

## The effect of pressure on the magnetic susceptibility of $\text{CeIn}_{3-x}\text{Sn}_x$ alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 6921

(<http://iopscience.iop.org/0953-8984/9/32/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 09:21

Please note that [terms and conditions apply](#).

## The effect of pressure on the magnetic susceptibility of $\text{CeIn}_{3-x}\text{Sn}_x$ alloys

G E Grechnev<sup>†</sup>, A S Panfilov<sup>†</sup>, I V Svechkarev<sup>†</sup>, A Czopnik<sup>‡§</sup>, W Suski<sup>‡</sup> and A Hackemer<sup>‡</sup>

<sup>†</sup> B Verkin Institute for Low Temperature Physics and Engineering, 47 Lenin Prospekt, Khar'kov 310164, Ukraine

<sup>‡</sup> W Trzebiatowski Institute of Low Temperature and Structure Research, PO Box 937, 50-950 Wrocław 2, Poland

Received 11 April 1997

**Abstract.** A transition from the Kondo state to an intermediate-valence state takes place in the quasibinary alloys  $\text{CeIn}_{3-x}\text{Sn}_x$  with cubic  $\text{AuCu}_3$ -type structure. The effect of pressure  $P$  up to 2 kbar on the magnetic susceptibility  $\chi$  of this system was measured at 78, 150, and 295 K. The value of  $d \ln \chi / dP$  obtained is well above those observed for similar RE compounds with stable valences. This derivative tends to decrease with temperature, and to increase (but not monotonically) with the tin content  $x$ . The experimental data on  $d \ln \chi / dP(x, T)$  were analysed in terms of the changes in the spin-fluctuation temperature  $T_{\text{sf}}$ .

### 1. Introduction

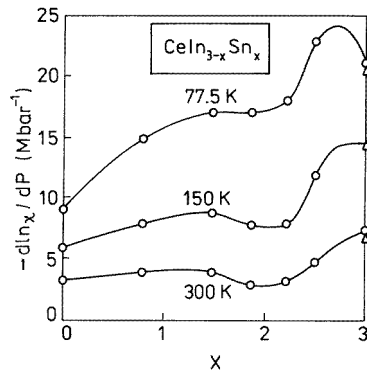
The magnetic susceptibility,  $\chi_f$ , of the rare-earth ions in metallic compounds provides information concerning the parameters of magnetic moment interactions with band electrons. These interactions occur either through an effective f-(spd) exchange,  $J$ , or through a splitting due to the crystal-field (CEF) interactions,  $\Delta_c$ . For favourable relationships of the above-mentioned quantities, these parameters can be determined from the temperature dependence of the magnetic susceptibility:  $\chi_f(T) = \chi_f(J, \Delta_c, T)$ . The effect of pressure on the magnetic susceptibility allows one to find a relation between the atomic volume and the above-mentioned parameters, which is important for the explanation of their microscopic nature. Therefore, we decided to investigate the temperature dependence of the magnetic susceptibility of the  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys under pressure.

The particular importance of the quasibinary solid solutions of the  $\text{CeIn}_{3-x}\text{Sn}_x$  type with the cubic  $\text{AuCu}_3$ -type structure results from an observation that, in these alloys, according to the composition, a magnetic state or nonmagnetic Kondo lattice can exist, accompanied by continuous transformation into the intermediate-valence (IV) state (see e.g. [1, 2]). It is assumed that the threshold of the transformation corresponds to  $x = 2$  (see e.g. [3]), and according to [4] it is very sensitive to the applied pressure. Generally, the electronic properties of this system also show a strong dependence on the pressure [5]. In this paper, we report on measurements of the magnetic susceptibility under pressure up to 2 kbar, and the results are discussed in terms of the changes in the spin-fluctuation temperature,  $T_{\text{sf}}$ .

§ Author to whom any correspondence should be addressed; e-mail: czopnik@highscreen.int.pan.wroc.pl.

## 2. Experiments

The binary compounds  $\text{CeIn}_3$  and  $\text{CeSn}_3$  and their solid solutions were prepared by melting the stoichiometric quantities of the components in an arc furnace under a protective argon atmosphere. The purity of the starting materials was 4N for Ce, and 6N for In and Sn. The melting was followed by a prolonged annealing for eight days at 600 °C in vacuum. The samples have the following compositions:  $x = 0, 0.79, 1.48, 1.86, 2.21, 2.50,$  and  $3.0$ . The temperature dependences of their magnetic susceptibilities were examined over the temperature range  $T = 4.2\text{--}300$  K by the Faraday method in comparison with previous results [1, 6]. Since the agreement is very good, we do not show the data here.



