graphite-monochromated Mo $K\alpha$ radiation) was $a=7.6330(10)$ Å,

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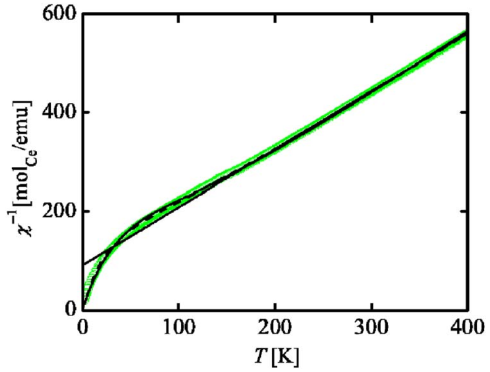

FIG. 1. (Color online) Inverse magnetic susceptibility of single-crystalline $\mathrm{CePt_4In}$ vs. temperature. The straight solid line is a fit to the experimental data of the Curie-Weiss law. The solid and dashed curves are fits of the Van Vleck formula, adapted to doublet-quartet and quartet-doublet schemes, respectively.

i.e., slightly larger than that derived from the polycrystalline data. This is an acceptable deviation for a measurement on the four-circle goniometer without special calibration. The EDXS analysis (equipment as above) of a few crystals yielded the chemical composition $\mathrm{Ce_{17}Pt_{67}In_{16}}$, in good agreement with the expected 1:4:1 stoichiometry ($\mathrm{Ce_{16.7}Pt_{66.6}In_{16.7}}$).

The magnetic properties were studied using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer in the temperature range 1.72–300 K and in external magnetic fields up to 5 T. The Seebeck coefficient was measured in the range 5–300 K using a standard differential method with pure copper as a reference material. X-ray absorption spectroscopy at the Ce-$\mathrm{L_{III}}$ threshold was performed at several different temperatures from room temperature down to 5 K at the EXAFS-1 beamline A1 of the Hamburger Synchrotronstrahlungslabor (HASYLAB/DESY) using a Si (111) double-crystal monochromator with $\mathrm{CeO_2}$ and $\mathrm{CeF_3}$ as the internal standards.

III. RESULTS AND DISCUSSION

A. Magnetic susceptibility

Figure 1 shows the temperature dependence of the reciprocal magnetic susceptibility, $\chi^{-1}(T)$, measured on a large amount (~300 mg) of nonoriented single crystals of $\mathrm{CePt_4In}$. Apparently, down to 1.72 K the compound remains paramagnetic. Above about 200 K, $\chi^{-1}(T)$ is linear and follows the Curie-Weiss law with the effective magnetic moment $\mu_{\mathrm{eff}}=2.6\mu_{\mathrm{B}}$ and the paramagnetic Weiss temperature $\theta_{\mathrm{p}}=-78$ K. The value of μ_{eff} is close to that calculated for a free $\mathrm{Ce^{3+}}$ ion ($2.54\mu_{\mathrm{B}}$) and implies the presence of well-localized magnetic moments. At lower temperatures $\chi^{-1}(T)$ strongly deviates from a straight-line behavior, most probably due to thermal depopulation of the CEF levels. The rather large negative value of θ_{p}, for a compound that does not order magnetically, may hint at a substantial Kondo screening effect.

In the whole temperature range studied, the experimental $\chi^{-1}(T)$ curve can be very well described in terms of the CEF model, e.g., by the Van Vleck formula adapted to the cubic symmetry of the Ce environment in $\mathrm{CePt_4In}$. In the case of $\mathrm{Ce^{3+}}$ ions experiencing a cubic CEF potential, the sixfold degenerate ground multiplet $^2F_{5/2}$ splits into a Γ_8 quartet and a Γ_7 doublet. Assuming that the Γ_7 doublet is the CEF ground state, the Van Vleck formula takes the form (see, for instance, Ref. 11)

$$\chi(T)=\frac{3}{8}\frac{a/T+b+(c/T-b)\exp(-\Delta/T)}{2+4\exp(-\Delta/T)}, \qquad (1)$$

where a and c are the low-frequency matrix elements, b is the high-frequency contribution, and Δ stands for the CEF splitting. Fitting Eq. (1) to the experimental data in the entire temperature range yields the following parameters: $a=0.8249\mu_{\mathrm{B}}^2$, $b=0.0157\mu_{\mathrm{B}}^2\ \mathrm{K}^{-1}$, $c=6.3695\mu_{\mathrm{B}}^2$, and $\Delta=323$ K. It is worth noting, that the consideration of the Γ_8 quartet being the ground state in $\mathrm{CePt_4In}$ results in a fit of slightly better quality (see Fig. 1), with the parameters: $a=1.3727\mu_{\mathrm{B}}^2$, $b=0.0383\mu_{\mathrm{B}}^2\ K^{-1}$, $c=1.8700\mu_{\mathrm{B}}^2$, and $\Delta=257$ K.

