High-pressure valence instability and T_c maximum in superconducting $CeCu_2Si_2$

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The high-pressure electrical resistivity of the Kondo compound $CeCu_2Si_2$ was investigated down to the subkelvin temperature range. The main result is the occurrence of a valence transition associated with a steep increase of the superconducting critical temperature T_c to about 2 K near 25 kbar. In the intermediate-valence phase, $\partial T_c/\partial P$ is negative, and no evidence for superconductivity is found above 1.2 K for $P > 100$ kbar. At pressures of the order of 200 kbar, the $\rho(T)$ curves between 0 and 300 K are similar to those for $LaCu_2Si_2$ at ambient pressure. The preceding results are discussed in terms of a two-component ($sd+f$) picture.

I. INTRODUCTION

The anomalous physical properties of many rare-earth (RE) compounds and alloys are due to the mixing of the localized $4f$ wave function with the conduction-band states.[1] While a general solution of the so-called "valence instability" problem is not yet available, considerable effort has been devoted by experimentalists to building a phenomenology that could account for the variety of practical situations. Taking single-impurity effects as a starting point, one generally discriminates[2] between integral-valent systems in which the resonant scattering of conduction electrons on the impurity site can lead to a strong coupling regime at 0 K (the Kondo effect), and intermediate-valence (IV) systems whose properties are dominated by quantum fluctuations between two configurations $4f^n$ and $4f^{n-1}+[5d\,6s]$. In the case of periodic compounds, genuine lattice effects develop at low temperatures and different ground states can result [magnetic ordering, "Fermi liquid" (FL), "Fermi gas" (FG), and superconducting]. In the case of cerium, the occurrence of superconductivity was long restricted to compounds with markedly nonmagnetic properties ($CeRu_2$, $CeCo_2$), which were considered to be tetravalent.

The observation of bulk superconductivity in the trivalent system $CeCu_2Si_2$ below $T_c \simeq 0.6$ K (Ref. 3) therefore raised considerable interest for this material. The normal-state properties are characterized by a very high density of states at the Fermi energy as indicated by the large linear electronic contribution to the specific-heat and the strong quadratic term in the electrical resistivity for $T \to 0$ K.[4] In the absence of superconductivity, the low-temperature ground state would thus be a Fermi liquid consisting of strongly correlated $4f$ quasiparticles, very similar to what is observed in $CeAl_3$ below 0.3 K. In this study, the stability of this extraordinary state with respect to a pressure-induced valence instability was investigated. The question of the origin of superconductivity in $CeCu_2Si_2$ was also addressed by tracking the critical temperature and transition width up to 100 kbar.

II. EXPERIMENT

The samples used in this study were $CeCu_2Si_2$ polycrystals prepared from the elements by arc melting measured amounts of Ce metal (99.99%-purity Rare Earth Products, Ltd), Cu (99.998%-purity, Materials Research Corporation) and Si (99.999%-purity, Goodfellow Metals). They actually belong to a series of 15 off-stoichiometric samples synthetized and investigated by Ishikawa *et al.*[5] Details on the preparation and characterization procedures can be found in that reference. The selected compositions (sample A: $Ce_{19.3}Cu_{42}Si_{38.7}$; sample B: $Ce_{19.7}Cu_{41}Si_{39.3}$) correspond to a slight *nominal* excess of copper, which is believed to result in more stoichiometric specimens.[6] The platelets for the high-pressure experiments (length times width $=0.8\times0.1$ mm) were cut from the ingots using a precision tungsten-wire saw,[7] then polished on sandpaper to a thickness of approximately 35 μm.

Two experimental setups corresponding to different temperature and pressure ranges were used for measurements on samples A and B, respectively. In the first one, a pressure up to 40 kbar was generated between two opposed, Bridgman-type, WC anvils. This assembly could be cooled to 50 mK in a few hours by use of a fast ^{3}He-^{4}He dilution unit.[8] The second device[9] was similar to the one developed by Wittig,[10] with synthetic-diamond anvils[11] loaded by a compact cryogenic CuBe press. The maximum pressure was as high as 200 kbar and the lowest accessible temperature about 1.2 K.