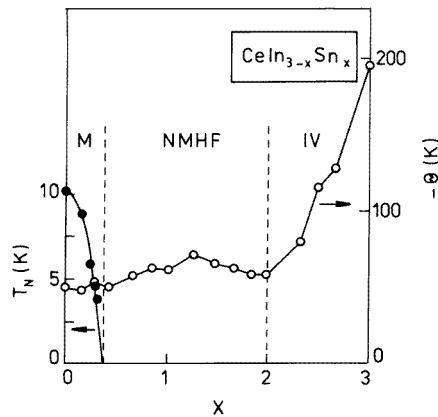
**Figure 1.** Changes in the magnetic susceptibility under pressure presented in the form of the derivatives  $d \ln \chi / dP$  versus the Sn concentration,  $x$ , for the  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys at different temperatures. The circles denote the present results (the error in the measurements does not exceed 10%), whereas the triangles represent the results of [8].

The magnetic susceptibility,  $\chi$ , was measured under pressure up to 2 kbar, produced using helium gas at 78, 150, and 300 K, with the help of a pendulum magnetometer located directly in a high-pressure cell [7]. The relative error of the experiment does not exceed 0.05%. The magnetic susceptibility of all of the samples investigated depends linearly on the applied pressure. The results are presented in figure 1 as the derivatives  $d \ln \chi / dP$ . The agreement of the present data with those obtained earlier for  $\text{CeSn}_3$  [8–10] is satisfactory. The results of [11], differing by an order of magnitude, are apparently erroneous. Although the single reported value of  $d \ln \chi(0) / dP = -12 \text{ Mbar}^{-1}$  for  $\text{CeIn}_3$  [12] is for the antiferromagnetic state, it is in reasonable agreement with the data resulting from figure 1, where the temperature dependence of this derivative is shown.

## 3. Results and discussion

As follows from figure 1, the derivatives  $d \ln \chi / dP$  increase with the decrease of temperature and with the increase of the Sn concentration,  $x$ . The concentration dependence is nonmonotonic, but exhibits an apparent minimum close to  $x = 2$ , and more pronounced curvature for  $x > 2$ , where the temperature dependence of the magnetic susceptibility is weaker. The average size of the pressure effects on magnetic susceptibility of the  $\text{CeIn}_{3-x}\text{Sn}_x$  is clearly larger than that detected for the compounds with stable magnetic moments (e.g. for  $\text{GdIn}_3$ ,  $d \ln \chi / dP = -2 \text{ Mbar}^{-1}$  at 78 K [7]).

The magnetic ( $T, x$ ) phase diagram of the quasibinary  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys is presented



**Figure 2.** The magnetic  $(T, x)$  phase diagram of the  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys. The meaning of the notation is: M—the magnetic Kondo state; NMHF—the nonmagnetic heavy-fermion state; and IV—the intermediate-valence state. Open circles correspond to the paramagnetic Curie temperature  $\Theta$ , and full circles correspond to the Néel temperature  $T_N$ .

in figure 2 [1, 2], and shows the sequence of development of the valence instability, in full agreement with existing theoretical prediction. In the range  $0 \leq x \leq 0.4$ , the alloys are dense Kondo systems, with antiferromagnetic order at low temperature. In this range, with the increase of the Sn concentration, the RKKY-type exchange interaction between the localized magnetic moments is replaced by the Kondo mechanism of demagnetization of these moments by the band electrons. In the concentration range  $0.4 \leq x \leq 2$ , the nonmagnetic heavy-fermion state (NMHF) develops, with a high value of the coefficient of electronic specific heat,  $\gamma$ , which reaches the maximum value  $\gamma = 240 \text{ mJ mol}^{-1} \text{ K}^{-2}$  [13] at  $x = 2$ , where a weakly marked intermediate-valence state appears (range:  $2 \leq x \leq 3$ ). At the same time, inelastic neutron scattering experiments [14] show that the growth of the Sn content  $x$  is accompanied by the collapse of the CEF splitting beyond  $x = 1$ , due to crossover with the Kondo energy increase.

Although in the x-ray absorption Ce  $L_{\text{III}}$  spectra the difference between the valences in  $\text{CeIn}_3$  and  $\text{CeSn}_3$  is not detectable (see table 1, where we collect together the data useful for further discussion of these compounds), the above-mentioned transition is reflected in a transformation of the electrical characteristics [4, 5, 16] and in a deviation of the lattice parameters of the alloys from Vegard's law (table 1). This transition is accompanied by a diminution of the electronic specific heat [13], and by a pronounced increase of the paramagnetic Curie temperature,  $\Theta$  (figure 2), which follows from the high-temperature approximation of the experimental dependencies  $\chi(x, T)$  by the Curie–Weiss law  $\chi(x, T) = C(x)/[T - \Theta(x)]$  [1].

