

**Magnetovolume effect in YbAgCu<sub>4</sub>**

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The magnetovolume effect, i.e., the atomic volume dependence of the magnetic susceptibility, has been investigated for the intermediate valence compound YbAgCu<sub>4</sub> in the temperature range of 4.2–300 K. The paramagnetostriction and the pressure dependence of the susceptibility were measured at low and high temperatures, respectively. It is found that the detailed behavior of the susceptibility cannot be explained within the framework of integer valence (Coqblin–Schrieffer model). The Anderson model, which in addition takes into account charge fluctuations, appears to be more appropriate and indicates that the *f*-level energy rather than its width is sensitive to the atomic volume change in YbAgCu<sub>4</sub>.

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**I. INTRODUCTION**

The intermetallic compounds, YbM<sub>4</sub> (*M* = Pd, Ag, Au, Zn, Cd, In, Tl), with the cubic C15b type structure, have Yb *f*-electron states with a large variety of properties ranging from localized levels to hybridized bands.<sup>1–6</sup> Despite numerous investigations, the main conditions and mechanisms of the evolution of the valence instability of the Yb ions are still not clearly understood.

An interesting system to study the origin of the valence instability is the continuous solid solution Yb(Ag–In)<sub>4</sub>. Here one of the end compounds of the alloy series, YbAgCu<sub>4</sub>, has the properties of a classical Kondo system,<sup>1</sup> i.e., the Yb ions follow the behavior of *J* = 7/2 integer-valent Coqblin–Schrieffer (CS) impurities,<sup>7,8</sup> or have properties very close to integer valence.<sup>8</sup> The other end compound of the alloy series, YbInCu<sub>4</sub>, has strong intermediate valence (IV) character in the low temperature phase and undergoes a unique isomorphous first-order phase transition to a heavy fermion state at *T<sub>V</sub>* ≈ 40 K at ambient pressure.<sup>4</sup>

The evolution of the electronic states in these alloys has been a subject of detailed experimental studies.<sup>4,9,10</sup> However, there is a marked disagreement among the data of the magnetic susceptibility,<sup>1,4</sup> and thus there is some uncertainty in the valence state of YbAgCu<sub>4</sub>. The present work is aimed at checking more carefully the valence of YbAgCu<sub>4</sub> and its sensitivity to pressure. For this purpose we study the magnetovolume effect,  $\partial \ln \chi / \partial \ln V$ , in the temperature range of 4.2–300 K. The experimental procedures are described in Sec. II. In Sec. III we present the results of our studies of the temperature and pressure dependence of the magnetic susceptibility, as well as the temperature dependence of the magnetostriction. The data obtained are discussed in Sec. IV in the framework of both the Coqblin–Schrieffer and the Anderson, impurity models. In Sec. V we summarize the results and present the conclusions of the paper.

**II. EXPERIMENTAL PROCEDURES**

A polycrystalline ingot of YbAgCu<sub>4</sub> was prepared from a stoichiometric mixture of elements (3*N*-purity Yb, 5*N*-purity Cu and Ag) by argon arc melting. Samples of appropriate sizes were spark-cut from the ingot after annealing in evacuated quartz tubes at 750 °C for a week.

The temperature dependence of the magnetic susceptibility at ambient pressure was measured by the Faraday method. To study the magnetovolume effect, we measured the magnetostriction in the temperature range of 4.2–150 K and the pressure dependence of the susceptibility at temperatures 78, 149, and 300 K. For the latter, we used a miniature automated pendulum magnetometer, which was placed directly into a high-pressure chamber. Hydrostatic pressure up to 2 kbar was applied to the sample using helium gas. The accuracy of the susceptibility measurement at this condition was better than 0.05%.<sup>11</sup>

The volume magnetostriction,  $\omega(H)$ , is defined from the longitudinal and transverse strains,

$$\begin{aligned} \omega(H) &= V(H)/V - 1 \\ &= \Delta V(H)/V = [\Delta L(H)/L]_{\parallel} + 2[\Delta L(H)/L]_{\perp}, \quad (1) \end{aligned}$$

and was measured by a three-terminal capacitance method in magnetic fields up to *H* = 8 T.<sup>12</sup>

