

Strong electronic correlations in CePt₄In

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Polycrystalline samples of CePt₄In and LaPt₄In were studied by means of X-ray powder diffraction, magnetic susceptibility, electrical resistivity and specific heat measurements. Some of the results have been compared to those reported previously for single-crystalline specimens. The physical properties of CePt₄In indicate that the magnetic moments of cerium are rather well localized and contribute to the Kondo-type scattering of conduction electrons in the presence of strong crystalline electric field.

Key words: *CePt₄In; CeInPt₄; strong electronic correlations; heavy fermion behaviour; Kondo effect*

1. Introduction

Usual behaviour of strongly correlated electron systems (SCES) is a highlight of present-day condensed matter physics. The SCES intermetallics based on cerium, ytterbium or uranium have unfilled 4f or 5f electronic shell which strongly interacts (hybridizes) with conduction and/or valence band states of s-, p-, and d-type. Depending on the strength of the f-ligand interactions, measured by the exchange integral J_{kf} [1], a variety of different low-temperature properties have been observed, spanning from long-range magnetic ordering, to formation of heavy quasi-particles (heavy fermions), and to fluctuating-valence state for low, intermediate and high values of J_{kf} , respectively. All these phenomena are directly related to the localization of f-electrons, namely the higher value of the exchange integral, the more delocalized character exhibit the f-electrons. In particular, in the intermediate-valence state they are only partly localized even at ambient temperatures.

For most compounds with well localized f-electrons, an important role of the crystalline electric field (CEF) effect is recognised. In the case of stable Ce³⁺ ions placed in a cubic environment, the six-fold degenerated ²F_{5/2} ground level splits into a Γ_7 doublet and a Γ_8 quartet separated by an energy Δ being of the order of 100–300 K. Usually,

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this phenomenon distinctly influences magnetic, thermodynamic and electrical-transport characteristics, studied as functions of temperature and magnetic field.

The cubic compound CePt₄In was originally classified in the literature as a valence-fluctuation system with strongly enlarged electronic contribution to the specific heat ($C/T \approx 1.75 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^2$ at 100 mK) and distinct CEF effect [2]. That interesting (yet physically rather questionable) coexistence of the opposing ground states motivated us to undertake comprehensive reinvestigations of physical properties of this particular compound. In the present paper, we briefly review and discuss hitherto obtained results of several experiments performed in wide ranges of temperature and magnetic field strength, on polycrystalline as well as on single-crystalline specimens.

2. Experimental

Polycrystalline samples of CePt₄In and of its non-magnetic reference system LaPt₄In were synthesized by conventional arc melting of stoichiometric amounts of the constituents (Pt foil, Ce and In pieces; purity 99.9%) under protective purified-argon atmosphere. The melted pellets were subsequently wrapped in molybdenum foil, sealed in evacuated silica tubes, and annealed at 900 °C for one month. The quality of the final products was examined by X-ray powder diffraction using a commercial Stoe diffractometer (CuK_α radiation, $\lambda = 1.54056 \text{ \AA}$) and by energy dispersive X-ray scattering (EDXS) analysis employing an EDAX PV9800 spectrometer attached to a Philips 515 scanning electron microscope.

High-quality single crystals of CePt₄In were grown using a conventional flux method, using elemental lead as a flux. The starting components (Ce, Pt, In as above, Pb pieces; purity 99.9%) were weighed in the atomic ratio 1:4:1:20, loaded into an alumina crucible, and sealed in a quartz ampoule under argon gas pressure of about 0.3 atm. The mixture was first heated up to 1030 °C, held at this temperature for 2 h, and then cooled down to 400 °C at the rate of 1–2 °C/h and finally down to room temperature upon switching off the furnace. Several well-faceted polyhedra-shaped single crystals with dimensions up to 0.6 mm were isolated from the flux by etching Pb in a solution of acetic acid and hydrogen peroxide. Their quality was checked by X-ray diffraction using an Xcalibur CCD Oxford Diffraction four-circle diffractometer (graphite-monochromated MoK_α radiation; $\lambda = 0.71073 \text{ \AA}$) and by microprobe EDXS analysis (equipment as above).

