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# Simple scaling behavior in the magnetic susceptibility of $CeSn_3$ under high pressure

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The static magnetic susceptibility $\chi$ of single-crystalline $CeSn_3$ is measured as a function of temperature $3 \leq T \leq 300$ K and hydrostatic pressure 1 bar$\leq P \leq 15$ kbar. The temperature and pressure dependence of $\chi$ is shown to be a function of a single characteristic spin-fluctuation energy $kT_{\text{sf}}$, i.e., $\chi T$ scales with $T/T_{\text{sf}}$. From the magnitude of the increase of $T_{\text{sf}}$ with pressure ($\partial \ln T_{\text{sf}}/\partial P \simeq +1.4\%$/kbar or $\partial \ln T_{\text{sf}}/\partial \ln V \simeq -7.6$) it can be indirectly inferred within a simple model that an increase in the $4f$ hybridization width $\Delta$, rather than a decrease in the $4f$ binding energy $\epsilon_{\text{ex}}$, is the dominant change in the magnetic state under pressure. These results imply that $CeSn_3$ would be best characterized as a trivalent Ce compound with a rather high spin-fluctuation temperature ($T_{\text{sf}} \simeq 200$ K) rather than as a compound with fractional valence. $\chi(T)$ appears to depend only very weakly on the relative orientation of the magnetic field. The Curie tail in $\chi(T)$ below 20 K is independent of pressure and is, therefore, very likely an impurity effect rather than an intrinsic property of the compound. It is suggested that scaling itself can be used to derive changes in both the valence $v$ and $T_{\text{sf}}$ in a single experiment.

## I. INTRODUCTION

It is useful to divide the magnetism of both local-moment and itinerant-electron metallic systems into four representative classes: (1) *stable magnetism*, as in Gd or Co; (2) *unstable magnetism*, as in $\gamma$-Ce or $ZrZn_2$; (3) *strongly enhanced* paramagnetism, as in $TiBe_2$ or Pd; (4) *Pauli paramagnetism*, as in Ta.[1] Whereas classes (1) and (4) are normally only very weakly influenced by a variation of the thermodynamic variables temperature $T$, and $P$, and magnetic field $H$, classes (3) and, in particular, (2) can react quite sensitively. High-pressure studies clearly offer the cleanest and most carefully controlled method to transport a given system from one class to another.[1]

Systems belonging to classes (1) or (4) are far from a magnetic instability; their magnetism is thus relatively well understood. So-called intermediate- or mixed-valence systems are believed to contain on the average a nonintegral easily variable number of local "magnetic" electrons per ion, and consequently belong to classes (2) to (3); the problem of the magnetism of intermediate-valence systems is one of prodigious complexity, surpassing in difficulty even the single-impurity Kondo problem [class (1)] which resisted solution for many years.

One fact which aided considerably in making the many-body Kondo problem amendable to solution is that the Kondo state can be described in terms of a single characteristic energy $kT_{\text{sf}}$ (here we assume the conceptual equivalence of the spin-fluctuation temperature $T_{\text{sf}}$ and the Kondo temperature $T_K$ whose magnitude is a measure of the degree of hybridization between local-moment and conduction-electron wave functions). The existence of a single characteristic energy implies that all Kondo anomalies are universal functions of $T/T_{\text{sf}}$, i.e., for the electrical resistivity $R = R(T/T_{\text{sf}})$ and for the magnetic susceptibility $(\chi T) = (\chi T)(T/T_{\text{sf}})$.[2] Such scaling has also been shown to hold within Fermi-liquid theory in the temperature range $T_{\text{sf}} < T \ll T_f$, where $T_f$ is the degeneracy temperature.[3] The equivalence of the Kondo and Fermi-liquid approaches, at least in the ground state, is well established.[2] Experimentally, the existence of the above universal scaling laws has been verified by high-pressure studies on the dilute Kondo system *Cu*Fe (Ref. 4) and on the archetypal Fermi liquid $^3$He.[5]

In the more complex intermediate-valence problem, the local magnetic state itself is unstable and a number of further characteristic energies besides $kT_{\mathrm{sf}}$ may be important: e.g., $\epsilon_{\mathrm{ex}}$ the binding or excitation energy of the magnetic electron, $\epsilon_{\mathrm{el}}$ the elastic energy associated with the large change in ionic volume with valence, $\epsilon_{\mathrm{int}}$ the interaction energy between the intermediate-valence ions. In spite of this potential complexity, we take the point of view that one should first establish experimentally the minimum number of characteristic energies necessary to satisfactorily describe the intermediate-valence phenomena found in a particular system.

In a significant work on the compound series $\mathrm{CeIn}_{3-x}\mathrm{Sn}_x$, Lawrence[6] has shown that $\chi T$ scales with $T/T_{\mathrm{sf}}$ to within 1% over a considerable range of the parameters $0.85 \leq x \leq 3$ and $73 \leq T_{\mathrm{sf}} \leq 200$ K, i.e., these compounds, which are normally considered to be at or within the intermediate-valence regime, can be characterized by a *single* energy $kT_{\mathrm{sf}}$. Lawrence and Béal-Monod,[7] Klasse *et al.*,[8] and Edelstein[9] have listed a number of Ce and Yb compounds where simple scaling laws seem to exist. Allen and Martin[10] have proposed that the binding energy of the Kondo singlet state is the driving force behind the $\gamma \rightarrow \alpha$ transition and volume collapse in elemental Ce and related solids, which is tantamount to implying $T/T_{\mathrm{sf}}$ scaling. Clearly, further careful experimental tests for simple scaling behavior are needed. Such quantitative tests can best be realized in high-pressure experiments which can be carried out reversibly on a single sample and are thus free of the metallurgical problems arising in studies on compound series.