**III. EXPERIMENTAL RESULTS**

The temperature dependence of the susceptibility,  $\chi(T)$ , of YbAgCu<sub>4</sub> is plotted in Fig. 1 together with the data reported in previous articles.<sup>1,4</sup> Our result exhibits a maximum at *T<sub>m</sub>* ≈ 44 K and reproduces well the single-crystal data of

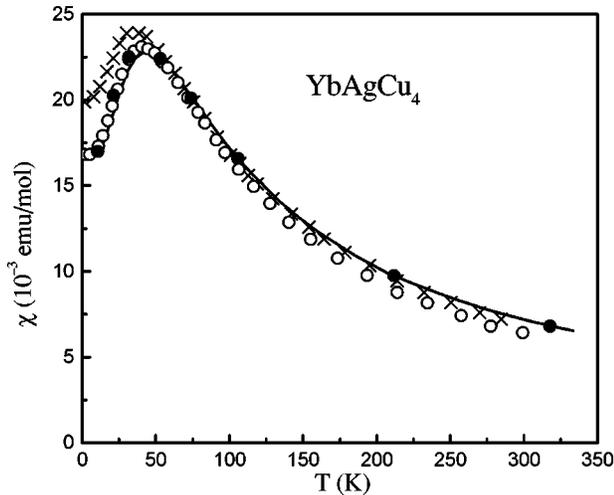


FIG. 1. The temperature dependence of the magnetic susceptibility of YbAgCu<sub>4</sub>. Data from the present work are given by the solid line, crosses represent data from Rossel *et al.* (Ref. 1), open circles are data from Sarrao *et al.* (Ref. 4), and a closed circle corresponds to the AI model fit.

Sarrao *et al.*<sup>4</sup> in the range of 4.2–100 K, but displays a slower decrease at higher temperatures. At low temperatures, both data sets lie appreciably below the curve first reported for YbAgCu<sub>4</sub> by Rossel *et al.*<sup>1</sup> The differences are, however, more quantitative than qualitative and could be the consequence of the sample quality.

Figure 2 illustrates the linear dependence of the magnetic susceptibility with pressure,  $\chi(P)$ , measured at the temperatures 78, 149, and 300 K. The volume magnetostriction,  $\omega(H)$ , defined earlier is proportional to the square of the magnetic field for all the temperatures used.<sup>12</sup> The quantity  $\partial \ln \chi / \partial P$  can be determined (i) from Fig. 2 or (ii) alternatively through the magnetostriction via

$$\frac{\partial \ln \chi}{\partial P} = \frac{\omega}{H^2} \frac{2V}{\chi}, \quad (2)$$

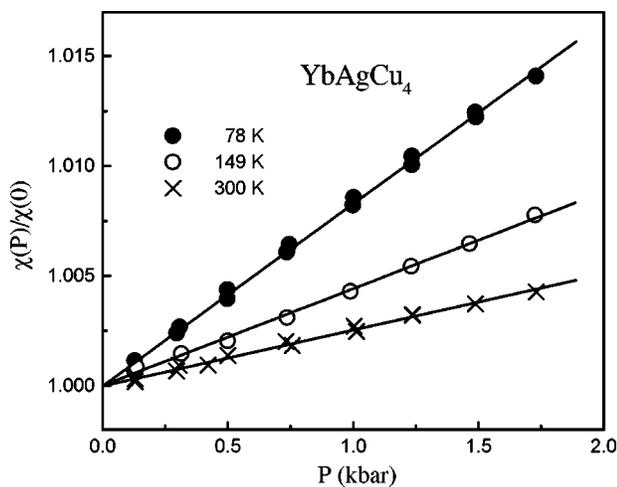


FIG. 2. The pressure dependence of the magnetic susceptibility of YbAgCu<sub>4</sub> at 78, 149, and 300 K.

