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LETTER TO THE EDITOR

Superconductivity and pressure-induced electronic topological changes in $CeCu_2Si_2$

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Abstract. Refined measurements are reported on the pressure dependence of the superconducting transition temperature in the heavy-fermion (HF) superconductor $CeCu_2Si_2$. Two characteristic pressures, $p_1 \approx 3$ GPa and $p_2 \approx 7.6$ GPa, delimit three ranges of the superconducting state. The present study confirms the unique behaviour of $CeCu_2Si_2$ in the series of HF superconductors. This particular behaviour is interpreted as resulting from two contributions: a smooth one due to the pressure-increased Kondo temperature and sharper additional features reflecting topological changes in the renormalized heavy bands.

Pressure appears as an experimental parameter of primary interest in the field of heavy-fermion (HF) physics. Volume reduction changes the strength of hybridization between conduction and f electrons and this in turn controls the behaviour of heavy-mass quasiparticles. This effect is reflected by the change of the Kondo temperature, T_K, or by that of the related characteristic electronic temperature, T^*. Typically a pressure $p \approx 10$ GPa can move T_K from ≈10 K to ≈100 K, i.e. it shifts the system from the HF to the mixed-valence regime. On the practical side, application of pressure allows one to follow the evolution of physical properties in one given sample. This is valuable since many aspects of the HF state appear very sensitive to sample preparation or contamination effects. Pressure has been repeatedly used in investigations concerning the specific superconductivity [1–7] which occurs in a few HF compounds with optimal transition temperatures ranging from $T_c \approx 0.5$ K to $T_c \approx 2$ K. Presently investigated U-based HF superconductors show a T_c decreasing with applied pressure, a trend opposite to that observed for T_K and T^* [8–11]. The latter 'anticorrelation' has been given a more quantitative basis by considering the Grüneisen parameters Γ_{T^*} and Γ_{T_c} ($\Gamma_X = \mathrm{d}\ln X/\mathrm{d}\ln v$, where v = volume) [12]. Both have large values in the HF state, similar magnitudes and opposite signs. The behaviour of $CeCu_2Si_2$, the only known example of a Ce-based HF superconductor at ambient pressure [1], is in stark contrast. For stoichiometric samples of this compound, T_c hardly changes up to $p \approx 2$ GPa [8, 13–15]; in the 2–3 GPa range a rapid increase is observed, followed by a gentle reduction at higher pressure [13–15]. Some non-superconducting starting samples can be made superconducting by applying moderate pressures ($p \approx$ a few 0.1 GPa) [16]. The previous non-monotonic behaviour was obtained with resistance measurements and is somewhat blurred due to a large broadening of the transition widths occurring at the same time. This motivated us to re-examine the pressure dependence of T_c in $CeCu_2Si_2$ using a different technique based on the use of a diamond anvil cell (DAC) and a.c. susceptibility.

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The present work is an extension of a preliminary study reported in [17]. The determination of $T_c(p)$ in $CeCu_2Si_2$ has an improved precision which primarily results from the special attention paid to obtaining hydrostatic conditions. These are of importance as thermal expansion measurements [18] and specific heat data under uniaxial stress [19] predict an opposite trend for stresses directed along and perpendicular to the tetragonal axis. Data are then interpreted as resulting from different contributions, one of which is due to pressure-induced topological changes in the renormalized band structure of $CeCu_2Si_2$. A calculation is presented for such effects.

For the present study, a polycrystalline sample was prepared by melting appropriate amounts of the pure elements in an arc furnace. Subsequently, the ingot was annealed for two days at 700 °C and five days as 1000 °C. The x-ray powder pattern showed only the reflections characteristic of the proper $ThCr_2Si_2$ structure. SEM analysis revealed that grains having stoichiometric composition and a.c. susceptibility for different parts of the ingot gave the same superconducting temperature $T_c = 690 \pm 15$ mK, close to the optimal value. The assembly of the DAC and the detection coils mounted in a helium-3 refrigerator has been described elsewhere [20]. Helium is used as a pressure-transmitting medium and pressure is measured at low temperature with the use of the ruby fluorescence scale. The pressure gradient or uniaxial stresses appear to be less than 0.05 GPa across the pressure chamber. After each pressure change, the cell was thermally cycled in order to remove possible parasitic stresses. Data were obtained for several loadings, on both increasing and decreasing pressure. The width of the superconducting transition detected by a.c. susceptibility was less than 0.03 K over all the investigated pressure range.

