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# Suppression of the structural phase transition in $CeCu_6$ by pressure and Au doping

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The heavy fermion compound $CeCu_6$ displays a structural phase transition from an orthorhombic to a monoclinic crystal structure at $T_m \approx 220$ K. Substituting larger Au for Cu atoms leads to an increase of the unit-cell volume at room temperature and a rapid suppression of the transition. On the other hand, a decrease of the unit-cell volume by the application of hydrostatic pressure reduces the transition temperature, too. To reveal the mechanism of the phase transition and to find an explanation of the different volume dependencies, we have investigated the dependence of the transition temperature on hydrostatic pressure and Au content ($x=0.0$, 0.05, 0.1, and 0.3) with a high-resolution dilatometer. The transition temperature drops linearly with increasing Au content $x$ and vanishes at $x \approx 0.14$. In $CeCu_6$ the thermal expansion and specific heat point clearly to a second-order transition. For Au contents of $x=0.0$, 0.05, and 0.1 we obtain a pressure dependence $dT_m/dP$ of $-17.0$ K/GPa, $-20.0$ K/GPa, and $-26.2$ K/GPa, respectively. The volume change by Au doping of $CeCu_6$ or by substituting Ce by a different rare-earth atom $R$ results in clearly different $T_m$ decreases for $T_m[V(R)]$ and $T_m[V(x)]$. However, if instead of the volume change, the change in the excess volume of the Cu(2) site is used, we obtain a uniform $T_m$ decrease of 320 K/Å$^3$. [S0163-1829(99)03741-8]

## I. INTRODUCTION

$CeCu_6$ transforms from a high-temperature orthorhombic ($Pnma$) to a low-temperature monoclinic ($P2_1/c$) phase with a very small distortion angle.[1] Within experimental resolution, neutron and x-ray diffraction measurements[1–3] indicate a second-order transition with the monoclinic strain $ab\cos\gamma$ as order parameter.[4] Ultrasonic investigations[5,6] have revealed a change in all measured elastic constants ($c_{ii}$; $i=1,\ldots,6$) and, especially, a complete softening of the transverse elastic constant $c_{66}$ at the transition temperature, which is also seen by a softening of the corresponding TA phonon (100) measured by neutron scattering.[1] In the few available specific-heat measurements[7] at higher temperatures no transition is visible and up to now the phase transition was not observed in the magnetic susceptibility,[3] optical conductivity,[8] thermoelectric power,[9] and Hall coefficient.[10] The electrical resistivity shows only a very small peak of less than 0.3 $\mu\Omega$ cm.[3,9,10]

The values of the transition temperature $T_m$ found in the literature scatter around 220 K, but show also significant lower temperatures [230 K (Ref. 2), 227 K (Ref. 11), 220 K (Refs. 3,12, and 6), 218 K (Ref. 5), 212 K (Ref. 11), 198 K (Ref. 6), and 168 K (Ref. 13)]. Suzuki *et al.*,[13] Noda *et al.*,[1] and Weber *et al.*[6] argue that these deviations are most probably caused by internal stress and impurities.

Ultrasonic measurements under hydrostatic pressure on a $CeCu_6$ sample with $T_m=168$ K show that external hydrostatic pressure shifts the transition temperature to lower temperatures with a rate of about $-20$ K/GPa.[13] This result was further confirmed by compressibility measurements at high quasihydrostatic pressure,[14] which showed the monoclinic phase to have a higher compressibility associated with slightly softer longitudinal elastic constants in comparison to the orthorhombic phase.

The transition is not only found in $CeCu_6$ but is a common feature of the homologous series $RCu_6$.[11,15–17] Yamada *et al.*[11] calculated with the thermal-expansion values of $CeCu_6$ the unit-cell volume for several $RCu_6$ compounds with $R=$La, Ce, Pr, Nd, and Sm at the respective transition temperature of each material and found a rapid decrease of $T_m$ with decreasing unit-cell volume $V$. The authors suggested that in $CeCu_6$ the pressure dependence of $T_m$ may be transformed to this volume dependence $T_m(V)$ by using the compressibility data of Oomi *et al.*[14]

A decrease of $T_m$ was also observed on Au-alloyed samples, although the lattice parameter are increased by Au doping at room temperature. For instance, in $CeCu_{5.9}Au_{0.1}$ the transition temperature is reduced to about 70 K (Ref. 18) and in parallel at this Au content the heavy-fermion system $CeCu_{6-x}Au_x$ is found to be between the Kondo- and Ruderman-Kittel-Kasuya-Yosida governed regions, leading to a non-Fermi-liquid behavior.[19]

To determine $T_m$ and its dependence on pressure, we investigated $CeCu_{6-x}Au_x$ with an Au content of $x=0.0$, 0.05, 0.1, and 0.3 by measuring the thermal expansion at ambient and higher pressures. In order to elucidate the order of the transition we have also performed a specific-heat measurement on $CeCu_6$.