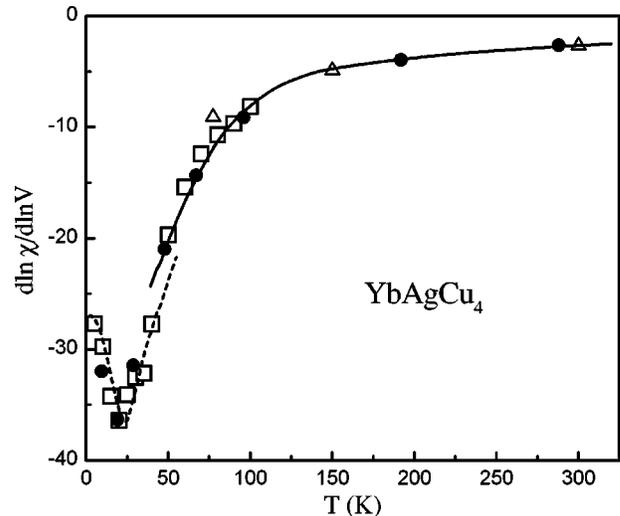


FIG. 3. The temperature dependence of the magnetovolume effect,  $\partial \ln \chi / \partial \ln V$ , of YbAgCu<sub>4</sub> estimated from  $\omega(H)$  (open squares) and  $\chi(P)$  (open triangles). The solid and dashed lines are the CS model with  $\Omega_K = -23$  and  $\Omega_K = -27$ , respectively. Closed circles represent the AI model fit with the parameters listed in Table I.

where  $\chi$  is the molar susceptibility (Fig. 1) and  $V$  is the molar volume ( $= 53.5 \text{ cm}^3$ ). The values of  $\partial \ln \chi / \partial P$  found from  $\chi(P)$  and  $\omega(H)$  were then converted to derivatives  $\partial \ln \chi / \partial \ln V$  [for a discussion of the bulk modulus  $B(T)$  see Sec. IV B] and plotted versus temperature in Fig. 3. They are in reasonable agreement with each other in the overlapping temperature range. The longitudinal magnetostriction data agree well with a previous measurement by Yoshimura *et al.* at  $T = 5 \text{ K}$ .<sup>13</sup> A less detailed version of the paramagnetostriction data has been published in a separate paper<sup>12</sup> in the context of (and in comparison with) other YbMCu<sub>4</sub> compounds.

#### IV. DISCUSSION

Keeping in mind that the properties of YbAgCu<sub>4</sub> are quite close to those of the integer valence limit of magnetic impurities, we will use two strategies to interpret the magnetic susceptibility data.

(1) The thermodynamics of the  $J = 7/2$  Coqblin–Schrieffer impurity model<sup>7</sup> has a universal behavior as a function of only one energy scale, namely the Kondo temperature  $T_K$ . This universality is an important advantage, which allows this model to be used for a rough preliminary interpretation.

(2) The Anderson model for impurities in the intermediate valence regime involves two energy scales, which can be associated with the charge and spin fluctuations, is a more complete (but also more involved) description of the phenomenon.<sup>14–16</sup>

##### A. Temperature dependence of the magnetic susceptibility

*The Coqblin–Schrieffer model:* In the CS model the susceptibility of noninteracting Kondo impurities follows a universal temperature dependence for a given total angular momentum  $J$ ,<sup>7</sup>

$$\chi(T)/\chi(0) = F_J(T/T_K), \quad (3)$$

where  $T_K$  is the characteristic Kondo temperature, the numerical results for the functions  $F_J(x)$  for  $J=1/2, 3/2, 5/2$ , and  $7/2$  are given in Ref. 7, and  $\chi(0)$  satisfies the Fermi liquid relation,

$$\chi(0) = C/T_K, \quad (4)$$

( $C$  is the Curie constant of the trivalent Yb ion). Hence, in the CS limit,  $\chi(T)$  is parametrized by only one energy scale,  $T_K$ ,<sup>7</sup> which for a fully degenerate  $J=7/2$  impurity (no crystalline fields) is given by

$$T_K = D \exp\left(\frac{\pi\varepsilon}{8\Gamma}\right) \equiv D \exp\left(\frac{1}{s}\right). \quad (5)$$

Here  $\Gamma$  is the hybridization width,  $\varepsilon$  is the location of  $f$  level relative to the Fermi energy, and  $D$  is the effective bandwidth. Both  $\varepsilon$  and  $s$  values are negative for YbAgCu<sub>4</sub>.

