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Kondo universality and energy scales in plutonium

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A B S T R A C T

The macroscopic properties of α and δ-plutonium were analyzed within the Fermi-liquid approach as well as the properties of a few model rare earth-based systems. The following major parameters in Pu were estimated within the single-site approximation: the characteristic Kondo energy, the *f*-electron shell occupation number, the effective degeneracy of the ground *f*-multiplet, the crystal field splitting energy. The ground state in δ-plutonium is a quantum superposition of two atomic states Pu^{3+} and Pu^{2+}. According to its macroscopic physical properties δ-Pu at low temperature is very close to the intermediate valence regime. The temperature dependence of the static magnetic susceptibility in plutonium was calculated. Since the universal Wilson criterion and the Kadowaki–Woods universal relation are valid in δ-Pu it can be considered as a Kondo system, while the position of α-plutonium in the general classification of solids remains a puzzle. The plutonium homology issue is discussed.

1. Introduction

Since its synthesis in the 40th XX to the beginning of the new century plutonium remains the most mysterious element without a well-defined position in the general classification of solids. The ground state issue in Pu is one of the major problems in fundamental solid state physics [1]. In the last few years plutonium is in the focus of the studies of the strongly correlated electron systems, both theoretical and experimental. Among the six allotropic modifications of Pu only two phases are stable at low temperatures and also at ambient conditions, namely α-Pu and δ-Pu stabilized by Ga and Al. These phases are interesting both for practical applications and for fundamental science. It is unknown whether α-Pu or δ-Pu could be superconducting or magnetically ordered at any external conditions. We cannot exclude other types of the ground states not typical in simple metals but rather common in the *f*-electron materials with strong electron correlations: Kondo-lattice with a nonmagnetic singlet ground state, non Fermi-liquid state, coexistence of magnetism and superconductivity in the heavy fermion regime, etc.

Several rare earth-based intermetallics demonstrate anomalous properties similar to plutonium. A concept of shifted homology of Pu and Ce has been suggested about a quarter century ago [2]. We consider Sm and Yb promising candidates regarding Pu homology. Universal features well-established for the rare earth-based compounds could be tested for Pu. The test for the Kondo universality was one of the motivations of the current study.

Another motivation was an attempt to establish the major energy scales in Pu. In metallic strongly correlated electron systems (SCES) the major interactions include: the Kondo interaction closely related to the hybridization of the *f*-electrons and the conduction band states, the crystal field potential (CF), the exchange coupling (RKKY), the spin-orbit coupling (SO), the possible (magnetic o phonon driven) coupling leading to superconductivity, the electron-phonon interaction [3].

The current work is focused on a quantitative analysis of anomalous plutonium properties caused by the *f*-electrons. We were aimed to provide a consistent set of parameters which allow to explain and calculate physical properties of Pu at low temperatures.

2. Results and discussion

The specific heat and the magnetic susceptibility are usually indicative of the ground state and phase transitions in solids. According to the experimental data (see [4] and references therein) Pu remains paramagnetic down to the lowest achievable temperatures. The magnetic susceptibility seems to be similar to the enhanced Pauli-like susceptibility with a week temperature dependence typical for the intermediate valence (IV) systems. One more fingerprint of the Kondo state is a value of the Sommerfeld coefficient. Both allotropic phases of plutonium stable at low temperature demonstrate the highest among all the elements values of the linear specific heat coefficient 65 и 17 mJ/(K^2 mol) in δ-Pu and α-Pu, respectively [4]. The rare earth-based (Ce, Sm, Yb) compounds, showing the values of the Sommerfeld coefficient close to that in Pu, belong to the class of IV systems with a strong degree

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of the *f*-electrons delocalization. Furthermore, many rare earth IV compounds demonstrate phase transitions accompanied by a volume collapse of the *f*-electron shell, a characteristic phenomenon of plutonium. As we see, even the first impression on the major macroscopic properties of plutonium suggests the IV regime, the nonmagnetic singlet (Kondo) ground state.