## II. SAMPLE PREPARATION

Single crystals of $CeCu_{6-x}Au_x$ with $x=0.0$, 0.05, 0.1, and 0.3 were grown by the Czochralski method under high-purity argon atmosphere. After an orientation of the grown crystals at room temperature using Laue diffraction, samples were spark cut to obtain oriented crystals. Their typical dimensions along the crystallographic axes range from 1 mm to 3 mm.

## III. EXPERIMENTAL METHOD

In order to measure the length changes of the samples generated by pressure and temperature variation we have miniaturized a usual capacitive dilatometer and mounted it in a gas-pressure cell. The movable capacitor plate is attached to a parallel spring suspension to enable a nearly frictionless length change and to preserve a parallel orientation of the capacitor plates to one another. Inevitably, the springs generate a small uniaxial pressure of about 0.1 MPa on the samples (for a sample area of approximately 0.5 mm$^2$). Normally, this uniaxial pressure contribution can be neglected against the applied hydrostatic pressure of several tens of MPa.

The temperature was changed by using a continuous helium-flow cryostat. The minimal achievable temperature is about 10 K due to the large heat transfer through the pressure tubes. The maximal pressure is limited to about 1.0 GPa and to the melting pressure of the pressure-transmitting medium because the free motion of the sample and of the movable capacitor plate is only guaranteed if the medium is gaseous or liquid. Since helium cannot intercalate the crystal lattice of $CeCu_{6-x}Au_x$ we have used it as pressure-transmitting medium to expand the temperature and pressure range as far as possible.

Typical thermal-expansion measurements were carried out in a temperature range from 10 K to 300 K along the three axes of the orthorhombic crystal structure neglecting the very small monoclinic distortion. The temperature was varied continuously at a constant rate of $\pm 7$ mK/s. The pressure dependence of the transition temperature was obtained by several subsequent thermal-expansion measurements at distinct constant pressures between 0.1 MPa and maximal 0.35 GPa.

The relative temperature control is better than 2 mK. Length changes of about $\Delta L/L = 10^{-8}$ could be resolved and the pressure is measured with a precision of 0.02 MPa. A more detailed description of the experimental setup will be published elsewhere.[20]

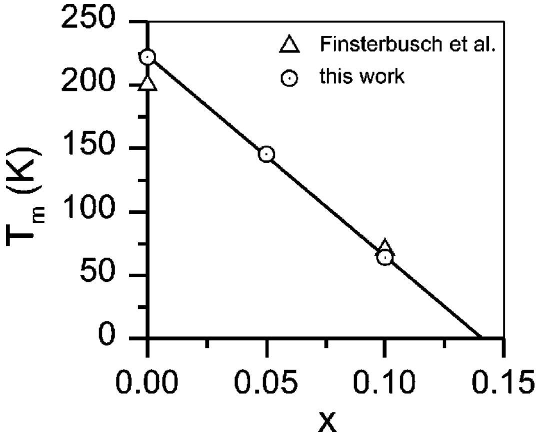

FIG. 1. The temperature of the structural phase transition of $CeCu_{6-x}Au_x$ as a function of Au content $x$ together with the values from Finsterbusch *et al.* (Ref. 18).

## IV. RESULTS AND DISCUSSION

The structural phase transition is clearly visible in the thermal-expansion coefficient along the three crystallographic axes of the investigated $CeCu_{6-x}Au_x$ samples with $x = 0.0$, 0.05 and 0.1 and is found to occur at 222 K, 146 K, and 64 K, respectively (see Fig. 1). The measured transition temperatures of $CeCu_6$ and $CeCu_{5.9}Au_{0.1}$ are in agreement with the values obtained from most of the authors (see Introduction) and from Finsterbusch *et al.*,[18] respectively. With increasing Au content the transition temperature drops linearly with $dT_m/dx \approx -15.8$ K/at.% Au. Extrapolating to lower temperatures, the transition vanishes at an Au content of about 0.14. Accordingly, we could not observe any phase transition in $CeCu_{5.7}Au_{0.3}$ between 10 K and 300 K.