Although the  $\chi(T)$  data reported in Ref. 1 (and shown in Fig. 1) are well described by Eqs. (3) and (4) with  $T_K = 131$  K, neither our results nor the single-crystal data<sup>4</sup> can satisfactorily be reproduced with such a one-parameter fit. From Eq. (4) the best value of  $T_K$  for our data appears to be 150 K. The main reason for the discrepancy is that the ratio,  $\chi(T_m)/\chi(0) = 1.38$ , markedly exceeds the universal CS model prediction of 1.21.<sup>7</sup> For  $T \geq 100$  K, the susceptibility of YbAgCu<sub>4</sub> is well represented by a Curie–Weiss law,

$$\chi(T) = \frac{C}{T - \Theta}, \quad (6)$$

with an effective magnetic moment in  $C$  of  $\mu_{\text{eff}} = 4.40 \mu_B$ , which is close to  $4.53 \mu_B$  for the free Yb<sup>3+</sup> ion, and a paramagnetic Curie temperature,  $\Theta \approx -39$  K, which agrees with previous estimations (see data collected in Ref. 2). However, the universal behavior of the CS model predicts that  $|\Theta| \approx 0.4 T_K \approx 60$  K,<sup>7</sup> which is about 50% larger than the experimental value.

There are three possible reasons for this disagreement. (i) A crystalline field splitting (CF) of the  $J=7/2$  multiplet would affect more the low  $T$  behavior than the high  $T$  susceptibility, but could effectively reduce the Kondo temperature. However, the overall CF splitting in YbAgCu<sub>4</sub> has been found to be less than  $T_K$ ,<sup>17,18</sup> so that the CF corrections seem to be too small to explain the discrepancy. (ii) The intersite interaction between the Yb-moments mediated by the conduction electrons [Ruderman–Kittel–Kasuya–Yosida (RKKY) type] could renormalize both the Kondo temperature and the Curie–Weiss temperature, as well as reduce the effective magnetic moment. Although there has been no reliable estimation of this contribution for YbAgCu<sub>4</sub>, one can infer from the properties of the compounds surrounding YbAgCu<sub>4</sub> (Refs. 3 and 5) that it should be small (compared to  $T_K$ ) and the correlations are probably of the antiferromagnetic type which can only aggravate the disagreement. From the theoretical point of view, intersite diagrams carry an additional factor  $1/(2J+1) = 0.125$  and are in that sense expected to be less relevant. (iii) Another possible scenario for

TABLE I. Magnetic and electronic parameters of YbAgCu<sub>4</sub> (see the text).

	Parameters	Present work	Previous works
Experiment	$T_m$ (K)	$44 \pm 1$	
	$\chi(T_m)/\chi(0)$	1.38	
	$\Theta$ (K)	-39	-31 <sup>a</sup>
	$\mu_{\text{eff}}$ ( $\mu_B$ )	4.40	4.28 <sup>a</sup>
CS model <sup>b</sup>	$T_K$ (K)	150	131, <sup>a</sup> 150 <sup>c</sup>
	$-\Omega_K$	$27 \pm 1$	18.6 (27.8), <sup>d</sup> $\approx 30^e$
AI model <sup>f</sup>	$\Gamma$ (K)	$510 \pm 50$	516 <sup>g</sup>
	$\varepsilon/\Gamma$	$-9.9 \pm 0.3$	$-9.9^g$
	$\partial \ln \Gamma / \partial \ln V$	$0.5 \pm 1$	
	$\partial \ln(\varepsilon/\Gamma) / \partial \ln V$	$-7.4 \pm 0.3$	

<sup>a</sup>Reference 1.

