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Evidence for valence fluctuation in the CeSn_3 compound

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Abstract. We present the experimental results of magnetisation, magnetic susceptibility (at normal pressure and under a pressure of 6 kbar), electrical resistivity and thermal expansion, performed on a single sample of CeSn_3 . These measurements were done over the temperature range of $1.4 < T < 300$ K.

We used an extension of the Ramirez-Falicov theory outlined by Alascio *et al* to show that these and previous specific heat and thermopower results can be related by including a mixing between the two possible Ce configurations.

1. Introduction

Although the reduction of the CeSn_3 lattice parameter relative to the expected value for $\text{Ln}^{3+}\text{Sn}_3$ has been known for more than forty years (Rossi 1933) and its anomalous magnetic susceptibility was pointed out fifteen years ago (Ferro-Ruggiero and Olcese 1964), it was only a few years ago that this compound was 'rediscovered' by solid state physics in the framework of the intermediate valence studies.

The aim of this paper is to collect the experimental evidence on magnetic, thermal and transport properties to show that they can all be related, not only qualitatively but also quantitatively, using the pattern of valence fluctuations, as proposed by Maple and Wohlleben (1973).

To describe the magnetic and thermal properties, we have used the model developed by Alascio *et al* (1973), which has a similar high- and low-temperature limit to the one by Wohlleben (1976), but it takes better account of the 4f Ce level occupancy at intermediate temperatures.

The accessible Ce configurations are $5d^14f^1(\text{Ce}^{3+})$ and $5d^24f^0(\text{Ce}^{4+})$, with total angular moments of $J = 5/2$ and $J = 0$, respectively.

The model was initially proposed as an extension of the Ramirez-Falicov (1971) theory of the α - γ transition in Ce to include the hydridisation effect of the 4f state with the conduction band, taking the highly correlated character of the f levels into account.

The Ce valence, as a function of temperature (T), is given in this model by

$$v(T) = 4 - 6\Phi/(1 + 5\Phi) = 4 - n(T) \quad (1)$$

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where n is the occupation number of the f level and Φ is given in terms of the f level parameters by (Coqblin and Blandin 1968):

$$\Phi(T) = \frac{1}{2} + \frac{1}{\pi} \text{Im} \psi \left(\frac{1}{2} + \frac{\Delta}{2\pi k_B T} + i \frac{2Bn - E}{2\pi k_B T} \right) \quad (2)$$

where $\text{Im} \psi$ is the imaginary part of the digamma function. The factor Δ accounts for the hybridisation of the localised and conduction states, and represents the f level width described by a Lorentzian distribution. In the interconfigurational fluctuation scheme it is connected with the lifetime of the electron in this level, i.e. $\tau = h/\Delta$. The factor B denotes the Coulomb interaction between an electron in the f shell and a hole in the conduction band (Falicov and Kimball 1969).

We can identify $2Bn - E$ with the excitation energy (E_{ex}) of the valence fluctuation theory:

$$2Bn - E = -E_{\text{ex}}. \quad (3)$$

At low temperatures we consider E_{ex} to be independent of T , which implies neglecting the temperature variation of n in equation (3). Clearly this approximation is valid in the range $k_B T < E_{\text{ex}}$ where the measurements are performed.

From equations (1) and (2) it is possible to find the temperature dependence of n . Particularly at $T = 0$ it takes the simple form:

$$n(0) = \left(3 - \frac{6}{\pi} \tan^{-1} \eta \right) \left(\frac{7}{2} - \frac{5}{\pi} \tan^{-1} \eta \right)^{-1}$$

with $\eta = E_{\text{ex}}/\Delta$.

A large discussion on the possible values of η respecting the valence states in Ce and Yb intermetallic compounds was done by Sales (1977).

2. Experimental results

All the measurements reported here were performed on a single sample, provided by G Olcese† in 1978, to avoid possible discrepancies due to different sample preparations.

2.1. Magnetic measurements

2.1.1. Magnetisation. The magnetisation of this compound was measured by the extraction method over different ranges of applied field (H) and temperature, using the facilities of the CRTBT-CNRS of Grenoble. Figure 1 shows the magnetisation (M) at 1.5 K and 4.2 K up to $H_{\text{max}} = 150$ kG, where the rapid saturation of the magnetic impurities is apparent (the used Ce is 99.95% pure). The M versus H dependence of $\text{CeSn}_3(M_{\text{Ce}})$ is expected to be linear up to almost 80 kG, because of the ratio $x = \mu_B H_{\text{max}}/k_B \Delta \simeq 8 \times 10^{-2}$ ($\Delta = 120$ K, as will be evaluated later).