The effect of pressure on the phase diagram presented in figure 2 is qualitatively equivalent to increase of the Sn concentration  $x$  [4, 15]. It seems that establishing some quantitative relationship between  $P$  and  $x$  does not have much value. First, the behaviour of the bulk modulus  $B(x)$  in this system is unknown, and its values for the two binary compounds show large discrepancies (see table 1). Moreover, in the development of the valence instability of the  $\text{CeIn}_{3-x}\text{Sn}_x$  system, there is competition among various mechanisms. In particular, negative ‘chemical’ pressure in the system (table 1) apparently contracts in response to this process, shifting the phase boundary towards higher  $x$  (it may be that in the  $\text{CePb}_3$  compound, which is isoelectronic with  $\text{CeSn}_3$ , the intermediate-valence

**Table 1.** Physical characteristics of CeIn<sub>3</sub> and CeSn<sub>3</sub> compounds. The notation is as follows:  $\Omega$ —the molar volume;  $B$ —the bulk modulus;  $v$ —the valence;  $\gamma_e$ —the electronic specific heat coefficient;  $\Delta_c = E(\Gamma_8) - E(\Gamma_7)$ —the crystal-field splitting;  $\Theta$ —the paramagnetic Curie temperature;  $T_N$ ,  $T_K$ , and  $T_{sf}$ —the Néel, Kondo, and spin-fluctuation temperatures, respectively; and  $G_i = \partial \ln E_i / \partial \ln V$ —the Grüneisen parameter. The indices X, n, h, s, r, and m denote x-ray, neutron, thermal, ultrasound, resistivity, and magnetic data, respectively.

Characteristics	CeIn <sub>3</sub>	Reference	CeSn <sub>3</sub>	Reference
$\Omega$ (nm <sup>3</sup> ) (300 K)	0.1031	[1, 4]	0.1053	[1, 4]
	(78 K) 0.1019	[4]	0.1036	[4]
$d \ln \Omega / dx$ (10 <sup>-3</sup> )	8.1	[1, 4]	4.2 (300 K)	[4]
			$\cong 0$ (78 K)	[4]
$B$ (Mbar)	0.54 <sub>s</sub>	[33]	0.54 <sub>s</sub>	[34]
	0.77 <sub>X</sub>	[35]	0.48 <sub>X</sub> ( $x = 2.7$ )	[35]
	0.67 <sub>X</sub>	[36]	0.43 <sub>X</sub>	[10]
	0.59 <sub>n</sub>	[15]		
$v$	3.02 <sub>X</sub>	[15]	3.02 <sub>X</sub>	[37]
$\gamma_e$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	62	[13]	65	[13, 23]
	140	[12, 33]	60	[38]
	60	[39]	55	[17]
			53	[40]
$G_e$	7 <sub>r</sub>	[15]	7 (78 K)	[34]
$\Delta_c$ (K)	150 <sub>n,s</sub>	[41, 42]	< 35	[42]
	120 <sub>n</sub>	[43]	66 <sub>h</sub>	[17]
	100	[44]		
	$\approx T_K$	[15]		
$-\Theta$ (K)	50	[1]	195	[1]
$T_N$ (K)	10.0–10.2	[1, 41]	—	
$G_m \equiv G_N$	$\approx -2_{h,r,n}$ ( $P = 0$ )	[15]	—	
$T_K$ (K)	$\leq 10_n$	[2]	75 <sub>h</sub>	[17]
	100	[33]	200	[38]
$T_{sf}$ (K)	< 100 <sub>n</sub>	[41, 2]	200 <sub>m</sub>	[1, 8, 45]
	$\approx 90_{m,X}$	[45]	$\approx 260_n$	[2]
$G_{sf}$	—		7.6 <sub>m</sub>	[8]

state is not formed [17], because of the larger molar volume:  $\Omega(\text{CePb}_3)/\Omega(\text{CeSn}_3) = 1.1$  [18]). As was mentioned previously, a deviation from a linear  $\Omega(x)$  dependence is observed for  $x > 2$ , and thus the same relation,  $x/P$ , does not hold for the whole system [4].

Now, the magnetic susceptibility under pressure will be discussed. At first, it was assumed, as in the papers [7, 19, 20], that it is possible to adjust an adequate theoretical model,  $\chi_f[Y_i(x), T]$ , with the experiment, for selected  $x$ -values with suitable  $Y_i$ -parameters. Then, using the measured magnetovolume effect,  $d \ln \chi / d \ln V \cong d \ln \chi_f / d \ln V$ , and the corresponding computed partial derivatives,  $\partial \ln \chi_f / \partial Y_i$ , for certain temperatures  $T_j$ , one can determine the unknown values  $d \ln Y(x) / d \ln V$  from the set of equations (where  $i \leq j$ )

$$\sum_i \left[ \frac{\partial \ln \chi_f(T_j)}{\partial Y_i} \right] \frac{d \ln Y_i}{d \ln V} = \frac{d \ln \chi(T_j)}{d \ln V}. \quad (1)$$

Furthermore, it will be shown that the fulfilling of this program for a selected system is

complicated by many unexpected factors, and the lack of additional pieces of information.