In $CeCu_6$ the transition is manifested by a mean-field behavior in the linear thermal-expansion coefficients (see left part of Fig. 2). We could not observe any hysteretic effects or discontinuous length changes. Additionally, we performed

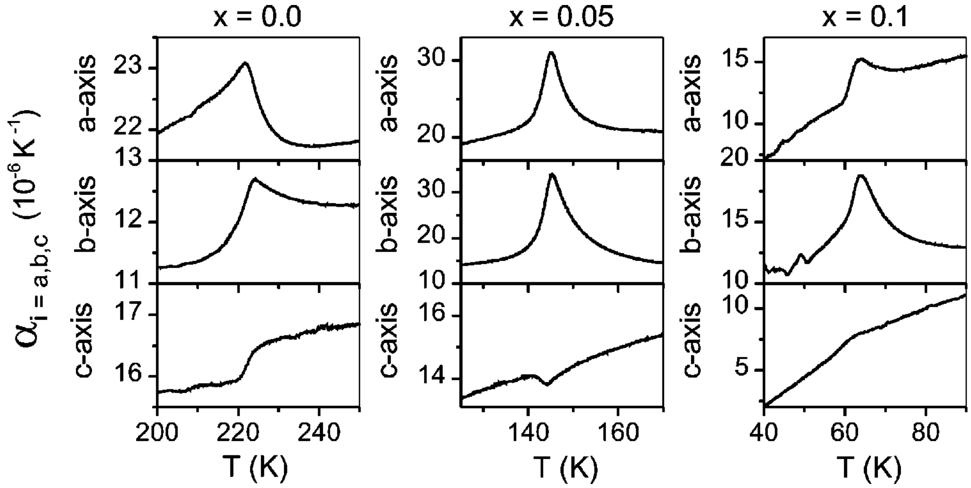

FIG. 2. The linear thermal-expansion coefficient of $CeCu_{6-x}Au_x$ in the vicinity of the structural phase transition along the *a*, *b*, and *c* axis as a function of temperature for Au content $x = 0.0$, 0.05, and 0.1 at ambient pressure. For $x = 0.3$ no signature of the transition can be found above 10 K.

a specific-heat measurement on $CeCu_6$ from 15 K to 250 K. Within the experimental resolution of $\sim 0.5\%$ no anomaly could be detected at $T_m$ against the large lattice background. These features point clearly to a second-order phase transition. The anisotropy of the unit cell is reflected by the different signs of the jump of the linear thermal-expansion coefficients $\Delta\alpha_i = \alpha_i(T > T_m) - \alpha_i(T < T_m)$ with $i = a, b, c$ along the three crystallographic axes. The jumps in the $b$ and $c$ axis with higher $\alpha_i$ values above the transition are opposite to that of the $a$ axis. They are obviously larger in the $a$ and $b$ axis direction, where the distortion evolves. In addition, the linear thermal-expansion coefficients along these directions show at $T_m$ anomalies, that are caused by fluctuations. Independent of the Au content, the $b$ axis exhibits in all samples the largest anomaly.

In $CeCu_{5.95}Au_{0.05}$ the signature of the transition is much larger than in $CeCu_6$ (see middle part of Fig. 2) but a clear indication of a positive or negative sign of the jump $\Delta\alpha$ is lost in comparison to $CeCu_6$. For this Au content hysteretic effects were found to be absent as in $CeCu_6$.

An even more diverse behavior is seen in the measurements on $CeCu_{5.9}Au_{0.1}$, where, in particular, along the $b$ axis remarkable discrepancies between different measurements were observed and further anomalies occur well below the transition. These measurements show a hysteresis between the heating and cooling curve. To test whether these effects were caused by the small uniaxial pressure contribution of the spring suspension we reduced slightly the small uniaxial pressure contribution from our experimental setup by increasing the initial distance of the capacitor plates, which is, however, traded off against a poorer experimental resolution. The right-hand side of Fig. 2 shows the thermal expansion of $CeCu_{5.9}Au_{0.1}$, which has been taken with such an extremely small uniaxial pressure contribution.

To show the effect of the uniaxial pressure contribution generated by the usual initial distance of our capacitor plates, we plot a typical result of such a measurement in Fig. 3 (the upper curves along the $a$ and $b$ axis). The jump and the anomaly along the $a$ axis have vanished and in the $b$ direction the size of the anomaly has dramatically decreased with, again, additional anomalies well below the transition.

In order to apply a really high uniaxial pressure, we have introduced an additional CuBe spring (see Fig. 4), which has been used in an earlier study to untwin a $La_{1-x}Sr_xCuO$ single crystal.[21] The spring and our dilatometer are made of the same material, which allows us to ignore additional thermal-expansion effects from the spring. We used this simple *in situ* technique to generate a high uniaxial pressure of about several tens of MPa along the three orthorhombic axes of $CeCu_{5.9}Au_{0.1}$ and measured in the same directions where the uniaxial pressure was applied (see Fig. 4). With the sample in this configuration the anomaly and the jump of the transition vanish along the $a$ and $c$ axis, while in the $b$ direction a small but clearly visible anomaly is present (see Fig. 3). The direction of the cusp at the transition is inverted, the anomalies at lower temperatures have disappeared, and no longer have hysteretic effects been found upon thermal cycling.