The experimental magnetic susceptibility data of single crystalline $\mathrm{CePt_4In}$ are similar to those obtained in Ref. 9 for a polycrystalline sample. In particular, in both studies $\chi^{-1}(T)$ shows a pronounced curvature below 150 K and a Curie-Weiss behavior at higher temperatures. The effective magnetic moments derived in the Curie-Weiss region is nearly same, yet the paramagnetic Weiss temperature found for our single crystals is roughly only one-third of the value reported by Malik *et al.* in Ref. 9. Their large value of θ_{p}, together with the strongly curved $\chi^{-1}(T)$ behavior at low temperatures, led the latter authors to the suggestion of the cerium ions in $\mathrm{CePt_4In}$ being in an intermediate-valence state. Applying a valence-fluctuation model that incorporates CEF effects[12] they obtained a fit of their susceptibility data with the Γ_7 doublet being the ground state and the Γ_8 quartet located about 480 K above this level. The parameters describing valence fluctuations, i.e., the energy difference between the $4f^1$ and $4f^0$ electronic configurations of cerium ions, E_{exc}, and the spin fluctuation temperature T_{sf}, were estimated to be only 325 K and 1–8 K, respectively. These values imply that Γ_7 is nearly degenerate with the $4f^0$ ground state, which is quite unusual for valence-fluctuation systems.

On the other hand, we have shown above that the susceptibility of $\mathrm{CePt_4In}$ can be completely described by the CEF effect acting on $\mathrm{Ce^{3+}}$ ions. Apparently, there is no need to involve valence fluctuations to reproduce the curvature in $\chi^{-1}(T)$ observed at low temperatures. Moreover, the present model yields a reasonable magnitude for the CEF splitting (260 or 320 K, depending on the CEF scheme), corroborated by our electrical transport results (see below).

B. X-ray absorption

Figure 2(a) presents the energy variation of the normalized x-ray absorption at the Ce-$\mathrm{L_{III}}$ threshold, $I(E)$, measured for $\mathrm{CePt_4In}$ at various temperatures. The spectra show one dominant main-transition line located at about 5.725 keV and small additional contributions on the pre-edge and high energy side. They can be described quite well by the overlap of four separate lines appropriate for a description of Ce

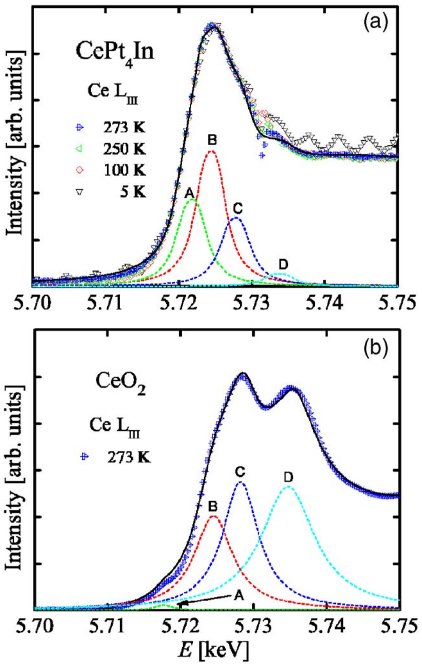

FIG. 2. (Color online) Normalized XANES spectra of (a) polycrystalline $CePt_4In$ (taken at 273, 250, 100, and 5 K), and (b) CeO_2 (measured at 273 K). The solid lines are the fitted core-absorption spectra. The dashed curves describe the respective contributions to the entire spectra (arctan backgrounds are omitted): (A) $2p \rightarrow 6s$ transition (B,C,D), $4f^1d^0$, $4f^1d^1$, and $4f^0$ configurations, respectively (for details see Refs. 13 and 14).

configuration, as reported for the absorption spectra of the reference materials CeF_3 and CeO_2.[13,14] Comparison with the fit results obtained for the latter compound [Fig. 2(b); note the contribution D, which describes the $4f^0$ configuration] clearly indicates an essentially trivalent state of the Ce ions in the compound studied. Apparently, this configuration remains nearly unaltered at least down to 5 K. Thus these experiments do not provide any evidence for the existence in $CePt_4In$ of valence fluctuations, presumed in Ref. 9. On the contrary, the XANES results seem to support the analysis of the magnetic properties of this compound in terms of the scenario of localized $4f$ electrons.