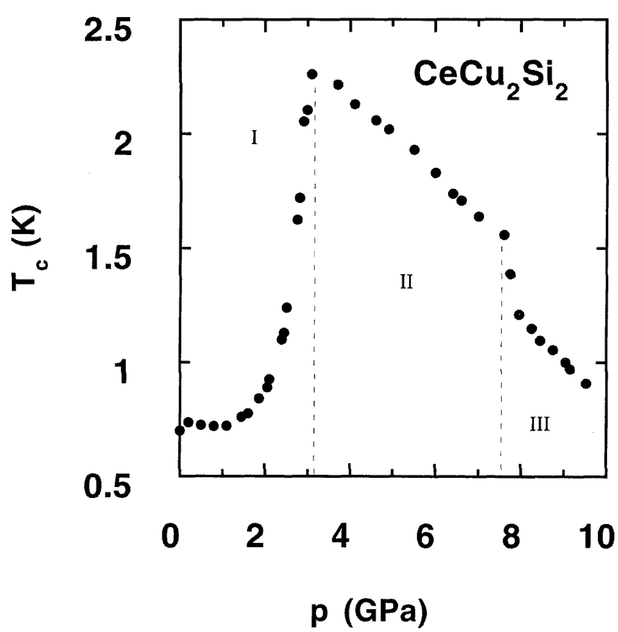

Figure 1. The change of the superconducting transition temperature of $CeCu_2Si_2$ with pressure. $p_1 \approx 3.1$ GPa and $p_2 \approx 7.6$ GPa (vertical dashed lines) delimit three different superconducting regimes.

Figure 1 shows the $T_c(p)$ curve obtained for pressures up to $p \approx 9.5$ GPa. The initial increase characteristic of slightly off-stoichiometric samples is absent from the present data which confirm the non-monotonic behaviour previously observed. T_c reaches its maximum value at $T_c^{\max} \approx 2.3$ K for $p_1 \approx 3.1$ GPa. Moreover, several additional features are also revealed: (i) the upward change at p_1 has a cusp like form; (ii) a second downward cusp is observed at $p_2 \approx 7.6$ GPa; (iii) between p_1 and p_2, T_c falls in an approximately linear function with $T_c(p) = 2.806$ K at $0.168p$; (iv) above p_2, after a cross-over region, a second linear range is observed with $T_c = 2.790$ K at $0.192p$. The changes at the two cusps are perfectly reversible as established by increasing and decreasing pressure through p_1 and p_2, respectively. p_1 and p_2 thus define three different superconducting states of $CeCu_2Si_2$: (I) for $p < p_1$, (II) for $p_1 < p < p_2$, (III) for $p > p_2$.

The linear regimes in ranges (II) and (III) are reminiscent of the linear decrease of $T_c(p)$ observed in U-based HF superconductors. In the case of UPt_3 and UBe_{13} [8, 11] the agreement is even approximately quantitative for $\mathrm{d}T_c/\mathrm{d}p$. As quoted above, quantitative considerations are rather expressed in terms of Grüneisen parameters. Writing:

$$T_c \approx \Theta_{eff} \exp\left(-1/\lambda_{eff}\right) \tag{1}$$

where $\Theta_{eff} \propto T_K$ and $\lambda_{eff} \propto N(\epsilon_F) \propto 1/T_K$ due to the narrow f-band character of the HF superconductivity, one gets:

$$\Gamma_{T_c}/\Gamma_{T^*} \approx 1 + \ln\left(T_c/\Theta_{eff}\right). \tag{2}$$

Therefore, anticorrelation holds for $T_c \approx 0.1\ \Theta_{eff}$, an order of magnitude which appears to be met in samples with optimal T_c. In $CeCu_2Si_2$ at room pressure, $\Gamma_{T_c} \approx +4$ (using the bulk modulus, $B \approx 110$ GPa [21]), while $\Gamma_{T^*} \approx 70$–80 [14, 18]. The only way to estimate Γ_{T^*} in regime (II) is by using resistivity measurements [13, 16], though this way is known to be rather uncertain for precise determination [12, 18]. Just above p_1, the shift of the temperature of the maximum resistivity, $T_{\max}$, provides $\Gamma_{T_{\max}} \approx 20$, while the change of A, the ρ versus T^2 law coefficient, gives $\Gamma_A \propto 2\Gamma_{T^*} \approx 55$ [13]. At the same pressure $\Gamma_{T_c} \approx -8$. Though the absolute values for the above electronic Grüneisen parameters are several times lower than for U-based HF superconductors, the anticorrelation between Γ_{T^*} and Γ_{T_c} above p_1 is satisfactory, and reinforces the similarity between regime (II) and the latter case. It is thus natural to conclude that regime (II) reflects the mean evolution of T_c expected for narrow-band superconductivity. Now we have to explain the unique features of $T_c(p)$ in $CeCu_2Si_2$ as compared to other HF superconductors. Equation (1) also predicts that T_c may go through a maximum as a result of the increasing trend of $T_K(p)$. However, the process is smooth and it is not possible to justify the cusps observed at p_1 and p_2 in this way. Another possibility for $T_c(p)$ results from a low T_c value at $p = 0$ due to a low coherence temperature. The latter temperature increases with p and consequently T_c increases . This mechanism is again confronted with the difficulties related to the presence of sudden changes at p_1 and p_2.