In both cases, the samples were embedded in a soft-solid material (steatite) providing quasihydrostatic conditions (pressure homogeneity better than 10%). The pressure was deduced from the superconducting transition of a lead strip located very close to the sample inside the

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pressure cell. True four-lead resistivity measurements were performed with aid of a high-sensitivity (<0.5 nV) ac bridge.[12]

III. RESULTS AND DISCUSSION

A major difficulty in using Bridgman anvils for resistivity measurements is to determine the geometrical factor l/s of the specimen. This quantity can actually vary under pressure as a result of contact sliding, closing of cracks, and dimensional changes. In this work, the latter term was essentially limited to the normal compressibility effect by using bulk samples rather than compacted powders. However, one should be careful in assuming $l/s=$const with pressure, especially in the low-pressure regime where the pressure profile in the cell (steatite plus pyrophyllite) builds up with appreciable platic flow. We therefore measured the room-temperature (RT) resistivity of a larger specimen from the same batch as sample A by the Van der Pauw method in a maraging-steel piston-cylinder clamp. The results up to 20 kbar are presented in Fig. 1 (inset). The experimental ρ-P curve can be represented quite accurately by a straight line of

$$\rho=\rho_0+\lambda P \quad (1)$$

with $\rho_0=110$ $\mu\Omega$ cm and $\lambda=1.58$ $\mu\Omega$ cm/kbar. The geometrical factor for sample A can now be determined by fitting the Bridgman-anvil data at 15 and 19 kbar to the preceding curve (asterisks in Fig. 1). The fact that the next points (at 24.6, 32.3, and 38.5 kbar) approximately follow the extrapolation of Eq. (1) suggests that (i) the variation of l/s is weak in this pressure range and (ii) the ρ-P curve does not show a strong curvature up to 40 kbar. All the very-high-pressure data (i.e., for sample B) were therefore normalized with a constant l/s as indicated on the figure.

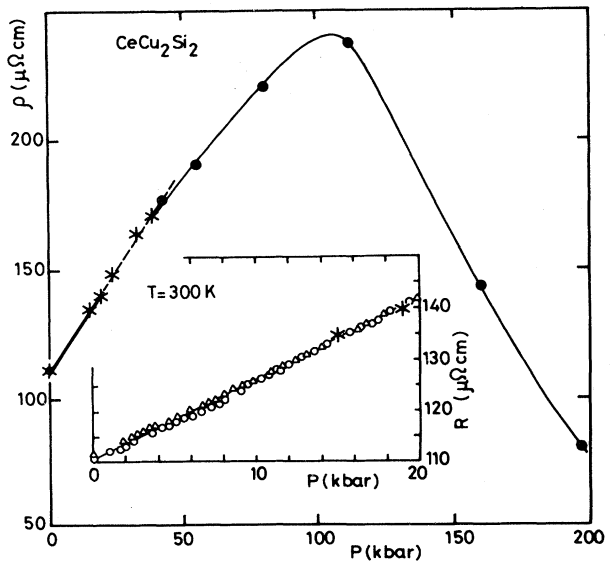

FIG. 1. Pressure dependence of ρ at room temperature for $CeCu_2Si_2$ A (*) and B (●). The dashed line is a linear extrapolation of the low-pressure data (see text). Inset: measurements up to 20 kbar in a hydrostatic pressure cell (sample from same batch as A), increasing (○) and decreasing (Δ)P.