<sup>b</sup>Reference 7.

<sup>c</sup>Reference 4.

<sup>d</sup>Reference 23.

<sup>e</sup>Reference 12.

<sup>f</sup>Reference 8.

<sup>g</sup>Reference 22.

the discrepancy is *charge fluctuations* in the Yb  $f$  shell, which will be discussed in more detail in the following in the context of Anderson's impurity model. In summary, the CS model is not sufficient to reproduce the details of  $\chi(T)$  in YbAgCu<sub>4</sub>. Nevertheless, the value  $T_K \approx 150$  K appears to be roughly correct, in view of our and previous estimations using different methods.<sup>4,6,17,19–21</sup>

*The Anderson impurity model:* Two energy parameters are of relevance for the degenerate Anderson impurity (AI) model with infinite  $U$ . The infinite Coulomb repulsion prevents the multiple occupation of the  $f$  level, which may then be either empty or occupied with one electron in  $(2J+1)$  possible states. The two energy scales correspond to the spin fluctuations (essentially the Kondo temperature) and the promotion of the  $f$  charge into the conduction band. Hence, the magnetic susceptibility  $\chi(T)$  now depends on two variables:

$$\Gamma \chi(T) = F_J\left(\frac{T}{\Gamma}, \frac{\varepsilon}{\Gamma}\right), \quad (7)$$

where  $\varepsilon$  is the  $f$ -level position measured from the chemical potential,  $A$  [denoted with  $(\varepsilon - A)$  in Ref. 14]. For given  $J$  the thermodynamic properties have been obtained numerically from the thermodynamic Bethe ansatz equations solving the model.<sup>14</sup> In the suitable region,  $F(x, y)$  was calculated as a function of  $\varepsilon/\Gamma$  in steps of 0.3 at eight selected  $T/\Gamma$  values between 0.02 and 0.6.<sup>14,15</sup> These results and the experimental data for  $\chi(0)$ ,  $\chi(T_m)/\chi(0)$ , and  $T_m$  allow, in principle, one to determine the  $f$ -level energy and its hybridization width.<sup>8,14,15</sup> For YbAgCu<sub>4</sub> the theoretical and experimental  $\chi(T)$  data agree closely over the temperature range used (see Fig. 1). The best fits for  $\Gamma$  and  $\varepsilon/\Gamma$  are listed in Table I (they slightly deviate from a previous estimation<sup>8</sup> based on the data of Rossel *et al.*<sup>1</sup>). The corresponding  $f$ -hole occupation number in the ground state,  $n_f(0) = 0.88 \pm 0.01$ , coincides with the experimental one (0.87).<sup>10</sup>

The preexponential factor can now be estimated by substituting the above mentioned values of  $T_K$  and  $\varepsilon/\Gamma$  into the standard expression (5) for the Kondo temperature. We obtain  $D \sim 7300$  K. A more rigorous estimate of  $D$  would involve an additional prefactor [the cutoff introduced *a posteriori* in the Bethe ansatz has to be related to the perturbative cutoff, see Eq. (4.29) of Ref. 15], which in our case enhances the cutoff to  $D \sim 10\,000$  K.

Thus the discrepancy in  $|\Theta|$  and  $T_K$  mentioned earlier for the CS model indeed has its origin in the charge fluctuations. Despite the rather weak valence admixture in  $\text{YbAgCu}_4$  it permits one, nevertheless, to separate the single parameter of the CS model,  $T_K$ , into its main constituents. This separation seems reliable enough since the same values of parameters follow from the just published analogous fitting of the AI model solution in noncrossing diagram approximation<sup>22</sup> (Table I).