In this paper we present high-pressure magnetic susceptibility measurements on $\mathrm{CeSn}_3$ which extend the work of Lawrence[6] to still higher values of $T_{\mathrm{sf}}$. Previous high-pressure studies[11-13] gave widely differing results and were also unable to test for scaling behavior or accurately determine $\partial \ln T_{\mathrm{sf}}/\partial P$ and $\gamma_{\mathrm{sf}} \equiv -\partial \ln T_{\mathrm{sf}}/\partial \ln V$. We verify scaling with $T/T_f$ and find $T_{\mathrm{sf}}$ to increase with pressure at the rate $+1.4\%$/kbar, giving $\gamma_{\mathrm{sf}} = +7.6$. This relatively low value of $\gamma_{\mathrm{sf}}$ for $\mathrm{CeSn}_3$ compared to other Ce systems allows us to conjecture that the predominant change in the magnetic state of trivalent Ce under external or lattice pressure is a broadening of the hybridization width $\Delta$ rather than a decrease of $\epsilon_{\mathrm{ex}}$; a similar conclusion was reached by Croft *et al.*[14] from their photoemission results on $\mathrm{CeAl}_2$ alloys. We also find the low-temperature ($T < 40$ K) Curie tail in $\mathrm{CeSn}_3$ to be essentially independent of pressure, which points to its origin as an impurity effect rather than as an intrinsic property of the homogeneous magnetic state of the compound.

## II. EXPERIMENT

A single crystal of $\mathrm{CeSn}_3$ (cubic $\mathrm{Cu}_3\mathrm{Au}$ structure) was prepared at the Ames Laboratory using standard Bridgman techniques. The Ce employed contains less than 40 ppm of rare-earth impurities (principally 17 ppm La, 4 ppm Pr, and less than 7 ppm Gd), less than 1500 ppm of interstitial impurities (500 ppm O, 40 ppm N, 690 ppm H, 94 ppm C, and 200 ppm F), and less than 260 ppm of all other impurities (principally 100 ppm Pt, less than 70 ppm Ga, 33 ppm Fe, 15 ppm Ta, 8 ppm Si, and 9 ppm Cl). The Sn is 99.999% pure. Sample 1 was prepared by spark cutting a section of the crystal to a cylinder approximately 4-mm diameter and 4-mm height with the ends of the cylinder perpendicular to the [111] direction. Sample 2 was cut from a nearby section of the same master crystal as sample 1. Sample 2 was then broken into approximately 30 randomly oriented pieces allowing a comparison of the single-crystalline and "polycrystalline" susceptibilities.

To measure the static magnetic susceptibility at ambient pressure, the standard Faraday method is used. The sample is placed in a small 5-g crucible made of ultrapure Cu which is supported in the center of a large superconducting solenoid set at 5.6 T main field and 6.4 T/m gradient field. The coils of this magnet are specially wound so that $H(dH/dz)$ is constant to better than 1% over a cylinder of 2-cm diameter and 5-cm height, thus obviating the necessity of maintaining a precisely constant position of the pressure clamp or crucible with respect to the magnet as the temperature is varied. In fact, moving the clamp up or down by ±1 mm causes a change in magnetic force of only a few micrograms which can be neglected.

High pressures are generated within the 5-mm-diam bore of a 90-g pressure clamp of standard design made of pure binary Cu-Be with $\mathrm{Al}_2\mathrm{O}_3$ anvils. The hydrostatic pressure cell consists of a thin-walled Delrin[15] tube with Cu-Be end stoppers filled with an *n*-pentan isoamyl pressure fluid. A tiny Pb superconducting manometer[16] is also included in the cell. Upon cooling from 300 to 3 K, the pressure decreases by 2—3 kbar.

The present temperature and pressure ranges of the apparatus are 2.5—350 K and 0—20 kbar, respectively. The temperature of the sample is determined using a calibrated carbon-glass thermometer[17] located only a few millimeters away from the pressure clamp. The sample tube is filled at 300 K with 1-Torr He exchange gas. Further details of the experimental apparatus are planned to be discussed in a future publication.[18]

## III. RESULTS OF EXPERIMENT

### A. Ambient pressure

Displayed in Fig. 1 is the static magnetic susceptibility at ambient pressure of a $CeSn_3$ single crystal (sample 1) with the 5.6-T magnetic field pointed along the [111] direction. The characteristic bell-shaped curve with a susceptibility maximum at $T_{max} \simeq 140$ K is clearly seen, in agreement with previous results[6,11,12,19]; in our measurements on sample 1, however, the low-temperature ($T < 40$ K) Curie tail is relatively small. In an effort to determine if the size of the Curie tail is sensitive to the orientation, mechanical state, or surface-oxidation state of the sample, the single crystal was broken up into 5 and then 30 randomly oriented pieces, allowed to oxidize in air several hours, and then remeasured. Aside from a slight ~1% suppression at all temperatures, the magnetic susceptibility of the same

