A CERIUM CONCENTRATED HEAVY FERMION?

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Abstract

The fcc-Ce_3In compound is presented as the best available approximation to reproduce the main magnetic properties of γ-Ce at low temperatures, where such pure phase does not exist. The electronic specific heat shows a maximum at 18K and an anomaly at 2.2K, with an entropy of 0.8 $R\ell n$ 4 at 32K. The susceptibility shows a broad maximum at 1.8K, while in the magnetization there are no trace of ordering up to 18 Tesla at 1.5 and 4.2K. We interpret the experimental results as governed by a quadruplet crystal field ground state, which undergoes a quadrupolar transition at 18K. At lower temperatures a Heavy Fermion ground state developes, with C_{el}/T = 500 mJ/Ceat.K^2 for $T \rightarrow 0$ and $\chi T/C_{el}$ = 0.11 emu K/J for T < 5K.

Key words: Specific Heat, Magnetization, Quadropolar Transition, Heavy Fermion.

Introduction

It is well known that metallic Ce undergoes two phase transitions between room and low temperature region, at normal pressure. The γ(fcc) to β(hcp) structural transformation at T = 326K (1) does not induce significant changes in the paramagnetic behaviour, but the β to α(fcc) transformation at T = 96K (1) is related with a nearly-trivalent to intermediate-valent transition. Due to these transformations the low temperature properties of Ce are well known in the α-phase and, after a hundred cycling process (2) in the β-phase. At room temperature the non-magnetic α-phase can be induced under a pressure of 7.6kbar (1). The low temperature properties of the γ-phase remain therefore unknown, except by the fact that the large value of the Curie-Weiss temperature θ_p = -50K (3) suggests the possibility of mixing between the localized and conduction electron states, as it was also put in evidence by resistivity measurements (4).

On searching for a system able to reproduce the main properties of γ-Ce at low temperature one finds that the highly concentrated Cerium compounds: β-Ce_3Al (5), Ce_3Sn (6) and Ce_3In (7), have the fcc-Cu_3Au crystalline structure. Both β-Ce_3Al and Ce_3In have a trivalent Ce-partner, but the last appears to be the most appropriated for this study because it forms in a unique phase and the In size approaches better the size of Ce. Furthermore, due to the relative Ce-In atomic volume, the electronic structure of Ce_3In is mainly dominated by the Ce-Ce contacts (Ce-In distances are larger than the sum of their respective atomic radius).

We present in this paper the specific heat and magnetic measurements performed on the Ce_3In compound which represents the best available approximation for the knowledge of the γ-Ce phase at low temperature.

Experimental Details

The starting materials, used for direct synthesis of the Ce_3In compound, were 99.9% pure Ce (Rare Earth Products Inc.) and 99.99% pure Indium (Koch-Light Co.). The sample (of about 2 grs) was prepared by the semi-levitation method on water cooled cooper crucible, under a pure and dry argon atmosphere. It was homogeneized by annealing in high vacuum at 700°C, for one week. The X-ray patterns are characteristic of the cubic $AuCu_3$ structure type, with a lattice parameter a = 5.06 Å, in agreement with the literature. Some extra lines, presumably due to traces of Ce_2In, were also detected. The magnetization measurements were performed in a vibrating sample magnetometer, operating in magnetic fields up to 2 Tesla and between 1.5 and 300K, and by an induction method at 1.5 and 4.2K in fields up to 18T (Service National des Champs Intenses, Grenoble). Specific heat measurements were performed in a semi- adiabatic He^3 calorimeter, using the standard heat pulse method, within a range of 0.5 to 30K.

Experimental results

The specific heat measurements were performed in the range of temperature between 0.4 and 32K. The usual subtraction of the phonon contribution done by taking the specific heat of the La_3In as reference compound cannot be made in this case because it becomes larger than the total Ce_3In specific heat (C_p) at about 25K (8). Due to the lack of a reference compound we extract the phonon contribution from the range of temperature(9 < T < 16K) where C_p follows the law $C_p = \gamma' T + \beta T^3$, with $\gamma' = 0.93$ J/K^2 mole and $\beta = 1.0 mJ/K^4$ mole. This β value corresponds to a Debye temperature of $\theta_D = 200K$, which is something larger than that of La_3In, $\theta_D = 170K$ (8). The electronic contribution can be calculated now as $C_{el} = C_p - C_D$, where C_D represents the Debye function for $\theta_D = 200K$. As shown in Fig.1, the C_{el} contribution has a maximum at 18K and another anomaly around 2.2K. The entropy gain of $C_{el}(T)$ is extracted from a C_{el}/T vs T plot (see fig.2) and reaches an 80% of Rℓn4 at 32K (see also fig.2). Such electronic entropy has to be related with a quartet ground state.