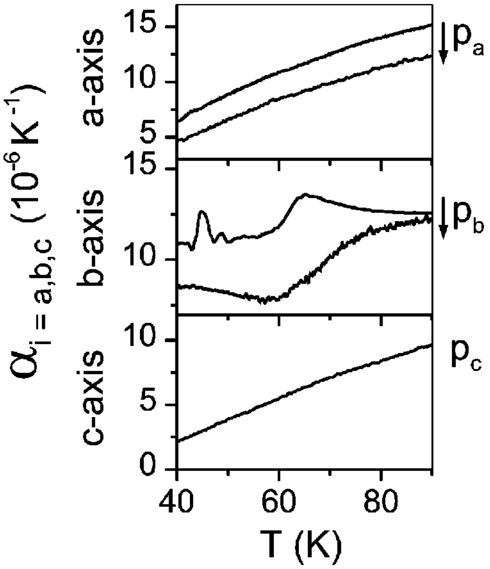

FIG. 3. The thermal-expansion coefficient of $CeCu_{5.9}Au_{0.1}$ along the three orthorhombic axes with an increased uniaxial pressure generated by the spring suspension of the dilatometer (upper curves for the $a$ and $b$ axis direction) and by the additional CuBe spring showed in Fig. 4 (lower curves for the $a$ and $b$ axis direction and curve for $c$ axis direction).

For other substances the extreme sensitivity on small uniaxial-pressure components has been reported by other authors, too. They are characteristic of the evolution of a twin structure recorded by thermal expansion.[22,21] Neutron-diffraction studies have revealed that the monoclinic phase is twinned with (100) as a common plane. Consequently, the evolution of the twin domains influences predominantly the thermal expansion along the $b$ direction. Unfortunately, for an ideal detwinning of $CeCu_{6-x}Au_x$, the uniaxial pressure should be applied along one of the [110] directions. In our restricted experimental space a measurement with such a spring is impossible. Since the uniaxial pressure generated by the CuBe spring has only a small shear contribution to support one direction of the distortion (see Fig. 4) the effect of our spring is difficult to estimate, but it can apparently suppress hysteretic effects and remove the anomalies at lower temperatures. The high sensitivity of the twin structure to stress application can also explain the increased ultrasonic absorption in the monoclinic phase, which is most probably caused by a coupling of sound waves to the twin boundaries.[12]

The influence of the twin formation seems to increase with growing Au concentration. In $CeCu_6$ and $CeCu_{5.95}Au_{0.05}$ we could not observe such effects and, furthermore, the signature of the transition in $CeCu_6$ indicates that in this case the transition is most likely not controlled by

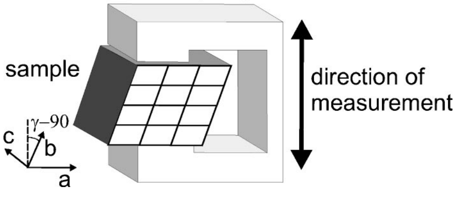

FIG. 4. The CuBe spring to generate a higher uniaxial pressure on the $CeCu_{5.9}Au_{0.1}$ crystal. Here, as an example, a measurement along the $b$ axis is illustrated.

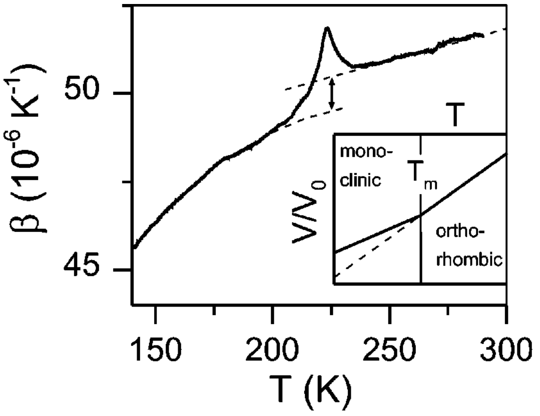

FIG. 5. The volume-expansion coefficient of $CeCu_6$ versus temperature in the vicinity of the phase transition. The inset shows a schematic view of the resulting volume change. Below the transition the unit-cell volume of the monoclinic phase is larger than the volume of the extrapolated orthorhombic phase (dashed line).

the twins. On the other hand, our thermal-expansion measurements of $CeCu_{5.9}Au_{0.1}$ along the *a* and *b* axis are, at the phase transition and below, influenced by the twins. In principle the *c* axis should not be affected by the twins. However, the orientation of the crystals with the Laue method is not precise enough to completely avoid in a measurement along the *c* axis minor contributions of the *a* or *b* axis.