A. Concentrated-Kondo to intermediate-valence transition

A selection of ρ-T curves covering the entire pressure range is presented in Fig. 2. The ambient-pressure results are in good agreement with those of other authors,[13,14] with a negative thermal coefficient of resistivity (TCR) below room temperature (RT), a flat maximum at about 67 K and a stronger one at $T_{max}=23$ K. The corresponding curve for sample B (not presented for clarity) shows essentially the same behavior; the lower maximum is still located at 24 K but the other is now slightly more pronounced and shifted to 92 K. Below T_{max}, ρ decreases steeply down to 0.67 K where superconductivity sets in. Assuming a quadratic temperature dependence of the normal-state resistivity below 1 K with a coefficient $\beta=10$ $\mu\Omega$cm/K^2,[4] our data [Fig. 3(a)] extrapolate to a residual resistivity $\rho_n(T=0)$ of only 6 $\mu\Omega$ cm, comparable to that found by other authors in good polycrystalline materials.[4] Upon applying the pressure, T_{max} gradually increases, and for $P>15$ kbar, both maxima merge into a very broad structureless anomaly. The maximum of this anomaly increases steadily with pressure, reaching RT for $P\simeq120$ kbar. Above 120 kbar, the ρ-T curves have a positive TCR over the entire temperature range and tend to a normal phonon-scattering behavior. The pressure dependence of T_{max} is summarized in Table I. It can also be noted that the amplitude of the resistivity maximum is enhanced by a factor ~1.7 between 0 and 80 kbar, then saturates or slowly decreases at higher pressures. The ρ-P curve at room temperature shown in Fig. 1 merely reflects the variation in amplitude and position of the resistivity anomaly. The large values of $\rho_{RT}(P)$ and its pressure derivative $\partial\rho_{RT}/\partial P$ up to 200 kbar suggest that even at the highest pressure, the resistivity still contains an appreciable contribution from anomalous *sd*-*f* scattering. Our results are therefore in contradiction with the conclusion of Aliev *et al.*[15] that cerium is in a 4+ valence state above 120 kbar. We note, however, that the general trends of the $\rho(T,P)$ dependence presented here agree qualitatively with the experimental results up to 140 kbar

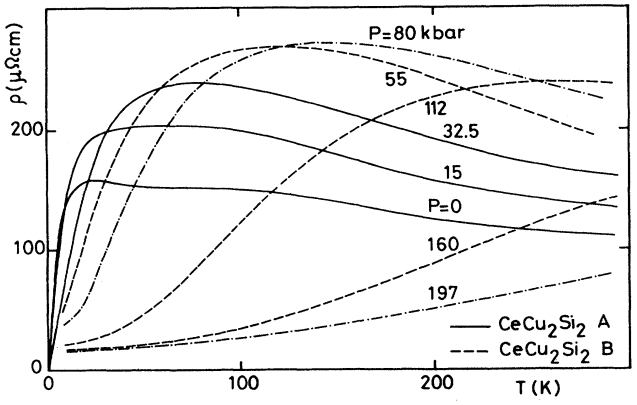

FIG. 2. ρ-T isobars of $CeCu_2Si_2$ A (solid lines) and B (dashed lines).

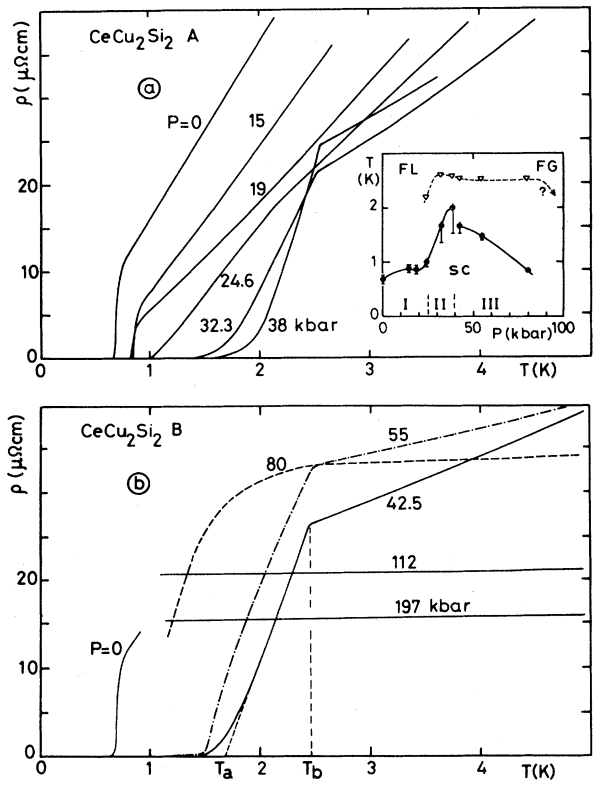

FIG. 3. (a) Low temperature resistivity and superconducting transition of $CeCu_2Si_2$ A as a function of pressure. Inset: Pressure dependence of T_a (●) and T_b (▽) as defined in Fig. 3(b) (see text). The apparent discontinuity at 40 kbar is a mismatch between the two different samples. (b) Low-temperature resistivity and superconducting transitions of $CeCu_2Si_2$ B at very high pressures.

previously reported by the same authors. Their observation of an initial decrease of $\rho_{RT}(P)$ up to 40 kbar (not seen in Fig. 1) is most likely due to undesired changes in the geometrical factor of the sample with pressure. Other discrepancies, such as the lower values of T_{max} in their experiment, can be due to sample problems, especially in view of the differences already existing between the curves at ambient pressure [$T_{max}(P=0)<10$ K and $\rho_n(T=0)>50$ $\mu\Omega$ cm Ref. (16)].

