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Thermodynamics of the first-order valence transition in $\mathrm{YbInCu_4}$

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We present measurements of the specific heat and complete elastic moduli of $\mathrm{YbInCu_4}$ as a function of temperature in order to complement existing thermal expansion data. Together these data allow a complete analysis of the thermodynamics of the first-order isostructural valence transition in $\mathrm{YbInCu_4}$. The Clausius-Clapeyron equation predicts well the measured pressure dependence of the valence transition temperature. Estimates of the Gruneisen parameter from thermodynamic measurements and from pressure-dependent magnetic susceptibility in both the high-temperature and low-temperature phases of $\mathrm{YbInCu_4}$ are in good agreement. On the other hand, a Gruneisen analysis of the change in Kondo temperature at the valence transition fails, emphasizing the importance of carrier-density changes associated with the valence transition, unlike in the case of the γ-α transition in elemental Ce. Finally, we address the issue of precursive rounding in the elastic moduli for temperatures greater than the valence transition temperature and argue that thermodynamically $\mathrm{YbInCu_4}$'s valence transition is indeed first order.
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$\mathrm{YbInCu_4}$ undergoes a first-order isostructural valence transition at 42 K in which the volume of the lattice increases by 0.5%.[1] This transition appears analogous to the γ-α transition in elemental Ce,[2] and the Kondo volume collapse (KVC) model,[3] at least qualitatively, provides insight into the physical mechanism producing the transition. In this model the strong spin-lattice coupling of the Kondo interaction produces a nonlinear feedback between f-electron population and lattice volume that leads to a first-order phase transition. For the case of γ-α Ce, this model predicts well the pressure-temperature phase diagram for the transition as well as the magnitude of the changes in physical properties across the phase boundary. However, for $\mathrm{YbInCu_4}$ the KVC model appears to be inadequate in explaining the quantitative details of the transition.[4]

One of the principal difficulties associated with achieving a better understanding of the physics of $\mathrm{YbInCu_4}$ is the great variations and inconsistencies among physical properties that have been reported in the experimental literature. It is generally agreed that, at some temperature or range of temperatures between 40 and 80 K, all physical properties that are coupled to the f-electron occupation number display large changes. However, the magnitude of the changes and their sharpness as a function of temperature vary widely, which makes a quantitative intercomparison of the measurements difficult. We have recently undertaken a program to synthesize flux-grown single crystals of $\mathrm{YbInCu_4}$,[5] which by Rietveld refinement of neutron-diffraction data have been shown to possess the smallest amount of site disorder for $\mathrm{YbInCu_4}$ yet reported (<2%, compared to ~5% for previous polycrystalline samples),[6] and to perform a complete set of physical measurements on these crystals in order to self-consistently characterize the properties of $\mathrm{YbInCu_4}$.[4,7–12]

Here, we report measurements of the specific heat and elastic moduli of $\mathrm{YbInCu_4}$, as well as the pressure dependence of the valence transition temperature $T_v(P)$ and of the magnetic susceptibility $\chi(T,P)$. These data, together with our previously published thermal expansion data,[4,5] allow a rather complete exploration of the thermodynamics of the isostructural valence transition in $\mathrm{YbInCu_4}$, and, in particular, permit us to identify the valence transition as strictly first order.

Single crystals of $\mathrm{YbInCu_4}$ were grown from an In-Cu flux as reported previously,[7] and bulk characterization (e.g., magnetic susceptibility, electrical resistivity, and powder x-ray diffraction) reveals that all such flux-grown crystals of $\mathrm{YbInCu_4}$ are essentially identical. Specific-heat data were obtained using a standard semiadiabatic heat pulse technique. The heater was a metallic thin film and the thermometer was an Allen-Bradley 100 Ω nominal carbon resistor. The addenda, which consisted of a 25 μm-thick sapphire plate, thermometer, and resistor, were measured separately,