In previous papers, various approaches were used for determination of the contribution of the f states,  $\chi_f$ , to the magnetic susceptibility of the compounds discussed, depending on the type of interaction of these states with band electrons. For example, De Gennaro and Borchì [21] have reported equations for  $\chi_f(T) = \chi_f(T, D, s, \Delta_c)$  for cerium in the Kondo region, with the presence of a CEF (here  $s = JN_F$ , where  $N_F$  is the electron density of states at the Fermi level, and  $D$  is the effective width of the conduction band). By means of a fitting of the corresponding parameters and the value of the RKKY indirect interaction, the experimental  $\chi(T)$  dependence for  $CeIn_3$  has been described [22]. In an analogous procedure for  $CeSn_3$  [11], the relation  $\chi_f(T) = \chi_f(T, E_{ex}, \Delta)$  was used, which was obtained for an intermediate-valence region in terms of the interconfigurational excitation energy,  $E_{ex}$ , and the hybridization width of the f level,  $\Delta$  (in this range, the CEF effects are strongly suppressed). Note that  $J = -V_{fc}^2/E_{ex}$ , and  $\Delta = \pi V_{fc}^2 N_F$  ( $V_{fc}$  is the matrix element of the mixing of the f level with the band states), and thus  $s \approx \Delta/E_{ex}$ . Therefore, both approaches operate using the same set of important energy parameters, but their numerical consistency in the region of the Kondo–IV state transition had not been checked.

The results of the parameter fits for the models mentioned are very sensitive to the details of the  $\chi_f(T)$  function. So their reliability depends on the accuracy of the extraction of this function from the experimental  $\chi(T)$  data (if one ignores the correctness—or otherwise—of the models applied). Unfortunately, due to the antiferromagnetic interaction, and the low value of the Ce moments, particularly in the Kondo and the intermediate-valence states, the non-f-electron contribution to the magnetic susceptibility in the materials discussed is quite substantial. There is no simple way to get rid of it.

Usually [1, 6], for  $\chi_f(T)$  the following expression can be used:

$$\chi_f(x, T) = \chi(x, T) - \chi_{La}(x, T) - \chi_{CW}. \quad (2)$$

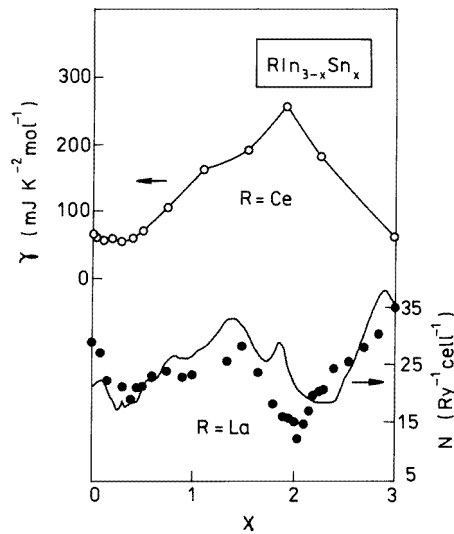
According to [1, 23], at low temperature the Curie–Weiss term  $\chi_{CW} = nC/(T - \Theta)$  results, in this system, from structural defects of the lattice, and for compositions close to  $x \approx 3$ , from an admixture of  $Ce_2Sn_5$  phase, which stabilizes a small number of Ce atoms in the form of the  $Ce^{3+}$  impurity. The number  $n$  of these ‘admixed’ atoms is different in different samples, and can reach up to 2%. Their contribution to the magnetic susceptibility ranges up to  $0.1\chi$  at  $T = 78$  K and  $x \approx 3$  [8, 23]. Their insensitivity to pressure is a favourable feature [8].

The background susceptibility (non-f-electron) contribution to equation (2), which contains the susceptibility of the conduction electrons and closed shells, is represented by  $\chi_{La}(x, T)$ , the magnetic susceptibility of the  $LaIn_{3-x}Sn_x$  alloys. This is the ‘nonmagnetic’ analogue of the system under consideration. Corresponding values of  $\chi_{La}(x, T)$  are given in [1, 24], and their magnitude is  $0.1\chi$  at  $T = 300$  K. The electronic part of the  $\chi_{La}(x, T = 78$  K) contribution exhibits clear oscillations with the considerable amplitude of  $\approx 3 \times 10^{-4}$  emu mol $^{-1}$  [1], and the extrema are strongly attenuated by temperature (by almost a factor of 1.5 in the 78–300 K range).