Electronic density of states (DOS) considerations provide an alternative approach to explaining why the observed $T_c(0)$ is four times smaller than the value extrapolated from the linear regime (II). From equation (1) and again assuming $T_c \approx 0.1\ \Theta_{eff}$, one finds that a reduction of the DOS by 40% is sufficient for a drop in T_c by a factor of four. Such a reduction can result from a static charge or spin-density wave. This hypothesis was recently proposed in order to explain the fact that the superconducting phase is embedded in a more general (H, T) phase diagram (for a review see [22]). However, this phase diagram seems to be related to non-static fluctuations as recently evidenced by NMR [23]. Consequently, such an origin for a reduced DOS appears uncertain until more direct evidence is obtained. Very recently, a semi-quantitative explanation for the (H, T) phase diagram has been obtained on the basis of topological changes occurring in the calculated renormalized electronic band structure [24]. We shall now examine how similar effects can modify $T_c(p)$. Pressure-induced topological changes give rise to the so-called '$2^{1/2}$-order transition' which may affect several quantities, as shown by Lifschitz [25]. Because the gap equation [26] has an integral form with a kernel defined in the vicinity of the Fermi level (ϵ_F), it will be significantly modified when a Van-Hove singularity lies close enough to ϵ_F. Such a mechanism has been invoked in the past to explain the pressure dependence of T_c in some elemental superconductors [27, 28]. In this case however, the 'anomalous' changes in T_c were limited to variations of a few per cent. Following the same spirit, the limiting form of the gap equation which defines T_c now reads:

$$g \int \frac{1}{\xi} \tanh\left(\frac{\xi}{2T_c}\right) \frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} = 1 \tag{3}$$

where g is a coupling constant, $\xi = \epsilon - \mu$ and μ is the chemical potential. Assuming a non-degenerate singularity at some critical point 'C' which belongs to the critical surface of constant energy $\epsilon \equiv \epsilon_c$ and has a quasimomentum $\boldsymbol{p_c}$ one can expand the energy spectrum of carriers as: $\epsilon = \epsilon_c + p_1^{*2}/2m_1 + p_2^{*2}/2m_2 + p_2^{*2}/2m_3$ in which $p_i^* = p_i - p_{ci}$. Each effective mass can be either positive or negative. Equation (3) can be separated into one integration performed in the vicinity of C which gives a singular contribution $I_{sing}(\mu,\ T_c)$, and one performed over the remaining part which gives a regular contribution, $I_{reg}(\mu,\ T_c)$. In shorthand notation, equation (3) reads: $A \equiv gI_{reg}(\mu,\ T_c) + gI_{sing}(\mu,\ T_c 0 = 1$. We now define T_c^{reg} as a solution of: $B \equiv gI_{reg}(\mu,\ T_c^{reg}) = 1$. Subtracting A from B and after the standard transformation of $I_{reg}(\mu,\ T_c^{reg}) - I_{reg}(\mu,\ T_c)$, one gets:

$$\frac{\upsilon(\mu)}{2} \ln\left(\frac{T_c^{reg}}{T_c}\right) = -I_{sing}\big(\mu,\ T_c\big) \tag{4}$$

$\upsilon(\mu)$ being a mean DOS at the Fermi level. Introducing the reduced momentum $q_i = p_i^* |m_i|^{-1/2}$, the integral is carried out using spherical or hyperbolic coordinates ($q_z = q \cosh\Psi,\ q_x = q \sinh\Psi \cos\Phi,\ q_y = q \sinh\Psi \sin\Phi$) depending on whether the effective masses have the same or different signs, respectively. One arrives at the same one-dimensional integral in both cases except for the sign which is 'plus' in the first case and 'minus' in the second:

$$I_{sing} = \pm \frac{\sqrt{|m_1 m_2 m_3| T_c}}{\pi^2 \hbar^3} \int_\eta^{\Omega/2T_c} \sqrt{x-\eta}\, \frac{\tanh x}{x}\, \mathrm{d}x. \tag{5}$$