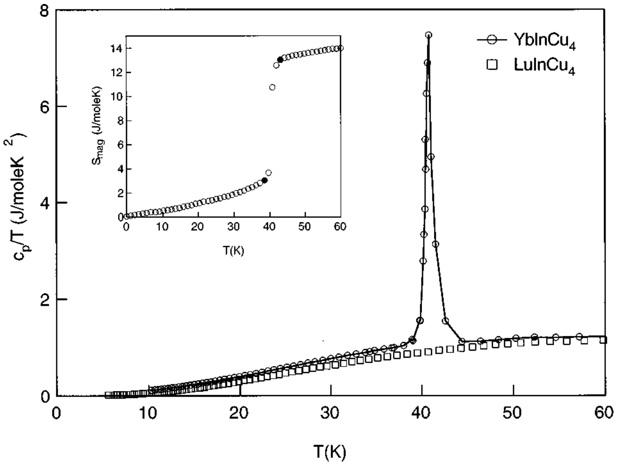

FIG. 1. Specific heat divided by temperature as a function of temperature for $YbInCu_4$ and $LuInCu_4$. The inferred magnetic entropy is shown in the inset. The latent heat associated with the valence transition is taken to be the change in entropy between the two solid symbols.

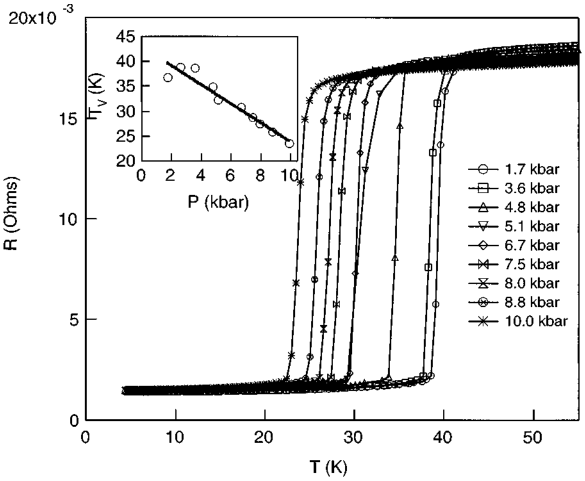

FIG. 2. Resistance as a function of temperature at various fixed pressures for $YbInCu_4$. The inset shows the inferred pressure dependence of the valence transition temperature.

as was the specific heat of the nonmagnetic isomorph $LuInCu_4$. The elastic moduli of $YbInCu_4$ were measured using resonant ultrasound spectroscopy (RUS),[13] a technique that, from the measurement of the mechanical resonances of a well-shaped, mm-sized single crystal, allows the simultaneous determination of all of a solid's elastic moduli. Because of this capability, only a single temperature sweep is required to obtain a complete set of elastic moduli data—a particularly important advantage when one is studying phase transitions that are sharp and hysteretic. The pressure dependence of the valence transition temperature was determined resistively, using a Be-Cu clamp-type pressure cell with flourinert as the pressure-transmitting medium. The absolute pressure at low temperature was measured using a lead manometer. The magnetic susceptibility as a function of temperature and pressure was measured using a novel pressure cell designed to fit in a commercial superconducting quantum interference device magnetometer.[14]

In Fig. 1 we show the specific heat of $YbInCu_4$ and of $LuInCu_4$ plotted as specific heat divided by temperature (c_p/T) vs temperature. Just above 40 K, c_p/T for $YbInCu_4$ rises from 1 J/mol K^2 to 8 J/mol K^2 in less than 1 K and then drops equally rapidly. Subtracting the $LuInCu_4$ data from that of $YbInCu_4$ allows an estimate of the ''magnetic'' specific heat of $YbInCu_4$, which includes effects from both the valence transition and the low-temperature mass enhancement of $YbInCu_4$ (the Sommerfeld coefficient of $YbInCu_4$ in the low-T phase is approximately 50 mJ/mol K^2). Integrating the ''magnetic'' specific heat gives the magnetic entropy shown in the inset of Fig. 1. The entropy jump ΔS at the valence transition is 10 J/mol K, taken as the difference between the two solid symbols in the figure. We know of two previous reports of specific-heat measurements through the valence transition in $YbInCu_4$.[1,15] Hauser *et al.* report an essentially linear increase of entropy from ~3 J/mol K at 40 K to ~11 J/mol K at 70 K. Felner *et al.* observe a two-peak structure (at ~40 K and ~60 K) in specific heat that leads to an integrated entropy of 13.3 J/mol K at 70 K. These three measurements yield similar entropy changes through the transition range. The differences can be ascribed to stoichiometric variations throughout the sample leading to broadened transitions. We stress that the single sharp peak in c_p/T in the present sample is consistent with the high quality observed in structural refinements and with a single homogeneous first-order phase transition.