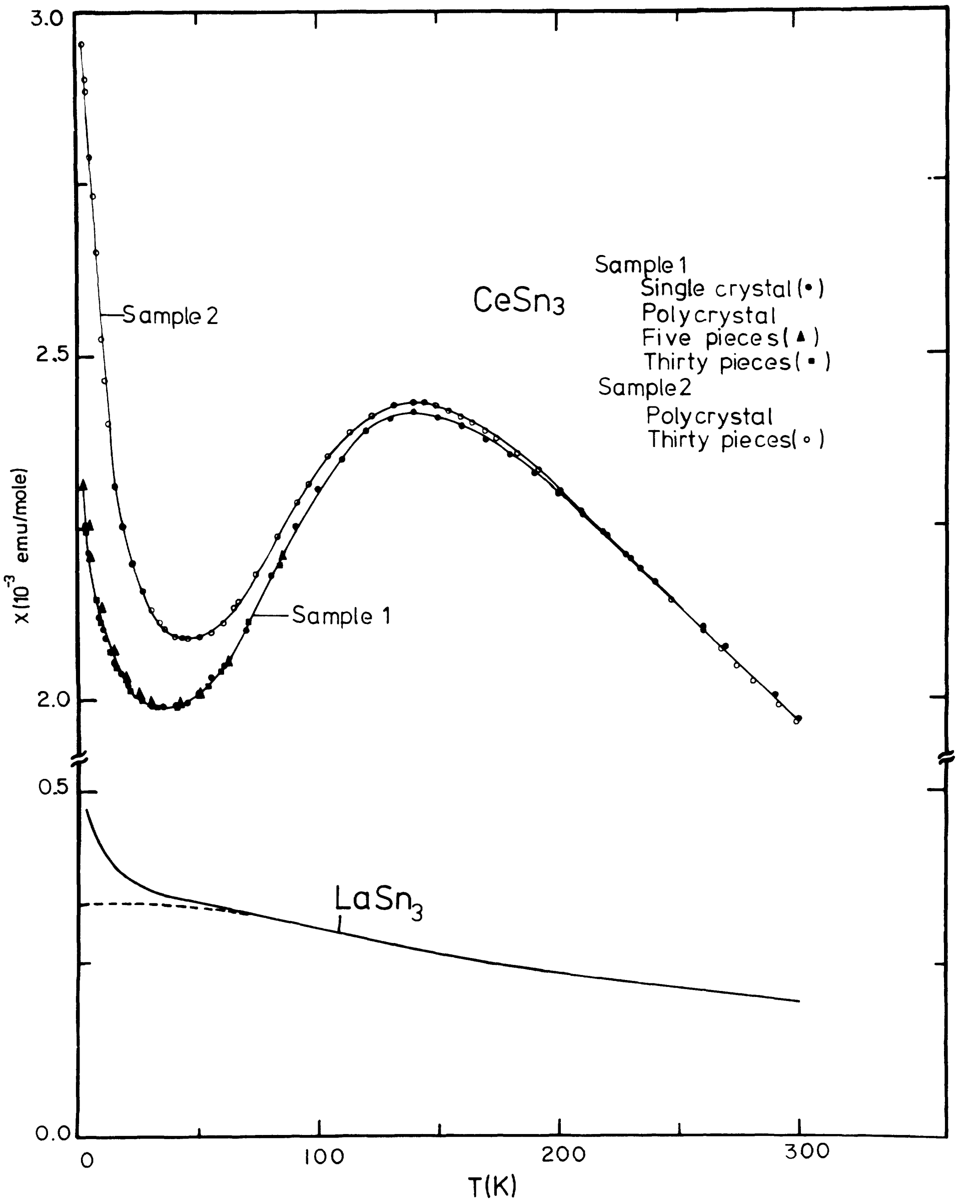

FIG. 1. Static magnetic susceptibility of $CeSn_3$ (present work) and $LaSn_3$ (Ref. 20) at ambient pressure vs temperature. For $CeSn_3$ the 5.6-T magnetic field is applied in the [111] direction. Single-crystalline $CeSn_3$ was also broken to give polycrystalline form. For better comparison polycrystalline data are scaled up by 1%. Dashed line for $LaSn_3$ has impurity Curie tail subtracted. Lines through data points drawn for clarity.

piece of material is identical in both clean single-crystalline and surface-oxidized polycrystalline forms (see Fig. 1).

Also shown in Fig. 1 is the susceptibility of polycrystalline sample 2. It seems significant that the susceptibility of sample 2, which was removed from an adjacent section (same height) of the master crystal as sample 1, should have a sizably larger Curie tail. In Fig. 2 a Curie-Weiss impurity susceptibility has been subtracted from the raw data. The agreement between the temperature dependence of the impurity-corrected susceptibilities is excellent over the entire temperature range above 5 K. The slight fall off in $\chi$-$\chi_{\mathrm{imp}}$ below 4 K is spurious, arising from the inaccuracy inherent in the subraction of two large numbers. The Curie constants of the impurity susceptibility $\chi_{\mathrm{imp}}$ of samples 1 and 2 are $2.6\times10^{-3}$ emu/mole and $7.9\times10^{-3}$ emu/mole, respectively, which would correspond to a *trivalent* Ce impurity concentration of 0.32% and 0.98% (Sereni's data[12] give 2.2% $\mathrm{Ce}^{3+}$). In this view, paramagnetic trivalent Ce is an impurity in its own $\mathrm{CeSn}_3$ matrix where the vast majority of all Ce ions appear nonmagnetic at low temperature ($\chi$ is temperature independent). Local strain fields could stabilize $\mathrm{Ce}^{3+}$ impurities.[6] The aforementioned mass spectrometric analysis, the variation in the apparent impurity concentration on samples from the same master crystal, the known sensitivity to the type of heat treatment carried out,[6] and the fact that the reference compound $\mathrm{LaSn}_3$ has a relatively small impurity concentration (see Fig. 1) all speak against non-Ce impurities as causing the Curie tail in $\mathrm{CeSn}_3$. It remains, however, an open question whether the low-temperature upturn is an impurity effect or is actually intrinsic to $\mathrm{CeSn}_3$. We will see shortly that the high-pressure results shed some light on this question.

### B. High pressure

Application of hydrostatic pressure to single-crystalline $\mathrm{CeSn}_3$ (sample 1) causes a reversible decrease in the magnetic susceptibility at room temperature, as seen in Fig. 3. From these data we obtain the pressure dependence $\partial\ln\chi/\partial P=(-0.67\pm0.05)\%/\mathrm{kbar}$ which gives $\partial\ln\chi/\partial\ln V=-K^{-1}\times(\partial\ln\chi/\partial P)=+3.6\pm0.3$, where the compressibility $K=1.84\times10^{-3}\ \mathrm{kbar}^{-1}$ is taken from Takke *et al.*[21] We compare this pressure dependence to the values $(-0.47\pm0.05)\%/\mathrm{kbar}$ from Zell *et al.*,[13] $(-0.8\pm0.4)\%/\mathrm{kbar}$ from Beille *et al.*,[11] and $-5.8\%/\mathrm{kbar}$ from Sereni.[12] The last value is clearly incorrect, being an order of magnitude too large.

In Fig. 4 it is seen that the application of pressure causes a decrease in the $\mathrm{CeSn}_3$ susceptibility, not