Here $x = \pm\xi/2T_c$, $\eta = \pm(\epsilon_c - \mu)/2T_c$ and Ω is a cut-off parameter dependent on the choice made for the integration domain about C. The signs in the definitions of ξ and η are the same as those appearing in the q dependence of ξ in this domain: $\xi = \epsilon_c - \mu \pm q^2/2$. According to equation (5), $I_{sing}(\mu,\ T_c)$ is positive when a topological transition results in the creation of a new pocket on the Fermi surface (FS) (see also [28]). The DOS acquires a singular increment which produces an increase of T_c. In the case of $CeCu_2Si_2$, a natural choice for T_c^{reg} should be close to the linear behaviour of range (II) and a negative singular contribution, $I_{sing} < 0$, is expected. The corresponding change of topology in the FS can consist of the disruption of a neck. On the other hand, the ambiguity introduced by separating I into I_{reg} and I_{sing} can be removed by considering the derivative $\mathrm{d}I_{sing}/\mathrm{d}\eta$. Thus, for a more convenient comparison with experimental data one better considers the pressure derivative of equation (4). To leading order on $(\epsilon_c - \mu)$, one has:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}p} \ln\left(\frac{T_c^{reg}}{T_c}\right) &\cong \frac{\mathrm{d}(\epsilon_c - \mu)}{\mathrm{d}p} \frac{\sqrt{|m_1 m_2 m_3|}}{2\pi^2\hbar^3 \upsilon(\mu)\sqrt{T_c}} J(\eta) \\ J(\eta) &= \int_\eta^\infty \frac{\tanh x}{x\sqrt{x-\eta}}\, \mathrm{d}x. \end{aligned} \tag{6}$$

A strong dependence of T_c on pressure comes mainly from the integral $J(\eta)$. According to its definition, $J(\eta)$ is a continuous function of η with $J \sim 1$ for $\eta \sim 1$. In particular $J(0) = 2\int_0^\infty x^{-1/2}\cosh^{-2} x \, dx = 2 \times 1.905\,56$. At both infinities, J tends towards zero but, as a result of the asymmetry linked to the topological transition, the asymptotes are different: $J(\eta) \approx 2\pi/\eta$ for large positive values of η and $J(\eta) \approx 2\ln(16\gamma|\eta|/\pi)/|\eta|^{1/2}$ for large negative η (γ is the Euler constant). Recalling the definition of η, one can see that the asymptotic form of $J(\eta)$ is more singular on the side of the transition which corresponds to the larger number of recesses of the FS, in accordance with a general rule [25].

The preceding analysis was based upon a quadratic dispersion law, for which case the singular part of the DOS, $\upsilon_{sing}(\mu)$, is proportional to $|\epsilon - \mu|^{1/2}$. It may happen, especially in the case of an f band with small dispersion, that on a wider range of momentum $\upsilon_{sing}(\mu)$ can be better approximated by a more general law, i.e. $|\mu - \epsilon_c|^{1-\alpha}$. For example, if the energy difference $(\epsilon - \epsilon_c)$ expansion starts from $(p_1^*)^4$ in one of the principal directions, one would then have $\alpha = 3/4$. In order to take this generalization into account, we substitute the integral

$$K_\alpha(\eta) = \int_\eta^\infty \frac{\tanh x}{x(x-\eta)^\alpha} \, dx \qquad (7)$$

for $J(\eta)$, with $1/2 \leqslant \alpha < 2$. So $J(\eta) = K_{1/2}(\eta)$.

A direct numerical evaluation proves that these integrals are poorly convergent for large values of η. It then proves more convenient to use the representation of this function in the form of the infinite sum:

$$K_\alpha(\eta) = K_\alpha(0) + \frac{4}{\sin\pi\alpha}\left(\frac{2}{\pi}\right)^\alpha \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{1+\alpha}} \left(\frac{\Im(\mathrm{i} + v_n)^\alpha}{(1+v_n^2)^\alpha} - \sin\frac{\pi\alpha}{2} \right) \qquad (8)$$

where $v_n = (2\eta/\pi)/(2n+1)$. As α is increased and approaches one, the asymmetry looks less and less pronounced.