To show that this 'saturation' is due to magnetic impurities (M_i) and not to an effect of change in the Ce valence, in figure 2 we show that the M_i versus H dependence (taking $M_i = M_{\text{meas}} - M_{\text{Ce}}$) can be described by a Brillouin function, which scales the H/T dependence.

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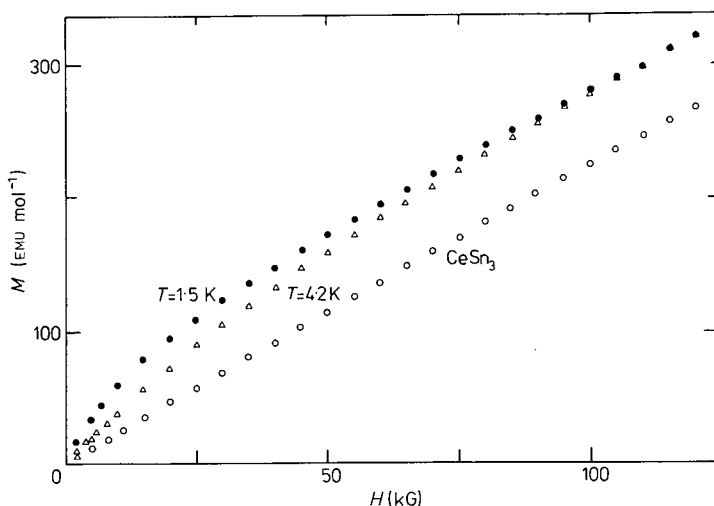


Figure 1. Total magnetisation versus applied field at $T = 1.5$ K (●) and $T = 4.2$ K (△). The open circles (○) denote the $CeSn_3$ magnetisation after subtracting that due to magnetic impurities from the results obtained for the impure crystal.

2.1.2. Magnetic susceptibility. The magnetic contribution of impurities has also been studied from the variation of the magnetic susceptibility (χ) in the low-temperature range (70 mK to 4.2 K) where the Ce contribution is negligible and this is displayed in figure 3.

Despite the anomalous behaviour below 2 K, probably due to an interaction between impurities via the conduction electrons, we can estimate the impurity contribution to the susceptibility in the region ($T > 2$ K) where the Curie-Weiss law fits.

Figure 4 shows the $\chi(T)$ results in the range between 4.2 K and 300 K. The low-temperature enhancement is due to impurities as discussed above, and the typical

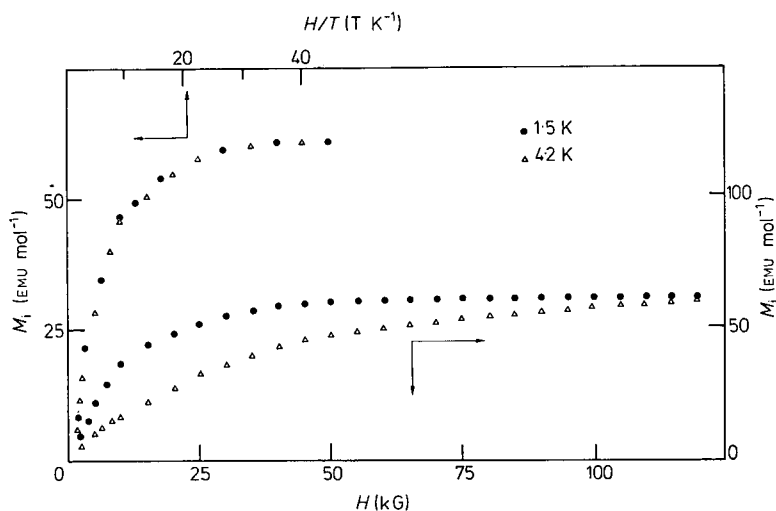


Figure 2. Magnetisation of the magnetic impurities (M_i) at $T = 1.5$ K (●) and $T = 4.2$ K (△) versus applied field and scaling of M with a Brillouin function of H/T .