Magnetic properties of CePt₄In and LaPt₄In were studied at temperatures ranging from 1.9 K up to 300 K and in external magnetic fields up to 5 T using a commercial Quantum Design MPMS-5 SQUID magnetometer. Electrical resistivity measurements were performed in the range 4–300 K employing a conventional four-probe method, on bar-shaped specimens with spot-welded electrical contacts. The transverse ($B \perp j$) magnetoresistivity was measured below 30 K in external magnetic fields up to 8 T. The Seebeck coefficient was measured at temperatures from 5 K up to room tempera-

ture using a standard differential method with pure copper as a reference. Heat capacity measurements were carried out over the temperature interval 2–400 K, employing a thermal relaxation technique [3] implemented in a commercial Quantum Design PPMS-9 platform.

3. Results

3.1. Crystal structure

The EDXS characterization revealed nearly single-phase character of all the poly- and single-crystalline samples with the compositions being close to the ideal 1:4:1 one. Figure 1 displays the X-ray powder diffraction pattern measured for polycrystalline $CePt_4In$, plotted together with the results of the crystal-structure refinement using a Rietveld method and the FullProf program [4].

Fig. 1. X-ray ($\lambda = 1.54056 \text{ \AA}$) powder diffraction pattern (open symbols) measured for polycrystalline $CePt_4In$. The solid line is a theoretical pattern refined using the Rietveld method. The solid ticks are the least-squared fitted Bragg positions. The lower solid curve is a difference between the experimental and theoretical patterns

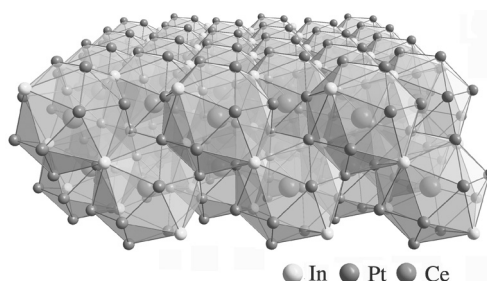
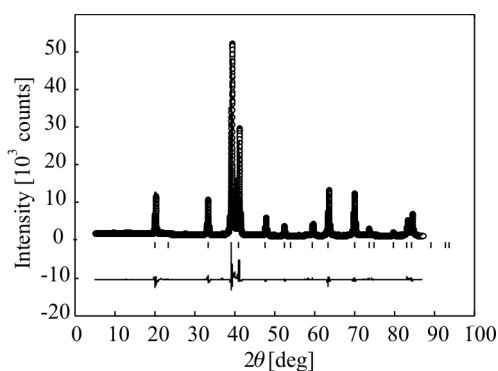


Fig. 2. Crystal structure of $CePt_4In$

The experimental data were analyzed within two different models proposed for this compound in the literature, namely cubic $MgCu_2$ type structure with some Ce-In disorder (space group $Fd\bar{3}m$) [5], and fully-ordered cubic $MgCu_4Sn$ type structure (space group $F\bar{4}3m$) [2, 6, 7]. For both models, all the Bragg reflections have identical positions and the X-ray profiles differ from each other only by intensities of the respective peaks. The performed structure refinements suggest that the $MgCu_4Sn$ type

model describes the unit cell of CePt₄In more accurately. In this structure, presented in Fig. 2, Ce atoms occupy only one inequivalent crystallographic position in the unit cell, namely the Wyckoff position 4*c*, which is surrounded within a cubic point symmetry by 16 nearest neighbours (12 Pt and 4 In). The shortest distances between Ce and the ligands are $d(\text{Ce-Pt}) = 3.1554(2) \text{ \AA}$ and $d(\text{Ce-In}) = 3.2957(2) \text{ \AA}$, while the distance between two neighbouring Ce atoms $d(\text{Ce-Ce})$ is as large as $5.3819(2) \text{ \AA}$. It is worth noting that the latter value is much higher than the Hill limit for Ce atoms (3.2 \AA).

The powder X-ray diffraction data yielded for CePt₄In the lattice parameter $a = 7.6112(2) \text{ \AA}$, being in reasonable agreement with the literature value ($a = 7.602 \text{ \AA}$ [2, 6]). For the non-magnetic counterpart LaPt₄In, the parameter $a = 7.6544(1) \text{ \AA}$ has been derived, which is also close to that reported before ($a = 7.648 \text{ \AA}$ [6]).