The maxima of the magnetic susceptibility in the  $LaIn_{3-x}Sn_x$  alloys can be connected with the enhanced Pauli paramagnetism, in qualitative agreement with the behaviour of the density of states (DOS) curve which follows from both experiment [24] and the  $N_F(x)$  calculation. Figure 3 shows the dependence

$$N_F(x) = (1 - x)N_F(q)(LaIn_3) + xN_F(q)(LaSn_3)$$

where  $q$  is the average valence of the alloy atoms, and the functions  $N_F(q)$  for  $LaIn_3$  and  $LaSn_3$  are calculated using the scalar relativistic LMTO-LDA method like in [25],



**Figure 3.** Coefficients of the electronic specific heat,  $\gamma$ , versus the Sn concentration,  $x$ , for  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys (upper part), and experimental (full circles) and calculated (thin line) values of the density of states,  $N_F$ , versus  $x$  for the  $\text{LaIn}_{3-x}\text{Sn}_x$  alloys (lower part).

including the f levels in the core states. Although the applied expression is simplified and does not include disorder effects in alloys, the result provides the magnitudes and the locations of the singularities of the experimental DOS in the  $\text{LaIn}_{3-x}\text{Sn}_x$  system fairly well (see figure 3). However, the corresponding modulation of the spin paramagnetism is far from the magnitude of the observed modulation of the magnetic susceptibility. Such a modulation, with deep diamagnetic anomalies, can be related to the orbital contribution [24]. Actually, in the general expression for the orbital magnetic susceptibility of the electrons in the lattice, together with the well known Landau–Peierls contribution there exist interband contributions of arbitrary sign [26]. Anomalous diamagnetism of the magnitude observed can be expected only when the Fermi level is located close to some points of degeneracy of the sp bands, where the magnetic susceptibility appears to diverge [27]. This is why deep and clear anomalies of the diamagnetic susceptibility are preserved in concentrated solid solutions, and at sufficiently high temperatures [28]. The correctness of the assumption about the nature of the diamagnetic anomalies in  $\text{LaIn}_{3-x}\text{Sn}_x$  alloys is confirmed by the accompanying anomalies in the thermoelectric power [24], which have similar sensitivity to the points of degeneracy of the bands [29].

From the calculations performed, and from those known from other papers [30], it follows that, at least on the symmetry lines  $\Gamma\Delta X$  and  $\Gamma\Delta R$  in the spectra of the compounds considered, there are the points of degeneracy for favourable levels of the band filling. Which of them are related to the observed diamagnetism should be analysed in a detailed way, separately.

Although the minima of the DOS correspond fairly well to those compositions for which anomalies of the diamagnetism exist [24], they have no direct relationship to the degeneracy. Even several equivalent points of degeneracy resulting from the symmetry of the lattice, as one of the conditions of strong diamagnetism, have a weak influence on the total DOS.

The spectra of the spd states of the compounds discussed do not follow the rigid-band model (see also [25]). Therefore, differences in location of the peaks of the DOS and the

points of degeneracy of the bands in the  $LaIn_{3-x}Sn_x$  and  $CeIn_{3-x}Sn_x$  systems are possible, enhanced by distinctions in the f–(spd) hybridization. This can give rise to errors that are hard to estimate in the evaluation of the  $\chi_f(x, T)$  contribution using equation (2).

Large pressure effects need the introduction of the corrections in  $\chi_f(T)$  (up to  $0.2\chi$ ) corresponding to the thermal expansion of the lattice, which has not been investigated in detail up to now. Finally, an assumption natural in common cases that  $d \ln \chi / dP \approx d \ln \chi_f / dP$  does not go undisputed for the systems considered. The magnitude of the background contribution to the  $d \ln \chi / dP$  derivative can appear to be of the same order as  $\chi_f$ , due to the sharpness of the modulation of  $\chi_{La}(x)$  (if it is preserved under the influence of the f–(spd) hybridization), and the significant shift of the Fermi level relative to the points of degeneracy, which follows from the electron transfer under pressure from the d to the sp band [25].

In this paper, we are forced to use the derivatives with respect to pressure, and not those with respect to volume, because the behaviour of the bulk modulus in the  $CeIn_{3-x}Sn_x$  system is unknown.

It may appear simpler to correct the values of the parameters found from  $\chi_f(T)$  than to perform a detailed analysis of the errors in the evaluation of  $\chi_f(T)$  and  $d\chi_f/dP$ . However, consideration of the  $CeIn_3$  case suggests the opposite conclusion. As a whole, the  $\chi(T)$  plot for this compound is explained successfully by the theory [21], with reasonable values of the fitted parameters. At the same time, we were unable to get a satisfactory description for the  $\chi_f(T)$  contribution with any choice of parameters, if just the  $\chi_{La}(300 \text{ K})$  background is taken into account in (2). Therefore, at this stage it is of primary concern to examine the main difficulties associated with the evaluation of the f-state contribution to the susceptibility. This examination can encourage a search for complementary properties, which will help to eliminate all obstacles in the evaluation of  $\chi_f(T)$ .