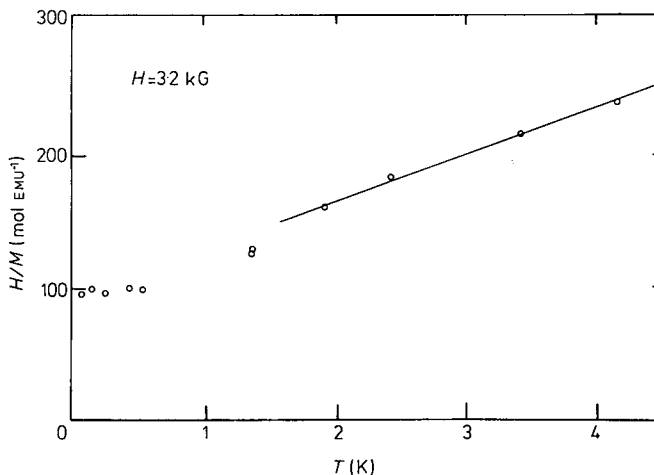


Figure 3. H/M versus T in the lower range of temperature, where the main contribution is due to impurities.

intermediate valence broadened maximum can be located at around 140 K. The decrease of $\chi(T)$ at high temperatures does not follow a Curie law exactly, indicating that at 300 K there is still a change in the Ce valence. The measurement was fitted with the function

$$\chi(T) = C_i/(T - \theta) + \chi_{Ce}(T) + \chi_0 \quad (4)$$

where $C_i = 0.018 \text{ EMU K mol}^{-1}$ and $\theta = -3.3 \text{ K}$ account for the impurity contribution. $\chi_0 = 0.5 \times 10^{-3} \text{ EMU mol}^{-1}$ is a temperature-independent contribution discussed later.

$\chi_{Ce}(T)$ is given, in the used model (Alascio *et al* 1973), by:

$$\chi_{Ce}(T) = C \frac{S^2}{1-n} \left[-\frac{\delta}{\delta E_0} \left(\frac{n}{S} \right) \right] \quad (5)$$

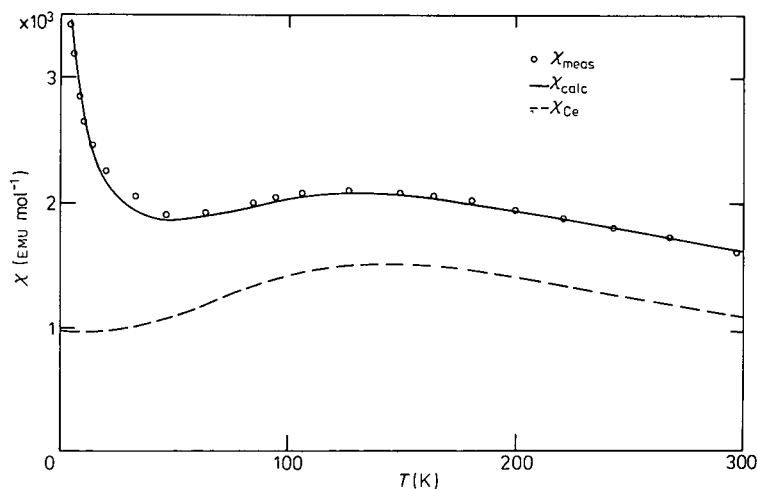


Figure 4. Measured magnetic susceptibility in the upper range of temperature (O), theoretical fit following equation (4) (full curve) and $\chi_{Ce}(T)$ contribution of equation (5) (broken curve) at normal pressure.

where $S = 1 - \frac{5}{6}n$ and the Curie constant is given by $C = Ng^2\mu_B^2 J(J+1)/3k_B = 0.805 \text{ EMU K mol}^{-1}$ for Ce (the constants have the classical values and $J = 5/2$ and $g = 6/7$). Since $n(T) = 6\Phi/(1 + 5\Phi)$, equation (5) results in the expression:

$$\chi_{Ce}(T) = \frac{(2J+1)C}{(2\pi)^2} \frac{1}{T} \frac{1}{1+4\Phi+5\Phi^2} \text{Re } \psi'$$

where $\text{Re } \psi'$ is the real part of the derivative of the digamma function and $\Phi(T)$ is the function defined in equation (2).