It is helpful to introduce ε_f – a parameter characterizing a fraction of an electron leaving the f-electron shell for the conduction band (positive ε_f) or a fraction of the conduction band electron occupying the f-shell (negative ε_f). So $-1 \leqslant \varepsilon_f \leqslant 1$. The first case ('electron') corresponds to Ce fluctuating between Ce^{3+} and Ce^{4+} states, the second ('hole') case – to Sm, Yb and Pu, fluctuating between the 2+ and 3+ configurations. The value of $|\varepsilon_f|$ is a deviation of an electron valence from the integer valence state, namely from the 'base' configuration which is responsible for the magnetic properties in Ce, Yb, Sm and Pu, the trivalent state. The ion valence is $3 + \varepsilon_f$ which reflect the symmetry of the 'electron' and the 'hole' IV cases. The effective (fractional) occupation of the base configuration $n_{f^n} = 1-|\varepsilon_f|$ is a very important parameter characterizing the magnetic properties of the IV system. The wave function of the IV system demonstrates the quantum mechanical superposition of the integer valence states (shown below very schematically):

$$|\psi\rangle = (1-|\varepsilon_f|)|4f^n\rangle + |\varepsilon_f||4f^{n-1}k\rangle \quad \text{for Ce}, \tag{1a}$$

$$|\psi\rangle = (1-|\varepsilon_f|)|5f^n k\rangle + |\varepsilon_f||5f^{n+1}\rangle \quad \text{for Pu, Sm, Yb}, \tag{1b}$$

k means any band electron state.

Pu, Ce and Sm are described in a similar way if they demonstrate the same value of ε_f. This fact is illustrated by Table 1.

We consider the single-site Kondo approximation as the simplest model for Pu at the current state. The Fermi-liquid expressions for the macroscopic properties of Kondo systems were provided by Rajan in [5]:

$$\gamma = N_A \pi^2 k_B < n_f > \frac{1}{3E_0}\frac{N-1}{N}, \tag{2}$$

$$\chi_{\text{static}} = N_A \pi \mu_{eff}^2 < n_f > \frac{1}{3E_0}. \tag{3}$$

The parameters of the model include the characteristic Kondo energy scale E_0, the fractional *f*-occupation $\langle n_f \rangle$, the magnetic degeneracy *N*. *N* as an effective parameter is somewhere between 2 and 6 in the case of the total angular momentum $J = 5/2$.

The ratio of the magnetic susceptibility (normalized by the squared effective moment) to the specific heat is called the Wilson number (Wilson ratio [6]) $R = N/(N-1)$. This number is between 1 and 2 in the majority of the Kondo systems.

In our preceding paper [7] we used CeNi as a homolog of Pu. It seems that cerium in CeNi has almost the same degree of delocalization of the *f*-electrons as δ-Pu. IV compound $Ce_{0.8}Th_{0.2}$ demonstrates higher degree of delocalization [8] but the same Sommerfeld coefficient as α-Pu. The parameters resulting from (2) and (3) are shown in Table 2.

The Wilson ratios for both Ce systems and δ-Pu are close to 1, indicative of the Kondo ground state. On the contrary, α-Pu fails in the Kondo universality test based on the Wilson ratio. In fact, the static magnetic susceptibility of this phase is much higher than the value expected from the Sommerfeld coefficient within the single-site model.

Table 1
Electronic configurations of Pu and its 4*f* homolog elements.