The facts supplied suggest the necessity of rejection of the sophisticated models given in [11, 21], and, for the time being, application of an empirical description of the susceptibility in terms of the spin-fluctuation temperature. In the paper [1], it has been shown that in  $CeIn_{3-x}Sn_x$  alloys, an effective magnetic moment  $\mu^2(x, T) = \chi_f T / C$  is with high accuracy a universal function of a single variable ( $T/T_{sf}(x)$ ) at  $0.8 \leq x \leq 3$  and  $4 \leq T \leq 350 \text{ K}$ . The susceptibility  $\chi_f$  is here found from expression (2), just with a contribution  $\chi_{La}(x, 300 \text{ K})$  (and for  $CeSn_3$  it is here found from expression (2), just with a contribution  $\chi_{La}(x = 3, T)$ ;  $C = 0.807 \text{ K emu mol}^{-1}$  is the Curie constant of the  $Ce^{3+}$  ion ( $J = 5/2$ )). For  $CeSn_3$ , this universality is preserved at least up to the pressure  $P = 14 \text{ kbar}$  [18] (see also reference [5], where pressure effects are discussed qualitatively for the whole system in terms of the behaviour of a single parameter,  $s = JN_F$ ). Moreover, also for  $CeIn_3$ , considerable deviation from this universality appears only at  $T < 100 \text{ K}$  [1]. Thus, it follows that practically all of the data of figure 1 can be described by the relation

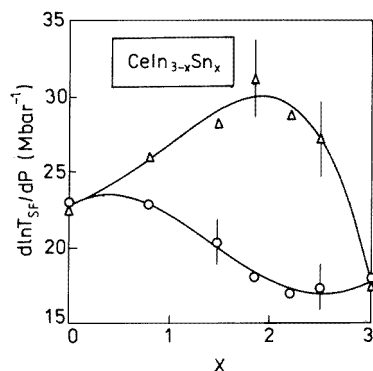
$$\frac{d \ln T_{sf}}{dP} = -\frac{d \ln \chi_f}{dP} \left( 1 + \frac{\partial \ln \chi_f}{\partial \ln T} \right)^{-1}. \quad (3)$$

At high temperatures, where the asymptotic Curie–Weiss law,  $\chi_f = C/(T - \Theta)$ , is followed, equation (3) is equivalent to the relation

$$\frac{d \ln T_{sf}}{dP} = \left( \frac{T}{\Theta} - 1 \right) \frac{d \ln \chi_f}{dP} \quad (4)$$

if  $T_{sf}$  is identical with  $-\Theta$  and  $dC/dP = 0$  due to the proximity of the real Curie constant, and its value for the free  $Ce^{3+}$  ion [1]. For calculation of the derivatives  $d \ln T_{sf}/dP$  according to (3) and (4), the interpolated forms of  $\chi_f(T, x)$  and  $\Theta(x)$  from [1]





**Figure 4.** The derivative  $d \ln T_{sf}/dP$  versus the Sn concentration,  $x$ , for the  $\text{CeIn}_{3-x}\text{Sn}_x$  alloys at different temperatures: circles—for  $T = 300$  K; triangles—averaged values for  $T = 78$  K and  $T = 150$  K. See the text for the explanation.

are used, as also are the derivatives  $d \ln \chi/dP$  from figure 1, assuming at present that  $d \ln \chi/dP = d \ln \chi_f/dP$ . The results are shown in figure 4, where the upper curve corresponds to averaged values at  $T = 78$  K and 150 K (the bars show the scale of the differences between them), and the lower curve corresponds to  $T = 300$  K (these points, obtained from both (3) and (4), are within the sizes of the bars, which represent here the magnitudes of the experimental errors).

One can note several peculiar features in figure 4.

(i) For  $\text{CeIn}_3$ , and for alloys with low concentration  $x$ , as well as for  $\text{CeSn}_3$  [8], the derivative  $d \ln T_{sf}/dP$  does not depend on temperature, in accord with the concept of a single characteristic energy in the  $\text{CeIn}_3$ – $\text{CeSn}_3$  system [1, 8] (neglecting the observation that the temperature dependence of the magnetic susceptibility of the alloys with low  $x$ -values, as was mentioned above, does not correspond fully to this concept).

(ii) An unexpected and intriguing feature is the discrepancy between  $d \ln T_{sf}/dP$  values corresponding to temperatures below 150 K and room temperature, for alloys with  $0.5 \leq x \leq 3$ ; for  $x \approx 2$  the derivatives differ by a factor of about 2.

(iii) At 300 K, the derivative  $d \ln T_{sf}/dP$  decreases relatively slow and monotonically, along with the increase of  $x$  (it might be that with a weak kink at  $x \approx 2$ ), while below  $T \approx 150$  K, the dependence  $d \ln T_{sf}/dP(x)$  exhibits a sharp maximum on the borderline between the NMHF and the intermediate-valence phases (at  $x \approx 2$ ).