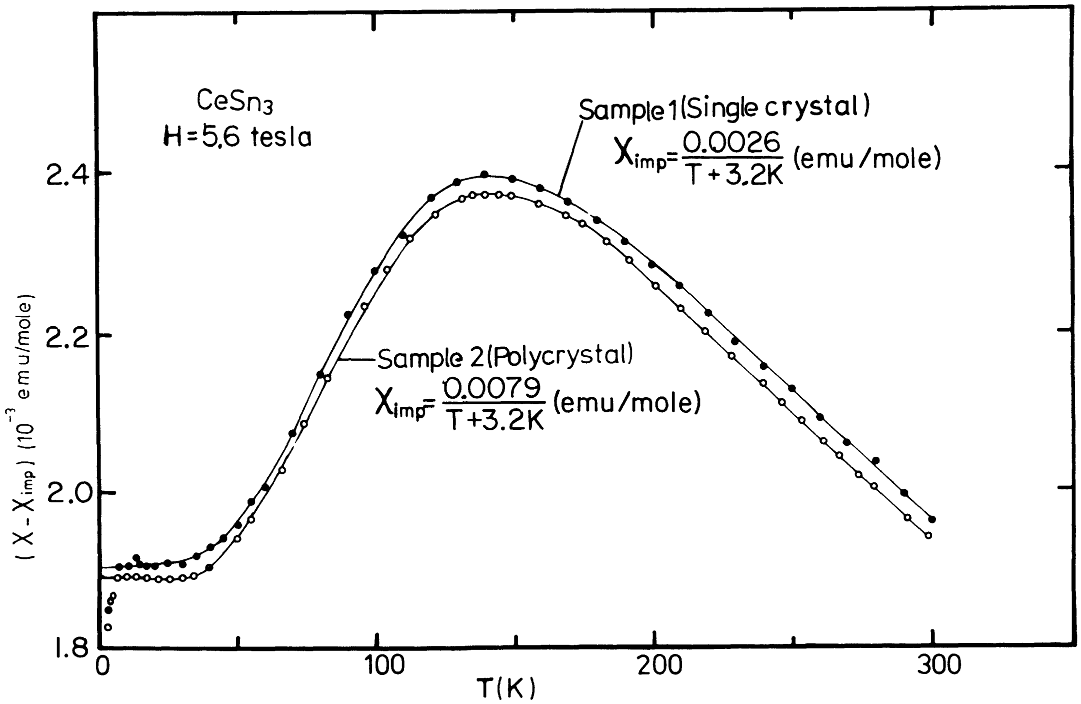

FIG. 2. Temperature dependence of magnetic susceptibility of two $\mathrm{CeSn}_3$ crystals after subtraction of a Curie-Weiss susceptibility $\chi_{\mathrm{imp}}$. Lines drawn for clarity.

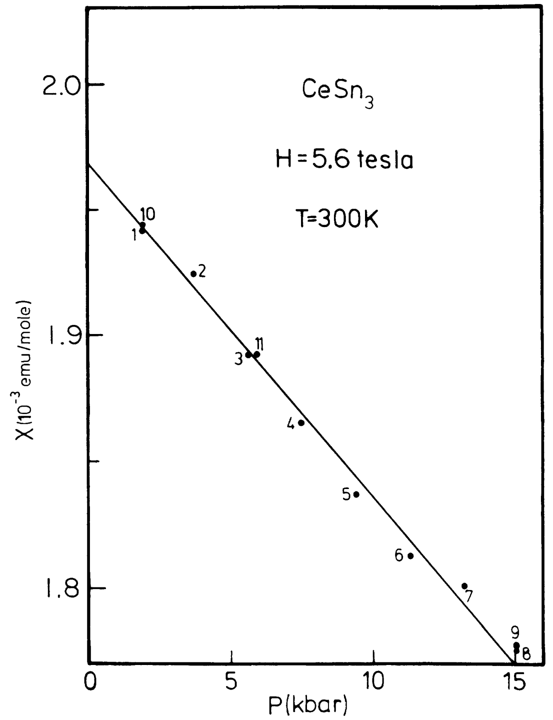

FIG. 3. Pressure dependence of magnetic susceptibility of single-crystalline $\mathrm{CeSn_3}$ (sample 1) at room temperature. Numbers give order of measurement. Susceptibility decreases reversibly with pressure. Straight line gives a least-squares fit with $\partial \ln \chi / \partial P = (-0.67 \pm 0.05)\%/\mathrm{kbar}$.

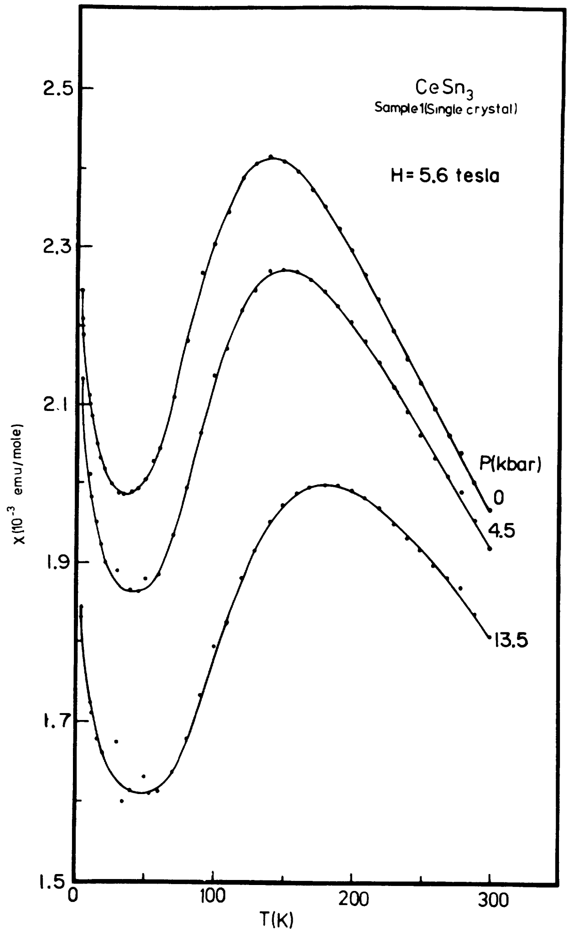

FIG. 4. Temperature dependence of magnetic susceptibility of $\mathrm{CeSn_3}$ at three pressures. Lines drawn for clarity. Pressures given are at room temperature; approximately 2.5 kbar is lost upon cooling.

only at room temperature, but over the entire temperature range to 3 K. The pressure dependence $|\partial \ln \chi / \partial P|$ rises sharply with decreasing temperature, almost tripling in value to 100 K. The temperature of the susceptibility maximum increases with pressure at the rate $\partial T_{\mathrm{max}} / \partial P \approx +3.4$ K/kbar. Very similar results were found by Zell *et al.*[13] on the Ce compounds $\mathrm{CeNi_2Ge_2}$, CeRhPt, and $\mathrm{Ce(Rh_{0.7}Pt_{0.3})_2}$. Sereni[12] also could resolve an increase in $T_{\mathrm{max}}$ with pressure for $\mathrm{CeSn_3}$.