The limit as $T \rightarrow 0$ is given by:

$$\chi_{Ce}(0) = \frac{6C}{\pi} \frac{S^2}{1-n} \frac{\Delta}{E_{ex}^2 + \Delta^2}. \quad (6)$$

By fitting equation (4) to the experimental values, we obtain $E_{ex} = 350 \text{ K}$ and $\Delta = 120 \text{ K}$, which means $\eta = 2.9$ and $n(0) = 0.41$ corresponding to a Ce valence of $v(0) = 3.59$. From equation (6) $\chi_{Ce}(0) = 0.99 \times 10^{-3} \text{ EMU mol}^{-1}$. We will use these values of E_{ex} and Δ to describe other physical properties of $CeSn_3$, in order to show that the model is able to describe not only the magnetic but also all the measurements we present here, that are connected with the Ce change of valence.

At room temperature the occupation number obtained with these parameters is $n(300) = 0.70$. This value will be compared later with that obtained from the lattice parameter.

2.1.3. Pressure effects. We have also studied the pressure effects on the magnetic susceptibility by applying a pressure of 6 kbar. The results are shown in figure 5, where it is possible to appreciate a similar behaviour to that found under normal pressure, but with a wider maximum a little shifted towards the higher temperature. The susceptibility values are reduced by a factor of 35% due to the effect of pressure.

As before, we fit the experimental results by using equation (4) (see the full curve in figure 5), obtaining values of $E'_{ex} = 440 \text{ K}$, $\Delta' = 170 \text{ K}$ (i.e. $\eta' = 2.6$) and $\chi'_0 = 0.1 \times 10^{-3} \text{ EMU mol}^{-1}$. For the magnetic impurities we used the same C_i and θ

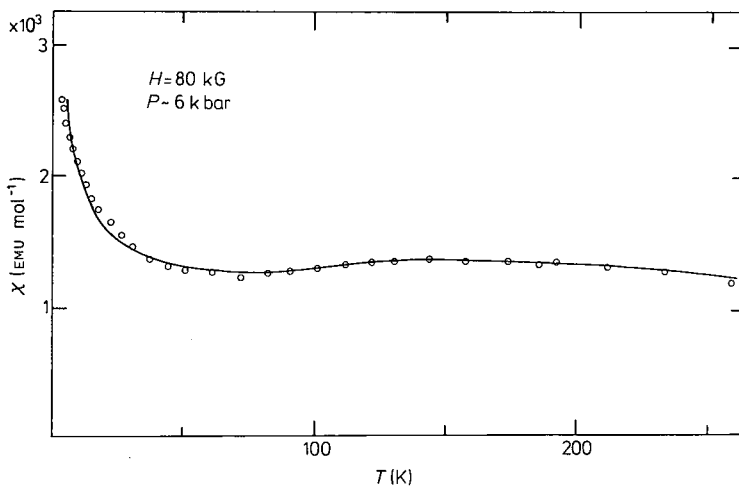


Figure 5. Measured susceptibility in the upper range of temperature (O) and theoretical fit (full curve) at a pressure of 6 kbar.

values, but a deviation from the proposed Curie–Weiss law is observed because of the high magnetic field applied ($H = 80$ kG) whose saturation effect becomes appreciable at low temperatures.

For $T = 0$ we get $n'(0) = 0.44$, a Ce valence of $v'(0) = 3.56$ and $\chi'_{\text{Ce}}(0) = 0.87 \times 10^{-3} \text{ EMU mol}^{-1}$, which means a ratio of $\Delta\chi(0)/\Delta p = 20 \times 10^{-6} \text{ EMU mol}^{-1} \text{ kbar}$.

2.2. Transport properties

2.2.1. Electrical resistivity. The resistivity (ρ) of CeSn_3 was measured in the temperature range between 4 K and 300 K, giving similar results to those of the previous work of Stalinski *et al* (1973). Our purpose was to compare the temperature dependence of ρ with the other physical properties when measured in the same sample.

In figure 6 the raw data for CeSn_3 is shown together with the difference in the values for LaSn_3 , to show how the Ce valence change enhances the resistivity.

At room temperatures we get $\rho_{300} = 35 \mu\Omega \text{ cm}$ and at low temperatures there is a residual resistivity of $\rho_{4.2} = 0.7 \mu\Omega \text{ cm}$, similar to that of LaSn_3 .

Although there is no reliable theoretical description of the valence effect on the electrical resistivity, we can make a qualitative comparison of $d(\Delta\rho)/dT$ with dn/dT as a function of T where $\Delta\rho = \rho(\text{CeSn}_3) - \rho(\text{LaSn}_3)$. In figure 8 we show values of $d(\Delta\rho)/dT$ and dn/dT where a clear maximum for both relations is seen to appear at around 100 K.