It follows from the above-mentioned properties of the derivative  $d \ln T_{sf}/dP$ , that the concept of a single characteristic energy for the  $\text{CeIn}_3$ – $\text{CeSn}_3$  system [1] is not valid. This conclusion corresponds closely to that based on the Néel temperature behaviour for  $\text{CeIn}_3$ – $\text{CeTi}_3$ – $\text{CeSn}_3$ – $\text{CePb}_3$  quasibinary alloys [31] far from the region of Kondo–IV-state transition.

In [15] it is assumed that for  $\text{CeIn}_3$  three energies are comparable:  $\Theta_{\text{RKKY}} \approx T_{\text{K}} \approx \Delta_{\text{c}}$ . Both latter ones,  $T_{\text{K}}$  and  $\Delta_{\text{c}}$ , are distinguished by high values of the Grüneisen parameter [19, 20]. The energy of the indirect f–f exchange can be estimated from the ratio  $\Theta_{\text{RKKY}}/T_{\text{N}} = -2.5$  for several compounds  $\text{RIn}_3$  [22]. The value  $\Theta_{\text{RKKY}} = -25$  K determined is actually close to the observed paramagnetic Curie temperature  $\Theta \approx -T_{\text{sf}}$  (table 1), whereas the usual normalization using the de Gennes factor for these compounds gives  $\Theta_{\text{RKKY}} = -1$  K. Apparently, indirect exchange in  $\text{CeIn}_3$  is substantially enhanced

under the influence of the Kondo effect, which is confirmed also by strong enhancement of the electronic specific heat in comparison to that of  $LaIn_3$  (figure 3). In this situation, it can be expected that the large pressure effect characteristic of the parameters of the Kondo system (e.g. the electronic Grüneisen parameter for  $CeIn_3$ ,  $G_e = 7$  (table 1)) could be expected also for  $\Theta_{RKKY}$ .

Consequently, all types of interaction which participate in the forming of the  $T_{sf}$ -parameter are responsible for its anomalously high sensitivity to the pressure, and the change of their relationships corresponds to the dependence of  $d \ln T_{sf}/dP$  on  $x$  and  $T$ . In particular, for multiplets  $J = 5/2$  split by the CEF, the excitation of all of the degrees of freedom at temperature  $T > \Delta_c$  results in the diminution of the importance of the CEF, and in increase of the Kondo temperature [5, 32]. The substantial temperature dependence of  $d \ln T_{sf}/dP$  is apparent in the region where  $T \approx \Delta_c$ , and disappears, together with the switching-off of the CEF effect in the intermediate-valence state at  $x = 3$ . In further analysis, we will explain the evolution of the ratio of the interaction parameters, and why the complicated composition of the phenomenological parameter  $T_{sf}$  is not reflected in the behaviour of  $\chi_f(T)$  at the temperatures and concentrations used.

Another important feature of the derivative  $d \ln T_{sf}/dP$  is the appearance of a low-temperature singularity on the borderline of the NMHF IV states (see figure 3), where according to current opinion a smooth transformation of the states should be observed [15]. At present, it is unclear whether this singularity appears due to unknown features of the borderlines, or due to singularities of the spd-band DOS curve, which shows a minimum exactly on this borderline (figure 3).

It is our intention to avoid any speculative conclusions. We are planning to return to detailed quantitative analysis of the results as soon as additional characteristics obtained for the systems investigated allow us to introduce the necessary corrections, and take into consideration side effects.

## References

- [1] Lawrence J 1979 *Phys. Rev. B* **20** 3770
- [2] Loewenhaupt M and Fischer K H 1993 *Handbook on the Physics and Chemistry of Rare Earths* vol 16, ed K A Gschneidner Jr and L Eyring (Amsterdam: North-Holland) p 163
- [3] Benoit A, Boucherle J X, Flouquet J, Sakurai J and Schweizer J 1985 *J. Magn. Magn. Mater.* **47+48** 149
- [4] Sakurai J, Hagiwara T, Murakami T, Komura Y, Kadomatsu H, Kurisu H and Fujiwara H 1984 *Solid State Commun.* **50** 71
- [5] Oomi G, Numata T and Sakurai J 1988 *Physica B* **149** 73
- [6] Dijkman W H, de Chatel P F and Aarts J 1980 *J. Magn. Magn. Mater.* **15+18** 970
- [7] Czopnik A, Panfilov A S and Svechkarev I V 1994 *Fiz. Nizk. Temp.* **20** 48 (Engl. Transl. 1994 *Low Temp. Phys.* **20** 39)
- [8] Shaheen S A, Schilling J S, Liu S H and McMaster O D 1983 *Phys. Rev. B* **27** 4325
- [9] Zell W, Keulerz K, Weidner P, Roden B and Wohlleben D 1982 *Valence Instabilities* ed P Wachter and H Boppert (Amsterdam: North-Holland)
- [10] Beille J, Bloch D, Voiron J and Parisot G 1977 *Physica B* **86+88** 231
- [11] Sereni J G 1980 *J. Phys. F: Met. Phys.* **10** 2831
- [12] Benoit A, Boucherle J X, Convert P, Flouquet J, Palleau J and Schweizer J 1980 *Solid State Commun.* **34** 293
- [13] Elenbaas R A, Schinkel C J and van Deudekan C J M 1980 *J. Magn. Magn. Mater.* **15+18** 979
- [14] Murani A P, Taylor A D, Osborn R and Bowden Z A 1993 *Phys. Rev. B* **48** 10 606
- [15] Morin P, Vettier C, Flouquet J, Konczykowski M, Lassailly Y, Mignot J-M and Welp U 1988 *J. Low Temp. Phys.* **70** 377
- [16] Sakurai J, Ohyama T and Komura Y 1985 *J. Magn. Magn. Mater.* **52** 320
- [17] Pillmayr N, Hilscher G, Perthold W, Sakurai J and Horie M 1990 *J. Magn. Magn. Mater.* **90+91** 414
- [18] Buschow K H J 1979 *Rep. Prog. Phys.* **42** 1373