3.2. Magnetic properties

The temperature variation of the inverse magnetic susceptibility, $\chi^{-1}(T)$, of polycrystalline CePt₄In is shown in Fig. 3. The $\chi^{-1}(T)$ dependence is linear above ca. 200 K and the experimental data can be well described in that temperature range by the Curie–Weiss law with the effective magnetic moment $\mu_{\text{eff}} = 2.44\mu_B$ and the paramagnetic Curie temperature $\theta_p = -133 \text{ K}$ (see the straight solid line in Fig. 3). The value of μ_{eff} is close to that calculated for a free Ce³⁺ ion ($2.54\mu_B$) and similar to that found for single-crystalline specimens ($2.6\mu_B$) [8], thus hinting at the presence of well localized magnetic moments. In turn, the large negative value of θ_p suggests the existence of strong Kondo interactions. According to Hewson [9], the characteristic Kondo temperature (in the absence of CEF effect) can be roughly estimated as $T_K = |\theta_p|/4 \approx 33 \text{ K}$. For single-crystalline CePt₄In, θ_p was found to be -78 K [8], hence yielding $T_K \approx 20 \text{ K}$.

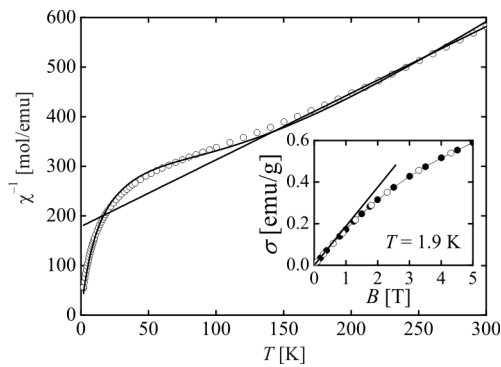


Fig. 3. Temperature dependence of the inverse magnetic susceptibility of polycrystalline CePt₄In; $B = 0.5 \text{ T}$. The solid straight line is a fit of the Curie–Weiss law to the experimental data. The solid curve is a fit to Eq. (1). The inset: magnetization of CePt₄In as a function of increasing and decreasing magnetic field (closed and open symbols, respectively)

Below 200 K, the $\chi^{-1}(T)$ curve strongly deviates from the rectilinear behaviour, in a manner characteristic of CEF effects. The Van Vleck formula adapted to a ground doublet–excited quartet CEF scheme (see the Introduction) has the form

$$\chi(T) = \frac{3 \frac{a}{T} + b + \left(\frac{c}{T} - b \right) \exp\left(-\frac{\Delta}{T}\right)}{8 + 4 \exp\left(-\frac{\Delta}{T}\right)} \quad (1)$$

where a and c are the low-frequency contributions, b is the high-frequency contribution, and Δ is the splitting energy. As shown by the solid curve in Fig. 3, this expression describes well the experimental data in the whole temperature range studied (i.e., 1.9–300 K) with the fitting parameters: $a = 0.2030 \mu_B^2$, $b = 0.0144 \mu_B^2 \cdot K^{-1}$, $c = 2.939 \mu_B^2$, and $\Delta = 395$ K. The latter value of Δ is not much different from that derived in a similar way for the CePt₄In single crystals ($\Delta = 323$ K) [8]. It is also worth reminding here that assuming an inverse level scheme (i.e., with the Γ_8 quartet being the ground level), one obtains slightly less satisfactory approximation of the experimental data and the CEF splitting is considerably smaller ($\Delta = 257$ K) [8].

The inset to Fig. 3 presents the magnetic field dependence of the magnetization σ measured for polycrystalline CePt₄In at 1.9 K with increasing and decreasing magnetic field. The $\sigma(B)$ curve exhibits a linear behaviour up to about 1 T. At higher fields, the magnetization tends to paramagnetic saturation, as expected of the ground doublet CEF state.