In contrast to the rather large changes with pressure observed in the intrinsic susceptibility of $\mathrm{CeSn_3}$ for temperatures above 40 K, the low-temperature Curie tail appears insensitive to pressure. We bring out this point in Fig. 5(a) where the subtraction of a *single* Curie-Weiss susceptibility $\chi_{\mathrm{imp}}$ is seen to result in a nearly temperature-independent intrinsic $\mathrm{CeSn_3}$ susceptibility for temperatures below 40 K at all three pressures. These results give strong evidence that the physical origin of the Curie tail differs entirely from that of the remaining susceptibility. This is exactly what would be expected if the Curie tail were not intrinsic but originated from stable paramagnetic impurities (about 0.3% $\mathrm{Ce^{3+}}$) within the $\mathrm{CeSn_3}$ matrix.

Somewhat more accurate experiments on the polycrystalline sample 2 (see Figs. 1 and 2) give identical results under high pressure as the single-crystalline sample 1, as seen in Fig. 5(b). For sample 2 the Curie tail can be described by a pressure-independent impurity susceptibility $\chi_{\mathrm{imp}}$ which would correspond to about 1% of $\mathrm{Ce^{3+}}$.

## IV. DISCUSSION

We now discuss the observed pressure and temperature dependence of the magnetic susceptibility of $\mathrm{CeSn_3}$ and the implications of these results for the understanding of stable- and fluctuating-valence systems in general.[22] In Ce systems the principal ef-

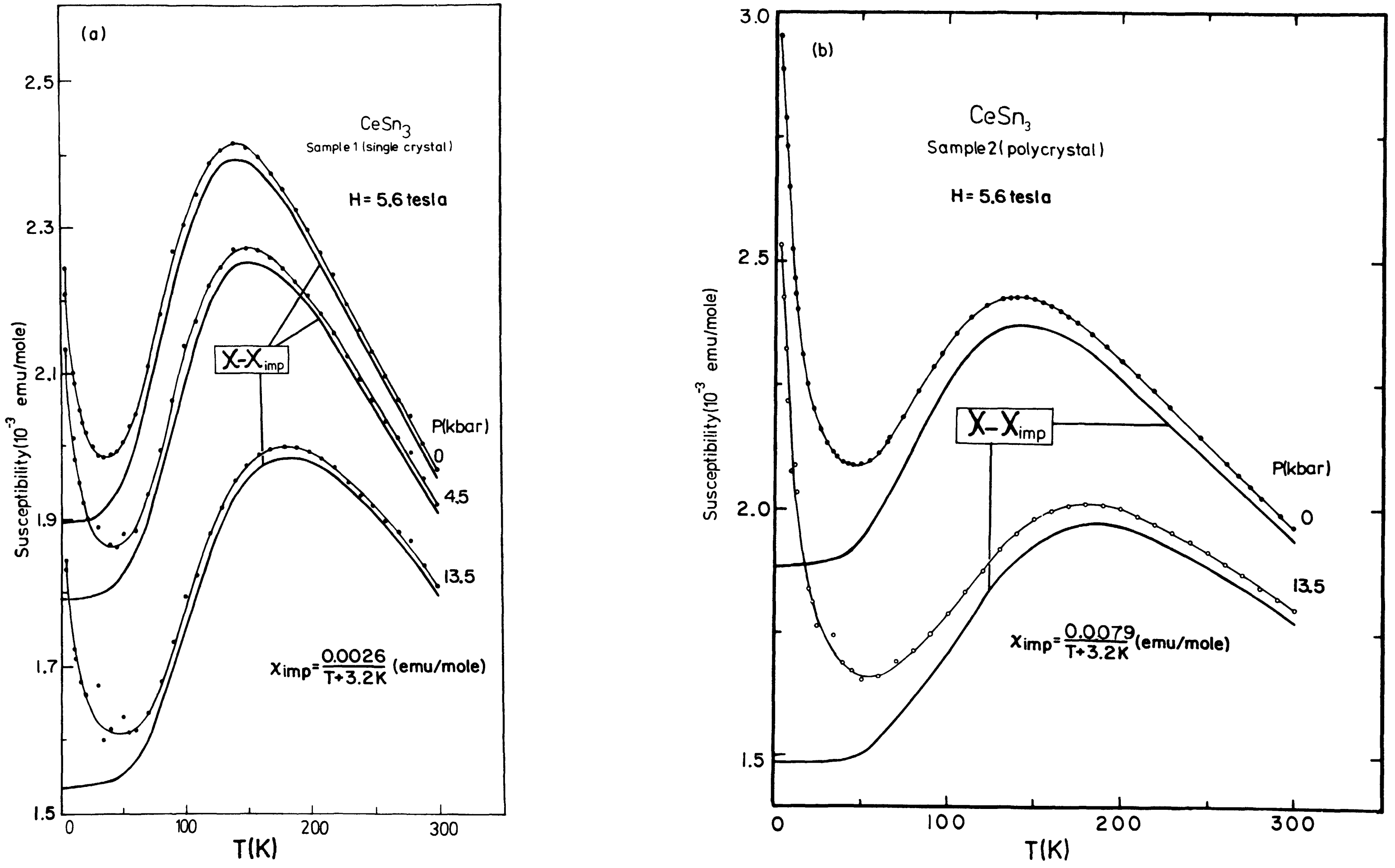

FIG. 5. Heavy solid lines give temperature dependence of susceptibility of (a) single-crystalline and (b) polycrystalline CeSn$_3$ after subtraction of a pressure-independent Curie-Weiss term $\chi_{imp}$ from the measured data.

fect of applying pressure is to delocalize each Ce's single $4f$ electron leading to a reduction in the effective moment.[1] The observed decrease with pressure of the magnetic susceptibility in $CeSn_3$ and other Ce systems[14,23] at all temperatures is simply an expression of this moment weakening. In Yb compounds, on the other hand, applying pressure will remove an electron from the filled $4f$ shell, thus enhancing the effective moment. Indeed, Zell *et al.*[24] have shown that in YbInAu the magnetic susceptibility *increases* with pressure at all temperatures below 300 K, the temperature $T_{\max}$ of the susceptibility maximum shifting to *lower* temperatures.