- [19] Panfilov A S, Svechkarev I V and Fawcett E 1993 *Physics of Transition Metals* vol II (Singapore: World Scientific) p 703
- [20] Panfilov A S, Pushkar' Yu Ya and Svechkarev I V 1993 *Fiz. Nizk. Temp.* **19** 96
- [21] De Gennaro S and Borchi E 1974 *Phys. Rev. B* **9** 4985
- [22] Buschow K H J, de Wijn H W and van Diepen A M 1969 *J. Chem. Phys.* **50** 137
- [23] Gschneidner K A Jr, Dhar S K, Stierman R J, Tsang T-W E and McMaster O D 1985 *J. Magn. Magn. Mater.* **47+48** 51
- [24] Toxen A M, Gambino R J and Welsh L B 1973 *Phys. Rev. B* **8** 90
- [25] Grechnev G E, Panfilov A S, Svechkarev I V, Buschow K H J and Czopnik A 1995 *J. Alloys Compounds* **226** 107
- [26] Hebborn J E and Sondheimer E H 1960 *J. Phys. Chem. Solids* **13** 105
- [27] Mikitik G P and Svechkarev I V 1989 *Fiz. Nizk. Temp.* **15** 295
- [28] Grechnev G E and Svechkarev I V 1985 *Fiz. Met. Metalloved.* **60** 723
- [29] Vaks V G, Trefilov A V and Fomichev S V 1981 *Zh. Eksp. Teor. Fiz.* **80** 1613
- [30] Hasegawa A and Yamagami H 1991 *J. Phys. Soc. Japan* **60** 1654
- [31] Rahman S, Timlin J, Crow J E, Mihalisin T and Schlottmann P 1990 *J. Appl. Phys.* **67** 5209
- [32] Maekawa S, Takahashi S, Kashiba S and Tachiki M 1985 *J. Phys. Soc. Japan* **54** 1955
- [33] Gao Q Z, Kanda E, Kitazawa H, Sera M, Goto T, Fujita T, Suzuki T, Fujimura T and Kasuya T 1985 *J. Magn. Magn. Mater.* **47+48** 69
- [34] Takke R, Niksch M, Assmus W, Luthi B, Pott R, Schefzyk R and Wohlleben D 1981 *Z. Phys. B* **44** 33
- [35] Oomi G, Tabata M and Sakurai J 1986 *J. Magn. Magn. Mater.* **54-57** 431
- [36] Vedel I, Redon A M, Mignot J-M and Leger J M 1987 *J. Phys. F: Met. Phys.* **17** 849
- [37] Wohlleben D and Rohler J 1984 *J. Appl. Phys.* **55** 1904
- [38] Umehara I, Kurosawa Y, Nagai N, Kikuchi M, Satoh K and Onuki Y 1990 *J. Phys. Soc. Japan* **59** 2848
- [39] Lin C L, Crow J E, Mihalisin T, Brooks J, Stewart G and Abou-Aly A I 1986 *J. Magn. Magn. Mater.* **54-57** 379
- [40] Cooper J R, Rizzuto C and Olcese G 1971 *J. Physique Coll.* **1** 1136
- [41] Lawrence J M and Shapiro S M 1980 *Phys. Rev. B* **22** 4379
- [42] Endoh D, Goto T, Tamaki A, Liu B, Kasaya M, Fujimura T and Kasuya T 1989 *J. Phys. Soc. Japan* **58** 940
- [43] Lassailly Y, Burke S K and Flouquet J 1985 *J. Phys. C: Solid State Phys.* **18** 5737
- [44] Evans S M M, Bhattacharjee A K and Coqblin B 1991 *Physica B* **171** 293
- [45] Weidner P, Keulertz K, Lohe R, Roden B, Rohler J, Wittershagen B and Wohlleben D 1985 *J. Magn. Magn. Mater.* **47+48** 75