We[4–6] (and others[1,16–18]) have previously reported a thermal expansion anomaly at the valence transition in $YbInCu_4$. The length of the sample increases by $\Delta L/L=0.15\%$ at the valence transition over a temperature range comparable to that of the specific-heat anomaly in Fig. 1. For a cubic material the volume change $\Delta V/V=3\Delta L/L$ in the limit of small ΔV and ΔL, and the Clausius-Clapeyron equation predicts $dT_v/dP=\Delta V/\Delta S$, where T_v is the valence transition temperature and P is pressure, so one can estimate the thermodynamically expected dT_v/dP for the valence transition from measured ΔL and ΔS. We infer $dT_v/dP=-2.5$ K/kbar. This prediction is in good agreement with our measured $dT_v/dP=-2$ K/kbar, inferred from the resistivity measurements shown in Fig. 2. Many other groups have also reported similar values for dT_v/dP.[1,15,16,19,20]

In many mixed-valence materials where Kondo effects are dominant, there are additional relationships among derivatives of the free energy, beyond those required by basic thermodynamics, that are found because of an experimentally observed scaling of the free energy.[21] Explicitly, if $F=F_N(T,V)+F_e(T,V)$, i.e., the free energy is composed of a ''normal'' contribution F_N and an electronic contribution F_e, which can be written as

$$F_e(T,V)=-Nk_BT_0-Nk_BTf[T/T_0(V)], \qquad (1)$$

where T_0, a characteristic temperature, has the dominant volume dependence in the free energy, one can define a Gruneisen parameter characterizing the strength of this volume dependence:

$$\Gamma=-d\ \ln T_0/d\ \ln V=(-B/T_0)dT_0/dP. \qquad (2)$$

One can also show that, in terms of measurable thermodynamic derivatives,

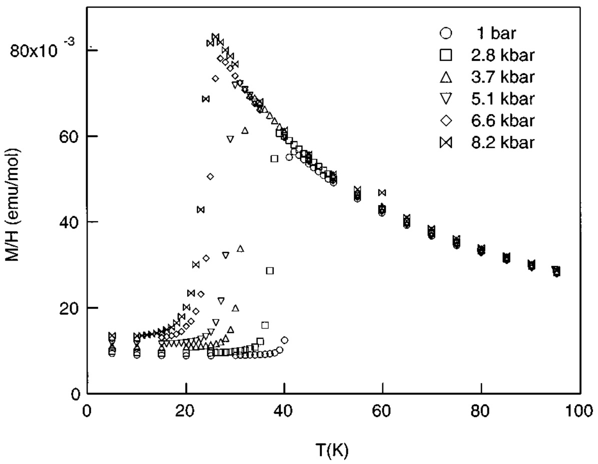

FIG. 3. Magnetic susceptibility of $\mathrm{YbInCu_4}$ as a function of temperature at various fixed pressures.

$$\Gamma = \beta V B_T / c_p , \tag{3}$$

where β is the thermal expansion, c_p the specific heat, and B_T the isothermal bulk modulus. To be precise, one should subtract the background lattice contribution to β and c_p, determined from measurements on nonmagnetic isomorphs, to correctly estimate the ''magnetic'' Gruneisen parameter from Eq. (3) (i.e., $\Gamma^{\mathrm{mag}} = \beta^{\mathrm{mag}} V B_T / c_p^{\mathrm{mag}}$). Naively, one might expect such a free-energy-scaling relationship to hold for $\mathrm{YbInCu_4}$, not only because many aspects of the physics can be described in a single-impurity Kondo picture (in particular T_v, the valence transition temperature, is approximately equal to T_0^+, the characteristic temperature of the high-temperature state)[4,7] but also because there is an observed scaling between the magnetic field required to induce the valence transition and the temperature at which the transition occurs that is strongly suggestive of a single underlying energy scale (perhaps associated with T_0^+).[9]