Figure 2 shows the logarithmic derivative of the ratio T_c^{reg}/T_c. A negative minimum occurs at $p_{infl} \approx 2.8$ GPa, and data are distributed in an asymmetric way about this value. The existence of an inflexion point, as well as its position, can be questioned, mainly because of the uncertainty remaining in the choice of T_c^{reg}. The error bars in figure 2 estimate this uncertainty together with the error resulting from the derivative procedure. In addition, one also has to consider that the overall curve can be shifted, again as a result of the uncertainty of the chosen T_c^{reg}. This is evaluated through the double-arrow segment in figure 2 by comparing the extrapolated linear regime of (II) with an extreme hypothesis of pressure-independent T_c^{reg}. Under such limits, the fitting procedure based on equation (6) can be carried out and consists of a linear transformation of the X and Y scales. The result is shown by the continuous line in figure 2. The corresponding mapping between η and p is: $\eta = 9(2.9 - p)$, with p expressed in GPa. Following Lifschitz [25], we can write $\eta = \eta_0(p_c - p)/p_c$. This gives the critical pressure as $p_c \approx 2.9$ GPa, located between p_{infl} and p_1, and $\eta_0 = (\epsilon_c - \mu(0))/2T_c \approx 26$. Retaining the mean value of 1.5 K for T_c, we obtain $\epsilon_c - \mu(0) \approx 80$ K for the distance of the critical energy from the Fermi level at zero pressure. A slightly improved fit to the data of figure 2 can be obtained in the lower-pressure range using equation (6) with $\alpha = 3/4$, but it deteriorates in the vicinity of p_{infl}. However, the characteristic energy scale deduced from this second fit is essentially the same as for $\alpha = 1/2$. This value of $\approx$80 K is significantly larger than $T_K(p=0) \approx 10$ K which scales with the width of the narrow quasiparticle band. It is also much larger than the energies associated with the characteristic magnetic fields, $H \approx 4$–6 T, involved in the (H, T) diagram for the so-called 'A-phase' transition [22], for which a mechanism based on

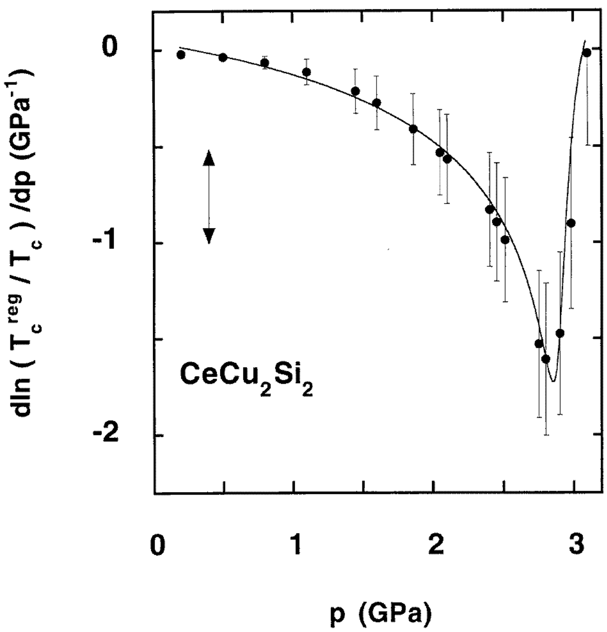

Figure 2. The logarithmic derivative of the ratio T_c^{reg}/T_c versus pressure below p_1. Error bars mainly reflect uncertainty in determining the derivative. The continuous line represents the prediction for a square-root cusp in the electronic DOS ($\alpha = 1/2$). The double arrow estimates the uncertainty in the position of the whole curve resulting from the choice of $T_c^{reg}(p)$.

field-induced topological change of the heavy quasi-particle bands has been proposed [24]. The order of magnitude of $\epsilon_c - \mu(0)$ rather suggests a mechanism involving crystal-field split sub-bands each having a width of approximately T_K. As the pressure is increased the sub-bands broaden and interfere, producing a topological change. In this context, it is interesting to recall that stoichiometric samples present two maxima in their temperature-dependent resistivity in range (I), one broad maximum in range (II) and a narrower one in range (III) [13, 16, 29]. On the other hand, the sharpness of the observed cusp indicates that the changes in the DOS are sharp as well. Bands should thus be rather well formed rather than smeared out due to a low coherence temperature. Of course, the crystal-field scheme can only give an approximate view of the problem and band calculations under reduced volume could certainly help in validating and refining the above scenario. Attempts to fit the drop above p_2 appear quantitatively more hazardous than in the case of p_1. This is due to the smaller jump amplitude occurring in a narrow pressure range and present data are still insufficient for checking the topological scheme near p_2.

In conclusion, the present re-examination of the evolution of T_c with pressure in $CeCu_2Si_2$ confirms the existence of two cusp like singularities at p_1 and p_2. Above p_1 and p_2, the observed linear decreases are presumably due to the general $T_K(p)$-controlled trend, characteristic of a narrow f-band superconductor. The rapid change of T_c below p_1 is qualitatively consistent with pressure-induced topological changes occurring in a well established band structure. Quantitatively, however the present analysis suggest larger energy scales than those involved in the magnetic-field-induced topological change.

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