### B. Magnetovolume effect

To study the magnetovolume effect, the data for  $\partial \ln \chi / \partial P$  have to be converted into  $\partial \ln \chi / \partial \ln V$  data. This requires knowledge of the temperature dependence of the bulk modulus  $B(T)$ , which unfortunately is not available for  $\text{YbAgCu}_4$ , except at room temperature [ $B(300 \text{ K}) = 1.08$  Mbar (Ref. 23)]. However,  $B(T)$  can be estimated using<sup>24,25</sup>

$$B(T) = B(0)_l - \frac{S}{\exp(\tau/T) - 1} + a[n_f(T) - n_f(300 \text{ K})]. \quad (8)$$

The first two terms on the right-hand side of Eq. (8) represent the empirical lattice contribution,<sup>25</sup> while the third term reflects the contribution due to the change of valence of the Yb ions with temperature.<sup>4</sup> The empirical parameters  $S$ ,  $\tau$ , and  $a$  have been determined for the compound  $\text{YbInCu}_4$ .<sup>4</sup> In view of the similarity of  $\text{YbAgCu}_4$  and the high-temperature phase of  $\text{YbInCu}_4$  (as well as the proximity of Ag and In in the same row of the periodic table and their small fraction in the compound content), we choose the same values as for the high-temperature phase of  $\text{YbInCu}_4$ , namely,  $\tau = 323$  K,  $S = 0.107$  Mbar, and  $a = 1.91$  Mbar.<sup>4</sup> The term  $B(0)_l$  in Eq. (8) is determined using the  $B(300 \text{ K})$  value mentioned previously. The difference in  $f$ -level occupation numbers for  $\text{YbAgCu}_4$ , i.e.  $[n_f(T) - n_f(300 \text{ K})]$ , is obtained from the experimental study of the  $L_{\text{III}}$  line edge in the x-ray absorption,<sup>5,10</sup> and is supported in addition by the linear relation between  $n_f$  and extra volume in the system due to the  $\text{Yb}^{2+}$  state admixture.

As estimated by Eq. (8) the  $B$  value at the lowest temperatures is about 6% less than the value  $B(300 \text{ K})$ , i.e., the corrections from the temperature dependence of  $B(T)$  are small. In Fig. 3 we present the data for  $\partial \ln \chi(T) / \partial \ln V$  using the assumed temperature dependence of  $B(T)$ . These data are discussed in the following in the context of the Coqblin–Schrieffer and Anderson models.

*Coqblin–Schrieffer model:* In the integer-valence limit, the magnetovolume effect is analyzed in terms of the volume

dependence of  $T_K$ , i.e., in terms of the temperature-independent Grüneisen parameter for the Kondo energy,  $\Omega_K \equiv -d \ln T_K / d \ln V$ .

Equations (3) and (4) yield

$$\frac{\partial \ln \chi}{\partial \ln V} = - \frac{d \ln T_K}{d \ln V} \left( 1 + \frac{\partial \ln \chi}{\partial \ln T} \right) \equiv \Omega_K \left( 1 + \frac{\partial \ln \chi}{\partial \ln T} \right). \quad (9)$$

We use the derivative of the experimental data (see Fig. 1) to determine  $\partial \ln \chi / \partial \ln T$  in Eq. (9), rather than the numerical differentiation of the universal theoretical curve, Eq. (3). The use of the derivative of the experimental data may extend the validity of this approach to the weak IV regime, as long as the parameter  $\varepsilon/\Gamma$  remains large as normally assumed for the CS limit.<sup>11</sup>

The Grüneisen parameter  $\Omega_K$  is then determined by fitting  $\partial \ln \chi / \partial \ln T$  obtained from Fig. 1 to the  $\partial \ln \chi / \partial \ln V$  data by making use of Eq. (9). At low temperatures ( $T \leq 60$  K) the fit yields the value  $\Omega_K = -27 \pm 1$ , while for higher temperatures a somewhat smaller value,  $\Omega_K = -23 \pm 1$ , is obtained. In Fig. 3 the dashed and solid curves show the result of this fit. The variation of  $\Omega_K$  with temperature indicates once more that a one-parameter scaling of  $\chi(T)$  is only a rough approximation to the properties of  $\text{YbAgCu}_4$ . Nevertheless, the uncertainty in the present estimate for  $\Omega_K$  is smaller than the one from the pressure dependence of the electrical resistivity,  $\rho(T)$ .<sup>23</sup> Under pressure the position of the maximum of the resistivity,  $T_{\rho m}$ , is shifted; assuming that this shift is proportional to  $T_K$  yielded  $\Omega_K = -18.6$ . On the other hand, the pressure dependence of the low-temperature  $T^2$  term, which is proportional to  $T_K^{-2}$ , gave  $\Omega_K = -27.8$ . Note that both estimates were obtained with no correction for  $B(T)$ . Bauer *et al.*<sup>23</sup> attributed their significant difference to micro-defects in the samples and believed that the former value of  $\Omega_K$  is more reliable. Our results unambiguously support the latter one. We choose  $\Omega_K = -27$  for our considerations in the following.