The volume-expansion coefficient $\beta = \Sigma_{i=a,b,c}\alpha_i$ derived from our measurements (see Fig. 5) reveals a smaller thermal expansion of the monoclinic phase resulting in a larger unit-cell volume compared to the volume of the unstable orthorhombic phase at low temperature. (This relative volume behavior is shown schematically in the inset of Fig. 5 as observed by Gratz *et al.*[3]) Consequently, the orthorhombic phase is stabilized under pressure and our measurements of the hydrostatic pressure dependence of $T_m$ show that with increasing pressure the transition is shifted towards lower temperatures for all investigated Au concentrations (see Fig. 6). For Au contents of $x = 0.0$, 0.05, and 0.1 we obtain a pressure dependence $dT_m/dP$ of $-17.0$ K/GPa, $-20.0$ K/GPa, and $-26.2$ K/GPa, respectively (see the insets of Fig. 6). With increasing Au content the transition temperature is suppressed more strongly under pressure.

As shown by Yamada *et al.*,[11] Vrtis *et al.*,[16] and Nakazato *et al.*[17] the structural phase transition is typical for the homologous series $RCu_6$ ($R$ = La, Ce, Pr, Nd, and Sm). Yamada *et al.* reported a very fast drop of $T_m$ with decreasing unit-cell volume,[11] which was estimated from the thermal expansion of $CeCu_6$ as mentioned in the Introduction. Following the idea of Yamada *et al.* we replot this curve, but owing to the more recent data of Vrtis *et al.*,[16] Nakazato *et al.*[17] and Endoh *et al.*[15] we are able to use the experimentally determined values of the unit-cell volume right at the transition. Figure 7 gives the transition temperature $T_m$ of $RCu_6$ and the investigated $CeCu_{6-x}Au_x(x = 0.0,\ 0.05,\ 0.1)$ samples as a function of the unit-cell volume $V$ at the transition temperature. In the rare-earth series $RCu_6$ the transition temperature $T_m[V(R)]$ grows linearly with increasing unit-cell volume with a rate of about 12.7 K/Å$^3$. Apparently, the transition does not occur in $RCu_6$ with a unit-cell volume smaller than 400 Å$^3$. Consequently, no such transition has been reported for $GdCu_6$, which has already at room temperature a unit-cell volume of only about 400 Å$^3$.[23]

In order to determine the influence of pressure on the transition via the unit-cell volume $T_m[V(P)]$ we use the unit-cell volume of the $CeCu_{6-x}Au_x$ samples as determined by x-ray[24] and neutron-diffraction studies[25] at room temperature. With our thermal-expansion measurements[20] we then