For $T < T_v$, it is straightforward to estimate Γ from both Eqs. (3) and (2). Although the Gruneisen parameter is relatively temperature independent for $T < T_v$, to be explicit we take data at $T = 10$ K: $\beta_{\mathrm{mag}} = -3 \times 10^{-6}\ \mathrm{K}^{-1}$,[4] $a = 7.143$ Å,[6] $c_p^{\mathrm{mag}} = 500$ mJ/mol K (Fig. 1), and $B_T = 10.5 \times 10^{11}$ erg/cm^3,[22] which together imply $\Gamma = 34.6$, a reasonable value for a heavy Fermion compound with Sommerfeld coefficient $\gamma = 50$ mJ/mol K^2.[21] In the single-impurity limit,[23] we know $T_0 = C/\chi(T=0)$, where C is the $J = \frac{7}{2}$ Curie constant, so a measurement of χ $(T=0)$ as a function of pressure allows us to determine Γ using Eq. (2). These data are shown in Fig. 3. We take χ (10 K) as an approximation of χ $(T=0)$, calculated T_0 for each P and from a linear fit to T_0 vs P find $dT_0/dP = -12.4$ K/kbar or $\Gamma = 30.6$, in good agreement with our thermodynamic estimate.

One can also estimate the Gruneisen parameter by looking at changes in the valence transition temperature and associating them with T_0.[4] Although this is not strictly correct for a first-order phase transition [the familiar Ehrenfest relation that can be derived from Eqs. (2) and (3) is only valid for second order phase transitions], it is often the case, as it is here, that such a calculation yields a reasonable result. If we assume $T_v = T_0^+$, from Fig. 2 we know $dT_v/dP = -2$ K/kbar, so Eq. (2) implies $\Gamma = 52$. Alternatively, one can take the literal definition of $\Gamma = -(V/T_0)\Delta T_0/\Delta V$. At the valence transition, we know $\Delta T_0 = 375$ and $\Delta V = 0.5\%$ which, using V and T_0 appropriate to the high-T phase, yields $\Gamma = 3000$, an unphysical value. Thus, every method of estimating Γ, both in the low-T phase and at the phase transition, gives a reasonable value of the Gruneisen parameter except for that in which ΔT_0 is directly associated with ΔV (i.e., when we make the assumption that the KVC model is a valid description of the valence transition). A similar observation has already been made in Ref. 4, where we argue that low carrier density is the driving mechanism behind the valence transition rather than Kondo volume collapse. The band structure of $\mathrm{YbInCu_4}$ is such that a small change in the Yb valence can give rise to large changes in effective conduction electron density of state.[10] Apparently, this nonlinear feedback is sufficiently strong to give rise to a first-order transition.

Finally, we consider the response of the elastic moduli to the valence transition in $\mathrm{YbInCu_4}$. Kindler *et al.* have performed the only measurement of the elastic constants of $\mathrm{YbInCu_4}$ as a function of temperature to date,[22] and these are the data that we have used for the bulk modulus in the above Gruneisen analysis. These measurements were performed on a Bridgman-grown single crystal that had a valence transition temperature of 65 K. They observed steplike drops in each of the measured elastic constants with transition widths (a few K) comparable to those of other physical measurements performed on their crystal. For the longitudinal elastic constant c_L, they also observed a Curie-Weiss-like temperature dependence that extended approximately 25 K above and below the valence transition temperature. The existence of this precursive rounding has significant consequences on the thermodynamic interpretation of the valence transition in $\mathrm{YbInCu_4}$. For a strongly first-order transition one expects no precursor effects in measured physical properties above T_v, whereas for a transition that is second order or weakly first order, precursor effects may be allowed by symmetry—as shown, for example, by Kindler *et al.* in their Landau analysis of the temperature dependence of their bulk modulus data.[22]

We have measured the elastic constants of a flux-grown single crystal of $\mathrm{YbInCu_4}$ as a function of temperature using RUS in order to determine if the elastic moduli depend on the valence transition temperature of the crystal (our crystals have $T_v = 42$ K whereas Kindler *et al.*'s crystal had $T_v = 65$ K) and to study the extent to which precursive rounding exists in our lower-T_v samples. In Fig. 4 we show the temperature dependence of representative resonance frequencies of our crystal. In general, a measured resonance frequency depends on a complicated linear combination of each of a solid's elastic moduli, so that modulus information cannot be extracted easily from the temperature dependence of an arbitrary resonance frequency. However, it is straightforward to infer best-fit values of all of the elastic constants at a given temperature from the complete set of resonance frequencies assuming that the size, shape, density, and crystallographic orientation of the sample are known.[13] Our fits at temperatures far above the valence transition are in good quantitative agreement with the results of Kindler *et al.*,[22] so here we focus only on the relative temperature dependence of the measured frequencies.