3.3. Electrical transport properties

Figure 4 presents the temperature variations of the electrical resistivity ρ measured on polycrystalline samples of CePt₄In and LaPt₄In. The overall shape of $\rho(T)$ of the La-based compound is characteristic of nonmagnetic metals and can be described by the Bloch–Grüneisen–Mott formula:

$$\rho(T) = \rho_0 + 4R\Theta_R \left(\frac{T}{\Theta_R} \right)^5 \int_0^{\Theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - KT^3 \quad (2)$$

where ρ_0 is the residual resistivity, the second term describes the electron-phonon scattering, and $-KT^3$ is an additional contribution to the resistivity representing the Mott s–d interband scattering. The least-squares fitting of Eq. (2) to the experimental data yielded the parameters $\rho_0 = 56.3 \mu\Omega \cdot \text{cm}$, $R = 0.177 \mu\Omega \cdot \text{cm} \cdot \text{K}^{-1}$, $\Theta_R = 65$ K and $K = 5 \times 10^{-7} \mu\Omega \cdot \text{cm} \cdot \text{K}^3$. The derived values of the parameters ρ_0 , R , and K are typical of nonmagnetic intermetallics, however the characteristic temperature Θ_R is much smaller than usually observed in La compounds (i.e. 200–300 K). This disparity may suggest that the model used for the description of the electrical resistivity of LaPt₄In is inappropriate and/or the compound itself exhibits some anomalous properties, as sometimes found for La-based intermetallics.

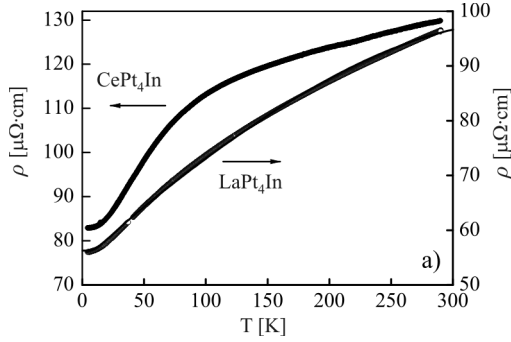


Fig. 4 Temperature dependences of electrical resistivities of polycrystalline CePt_4In and LaPt_4In . The solid line represents a fit of the Bloch–Grüneisen–Mott formula (Eq. (2)) to the experimentally determined resistivity of LaPt_4In

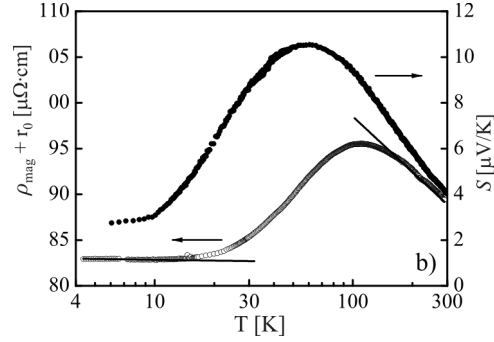


Fig. 5. Magnetic contribution to the electrical resistivity (open symbols) and thermoelectric power (closed symbols) of polycrystalline and single-crystalline CePt_4In in function of temperature in the semilogarithmic scale. The two straight solid lines are fits to Eq. (4)

The temperature dependence of the electrical resistivity of CePt_4In , displayed in Fig. 4 is typical of systems exhibiting an interplay of the Kondo and CEF interactions, e.g. CeAl_2 [10], CeNiGe_3 [11], $\text{Ce}_2\text{Ni}_3\text{Ge}_5$ [12, 13], CeNiGe_2 [14]. In particular, a broad hump in $\rho(T)$ seen in the temperature interval 20–200 K may be attributed to the Kondo-type scattering of the conduction electrons on the excited CEF level (i.e., Γ_8 quartet). In order to verify this presumption, the magnetic contribution, ρ_{mag} , to the total resistivity of CePt_4In was estimated. Assuming that the phonon contribution, ρ_{ph} , to the electrical resistivity of LaPt_4In properly approximates the ρ_{ph} term of the Ce-based compound, ρ_{mag} enlarged by temperature independent residual resistivity ρ_0 , can be calculated in the following manner:

$$\rho_{\text{mag}}(\text{CePt}_4\text{In}) + \rho_0(\text{CePt}_4\text{In}) = \rho(\text{CePt}_4\text{In}) - \underbrace{[\rho(\text{LaPt}_4\text{In}) - \rho_0(\text{LaPt}_4\text{In})]}_{\rho_{\text{ph}}} \quad (3)$$