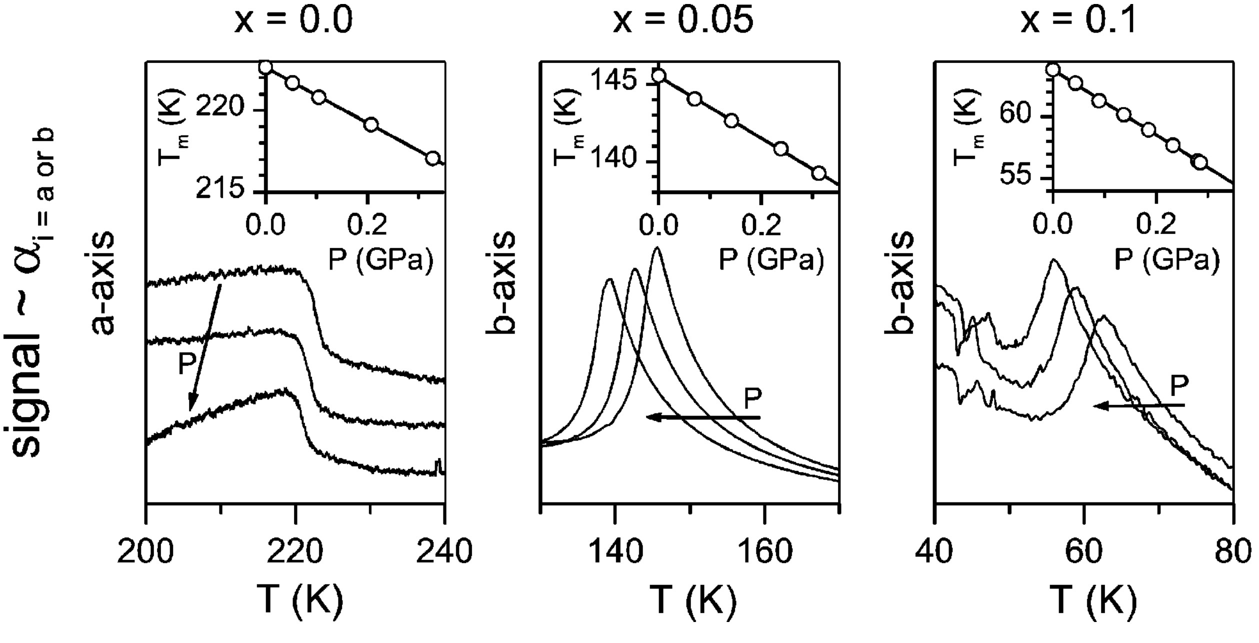

FIG. 6. The raw data of the thermal-expansion measurements under pressure of $CeCu_{6-x}Au_x$ with $x = 0.0$, 0.05, and 0.1. The data include the pressure and temperature dependence of the dielectric constant of the pressure-transmitting medium. For clarity only three different measurements are displayed in each plot. The presented data for $x = 0.0$ are taken at $P = 0$ GPa, 0.053 GPa, and 0.105 GPa, for $x = 0.05$ at $P = 0$ GPa, 0.142 GPa, and 0.313 GPa, and for $x = 0.1$ at $P = 0.043$ GPa, 0.185 GPa, and 0.280 GPa. The derived pressure effects $dT_m/dP$ for $x = 0.0$, 0.05, and 0.1 are $-17.0$ K/GPa, $-20.0$ K/GPa, and $-26.2$ K/GPa, respectively.

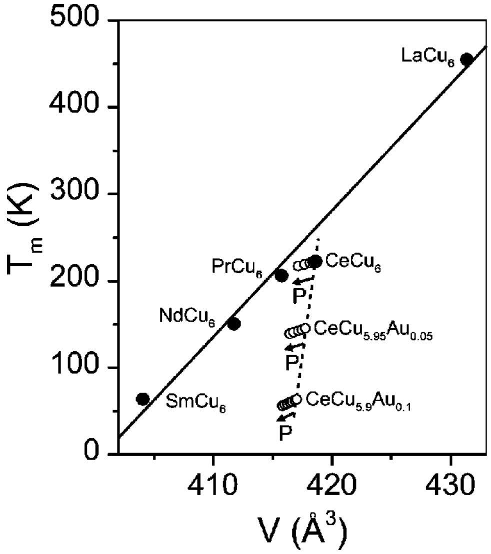

FIG. 7. The transition temperature $T_m$ of $R$Cu$_6$ and CeCu$_{6-x}$Au$_x$ as a function of the unit-cell volume at $T_m$. The $T_m(V)$ values of LaCu$_6$, NdCu$_6$, PrCu$_6$, and SmCu$_6$ are obtained from the data of Vrtis *et al.* (Ref. 16), Nakazato *et al.* (Ref. 17), and Endoh *et al.* (Ref. 15).

calculate the unit-cell volume at the transition temperature at ambient pressure. The volume at higher pressures is determined by using our measured bulk modulus values[20] at $T_\mathrm{m}$ of 93 GPa, 97 GPa, and 97 GPa for $x=0$, 0.05, and 0.1, respectively.

In contrast to the suggestion of Yamada *et al.*[11] the pressure-induced volume effect on the transition $T_\mathrm{m}[V(P)]$ of CeCu$_6$ does not follow the $T_\mathrm{m}[V(R)]$ curve but shows a clearly smaller slope (see the arrows in Fig. 7). This slope $dT_\mathrm{m}/dV(P)$ rises significantly with increasing Au content from 3.7 K/Å$^3$ over 4.7 K/Å$^3$ to 6.1 K/Å$^3$ for $x=0.0$, 0.05, and 0.1, respectively, which is not an effect of a changing bulk modulus because the bulk modulus remains almost constant.

$T_\mathrm{m}(V)$ of the investigated CeCu$_{6-x}$Au$_x$ samples at ambient pressure (marked in Fig. 7 by the dashed line) deviates even more drastically from the $T_\mathrm{m}[V(R)]$ curve. Already the pure CeCu$_6$ sample has a smaller $T_\mathrm{m}$, which is thought to be a consequence of a Ce valence slightly larger than three.[16] A similar valence change of Ce was observed in the isostructural series $R$Cu$_5$Sn.[26] With Au doping the unit-cell volume of CeCu$_{6-x}$Au$_x$ is increased at room temperature from about 420.06 Å$^3$ to 421.44 Å$^3$ for $x=0$ to 0.1, respectively. However, due to the sharp drop of the transition temperature with Au doping and the thermal expansion, the resulting unit-cell volume $V(x)$ at the transition temperature $T_\mathrm{m}$ decreases very slightly from 418.6 Å$^3$ to 417.02 Å$^3$ for the Au concentration $0 \leqslant x \leqslant 0.1$. From this observation it is clear that $T_\mathrm{m}$ is definitely not determined simply by the unit-cell volume.