The low-temperature regime ($T<T_{max}$) is most interesting because it reflects the emergence of a coherent ground state dominated by heavy quasiparticle excitations in the strongly correlated $4f$ resonance. At low pressures, the βT^2 term which is a genuine Fermi-liquid property,[4] can be observed only below 1 K in a magnetic field sufficient to quench superconductivity. On the other hand, a strong αT term is observed above T_c for $0 \leq P \leq 40$ kbar [Fig. 3(a)]. Applying pressure results in a steep decrease of α as reported in Table I. A similar term was actually found in several anomalous cerium compounds. Representative data are collected in Table II, together with the corresponding values of γ, the coefficient of the linear specific-heat term. The correlation existing between the two sets of data suggests that the coefficient α qualitatively tracks the variations of the renormalized $4f$ density of states. In the case of $CeCu_2Si_2$, this observation implies a drastic depression of the $4f$ resonance under pressure, as α decreases from 20.3 to less than 5 $\mu\Omega$ cm/K between 0 and 50 kbar.

Above 50 kbar, the ρ-T curves begin to exhibit appreciable upward curvature, with an inflexion point at increasingly higher temperatures. Such S-shaped curves, similar to those shown in Fig. 2 for $P=80$ and 112 kbar are typical for IV cerium compounds. A βT^2 regime is clearly observed over a significant temperature range for $P=80$, 112, and 160 kbar (Fig. 4). The values of β decrease steadily with increasing pressure (see Table I).[17] They are several orders of magnitude smaller than the $P=0$ value of Steglich *et al.*,[4] but comparable to that found, for instance, in $CeBe_{13}$ (Table II). Our results therefore indicate a transition from dense Kondo to IV as pressure increases. Such a phenomenon was already reported for $CeAl_2$ and $CeIn_3$. However, those systems are known to have a magnetically ordered ground state at ambient pressure, and the low-temperature properties essentially reflect the competition between magnetic ordering and $4f$ delocalization. On the other hand, the present situation corresponds to a more subtle crossover between two nonmagnetic ground

TABLE I. Resistivity data for $CeCu_2Si_2$ at different pressures.

P (kbar)	T_a (K)	T_b (K)	α ($\mu\Omega$ cm/K)	β ($\mu\Omega$ cm/K^2)	T_{max} (K)
0	0.68	0.72	20.3	10[a]	23–67
15	0.86	0.91	17.2		?–68
19	0.84	0.92	12.7		72
24.6	1.06	2.18	11.8		78
32.3	1.7	2.53	8.4		83
38	1.95	2.55	7.4		88
42.5	1.69	2.45	5		111
55	1.5	2.49	?	?	120
80	~0.85	~1.6		0.072	145
112	<1.2	<1.2		0.01	266
160	<1.2	<1.2		~0.001	
197	<1.2	<1.2		?	

[a]See Ref. 4.

TABLE II. Comparison between electronic properties of different Kondo-lattice and IV systems.

	α ($\mu\Omega$ cm/K)	β ($\mu\Omega$ cm/K^2)	γ J/mole K^2	α/γ	T_{max} (K)
$CeAl_3$	30[a]	35[b]	1.62[b]	18.5	34
$CeCu_2Si_2$	20.3[c]	10[c]	1.0[d]	20.3	23—67[c]
$CePd_3$	1.1[e,f]		0.039[f]	28.9	130[e,f]
$CeBe_{13}$		$1.96.10^{-3}$[g]	0.059[g]		245

[a]See Ref. 18.
[b]See Ref. 19.
[c]Present work.
[d]See Ref. 4.
[e]See Ref. 20.
[f]See Ref. 21.
[g]See Ref. 22.

states, namely, from a strongly interacting, $CeAl_3$-like Fermi liquid, to an IV state with relatively weak correlations and properties more similar to those of a Fermi gas.