C. Seebeck coefficient

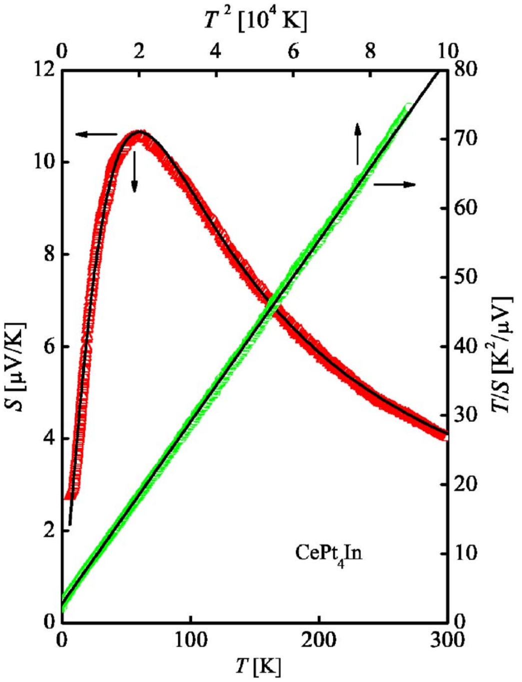

FIG. 3. (Color online) Temperature dependence of the Seebeck coefficient of single-crystalline $CePt_4In$, plotted in two different representations. The solid lines are fits of the experimental data to Eq. (2).

The temperature variation of the Seebeck coefficient, measured on a single crystal of $CePt_4In$, is displayed in Fig. 3. The $S(T)$ curve has a shape characteristic of systems possessing a peak in the density of states near the Fermi level, e.g., SCES. Assuming a Lorentzian shape of the f-electron peak, one can describe the thermoelectric power of such systems by the expression[15]

$$S_f(T) = \frac{2}{3}\pi^2 \frac{k_B}{|e|} \frac{T\varepsilon_f}{(\pi^2/3)T^2 + \varepsilon_f^2 + \Gamma_f^2}, \tag{2}$$

where ε_f is the distance of the f-electron peak from the Fermi level, and Γ_f denotes its half-width. As apparent from Fig. 3, the above formula describes quite well the experimental data yielding the following fitting parameters: ε_f=7.5 K (0.64 meV) and Γ_f=110 K (9.5 meV). It is worth noting that the obtained values are approximately one order of magnitude lower than those reported for IV systems (see, e.g., Ref. 15). Thus, also the thermopower data show that the $4f$ states in $CePt_4In$ are fairly well localized.

The approach given by Eq. (2) completely neglects the CEF effect and its influence on the density of states in heavy-fermion systems. Thus, the so-derived value of Γ_f cannot be considered as a proper measure of the Kondo temperature T_K. According to the Coqblin-Schrieffer model,[16–18] which describes the Kondo effect in the presence of strong CEF ($T_K \ll \Delta$), the position T_{max} of the characteristic broad maximum in $S(T)$ strongly depends on the CEF splitting. In the case of a two-level CEF scheme, T_{max} is related to the CEF splitting Δ as $T_{max}=\Delta/3$ (see Ref. 18). Using the latter formula one estimates Δ in $CePt_4In$ as being about 210 K. It should be noted that this latter value is reasonably close to those derived from the analysis of the magnetic susceptibility data.

IV. SUMMARY

The magnetic properties of single crystalline $CePt_4In$ have been interpreted in terms of a strong CEF effect. The experimental data were properly described by the Van Vleck-like formula, adapted either for the doublet-quartet or quartet-doublet schemes with the crystal field splitting Δ of the order of 260–320 K. A similar size of Δ was estimated from the peak position in the temperature dependence of the Seebeck coefficient. Both $\chi(T)$ and $S(T)$ are characteristic of systems with fairly localized magnetic moments. The rather stable $4f^1$ configuration of the Ce ions in $\mathrm{CePt_4In}$ has been supported by measuring the XANES spectra. The new results call for a thorough reinvestigation of the physical behavior of this interesting compound that was classified in the literature[9] as a valence-fluctuation system. Some of them, namely ultra-low-temperature electrical-transport and specific-heat measurements, are presently under way.

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