Differentiating Eq. (5) and omitting the term  $\partial \ln D / \partial \ln V \approx -1$ <sup>26</sup> (the variation of  $s$  is much more important than the one of  $D$ ) we have

$$\frac{\partial \ln s}{\partial \ln V} \approx s \Omega_K = 7.0 \pm 0.5. \quad (10)$$

This derivative is attributed to the CS model just conventionally because here we used the value of  $s$  which cannot be estimated reliably within the CS approach itself and, instead, had to be taken from the above mentioned AI-model-based analysis. Nevertheless, a quite similar value of  $\partial \ln s / \partial \ln V \approx 6$  was estimated for the high-temperature heavy fermion phase of  $\text{YbInCu}_4$ .<sup>26</sup>

*Anderson model:* The magnetovolume effect for the Anderson model can be decomposed into the contributions arising from the volume dependence of  $\varepsilon/\Gamma$  and of  $\Gamma$ . The result of the best fit of the AI model to the experimental data for  $\partial \ln \chi(T) / \partial \ln V$  is shown in Fig. 3. The volume derivatives obtained for the parameters  $\Gamma$  and  $\varepsilon/\Gamma$  are given in Table I. Because of some uncertainties in the data at  $T=0$ , both  $\chi(T)$  and  $\partial \ln \chi(T) / \partial \ln V$  curves were used simulta-

neously in the fitting procedure for the parameters  $\varepsilon/\Gamma$  and  $\Gamma$  themselves as well as their derivatives to get an unambiguous solution. A measure of this fit inconsistency is a small difference in the value of  $\Gamma$  of about  $\sim 8\%$  for the curves mentioned which is covered by the averaged  $\Gamma$  value uncertainty in Table I. The uncertainty in our estimate of  $B(T)$ , Eq. (8), is in fact not important; even if the  $T$  dependence of  $B$  is completely neglected, the derivative  $\partial \ln s / \partial \ln V = -\partial \ln(\varepsilon/\Gamma) / \partial \ln V$  just increases from 7.4 to 7.8, i.e., it remains within the error margin of the fit.

The data show unambiguously that for the compound considered the change in the  $f$ -level energy rather than the change in the hybridization width dominates the pressure dependence of  $\chi$ . Moreover, the volume dependence of  $\Gamma$  appears to be negligible, so that just one parameter is representative in the pressure dependence of the magnetic susceptibility. This explains the approximate validity of Eq. (9) in the IV region, as well as the close agreement found for  $\partial \ln s / \partial \ln V$  within both the CS [Eq. (10)] and the AI (Table I) models.

The value of the parameter  $\partial \ln \Gamma / \partial \ln V$  is mostly determined by the high temperature tail of the susceptibility (Curie–Weiss law), where the influence of the RKKY-like interaction between Yb ions cannot be fully excluded. The  $f$ – $f$  interaction is in the first place mediated by the conduction electrons, but the magnetoelastic effect is also expected to contribute through low-frequency phonons. Our data lead to a value of the derivative  $\partial \varepsilon / \partial \ln V$  of  $3.2 \pm 0.5$  eV. This result is in good agreement with the *ab initio* value of about 3 eV calculated for this derivative for Yb metal,<sup>27</sup> and the similarity of these values supports our confidence in the reliability of our fits. The value of Ref. 27 is maximal and stable in a wide vicinity of the equilibrium atomic volume and should be taken as more or less universal for metallic Yb systems. Hence, this agreement with the calculated value leaves no room for a significant contribution of  $\partial \ln \Gamma / \partial \ln V$  to  $\partial \ln s / \partial \ln V$ . The hybridization is expected to increase under compression because a reduced volume increases the overlap between the  $f$ -wave functions with the conduction states. However, with our data we were not able to resolve the sign of  $\partial \ln \Gamma / \partial \ln V$  within the uncertainty of the analysis. Unfortunately, there are not enough measurements on Yb systems under pressure<sup>28</sup> to conclude on some universal behavior of Yb compounds, and further experimental tests are needed.