Ion	Pu	Ce	Sm
Base configuration f^n	Pu^{3+}: $5f^5$ ($\varepsilon_f = 0$)	Ce^{3+}: $4f^1$ ($\varepsilon_f = 0$)	Sm^{3+}: $4f^5$ ($\varepsilon_f = 0$)
Alternative configuration $f^{n\pm1}$	Pu^{2+}: $5f^6$ ($\varepsilon_f = -1$)	Ce^{4+}: $4f^0$ ($\varepsilon_f = 1$)	Sm^{2+}: $4f^6$ ($\varepsilon_f = -1$)
f-electron count ($n - \varepsilon_f$)	$5 - \varepsilon_f$	$1 - \varepsilon_f$	$5 - \varepsilon_f$
valence	$3 + \varepsilon_f$	$3 + \varepsilon_f$	$3 + \varepsilon_f$
fractional *f*-occupation	$n_{f^n} = 1-\|\varepsilon_f\|$	$n_{f^n} = 1-\|\varepsilon_f\|$	$n_{f^n} = 1-\|\varepsilon_f\|$

Table 2
The parameters of the single-site Kondo model and macroscopic properties of two Pu phases and the corresponding Ce-based model systems.

	$Ce_{0.8}Th_{0.2}$	CeNi	α-Pu	δ-Pu
γ (mJ/mol K^2)	12.8 (17.4)	65	17	65
χ (0) (μemu/mol)	540	2000	510	550
E_0, meV	138	26	98	26
ε_f	>0.2	0.15	?	−0.15
R_{exp}	1.06	1.05	4.3	1.22
R_{calc}	1.2	1.2	1.2	1.2
N_{calc}	6	6	6	6

In the simple calculation described above the value of the magnetic degeneracy *N* was taken as 6. However the choice of *N* is not that trivial since the CF interaction lifts this degeneracy in real systems. The ratio the Kondo energy and the CF energy plays a key role. If $E_0 >> \Delta_{CF}$ then all the components play a role, $N = 6$, in the opposite case $E_0 << \Delta_{CF}$ $N = 2$.

At the current state no direct experimental estimates of the CF strength are available for Pu. In α-Pu the Pu ions are occupying different crystallographic positions with different point symmetry. In δ-Pu stabilized by Ga and Al the CF environment of Pu is distorted. Due to these reasons we will discuss the CF problem in Pu in terms of the average splitting $\langle \Delta \rangle_{CF}$ leaving aside the fine structure.

Again rare earth-based compounds provide a clue. In the majority of cerium-based systems $\langle \Delta_{CF} \rangle$ is within 10 to 30 meV. For Pu intermetallics experimental information is very scarce. In the Kondo system $PuPd_2Sn$ $\langle \Delta_{CF} \rangle$ is about 9.5 meV [9]. As to the compounds with well-established 3+ state, rare earth ions and actinides demonstrate the same magnitude of the CF splitting in trichlorides. In particular, $\langle \Delta_{CF} \rangle$ for Pu^{3+} in $LaCl_3$ matrix is about 60% of $\langle \Delta_{CF} \rangle$ for Ce^{3+} and 80% for Sm^{3+} [10]. This matrix is nonmetallic, however experimental information collected on the CF effects in trichlorides is full and reliable. So our estimate for the most probable range for $\langle \Delta_{CF} \rangle$ in Pu based on the comparison with rare earth ions is 5 to 30 meV.

Two equations, namely (2) and (3), allow us to estimate *N* if we consider a pair out of three variables E_0, $\langle n_f \rangle$ and *N* to be dependable. In fact the Kondo energy depends on valence, almost integer valence corresponds to small E_0 (heavy fermion regime) while smaller $\langle n_f \rangle$ corresponds to the IV with high E_0. A reasonable linear dependence valid in the range of $\langle n_f \rangle$ 0.7 to 0.95 is: $\langle n_f \rangle = 1 - 0.00523\ (\text{meV}^{-1}) E_0$. By making use of this dependence we got $N = 5.4$ for the Δ-phase. Such value of *N* is indicative of the CF strength a smaller than the Kondo energy ($\langle \Delta_{CF} \rangle \sim 20$ meV or smaller).