The next step is to attempt to account for the detailed temperature and pressure dependences of $\chi$. In the following we assume that the susceptibility is a function of temperature $T$, a spin-fluctuation temperature $T_{\rm sf}$, and the valence $v$, i.e., $\chi=\chi(T,T_{\rm sf},v)$. The valence $v$ is directly related to the time-averaged number of electrons $n$ in the $4f$ state, i.e., for Ce, $v=4-n$. Both $T_{\rm sf}$ and $v$ are, in principle, dependent on temperature and pressure. To extract these dependences from experiment, an accurate microscopic theory of the mixed-valence state is required which is at present lacking.[22,25] Various phenomenological models have been developed[22,25,26]; however, it is an open question whether these models are sufficiently accurate to allow the extraction of reliable values for $T_{\rm sf}(T,P)$ and $v(T,P)$. In such a situation it would seem prudent to attack the full mixed-valence problem from the stable-valence side where one would hope to find the magnetic state dependent mainly on the value of $T_{\rm sf}$, with $\partial v/\partial T \simeq \partial v/\partial P \simeq 0$. If only one characteristic energy $kT_{\rm sf}$ is important, one could hope to find simple scaling laws in the physical quantities. Indeed, the fact that in a number of Ce and Yb systems[7–9,22,24,27] the impurity-corrected value of $\chi(0)$ seems correlated with that of $T_{\max}$ [the smaller $\chi(0)$, the larger $T_{\max}$] would hint at the existence of such scaling laws. Perhaps the clearest evidence for scaling was provided by Lawrence[6] who showed that the susceptibility of $CeIn_{3-x}Sn_x$ could be described as a function of the single scaled variable $T/T_{\rm sf}$ for a wide range of $x$ and $T$; he obtained $\chi T/C=f(T/T_{\rm sf})$ where $C$ is the Curie constant for $Ce^{3+}$.

Both absorption edge[28] and lattice-constant[6] studies indicate that Ce in $CeIn_3$ ($CeSn_3$) is in (very near) the trivalent state. That Ce in $CeSn_3$ has a slightly higher valency than in $CeIn_3$ is supported by the absence of magnetic ordering and the higher value of $T_{\rm sf}$ in the former. Application of high pressure will certainly push $CeSn_3$ further towards the intermediate-valence regime[1] and it is of considerable importance to determine how long the simple scaling laws will hold. It is conceivable that mixed-valence phenomena will need to be divided up into two temperature regions: a low-temperature regime where it is energetically more favorable for the $4f$ sites to become strongly correlated and form band states and a high-temperature region where the individual $4f$ sites are uncorrelated and the single-impurity model applies.[29] In any case, if pressure causes, in addition to changes in $T_{\rm sf}$, a sizable increase in the valence of $CeSn_3$, it will no longer be possible to fit the susceptibility to a simple scaling law with a single characteristic energy.

In Fig. 6 we plot $\chi T/C$ vs $\ln T$ for both single-crystalline and polycrystalline samples. To obtain the $4f$-electron contribution, the susceptibility of the reference compound $LaSn_3$ in Fig. 1 has been subtracted. For lack of a measurement, $\chi_{\rm LaSn_3}$ is assumed pressure independent; considering the relatively small temperature dependence of $\chi_{\rm LaSn_3}$ and the anticipated small decrease in $\chi_{\rm LaSn_3}$ of 1–2 % for 15 kbar,[30] this would seem to be a good assumption. $C=0.807$ emu K/mole is the Curie constant for $Ce^{3+}$. $\chi T/C$ can thus be looked on as the square of the relative magnetic moment $[\mu(T)/\mu(\infty)]^2$, where $\mu(\infty)$ designates the high temperature or $Ce^{3+}$ moment. When the susceptibility has reached the full paramagnetic $Ce^{3+}$ value, then $C\chi/T=1$ and $\mu(T)=\mu(\infty)$.

In Fig. 6 we see that the effective moment $\mu(T)$ gradually rises from a negligible value in the nonmagnetic low-temperature state to a value within 20% of $\mu(\infty)$ by 300 K. If we use for discussion purposes the expression $\chi=C/(T+T_{\rm sf})$,[26] then $T=T_{\rm sf}$ implies $\chi T/C=\frac{1}{2}$, giving from Fig. 6 $T_{\rm sf}=200$ K at atmospheric pressure, in agreement with Lawrence.[6] To saturate $\mu(T)$ we thus need temperatures $T \gg T_{\rm sf}=200$ K. The application of pressure is seen to shift the $\chi T/C$ curve bodily to higher temperatures *without any detectable change in shape*, as seen in Fig. 7. This implies that the universal behavior of $\chi T/C$ on $T/T_{\rm sf}$ pointed out by Lawrence[6] for $CeIn_{3-x}Sn_x$ also holds for $CeSn_3$, which has been pushed further toward the strongly mixed-valence regime by high pressure.

From Figs. 6 and 7 we thus see that 13.5-kbar pressure increases $T_{\rm sf}$ from 200 to 240 K, giving $\partial \ln T_{\rm sf}/\partial P = +1.4\%/\text{kbar}$ for both single-crystalline and polycrystalline samples. It is interesting to note that $T_{\rm sf}(13.5\ \text{kbar})/T_{\rm sf}(0\ \text{kbar}) = 1.2 \approx \chi(0\ \text{K},\ 0\ \text{kbar})/\chi(0\ \text{K},\ 13.5\ \text{kbar}) = 1.27$, where $\chi_{\rm LaSn_3}(0\ \text{K})$ has been corrected. We have, therefore, a rough verification of the dependence $\chi(0\ \text{K}) \sim 1/T_{\rm sf}$ or $T\chi(0\ \text{K}) \sim T/T_{\rm sf}$, which implies scaling behavior also at the lowest temperatures. The only approximate nature of this verification is satis-