Figure 5 presents the $(\rho_{\text{mag}} + \rho_0)(T)$ curves obtained in this way in a semilogarithmic scale. At high temperatures, ρ_{mag} increases logarithmically with decreasing the temperature down to about 150 K, goes over a broad maximum located at about 100 K and then decreases down to about 10 K. At lower temperatures another $-\ln(T)$ region can be noticed. According to Cornut–Coqblin [10], the two logarithmic slopes in $(\rho_{\text{mag}} + \rho_0)(T)$ of CePt_4In can be interpreted as a result of Kondo scattering of the conduction electrons on the CEF levels, i.e. Γ_8 quartet and Γ_7 doublet at high and low temperatures, respectively. Least-squares fitting of the formula [16]:

$$(\rho_{\text{mag}} + \rho_0)(T) = \rho_0^\infty - c_K \ln(T) \quad (4)$$

to the experimental data, yielded the parameters $\rho_0^\infty = 139$ and $83 \mu\Omega\cdot\text{cm}$, and $c_K = 8.7$ and 0.1 for the high- and low-temperature regions, respectively. Consequently, the CEF splitting Δ can be roughly estimated as being of the order of 100–150 K.

The temperature dependence of the Seebeck coefficient measured for single-crystalline CePt₄In is plotted in Fig. 5 in a semilogarithmic scale. As reported in Ref. [8], the broad maximum, well visible at $T_{\text{max}} \approx 60\text{--}70$ K, is characteristic of dense Kondo systems and allows one to estimate the CEF splitting to be $\Delta = 3T_{\text{max}} \approx 180\text{--}210$ K [15].

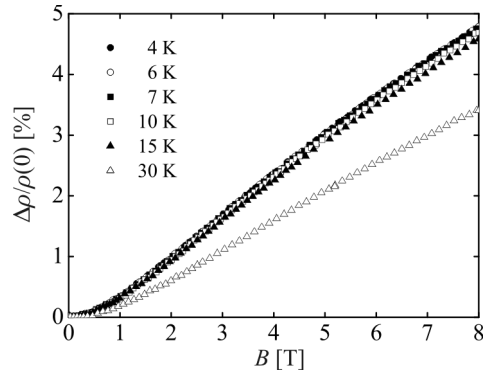


Fig. 6. Field dependences of the magnetoresistivity of polycrystalline CePt₄In measured at several temperatures

Upon applying external magnetic fields, the low-temperature resistivity of CePt₄In gradually increases with rising the field strength (Fig. 6). At 4 K, the magnetoresistivity, defined as $\Delta\rho(B)/\rho(0) \equiv [\rho(B) - \rho(B=0)]/\rho(B=0)$, is about 5% in the field of 8 T. This magnitude of $\Delta\rho(B)/\rho(0)$ remains nearly unchanged up to about 15 K, while at higher temperatures it rapidly decreases towards zero. The observed behaviour, being typical of non-magnetic metals, is however highly amazing for CePt₄In, as it is opposite to negative magnetoresistivity expected for dense Kondo systems in an incoherent single-ion regime.

3.4. Specific heat

Figure 7 displays the temperature dependences of the specific heat of CePt₄In and LaPt₄In, plotted as the C/T ratio in a semilogarithmic scale. Above ca. 100 K, the two curves nearly overlap, thus indicating that in this temperature range the specific heat is dominated by an almost identical phonon contribution. At lower temperatures a distinct (and systematically increasing with decreasing T) difference between $C(T)/T$ of Ce and La compounds is observed, most probably due to combined contributions from Schottky and Kondo interactions in the CePt₄In compound. However, any quantitative analysis of this effect is hampered by large experimental uncertainty. Discussion of the low-temperature behaviour of the specific heat of both compounds has recently been presented in Ref. [17]. The electronic specific heat ratio $\Delta C/T$ measured for CePt₄In in zero magnetic field strongly increases with decreasing temperature below 20 K (where

$\Delta C/T$ is of the order of $100 \text{ mJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$) down to about 250 mK, where a broad maximum ($\approx 1.75 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^2$) occurs. At lower temperatures, $\Delta C/T$ slightly diminishes and finally saturates at the value of about $1.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$.