Up to now we have not considered the anisotropy of these compounds. To get better insight into the anisotropy of CeCu$_{6-x}$Au$_x$ we try to evaluate the uniaxial pressure dependencies of the transition temperature. To our knowledge, up to now no literature data about the uniaxial pressure dependencies are available. In principle, our thermal-expansion measurements could reveal these dependencies via the Ehrenfest relation:

$$\frac{dT_\mathrm{m}}{dp_i} = V_\mathrm{mol} T_\mathrm{m} \frac{\Delta\alpha_i(T_\mathrm{m})}{\Delta C_p(T_\mathrm{m})}, \quad i=a,b,c. \tag{1}$$

Unfortunately, the twin formation makes a proper determination of $\Delta\alpha_i(T_\mathrm{m})$ difficult. In addition a specific-heat anomaly is not detectable as mentioned above. However, our value for the hydrostatic pressure dependence $dT_\mathrm{m}/dP$ allows us to calculate the anomaly in the specific heat

$$\Delta C_p(T_\mathrm{m}) = T_\mathrm{m} V_\mathrm{mol} \left(\frac{dT_\mathrm{m}}{dp_i}\right)^{-1} \sum_{i=a,b,c} \Delta\alpha_i(T_\mathrm{m}), \tag{2}$$

and hence the stress dependencies $dT_\mathrm{m}/dp_i$. This method can be used for CeCu$_6$ because the thermal-expansion measurements are apparently not influenced by twin domains for this compound. The resulting specific-heat anomaly $\Delta C_p(T_\mathrm{m}) \approx -0.35$ J mol$^{-1}$ K$^{-1}$ for CeCu$_6$ is indeed far below the resolution of our specific-heat measurement. We derive a uniaxial pressure dependence along the orthorhombic $a$, $b$, and $c$ axis of 48.6 K/GPa, $-43.5$ K/GPa, and $-22.1$ K/GPa, respectively. This large anisotropy cannot be understood by simply considering the change of lattice parameters. To get an idea of the origin of the $T_\mathrm{m}$ changes we have to discuss the internal changes of the unit cell with Au and $R$ substitution.

Ruck *et al.*[27] reported that the Au atoms occupy exclusively the Cu(2) site[28] in CeCu$_{6-x}$Au$_x$ for $x \leqslant 1.0$, because this site has the largest interatomic spacing, i.e., a large excess volume if occupied by a Cu atom. Vrtis *et al.*[16] found that the Cu(4), which is a nearest neighbor to the Cu(2) site, shows the largest displacement at the orthorhombic-monoclinic transition and may be triggering the transition. The Cu(2) site is the only Cu site that is surrounded by the maximum number of four $R$ atoms. Larger $R$ atoms lead, therefore, to an increase of the entire Cu(2) coordination polyhedron and, conseqently, to a larger excess volume. On the other hand, replacing the Cu(2) by a larger Au atom reduces this volume. The correspondence of the dependence of the transition temperature on Au content and $R$ ion radius suggests that the excess volume at the Cu(2) site causes the transition, giving the system a possibility to minimize its free energy by a distortion. With this assumption it would be evident that the unit-cell volume is not the decisive parameter and that a change in the excess volume by introducing larger Au atoms in the Cu(2) site will dramatically reduce $T_\mathrm{m}$. Using the available data of atom positions [CeCu$_6$,[25] LaCu$_6$,[16] PrCu$_6$,[16] NdCu$_6$,[16] and SmCu$_6$ (Ref. 29)] we tried to estimate the excess volume per Cu(2) site by subtracting the volume of the ion occupying the Cu(2) site from the free volume of the Cu(2) site itself, i.e.,

$$\Delta V_{\mathrm{Cu}(2)} = (4/3)\pi\{\langle r_{\mathrm{Cu}(2)}\rangle^3 - [x r_\mathrm{Au}^3 - (1-x) r_\mathrm{Cu}^3]\}. \tag{3}$$

Here, $\langle r_{\mathrm{Cu}(2)}\rangle$ is the mean distance between the center of the Cu(2) or Au ion and its neighbors, and $r$ is a typical ion radius of Cu or Au ions in metals with 1.278 Å and 1.442 Å, respectively.[30] The size of the $R$ ions was estimated with a valence of three with eightfold coordination.[31] This may only be a crude estimate, but fortunately the abso-