Another qualitative comparison can be made if we consider the rise of ρ produced by the increment of the Ce magnetic moment. The coupling between the spin of the 4f electron and the conduction electron should give a magnetic resistivity contribution of the form:

$$\rho_m = A n_i.$$

n_i is generally connected with the magnetic impurity concentration, in this case $n_i \equiv n(T)$ describes the experimental behaviour.

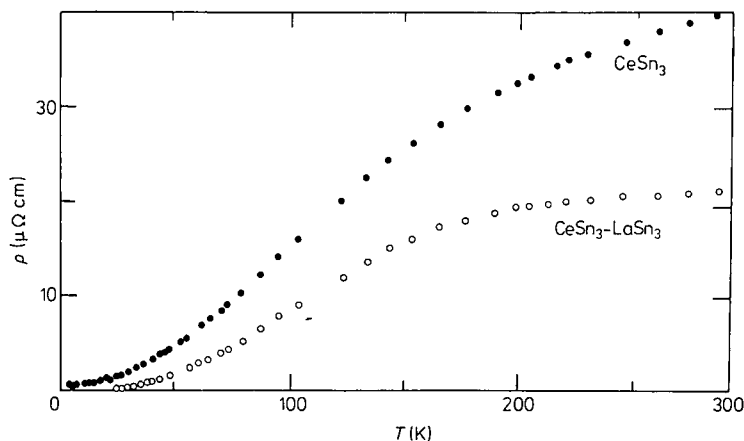


Figure 6. Measured electrical resistivity of CeSn_3 over the range 4.2 K to 300 K (●) and the difference from the reference sample of LaSn_3 (○).

2.2.2. *Thermopower.* For the thermopower we refer to the measurements made on another sample (Cooper *et al* 1971) also prepared by G Olcese. Here again the lack of a theoretical description prevents a qualitative comparison. However, we note the coincidence between the temperature of the maximum thermopower value and $E_{\text{ex}} - \Delta = 230$ K (see figure 7). This makes sense if we consider the Seebeck coefficient (S) as a measure of the change in the density of states (see equation (7a) below), which reaches a maximum at $E_{\text{ex}} - \Delta$. The large values observed allow us to consider S as due only to diffusion effects (S_{D}).

Assuming that the 's' density of states is approximately constant and the mean free path is inversely proportional to the 'f' density of states (D_f), we obtain

$$S_{\text{Df}} = -\frac{\pi^2 k_{\text{B}}^2}{3|e|} \left(\frac{\partial}{\partial E} \ln D_f(E) \right)_{E=E_f} \quad (7a)$$

(e being the electron charge) for $k_{\text{B}}T \ll \Delta$ and E_{ex} (Barnard 1972, equation (6.6)).

Using a Lorentzian density of states of width Δ and centred at E_{ex} , we obtain (in $\mu\text{V K}^{-1}$):

$$S_{\text{D}}(T) = \frac{2\pi k_{\text{B}}^2 T}{3e} D(E)^{-1} \frac{E_{\text{ex}} \Delta}{(E_{\text{ex}}^2 + \Delta^2)^2} = 0.2 T \quad (7b)$$

which is compared with the low-temperature experimental values also seen in figure 7.

2.3. Thermal properties

2.3.1. *Thermal expansion.* The thermal expansion coefficient (α) at temperatures between 1.2 K and 300 K was measured in our sample by Pott and Schefzyk (1979) using the capacitance method, and compared with that of LaSn_3 in order to obtain the contribution due to the Ce valence change as a function of temperature (see figure 8):