A similarly strong volume dependence of  $s$  is known to exist for Ce compounds with unstable valence of  $\partial \ln s / \partial \ln V \approx -7$ .<sup>29,30</sup> The opposite sign of this derivative is just the consequence of the electron–hole asymmetry of Ce and Yb (Ce has one  $f$  electron and Yb has one  $f$  hole) with the valence change having the same sign.<sup>26</sup> There is, however, an important difference in the origin of the volume dependence of  $s$  between Ce and Yb. It is generally accepted that in Ce and its compounds the change in the hybridization with pressure dominates over the shift in the  $f$ -level position.<sup>29,31</sup> Thus the volume collapse of Ce (first-order valence phase transition) was explained<sup>29,30</sup> in terms of a change of the Kondo temperature with pressure, but induced by a change in the hybridization width, rather than a change in the  $f$ -level posi-

tion. But most likely the specific origin of the  $s(V)$  dependence is of no importance for the Kondo volume collapse model. Similarly, the pressure dependence of the susceptibility of the IV compound CeSn<sub>3</sub> (Refs. 11 and 31) was interpreted as due to a change in the hybridization,<sup>31</sup> although it is impossible to separate the two mechanisms ( $f$ -level position and  $\Gamma$ ) using only the susceptibility data within the CS model, since they only enter the parameter  $T_K$ .<sup>31,32</sup> In the case of CeSn<sub>3</sub> this conclusion was reached based on the complete set of data on the stability of the  $f$ -level energy in Ce systems.<sup>31</sup> It is also generally believed that the hybridization matrix element in Ce systems is much larger than for Yb compounds.

The fact that the numerical values of the derivatives  $|\partial \ln s / \partial \ln V|$  of YbAgCu<sub>4</sub> and Ce systems agree appears to be accidental, since their origin is dramatically different. The Kondo volume collapse model fails to explain the first-order phase transition in Yb(Ag–In)Cu<sub>4</sub> solid solutions. This is particularly evident from the rather small volume jump at the transition.<sup>10</sup> One plausible explanation of the transition is as an entropy-driven transition between phases with large and small Kondo temperatures.<sup>33</sup> Deeper insight into the microscopic parameters of this  $f$ -state transformation with pressure is needed, to hopefully identify the correct mechanism of this intriguing phenomenon.<sup>10,33–36</sup>

## V. CONCLUDING REMARKS

In the present study of the magnetovolume effect of YbAgCu<sub>4</sub> we were able to separate the contributions of the atomic volume dependence of the  $f$ -level width and the  $f$ -level energy. This separation was possible despite the weak admixture of the divalent Yb configuration. The two parameters are usually integrated in one effective characteristic temperature  $T_K$ .

Based on the Anderson impurity model we conclude that in YbAgCu<sub>4</sub> the volume dependence of the  $f$ -level energy largely surpasses that of the hybridization width. This is in contrast to the situation in Ce systems where the pressure dependence of the hybridization width is believed to be the dominant quantity. The validity of this conclusion for other Yb compounds is still the subject of further investigations.

Such data are of special interest because at present there are no reliable *ab initio* theoretical calculations of the general trends of the  $f$ -level position for the relevant IV regime and of its hybridization width with the band states. They could help to gain insight into the microscopic mechanisms of valence and phase stability, as well as to study the effects of other interactions like  $f$ – $f$  exchange between sites and crystalline field splittings.

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