The temperature dependence of the static magnetic susceptibility in δ-Pu was calculated by the single-site model using the values of the relevant parameters mentioned above. The calculation procedure is described in [5], the temperature dependence is governed by the Kondo energy, effective valence and the ratio of the Kondo energy to the halfwidth ($\Gamma/2$) of the spectral function (see [5]). The outcome is shown on Fig. 1. One curve represents the temperature dependence within the non-crossing approximation (NCA) [11] with $\Gamma/2 = E_0$, another – with the ratio of these parameters similar to the one observed experimentally in the IV system CeNi [12]. The second curve shows relatively week temperature dependence of the magnetic susceptibility at $T < 150$ K. This is consistent with the experimentally observed almost temperature-independent static magnetic susceptibility of Pu. In particular, in the δ-phase the magnetic susceptibility is almost constant with a value of about 550 μemu/mol. At $T > 150$ K the calculated susceptibility goes down which is not reflected in experiments, the experimental

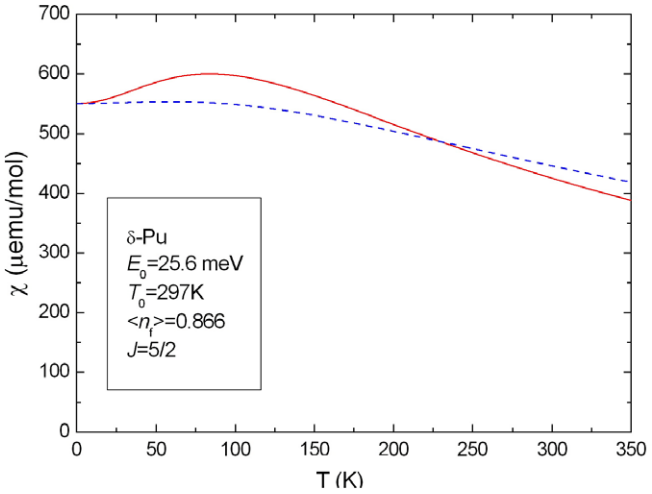

Fig. 1. Calculated temperature dependence of the static magnetic susceptibility of δ-plutonium. Solid line – NCA susceptibility for the parameters indicated in the insert and the text. Dashed line – single-site susceptibility for $T_0 = E_0/k_B = 297$ K and $\Gamma/2$=492 K.

one stays at the same level up to 350 K (see [4]). Thus the problem of peculiar magnetic susceptibility of plutonium remains but shifted to the higher temperature range.

In addition to the Wilson ratio the Kondo systems demonstrate other universal laws and relations: the T-squared law for the temperature dependence of the resistivity [13] $\rho(T) = A \times T^2$ at low temperature, the Kadowaki–Woods relation of the resistivity coefficient A and the specific heat Sommerfeld coefficient (see [14] and references therein). α and δ-Pu demonstrate the values of A: 1.1×10^{-2} and 0.88×10^{-2} (μΩ cm/K^2), respectively. According to the value of A δ-plutonium is very close to the universal line on the A-γ diagram (see [14]), as many Ce, Sm and Yb Kondo systems. As to the α-phase, it again fails in the Kondo universality test.

3. Conclusion

The single-site approximation seems to work quite well for the macroscopic properties of δ-Pu at $T < 150$ K. This phase at low temperatures follows the universal Wilson and Kadowaki-Woods relations indicative of the IV regime of the 5f electrons. The major energy scales were estimated in δ-Pu: the Kondo energy $E_0 = 25.6$ meV ($T_0 = 297$ K), the CF energy is between 5 and 20 meV. The fractional f-occupation in δ-Pu seems to be close to 0.866 yielding the f-count 5.13. Recent theoretical calculations also point to the IV regime with the f-count of about 5.3 [15].

α-Pu fails in the Kondo universality tests despite of Pauli-like static magnetic susceptibility and large Sommerfeld coefficient. If this system belongs to the Kondo domain the Kondo physics of α-Pu must be very complex. Inelastic neutron scattering could provide a clue to solve the α-Pu puzzle.

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