The magnetic susceptibility (χ) was measured in the range of temperature between 1.8 and 300K. The Curie constant (C) is extracted from a χ^{-1} vs T plot, see fig.3, where the slope for T > 70K corresponds to a value of C = 0.78 emuK/Ceat., close to the Ce^{3+} free ion value, in agreement with previous measurements (7). The temperature at which C reaches the full value is coherent with the fact that the specific heat does not evidence any Schottky contribution up to 30K, suggesting that the Γ_8-Γ_7 splitting, due to the Crystalline Field (CF), has to be larger than 70K.

The large negative value of the Curie-Weiss temperature $\theta_p = -50K$ cannot be explained by a dole CF effect and it is an indication of a localized-conduction electron state hybridization (9), which changes with temperature as the exited CF level reduce its thermal population. The continuous downwards curvature of $\chi^{-1}(T)$ for T< 70K is also a characteristic of a quartet ground state. At very low temperature (2.5 < T < 5K), $\chi^{-1}(T)$ recovers a Curie-Weiss behaviour with a Curie constant value of C' = 0.30 emuK/Ceat. and $\theta'_p = -1.85K$. Finally, $\chi(T)$ has a maximum (of 0.074 emu/Ceat.) at 1.8K, as shown in the inset of fig.3.

The magnetization measurements were taken at 1.5 and 4.2K under magnetic fields up to 18 Tesla (see fig.4). At the maximum applied field there is no evidence of magnetic saturation and the slope (or M/H ratio) is similar at both temperatures: 9.10^{-3} emu/OeCeat. The magnetization curve at 1.5K (bellow the maximum of χ) does not show any evidence of magnetic order. The Saturation Magnetization (Ms) can be obtained appling the Akulov criterium ($M=Ms-A/H-B/H^2$). Here we obtain Ms= $0.97\mu_\beta$/Ceat., again without significative difference between 1.5 and 4.2K (see the inset of fig.4).

Discussion

The entropy gain up to 32K (0.8Rℓn4) and the continuous downward curvature of $\chi^{-1}(T)$, indicate that the low temperature behaviour of Ce_3In is dominated by the presence of a quartet or eventually two doublets with a small energy splitting. The temperature dependence of $C_{el}(T)$ cannot be described in terms of Schottky anomalies originated in the small CF splitting because the $C_{el}(T)$ values at 2K and 18K are not compatible with the entropy gain at those temperature.

The θ_p value extrapolated from T> 70K coincides with that of Ce in its γ-phase (3), as a confirmation of Ce_3In as a good choise for a comparison. If we take the large negative θ_p value as an indication of localized-conduction electron state mixing (9), its temperature dependence (from θ_p= -50K at 70K and θ_p= -1.8K at 4K) makes evident that the strengh of such mixing is of the order of the CF splitting and depends on the thermal population of the excited states (10).

We will analyse now the low temperature C_{el} anomaly. The symmetry of the anomaly with respect to the maximum at 2.2K in a δC_{el} vs ℓnT plot (where $\delta C_{el} = C_{el} - \gamma' T$) excludes a magnetic origin, while the decrease of $\delta C_{el}/T$ vs T indicates that a gap opens in the electronic density of states (11). Although the maximum of $\chi(T)$ at 1.8K suggest the possibility of magnetic correlations, we notice that the ratio $\chi T/C_{el}$ = 0.11 emu K/J is constant between $1.5 < T < 5K$, as expected for a Fermi Liquid system.

From the low temperature properties we can say that Ce_3In behaves as a Heavy Fermion (HF) system, with C_{el}/T = 680 mJ/K^2 Ceat. at 1.8K, becoming a Kondo-Lattice below 2K, with C_{el}/T = 500 mJ/K^2Ceat. for $T \to 0$. The original characteristic of this HF is the extremely short Ce-Ce distance, d = 3.55 Å, which does not follow the usual criterium concerning the large distance between Ce atoms in the typical Ce HF systems.