$$\alpha_{\text{v}}(T) = \alpha(\text{CeSn}_3) - \alpha(\text{LaSn}_3).$$

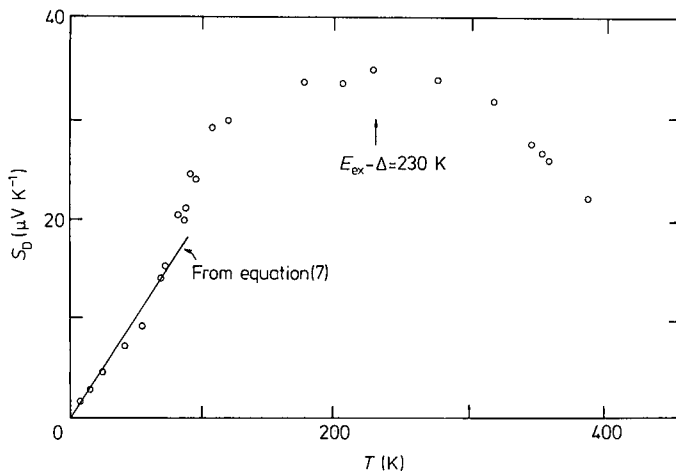


Figure 7. CeSn_3 thermopower over the range 4.2 K to 400 K (after Cooper *et al* 1971). Note the coincidence of $E_{\text{ex}} - \Delta = 230$ K with the temperature of the maximum and the initial slope with the value obtained in equation (7a) (see the text).

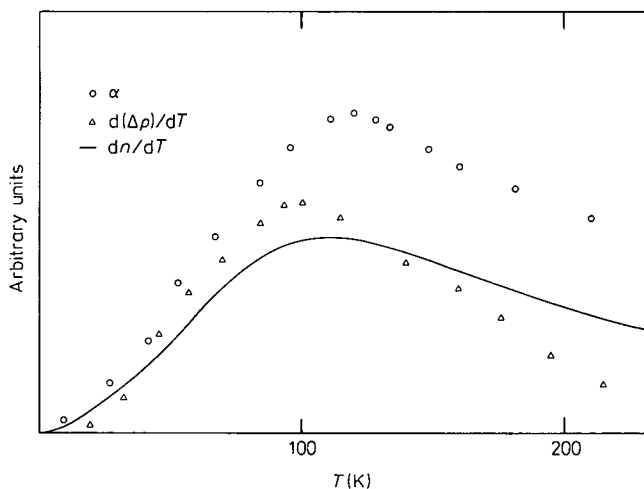


Figure 8. Thermal expansion (O), derivatives with respect to the temperature of the Ce valence contribution to the electrical resistivity (Δ) and the calculated derivative with respect to the temperature of the occupation number (full curve) versus temperature.

As this compound has the cubic structure Cu_3Au , one can write $\alpha_v(T) = L^{-1} d(\Delta L)/dT$, where ΔL is the observed expansion and L the sample length. If we suppose that ΔL is due only to the Ce change of valence (the Sn thermal expansion was subtracted using the data for LaSn_3), only one half of the atoms contribute to ΔL , and then

$$\Delta L(T) = \frac{1}{2} \Delta n(T) (L^{3+} - L^{4+}). \quad (8)$$

The factor $(L^{3+} - L^{4+})$ can be obtained considering the Ce ionic radius (r^i) in both ionic states (i.e. $r_1^{3+} = 1.034 \text{ \AA}$ and $r_1^{4+} = 0.94 \text{ \AA}$, Olcese 1969) as illustrated in figure 9. For the lattice parameter (a) we obtain $a^{3+} = 4.740 \text{ \AA}$ and $a^{4+} = 4.675 \text{ \AA}$, and taking

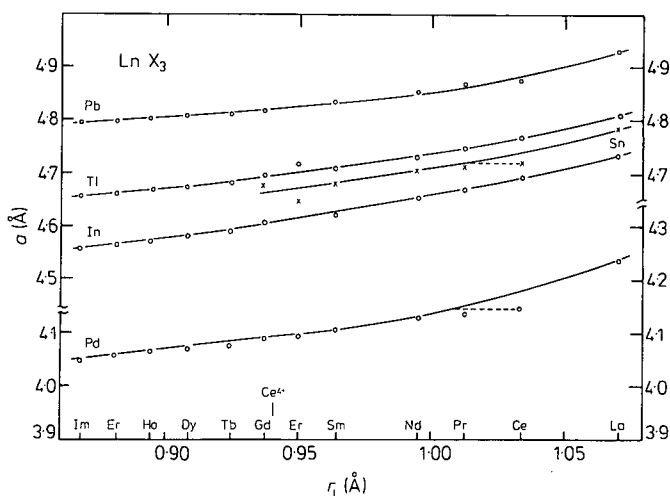


Figure 9. The lattice parameter of La compounds with crystal structure Cu_3Au versus 3^+ ionic radius and Ce^{4+} ionic radius (after Olcese 1969).