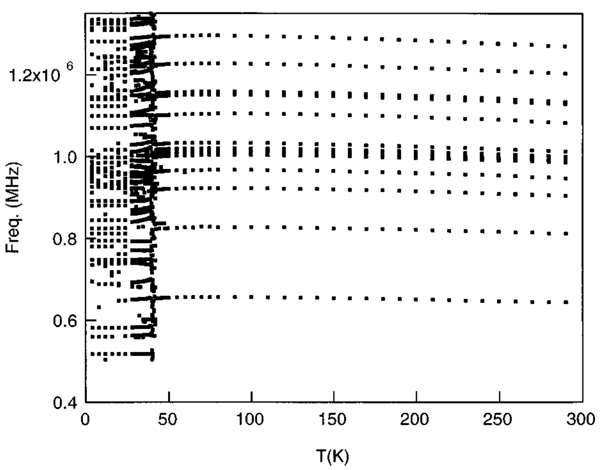

FIG. 4. Measured resonance frequencies of a single crystal of $YbInCu_4$ as a function of temperature.

To first order, the frequencies in Fig. 4 are temperature independent at high temperature, drop sharply over a very narrow range of T (~ 1 K), and are temperature independent at low temperature. Unfortunately, because of the very rapid change in frequencies at T_v, we are unable to track individual resonances through the valence transition and are also unable to obtain a self-consistent elastic constant fit to the measured frequencies below T_v. This is presumably due to the significant strain induced by the volume expansion, a not uncommon effect associated with such large volume changes. Furthermore, on warming back above T_v, the measured frequencies are not reproducible, suggestive of microcracking and strain-induced disorder, a phenomenon also observed in our resistivity data.[7] Despite these experimental complications, two general conclusions can be drawn from our RUS data. The data of Kindler *et al.*,[22] at least away from the valence transition, are sound, and the ''background'' elastic constants are independent of the precise T_v of a crystal. Near the valence transition it is not clear that the Landau-type analysis of Kindler *et al.*[22] is appropriate for samples with lower T_v. Although this conclusion may be clouded because of our inability to track resonances through the transition, it appears that the essentially symmetric softening that Kindler *et al.*[22] observed for c_L near T_v is not reproduced in any of our resonance frequency data.

In order to address the issue of precursive rounding in the elastic constants at temperatures greater than T_v, we show in Fig. 5 the temperature dependence of one of the resonance frequencies shown in Fig. 4. Again, data are only shown for $T > T_v$ because we are unable to track the evolution of a particular resonance frequency below T_v. One should note that this is true of all resonance frequencies, even those that are not coupled to the bulk modulus—in an RUS measurement on a sample with near-unity aspect ratios, the lowest frequency modes depend purely on shear moduli and are thus uncoupled to the bulk modulus—an observation entirely consistent with Kindler *et al.*'s finding that all elastic moduli drop appreciably at the valence transition. In the KVC model, only the bulk modulus should show such a change, because the dominant functional dependence is the volume dependence of the f-electron occupation number n_f and the bulk modulus is the appropriate conjugate susceptibility. Presumably, the origin of the observed changes in all elastic moduli is the splitting of the Yb $J = \frac{7}{2}$ multiplet by crystal-electric fields, observed for $YbInCu_4$ by Severing *et al.* for $T > T_v$,[24] which give rise to anisotropies in the f-electron wave functions and therefore in the volume dependence of n_f, thereby allowing coupling to moduli other than the bulk modulus.