In order to extract more information on the CF ground state of this compound we can study the low temperature magnetic parameters (i.e. C' and Ms) within the context of a small derivation from the cubic symmetry. In other words we will assume a small tetragonal distortion in the system at hand. The experimental values C' = 0.3 emu K/Ceat. and Ms = $0.97\mu_\beta$/Ceat. are consistent with a $\Gamma^2_{t_7}$ doublet ($\Gamma^2_{t_7} = b|\pm 5/2\rangle + a|\mp 3/2\rangle$) where b = 0.8 and a = 0.6 (12). These b and a values agree with a small splitting between the $\Gamma^2_{t_7}$ and Γ_{t_6} doublets, which in a cubic symmetry belong to the Γ_8 quartet.

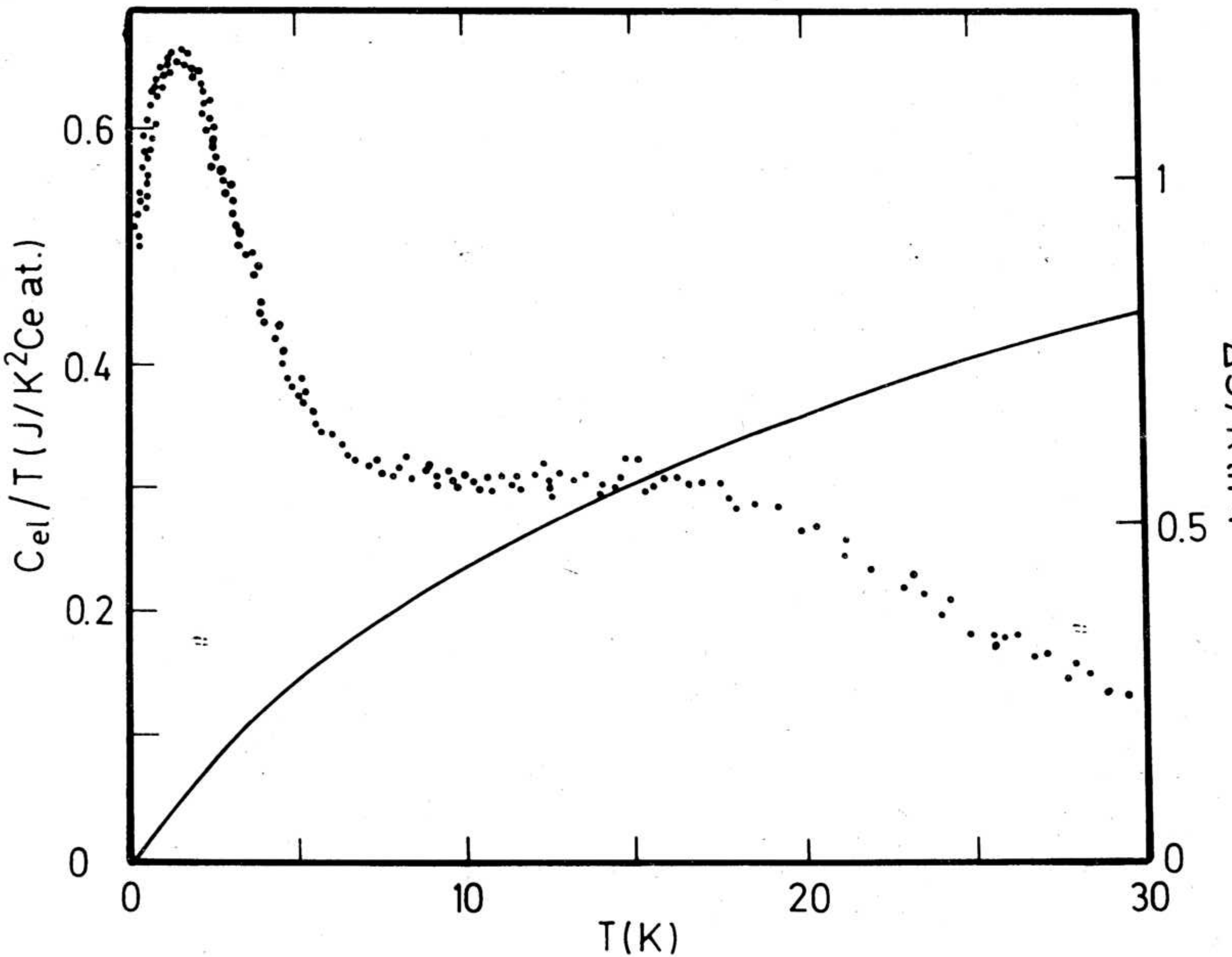
Such a CF level scheme was studied by Desgranges et al. (13) for a quartet ionic ground state split into two doublets. In fig.5 we compare the experimental results with the theory and we find that our measurements can be qualitatively described by the ratio $\Delta/T_K = 1$ (where Δ is the CF splitting and T_K the Kondo temperature), which indicates that both hybridization and CF splitting are within the same range of energy. Nevertheless, an accurate comparison between experiment and theory shows that the upper C_{el} maximum (at 18K) is something sharper than the predicted by the theory.