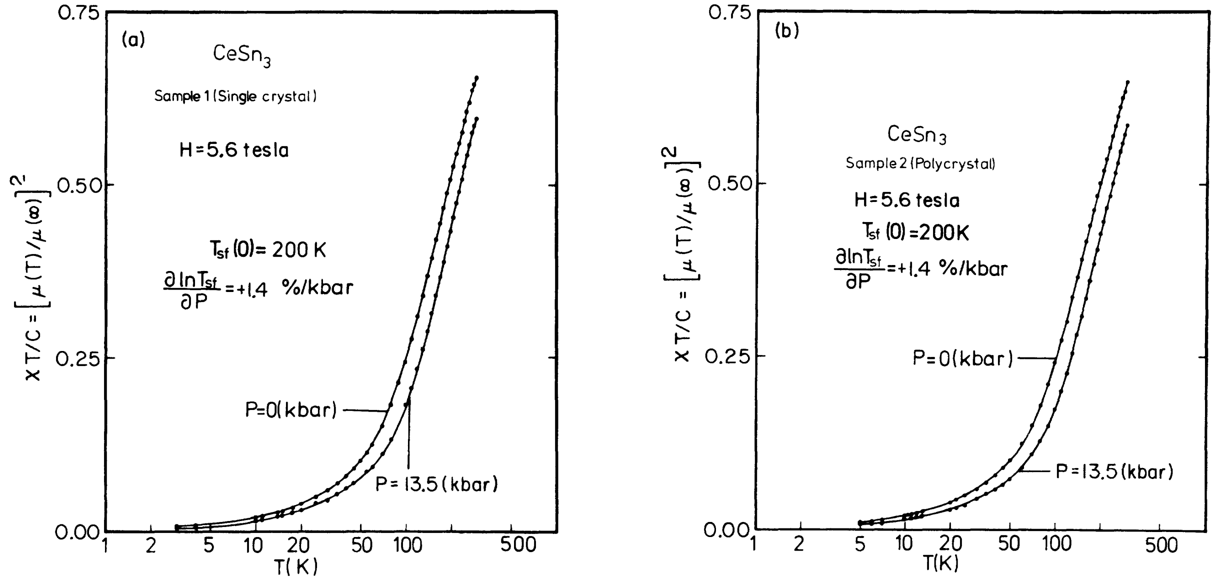

FIG. 6. Relative moment squared vs $\ln T$ for (a) single-crystalline and (b) polycrystalline CeSn$_3$. $T_{sf}$ increases with pressure.

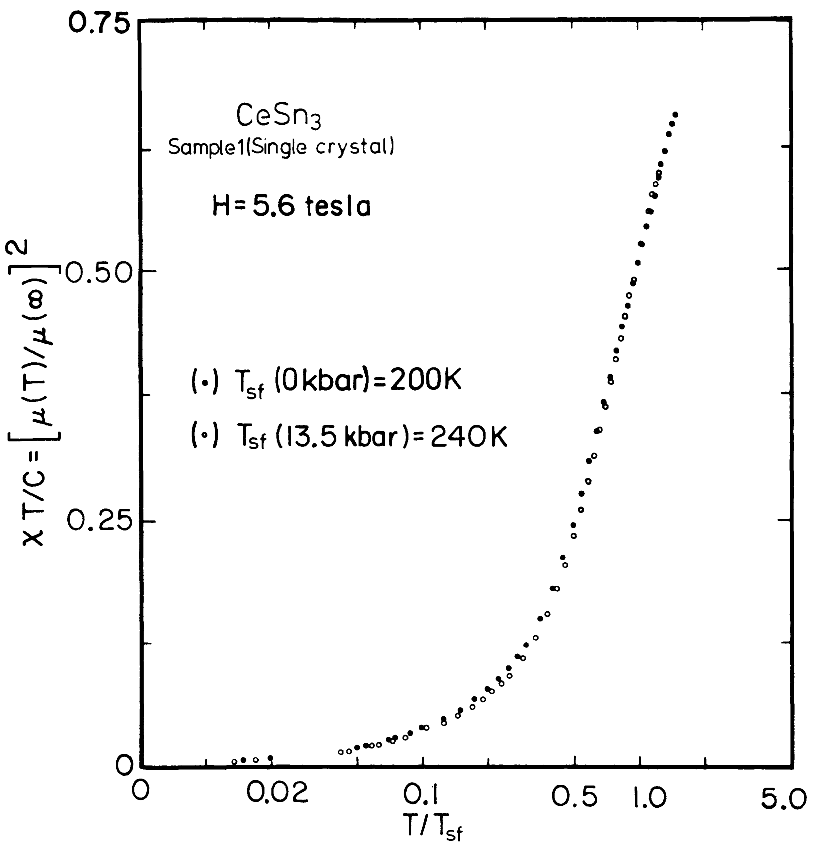

FIG. 7. Relative moment squared vs $\ln(T/T_{sf})$ for single-crystalline CeSn$_3$. Within experimental uncertainty both data overlap at all temperatures, confirming the scaling law $\chi T/C = f(T/T_{sf})$.

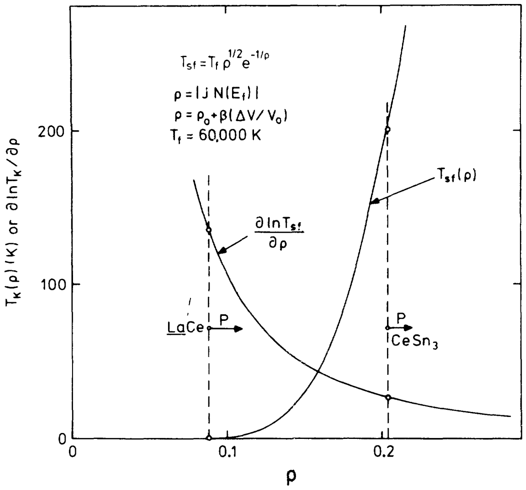

FIG. 8. $T_{sf}$ and $\partial \ln T_{sf}/\partial \rho$ vs $\rho$. Ordinate scale same for both quantities. From value of $T_{sf}$, both $\rho$ and $\partial \ln T_{sf}/\partial \rho$ can be estimated. Pressure increases both $\rho$ and $T_{sf}$ but decreases $\partial \ln T_{sf}/\partial \rho$.

factory considering the corrections in the raw data involved and the unknown pressure dependence of $\chi_{LaSn_3}$.