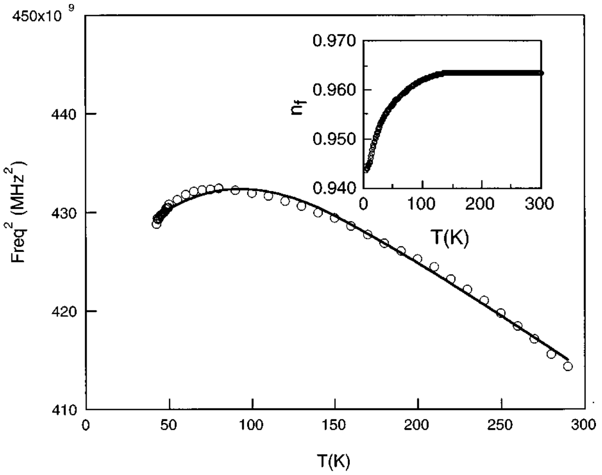

FIG. 5. The experimentally observed temperature dependence of a particular resonance frequency (open symbols) of $YbInCu_4$ and the predicted temperature dependence (solid line) due to a model described in the text. The inset shows the theoretically predicted temperature dependence of the f occupation number, n_f. See text for details.

If one allows such a coupling of the valence transition to each of the elastic moduli, one can explore the temperature dependence of a particular resonance frequency as representative of the overall elastic response. In Fig. 5, we show that the temperature dependence of a measured resonance frequency (plotted as frequency squared so as to have the temperature dependence appropriate to an elastic modulus) can be well described by two contributions—a background lattice term and a contribution due to the temperature dependence of n_f *in the absence of a valence transition.* The background contribution is estimated by the Varshni function,[25] an expression that has been found empirically to describe well the temperature dependence of the lattice contribution to the elastic moduli:

$$c_{ij}^{L}(T) = c_{ij}^{0} - S/[\exp(\tau/T) - 1] \tag{4}$$

with $c_{ij}^{0} = 435 \times 10^9$ MHz^2, $S = 41 \times 10^9$ MHz^2, and $\tau = 323$ K. In the noncrossing approximation, Bickers, Cox, and Wilkins have calculated the temperature dependence of n_f as a function of the Kondo temperature of a system[23] (see inset, Fig. 5). We have previously inferred a value for the Kondo temperature for $YbInCu_4$ for $T > T_v$ and have performed L_{III} measurements to verify the accuracy of Bickers, Cox, and Wilkins' prediction for $n_f(T)$ for $YbInCu_4$.[4] This contribution to the elastic constant, again most simply understood as due to the volume dependence of n_f, can be written as $c_{ij}^{f}(T) = a[n_f(T) - n_f(300)]$, where $a = 732 \times 10^9$ MHz^2 is a temperature-independent constant.[26] The fitted $c_{ij}(T) = c_{ij}^{L}(T) + c_{ij}^{f}(T)$, shown as the solid line in Fig. 5, agrees remarkably well with the data, given the simplicity of our model. Again it should be pointed out that the $c_{ij}^{f}(T)$ contribution is not an effect due to the valence transition but rather to the normal evolution of $n_f(T)$. Recent RUS measurements on $YbAgCu_4$ (in which there is no valence transition) bear this out.[27] Therefore, we argue that there are no precursor effects in the elastic moduli associated directly with the valence transition in $YbInCu_4$ and that, consistent with our specific-heat data, the transition is thermodynamically first order.

In summary, we have shown that the isostructural valence transition that occurs in $YbInCu_4$ is thermodynamically first order. Although rather obvious from this and previous data, the conclusion that $YbInCu_4$ displays a first-order transition is somewhat at odds with the observed magnetic-field temperature scaling[9] that suggests the existence of a single energy scale associated with the transition. Typically, two energy scales are required (e.g., the van der Waals equation of state) to give rise to a first-order phase change, whereas only one seems to be present in $YbInCu_4$. As regards the mechanism underlying the transition, although a Gruneisen analysis of the free energy both above and below the valence transition appears reasonable, the change in volume at the valence transition is insufficient to explain the observed change in Kondo temperature. This is in striking contrast to the case of γ-α Ce, where the Kondo volume collapse model quantitatively explains the observed transition. Although more work is needed to elucidate the detailed nature of the high-T state in $YbInCu_4$, and in particular, to evaluate the effects of the observed crystal field splitting of the Yb multiplet on the valence transition, a single-impurity description of this state may be inadequate, and it appears that the hybridization of individual crystal-field multiplets and density-of-state effects must be considered in order to adequately describe $YbInCu_4$'s isostructural valence transition.

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