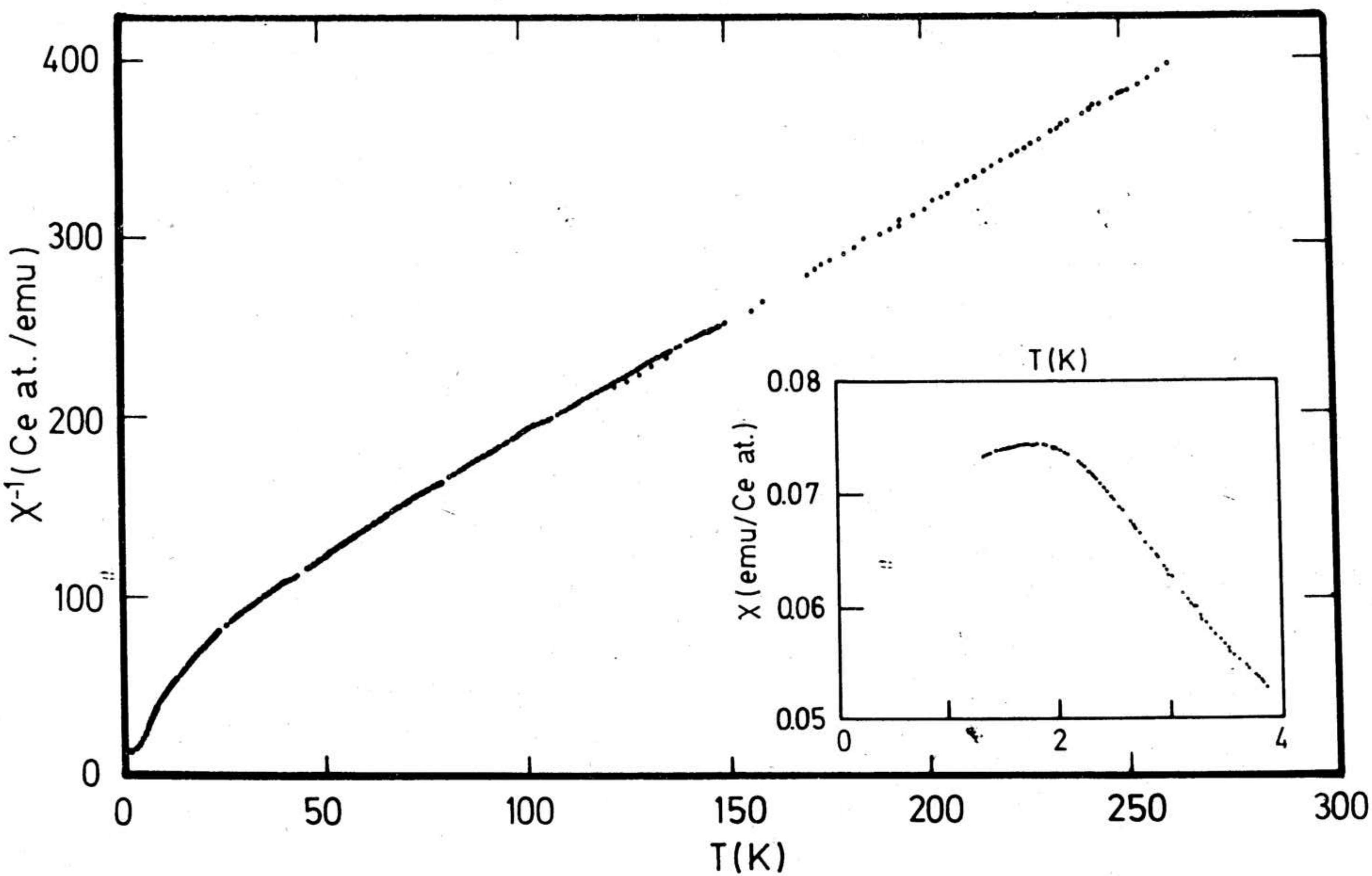
The shape of this specific heat anomally suggests that the degeneracy of the CF ground state (Γ_8) is reduced due to a change in the local Ce symmetry. The possibility of a structural martensitic-like transformation is excluded by resistive measurements at normal pressure (14). The electrical resistance of Ce_3In does not show any anormaly around 18K, although structural instabilities are induced at pressures above 14kbar for T > 20K (see also ref. 14). An important feature of the normal pressure measurements is the drastic reduction of the resistivity below 10K, in the region of temperature where the coherence effects are expected to develop (see in fig. 2 the starting of the upward curvature of C_{el}/T at that temperature).