Upon applying external magnetic field of 0.5 T, the maximum in $\Delta C(T)/T$ disappears, and the $\Delta C/T$ curve shows $-\ln T$ behaviour over almost a decade in temperature, in a manner characteristic of non-Fermi liquid systems [18].

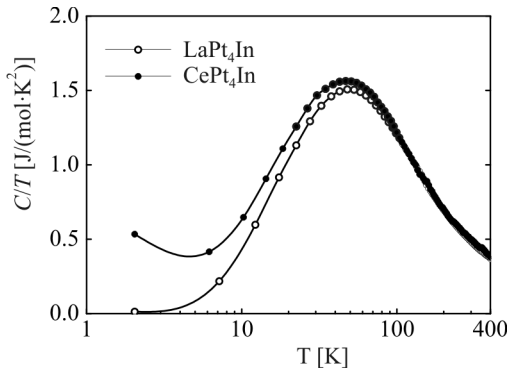


Fig. 7. Temperature dependences of the C/T ratio of single-crystalline CePt_4In and polycrystalline LaPt_4In in a semilogarithmic scale

In stronger fields, a regular Fermi liquid-like behaviour ($\Delta C(T)/T \approx \text{const}$) is recovered. The analysis of the temperature dependence of the magnetic entropy of CePt_4In suggests that the anomaly observed at $T^* = 250 \text{ mK}$ in $\Delta C/T(T)$ measured in zero magnetic field is due to some sort of short-range magnetic ordering of the cerium magnetic moments. The characteristic Kondo temperature, estimated from the relation $\Delta S(T_K) \approx 0.68R \ln 2$ [19], where ΔS is the excess entropy, is about 9–10 K.

4. Discussion and summary

CePt_4In was initially reported as an intermediate valence system with distinct CEF effect [2]. That conclusion was based mainly on the results of magnetic susceptibility measurements which showed a strong deviation from the Curie–Weiss law at low temperatures. In contrast, the opposite statement on local character of the $4f$ electrons in CePt_4In has recently been formulated in Ref. [8]. The rather stable $4f^1$ configuration of Ce ions was evidenced by measuring the XANES spectra at several temperatures down to 5 K. All these curves exhibited almost identical shapes, governed by the $4f^1 d^0$ and $4f^1 d^1$ contributions with no sign of the $4f^0$ configuration. The results discussed in the present paper corroborate the previous findings. The curvature in $\chi^{-1}(T)$ was explained in terms of the CEF model with Δ of the order of 250–350 K. Moreover, the presence of well localized magnetic moments of cerium in CePt_4In can be anticipated from the temperature variations of the electrical resistivity, the thermoelectric power (see also Ref. [8]) and the specific heat (see also Ref. [17]). All these characteristics show some features typical of dense Kondo systems with strong CEF effect, in which

$T_K \ll \Delta$. In particular, the ultra-low temperature specific heat data revealed a short range magnetic ordering of the Kondo-screened magnetic moments at the temperature of 250 mK, consistent with the presence of well localized magnetic moments [17].

Most surprisingly, the results of magnetoresistivity measurements, performed on polycrystalline CePt₄In, seem to contradict the Kondo scenario with T_K of the order of 10 K (as derived from the entropy analysis). The values of the magnetoresistivity are positive in the whole temperature range studied, as expected of simple metals rather than of dense Kondo systems above the coherence temperature. Somewhat problematic are also different values of the CEF splitting derived from the analysis of the magnetic susceptibility (250–350 K) and the electrical resistivity (100–150 K), as well as rather large discrepancies (9–33 K) in values of the Kondo temperature estimated from the magnetic susceptibility and magnetic entropy data.

Thus CePt₄In seems to be a dense Kondo system with localized magnetic moments which experience strong CEF effect of cubic symmetry. The screened moments of the ground doublet probably exhibit some short-range magnetic ordering at very low temperatures. The character of that ordering as well as the characteristic energy scales of the system (T_K and Δ) awaits verification by inelastic and elastic neutron scattering experiments, respectively.

Acknowledgements

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