The residual resistivity $\rho_n(0)$ extrapolated from the normal state also exhibits an unusual pressure dependence: It first increases from $\simeq 6$ $\mu\Omega$ cm at $P=0$ to more than 30 $\mu\Omega$ cm at 80 kbar just before the disappearance of superconductivity. The additional scattering cannot be due solely to the cold working produced by nonhydrostatic pressure components, since a decrease of $\rho_n(0)$ by more than 50% follows at even higher pressures. This variation probably involves effects of both impurity scattering and band structure of the host. In dilute alloys such as *Y*Ce, cerium impurities can contribute about 12 $\mu\Omega$ cm/at. % in the strong-coupling limit ($T \ll T_K$).[23] A concentration of a few-percent cerium atoms in distorted lattice sites is quite possible in this system, considering the aforementioned stoichiometry problems. On the other hand, studies of the IV compound $CePd_3$ (Ref. 24) have shown that the impurity scattering cannot be treated in a simple Mathiessen-rule picture. Semimetallike situations should be considered in the complicated narrow-band structure of such compounds.

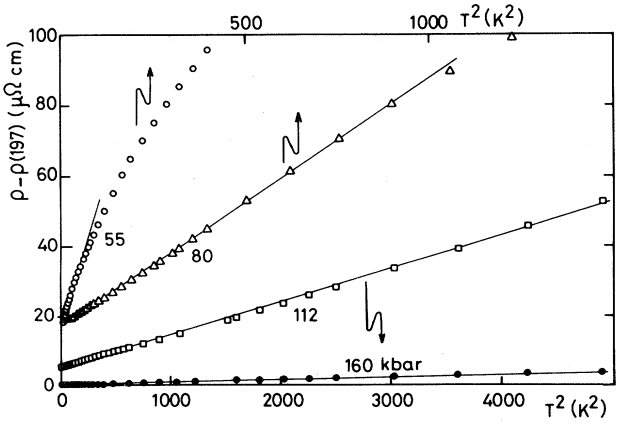

FIG. 4. T^2 plot of the low-temperature resistivity of $CeCu_2Si_2$ B above 50 kbar.

B. Superconducting properties

Figure 3 shows the superconducting transition of $CeCu_2Si_2$ at different pressures. For clarity, the data for samples A and B (also, corresponding to different pressure ranges) are plotted as separate diagrams. In the case of sample A, the transitions were checked to be independent of the measuring current, so long as Joule heating remained negligible. This observation ensures that the resistive transition is not a spurious percolative effect due to tenuous superconducting channels, but affects large regions of the sample.

At ambient pressure, the resistivity curves for samples A and B coincide within 0.5% below 5 K. This remarkable agreement confirms the observation by Ishikawa *et al.*[5] that superconductivity is quite insensitive to stoichiometry on the copper-rich side of the phase diagram. The critical temperature taken at the midpoint of the resistivity drop is $T_c = 0.70 \pm 0.01$ K, for both samples, in good agreement with the susceptibility results ($T_c = 0.67$ K). The transition width $\Delta T_c \simeq 50$ mK is indicative of a good sample homogeneity.

On increasing pressure, T_c first rises slowly between 0 and 15 kbar, then seems to level off up to $\simeq 20$ kbar [see inset in Fig. 3(a)]. The transition width is about the same as at zero pressure, but the resistivity drop is strongly reduced. The latter feature actually corresponds to a smaller normal-state resistivity at T_c, in accordance with the decrease of β (observed) and α (anticipated) under pressure.

Between 20 and 30 kbar, both the critical temperature and the shape of the transition change drastically. This crossover region is best characterized by the 24.6-kbar curve: The original transition below 1 K has completely disappeared and a new faint knee appears on the curve around 2 K. Below this temperature, the resistivity decreases very gradually and vanishes only for $T < 1$ K.

At higher pressures the transition becomes more pronounced with a sharp kink at $\simeq 2.5$ K. However, its width ($\Delta T_c \sim 0.5$ K) is still about 1 order of magnitude larger than at ambient pressure. Above 50 kbar the ρ-T characteristics have a downward curvature in the transition region. At 80 kbar, the transition extends from ~ 2 K to less than 1 K, and the zero-resistivity state is not achieved in our experimental window. For $T > 100$ kbar,

the results give no evidence for a superconducting transition down to 1.2 K.