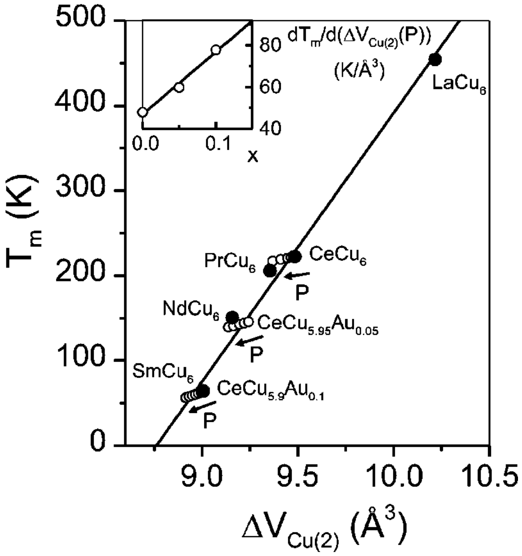

FIG. 8. The transition temperature $T_m$ of $R$Cu$_6$ and CeCu$_{6-x}$Au$_x$ from Fig. 7 as a function of the excess volume at the Cu(2) site. In the inset the excess volume dependence of $T_m$ derived by application of hydrostatic pressure is shown as a function of the Au content.

lute value of the excess volume is not important, since we consider only the relative changes of $\Delta V_{Cu(2)}$. In Fig. 8 the transition temperatures from Fig. 7 are plotted as a function of the $\Delta V_{Cu(2)}$ values calculated by this method.

Surprisingly, our simple calculation of $\Delta V_{Cu(2)}$ yields volume dependencies of the transition temperature $T_m[V(R)]$ and $T_m[V(x)]$ as a function of $\Delta V_{Cu(2)}$, which coalesce very well on one line with a slope of about 320 K/Å$^3$ (see Fig. 8). This supports the idea that the excess volume of the Cu(2) site is a key factor of this transition.

In contrast, the external pressure dependence $T_m[V(P)]$ as a function of $\Delta V_{Cu(2)}$ shows significant deviations. This has to be expected because we have no information on the true changes of $\Delta V_{Cu(2)}$ but could only estimate values from the unit-cell contraction under pressure. Any nonhomogeneous changes of the relative atom positions of the Cu(2) coordination polyhedron under pressure will result in a erroneous estimation of the pressure dependence of $\Delta V_{Cu(2)}$.

The existence of the excess volume at the Cu(2) site suggests that the surrounding atoms (10 Cu and 4 $R$ ions) have no possibility to come closer to this atom, which will lead to prestressed bondings. Therefore the coordination polyhedron of the Cu(2) site will form a less compressible structural element within the unit cell, which results in a smaller decrease of the excess volume under pressure compared to the lattice parameters. Hence, we expect a smaller slope of $T_m[V(P)]$ for CeCu$_6$ in comparison to $T_m[V(R)]$ and $T_m[V(x)]$ as is indeed found in the experiment (see Figs. 7 and 8). If the coordination polyhedron of the Cu(2) site expands upon the introduction of the large Au atom the prestress will be reduced, resulting in a more uniform compressibility within the unit cell. Indeed, with increasing Au doping the slope of $T_m[\Delta V_{Cu(2)}(P)]$ increases, as may be seen in the inset of Fig. 8. Surprisingly, a simple extrapolation of the concentration dependence of the slope $dT_m/d[\Delta V_{Cu(2)}(P)]$ for an Au content of $x=1.0$ gives approximately a slope of 349 K/Å$^3$, which is almost the same value as found for $R$ substituting or Au doping.

## V. SUMMARY

In conclusion, we have determined the transition temperature of the monoclinic to orthorhombic phase transition of CeCu$_{6-x}$Au$_x$ in dependence of the Au content and higher static pressure. The transition temperature $T_m$ falls linearly with increasing Au content $x$ and vanishes at an Au content of approximately 0.14. In CeCu$_6$ the thermal-expansion measurements point clearly to a second-order transition, as does the lack of an anomaly in the specific heat at $T_m$. With increasing Au content the influence of the twin domains begins to dominate the thermal expansion but can be minimized by application of a small uniaxial pressure. For Au contents of $x=0.0$, 0.05, and 0.1 we obtain a pressure dependence $dT_m/dP$ of $-17.0$ K/GPa, $-20.0$ K/GPa, and $-26.2$ K/GPa, respectively.

The volume change by substituting the rare-earth atom $R$ or by Au doping CeCu$_6$ results in clearly different $T_m$ decreases for $T_m[V(R)]$ and $T_m[V(x)]$. However, if instead of the volume change the change in the excess volume of the Cu(2) site, $\Delta V_{Cu(2)}$, is used, we obtain a uniform $T_m$ decrease of 320 K/Å$^3$. We interpret the difference between the volume dependence of $T_m$ by doping $T_m[V(R \text{ or } x)]$ and pressure application $T_m[V(P)]$ as a consequence of a nonuniform compressibility within the unit cell. With increasing Au concentration, the compressibility becomes more uniform because the large Au atom softens the initially almost incompressible Cu(2) coordination polyhedron and the volume dependence of $T_m[\Delta V_{Cu(2)}(P)]$ and $T_m[\Delta V_{Cu(2)}(R \text{ or } x)]$ converge.

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