From the above value of $\partial \ln T_{sf}/\partial P$ we obtain, using the known compressibility,[21] $\gamma_{sf} \equiv -\partial \ln T_{sf}/\partial \ln V \approx +7.6$ for $CeSn_3$. It is of interest to compare $\gamma_{sf}$ for this concentrated Ce system which is at or near mixed valency with values for very dilute single-impurity Kondo systems with Ce impurities[4]: For *La*Ce, $T_{sf} \simeq 0.2$ K and $\gamma_{sf} \approx +50$; for *Y*Ce, $T_{sf} \simeq 40$ K and $\gamma_{sf} \approx +30$. By comparing these three Ce systems, there appears to emerge the trend that $\gamma_{sf}$ increases as $T_{sf}$ decreases. A similar rough correlation may hold for 3*d*-impurity systems.[4]

As an aid in understanding this apparent correlation, we invoke a Kondo-type model and plot in Fig. 8 the Kondo or spin-fluctuation temperature given by[31]

$$T_{sf} = T_f \rho^{1/2} e^{-1/\rho} , \tag{1}$$

and its derivate $\partial \ln T_{sf}/\partial \rho$ as a function of

$$\rho = |JN(E_f)| = |V_m^2 N(E_f)/(2\epsilon_{ex})| , \tag{2}$$

where $N(E_f)$ is the density of states, and the negative exchange parameter $J$ is related to $\epsilon_{ex}$ and the mixing matrix element $V_m$ as given by Schrieffer[32] for a spin-$\frac{1}{2}$ system. We use here a free-electron-like value of the degeneracy temperature $T_f = 60\,000$ K and assume $\partial T_f/\partial \rho = 0$. From Eq. (1) or Fig. 8 it is immediately clear that the observed positive value of $\partial T_{sf}/\partial \rho$ must imply that $\rho$ increases with pressure. From Eq. (2) we see that an increase in $\rho$ can arise either from an increase in the hybridization width $\Delta \sim V_m^2 N(E_f)$ or from a decrease in $\epsilon_{ex}$, or both. If we now assume that $\Delta$ *increases* with pressure and is a linear function of volume change, whereas $\epsilon_{ex}$ remains constant, it follows that $\partial \rho/\partial \ln V$ is a negative constant for all values of $\rho$. From the expression

$$\gamma_{sf} = \frac{-\partial \ln T_{sf}}{\partial \ln V} = \left[\frac{-\partial \rho}{\partial \ln V}\right]\left[\frac{\partial \ln T_{sf}}{\partial \rho}\right] = \left[\frac{-\partial \rho}{\partial \ln V}\right]\left[\frac{1}{2} + \frac{1}{\rho}\right]\left[\frac{1}{\rho}\right] , \tag{3}$$

it then follows that $\gamma_{sf}$ should be positive and *decrease* as $\rho$ (and thus $T_{sf}$) increases, as found in experiment as discussed above for Ce systems. In fact, using the above values of $T_{sf}$, we can then estimate from Eqs. (1) and (3) that $\gamma_{sf}(La\text{Ce})/\gamma_{sf}(CeSn_3) \simeq 5.1$ compared with the experimental value of 6.6. This agreement is surprisingly good (for *Y*Ce, experiment gives twice the estimated value). From Eqs. (1) and (3) we obtain $\partial \ln \rho/\partial \ln V \simeq -1.4$ for $CeSn_3$, compared to the value $\sim -4$ for *La*Ce (Ref. 4); this decrease in magnitude is to be expected for constant $\partial \rho/\partial \ln V$.

If, on the other hand, we assume that $\epsilon_{ex}$ *decreases* with pressure and is a linear function of volume change, whereas $\Delta$ remains constant, it then follows that $\partial \rho^{-1}/\partial \ln V$ is a positive constant for all values of $\rho$. Since $\partial \rho/\partial \ln V = -\rho^2(\partial \rho^{-1}/\partial \ln V)$, it would follow from Eq. (3) that $\gamma_{sf} \sim (\rho/2) + 1$ and the value of $\gamma_{sf}$ would be expected to increase as pressure increases $\rho$ (and thus $T_{sf}$), contrary to experiment.

Within the above Kondo-type model with the above assumptions, it can thus be inferred from the present results on $CeSn_3$ that the observed increase of the spin-fluctuation temperature with pressure originates from an increase in the hybridization width $\Delta$, the excitation energy remaining essentially constant.

Studies of the photoemission spectrum,[11,33] $L_{III}$-absorption edge,[28] Compton[34] scattering, positron annihilation,[35] and muon-spin rotation,[36] when taken together, give convincing evidence that in numerous $\gamma$- and $\alpha$-like Ce systems (usually considered to be barely integral and strongly mixed valence, respectively) the 4*f*-occupation number is essentially integral in both cases with a 4*f*-stabilization energy $\epsilon_{ex}$ near 2 eV. In fact, Allen and Martin[10] have gone one step further and proposed that Ce's $\gamma$-$\alpha$ transition with its large volume collapse is driven by the binding energy of a Kondo ground state. From lattice-constant[6] and neutron scattering measurements,[7] $CeSn_3$ would appear to be no exception to the above trend. Further evidence for the stability of $\epsilon_{ex}$ and the $Ce^{3+}$ state to environmental changes is provided by the present observation of simple scaling in $T/T_{sf}$ and the indicated insensitivity of $\epsilon_{ex}$ to pressure.

The existence or nonexistence of such simple one-energy scaling laws as demonstrated by Lawrence[6] for $CeIn_{3-x}Sn_x$ and here for $CeSn_3$ under pressure are of importance for attaining an understanding of the intermediate-valence state. One should, after all, only incorporate into a given model the absolute *minimum* number of characteristic energies necessary to describe the given phenomena. Further experimental work is needed, in particular within the strongly mixed-valence regime, to test the generality of such scaling relations.

Whereas in $CeSn_3$ it appears that $T_{sf}$, and not the valence $v$, is initially sensitive to pressure, it would be expected that at sufficiently high pressures both quantities should change significantly. From this point on, simple scaling would break down. We would like to propose, in fact, *the use of the requirement of scaling in two energies to determine the actual variation of* $T_{sf}$ *and* $v$. For Ce systems such a two-parameter scaling law might take the form $\chi T/C=[4-v(P)]f(T/T_{sf}(P))$. The effective moment would thus go to zero as Ce's valence approaches 4. This method would, if successful, allow the determination of *two* characteristic energies using only a *single* experimental technique. From the accuracy of the scaling in Fig. 7, the proposed two-parameter scaling law allows the estimate that in $CeSn_3$ the $4f$-electron number remains constant under a pressure change of 13.5 kbar to within about 2%, even though $T_{sf}$ increases by 20% as the sample volume decreases by 2.5%. Lawrence's studies[6] on $CeIn_{3-x}Sn_x$, when analyzed in this manner, give a similarly small valence change across the compound series where $T_{sf}$ has tripled in value. We feel that our proposed method of estimating changes in $T_{sf}$ and $v$ is worthy of further study.

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