Within the Ce compounds with a quartet as a CF ground state, CeB_6 shows significative similarities with Ce_3In. Under an applied magnetic field of 1.8 Tesla, the specific heat of CeB_6 also shows a bump at about 2K (related to the zero field antiferromagnetic transition) and a maximum at 4K which increases under magnetic field (15). From neutron measurements the maximum at 4K was found to be related to a Quadrupolar transition (16). The electrical resistivity (under magnetic field) behaves with the same temperature dependence as in Ce_3In: the coherence effects appear below the Quadrupolar transition, where the Kondo-Lattice ground state starts to develop (17). From these similarities one can say that also the Γ_8-CF ground state of Ce_3In undergoes a Quadrupolar transition (at 18K) which splits the four fold degeneracy into two doublets.

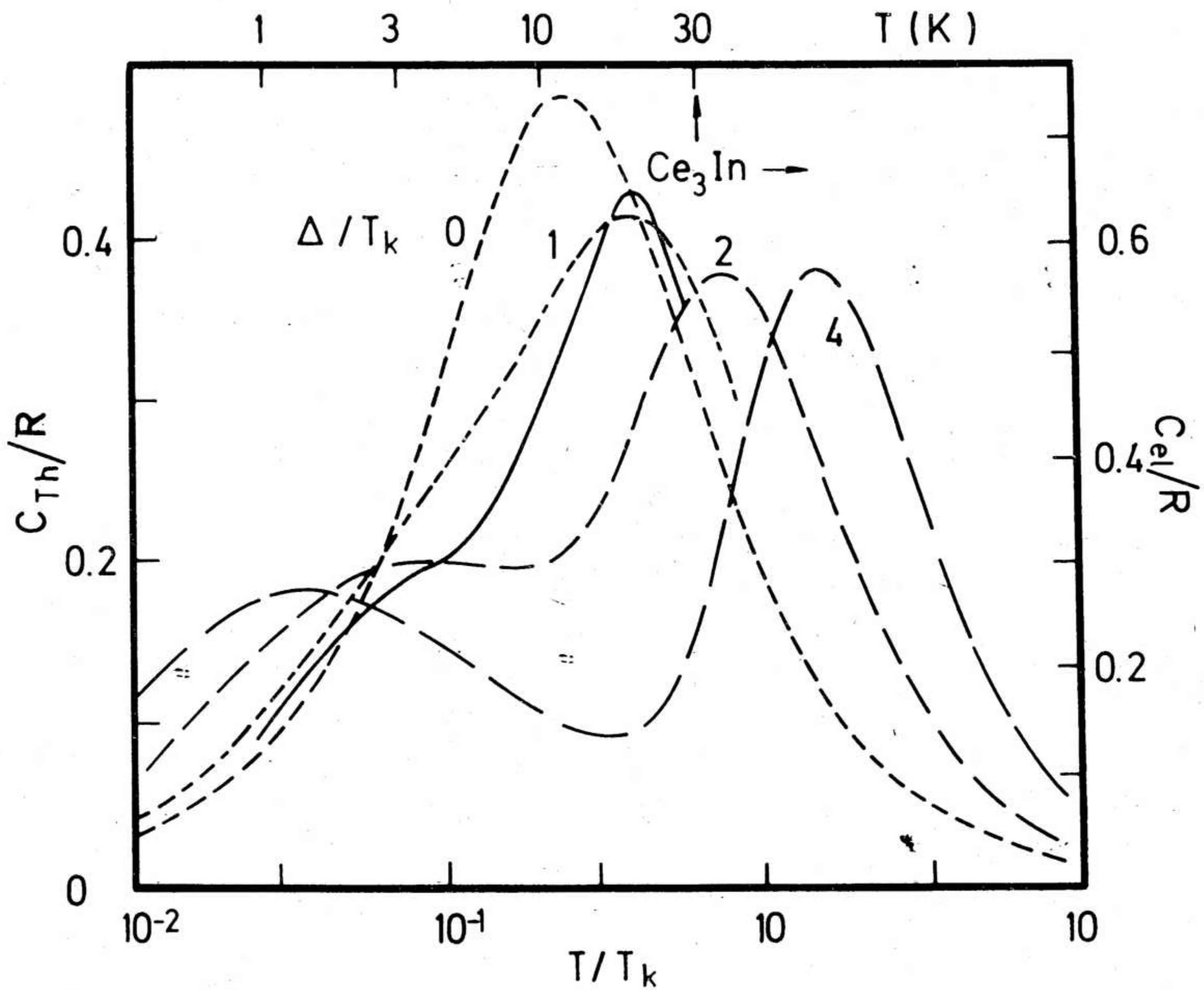
Conclusions

We have shown that the fcc compound Ce_3In, proposed as the best approach to the Ce behaviour in its γ-phase at low temperatures, is characterized by = i) a HF ground state with: $(C_{el}/T)_{max}$ = 680mJ/K^2 Ceat., three times larger Ce concentration and 20% smaller Ce-Ce distance than $CeAl_3$, ii) an onset of a gap in the electronic density of states correlates with the coherence effects in the electrical resistance, and iii) a Γ_8-CF ground state at high temperatures, which undergoes a Quadrupolar transition at 18K. Neutron diffraction measurements should confirm this point.


0.6
0.4
0.2
0
Cel / T (J / K2Ce at.)
1
0.5
0
ΔS / R ln 4
0
10
20
30
T(K)



X-1 (Ce at. /emu)
400
300
200
100
0
0
50
100
150
200
250
300
T (K)
T (K)
X (emu/Ce at.)
0.08
0.07
0.06
0.05
0
2
4



T (K)
1
3
10
30
Ce3In →
Δ / Tk
0
1
2
4
C_Th/R
0.4
0.2
0
C_el/R
0.6
0.4
0.2
10^-2
10^-1
10
10
T/Tk