$L = aN$ we finally get $(L^{3+} - L^{4+}) = 0.065 N \text{ \AA}$ (N being number of cells). $\Delta n(T)$ between 1.2 K and 300 K has been evaluated in §2.1.2 to give 0.29, which results in $\Delta L = 9.42 \times 10^{-3} \text{ \AA}$. This value is in very good agreement with the measured value of $\Delta L = 9.87 \times 10^{-3} \text{ \AA}$.

2.3.2. *Specific heat.* The low-temperature specific heat can be evaluated as $C_v = \gamma T$, with

$$\gamma = \frac{1}{3} N \pi^2 k_B^2 (\delta(E_f) + D(E_f)) \quad (9)$$

where $\delta(E_f)$ is the conduction band density of states and $D(E_f)$ the broadened 'f' level contribution, both at the Fermi energy.

From $LaSn_3$ we have $\frac{1}{3} N \pi^2 k_B^2 \delta(E_f) = 10.96 \text{ mJ K}^{-2} \text{ mol}^{-1}$ (Bucher *et al* 1968). The f level contribution (in $\text{mJ K}^{-2} \text{ mol}^{-1}$) is (using the values obtained in §2.1.2)

$$\frac{N \pi^2 k_B^2}{3} D(E_f) = \frac{N \pi^2 k_B^2}{3} \frac{(2J + 1)\Delta}{\pi(E_{ex}^2 + \Delta^2)} = 45.06.$$

Substituting into equation (9) we have $\gamma = 56 \text{ mJ K}^{-2} \text{ mol}^{-1}$. This value has to be compared with the experimental one, also measured by Cooper *et al* (1971), who obtained $\gamma = 53 \text{ mJ K}^{-2} \text{ mol}^{-1}$, again in very good agreement with our results.

3. Discussion of results

An accurate analysis of χ as $T \rightarrow 0$ reveals the following points.

(i) The enhancement of χ is essentially due to impurity effects and is not related to the valence of Ce, and the remanent susceptibility: $\chi_{meas} - \chi_{imp} = \chi_{Ce}(0) + \chi_0$, has zero slope in accordance with the third law of thermodynamics.

(ii) The temperature-independent term χ_0 , has no clear origin. There are probably two causes; the band Pauli-like paramagnetism and a Van Vleck contribution due to the first L-S Ce excited level with $J = 7/2$. This means that $\chi_0 = \chi_\rho + \chi_{vv}$ (the Sn contribution is not considered because it is two orders of magnitude smaller). Taking $\chi_\rho = N \mu_B^2 \delta(E_f) = \mu_B^2 (3/\pi^2 k_B^2) \gamma$ we have (using the γ of $LaSn_3$): $\chi_0 = 0.15 \times 10^{-3} \text{ EMU mol}^{-1}$, which is similar to χ_0 . The calculated Van Vleck contribution is $\chi_{vv} = 0.25 \times 10^{-3} \text{ EMU mol}^{-1}$. This can explain the χ_0 value at normal pressure but it does imply a very large dependence of the position of the $J = 7/2$ level with pressure.

It remains an open question as to whether some contribution due to the Stoner enhancement from the two 5d electrons of the band exists.

We have obtained a pressure dependence of E_{ex} of $\Delta E_{ex}/\Delta p = 15 \text{ K kbar}^{-1}$, smaller than the 42.53 K bar^{-1} value proposed for pure Ce (Alascio *et al* 1972). In a previous work (Sereni *et al* 1979) we proposed a general relation between the Ce ionic radius and E_{ex} , valid for a number of cubic compounds. This relation allows us to evaluate a sort of compressibility factor for Ce (in bar^{-1}) as follows:

$$\chi_{Ce} = r_i^{-1} (\Delta r_i / \Delta p) = r_i^{-1} (\Delta r_i / \Delta E_{ex}) (\Delta E_{ex} / \Delta p) = 0.4 \times 10^{-6}$$

which results in a value smaller than that measured on $CeSn_3$ by Beille *et al* (1977), namely $2.3 \times 10^{-6} \text{ bar}^{-1}$, but clearly of the same order of magnitude.

We conclude from this work that a number of thermodynamic properties of $CeSn_3$ can be compared successfully with the predictions of a very simple model which has already been applied to pure Ce (Alascio *et al* 1973). The theoretical model emphasises

the local picture, considering the sample as an aggregate of f level ions hybridised with conduction electrons.

The temperature dependence of the Ce valence has been shown as being able to be described by only two parameters: E_{ex} and Δ .

Acknowledgments

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