The results are summarized in the inset of Fig. 3(a) where the superconducting transition temperature is plotted as a function of pressure. Above 20 kbar, defining T_c becomes ambiguous and two characteristic temperatures were taken to represent the shape of the transition [see curve at 42.5 kbar in Fig. 3(b)]. T_b corresponds to the initial departure from the normal-state behavior, and T_a to the linear extrapolation of the transition curve to $\rho=0$. The values of T_a and T_b at various pressures are also listed in Table I.

Three distinct pressure regions can be defined, according to their superconducting properties. In region I ($P<20$ kbar), T_c is low, the transition is narrow and $\partial T_c/\partial P$ is small. The cerium ions are trivalent, as noted previously, and $CeCu_2Si_2$ can be regarded as a Kondo-lattice system. Region II ($20<P<40$ kbar) is characterized by the increase of T_c and, more specifically, by the large value of $\partial T_c/\partial P$ and the considerable broadening of the transition. At $P\sim 40$ kbar, T_c goes through a maximum, then decreases steadily in Region III up to 80 kbar. The transition remains very broad in this pressure range too.

In Region I, the relative insensitivity of T_c to pressure contrasts with the drastic increase of the Kondo coupling revealed by the normal-state resistivity (see variations of α in Table I). It seems therefore unlikely that superconductivity in this system be primarily due to heavy $4f$ quasiparticles. We instead suggest describing it in terms of two components with *sd* and *f* character, respectively. The strong magnetic fluctuations on the trivalent cerium ions preclude superconductivity even at 1 K, so long as the $4f$ states at different sites remain essentially uncorrelated. As the coherent Fermi-liquid ground state builds up for $T\sim T^*\simeq 0.3$ K, the pair-breaking rate decreases and superconductivity can set in. The correlation of both mechanisms—formation of heavy fermions and superconductivity—is substantiated by the drop of the specific-heat coefficient γ at T_c and its gradual reappearance as the normal state is restored in a magnetic field.[25]

The rapid changes observed in Region II are ascribed to a valence transition of the cerium ions from 3 to $3+\epsilon$. This interpretation is supported by the change of sign of the low-temperature thermoelectric power from negative to positive[26] in the same pressure range. The pressure limits assigned here are indeed somewhat arbitrary, and the crossover might be even more localized around 25 kbar. In the event of a large volume decrease accompanying the partial $4f$ delocalization, changes in the phonon spectrum of the host can play a role in the observed enhancement of T_c.

In the IV phase (Region III), the T_c values are comparable to those found in lanthanum and, more recently, in the high-temperature phase of $LaIr_2Si_2$ ($T_c=1.6$ K).[27] The negative dT_c/dP in this region is the usual effect of a *d*-band broadening. The high-pressure phase of $CeCu_2Si_2$ may therefore correspond to the zero-pressure phase of $LaCu_2Si_2$ which is not superconducting.

The enormous broadening of the superconducting transition is a puzzling issue. It cannot be due to structural disorder induced by pressure since a sharp transition was recovered after releasing the pressure from 38 kbar to 0. It is also noteworthy that the same effect was obtained in two separate pressure-cells with different dimensions. If the transition width of about 1 K at 40 kbar is representative of the inhomogeneities of the material, one must invoke a sharp increase of the pair-breaking rate to explain the narrow transition at $P=0$. Conversely, the effect of disorder may become critical in the 40—80 kbar range: The properties of $CeCu_2Si_2$ in this region are indeed similar to those of $CePd_3$ at ambient pressure, a situation where the drastic scattering produced by low impurity concentrations remains unexplained. This question is certainly related to the anomalous enhancement of $\rho_n(0)$ discussed above. It would be interesting to extend the experiments to $T<1$ K for $P>80$ kbar and look for a possible narrowing of the superconducting transition.

IV. CONCLUSION

This study substantiates the occurrence of a valence transition in $CeCu_2Si_2$ around 25 kbar. The quite unusual pressure dependence of T_c is tentatively interpreted in a two-component picture. Isothermal compression or high-pressure *L*-edge experiments should be undertaken to look for anomalous volume changes in this system. Critical-field measurements above 40 kbar would help to clarify the mechanisms of superconductivity in the IV phase of this compound.

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