References

1 - D.C. Koskenmaki and K.A. Gschneidner, Jr., "Handbook on the Physics and Chemistry of Rare Earths", Ed. K.A. Gschneidner Jr. and L. Eyring, North-Holland Pub. Co. 1978, Chapter 4.

2 - J.M. Lock, Proc. Phys. Society (London) B70, 566 (1957).

3 - R.V. Colvin et al, Phys. Rev. 122, 14 (1961)

4 - T.G. Ramesh and V. Shubha, J. Phys. F 10, 1821 (1980).

5 - W.B. Pearson, "Handbook of Lattice-Spacing and Structures of Metals", Pergamon Press, Vol.2, p.539 (1970).

6 - "Pearson's Handbook of Crystallographic Data for Intermetallic Phases", by P. Villars and L.D. Calvet, A.S.M., 1985.

7 - L. Colombo and G.L. Olcese, Rend. Acad. Naz. dei Lincei 35, 12 (1963).

8 - F. Heiniger et al., Phys. Rev. B8, 3194 (1973).

9 - H.R. Krishna-murthy et al., Phys. Rev. Lett. 35, 1101 (1975).

10 - D. Wohlleben and B. Wittershagen, J. Magn.& Magn.Mater. 52, 32 (1985).

11 - N. Grewe, Solid State Commun. 50, 19 (1984).

12 - G. Fisher and A. Herr, Phys. Stat. Sol. (b) 141, 589 (1987).

13 - H.U. Desgranges and J.W. Rasul, Phys. Rev. B32, 6100 (1985).

14 - J.D. Thompson et al., J. Less Common. Metals 127, 385 (1987).

15 - T. Fujita et al., Sol. State Commun. 35, 569 (1980).

16 - C. Vettier et al, J. Mag. Mag. Mat. 63-64, 18 (1987).

17 - T. Kasuya et al., "Valence Flutuations in Solids", Ed. L. Falicov, W. Hambe, M.B. Maple. North Holland Pub. C. 1981, p. 215.

Figure captions

Figure 1: Temperature dependence of C_{el}/T (points) and of the entropy (continuous curve).

Figure 2: Temperature dependence of the inverse of the magnetic susceptibility. Inset: maximum of the susceptibility at 1.8K.

Figure 3: Comparison of the Ce_3In electronic specific heat (C_{el}: continuous line) with the Desgranges and Rasul model (C_{th}:dashed lines), in units of the gas constant: R