Valence fluctuation mediated superconductivity in CeCu$_2$Si$_2$

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Abstract

It has been proposed that there are two types of superconductivity in CeCu$_2$Si$_2$, mediated by spin fluctuations at ambient pressure, and by critical valence fluctuations around a charge instability at a pressure $P_v \approx 4.5$ GPa. We present in detail some of the unusual features of this novel type of superconducting state, including the coexistence of superconductivity and huge residual resistivity of the order of the Ioffe-Regel limit, large and pressure dependent resistive transition widths in a single crystal measured under hydrostatic conditions, asymmetric pressure dependence of the specific heat jump shape, unrelated to the resistivity width, and negative temperature dependence of the normal state resistivity below 10 K at very high pressure.

Key words: CeCu$_2$Si$_2$, superconductivity, valence fluctuations

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Introduction

The heavy fermion (HF) family has been a constant source of scientific interest for many years, owing to the rich variety of electronic properties and competing ground states. These can be be tuned within an experimentally accessible region of pressure, magnetic field, or chemical substitution. Many of the most interesting features of these compounds are found where the localised $f$ electrons are on the border of itinerancy, and strong interactions with the more loosely bound conduction electrons have a hugely important effect.

Superconductivity is one of the most striking properties of many HF Ce compounds. The superconducting pairing mechanism is still not fully understood, but the presence of a local magnetic moment at each Ce site strongly disfavours a phonon-mediated interaction.

The leading candidate for the pairing mechanism in HF superconductors has been mediation by low energy spin fluctuations around a so-called magnetic quantum critical point (QCP). This is where the magnetic ordering temperature is driven to zero at a pressure $P_c$, if pressure is the control parameter, and quantum fluctuations between competing ground states dominate the properties of the system. For example in CePd$_2$Si$_2$ and CeIn$_3$, superconductivity was found in a small dome around the QCP, but only in samples of very high purity, where the electronic mean free path exceeded the superconducting coherence length $\xi$ [1]. The nature of the singularity at $P_c$ has usually been treated as second order, however this view may not be entirely correct [2].

The heavy fermion superconductor CeCu$_2$Si$_2$ has a very unusually shaped superconducting region in the pressure-temperature phase diagram, and its isoelectronic parent compound CeCu$_2$Ge$_2$ displays very similar behaviour under larger compression. It was recently shown that the addition of Ge impurities to CeCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ separates the superconducting region into two separate domes, centred on the antiferromagnetic QCP and a valence transition respectively [3]. We have argued that CeCu$_2$Si$_2$ has a second mechanism of superconductivity at high pressure, where critical valence fluctuations, between Ce $4f^{n}$ and...
4f\textsuperscript{n−1} + [5d\textsuperscript{6}s\textsuperscript{6}] electronic configurations form the basis of the pairing mechanism\cite{4, 5}. These are associated with a nearly first order valence instability, analogous to the Ce α − γ transition with a critical end point close to zero temperature. There is a good deal of evidence for an abrupt change in Ce valence, along with several anomalies in the normal state, close the pressure at which \(T_c\) attains its maximum value of around 2.5 K.

The superconducting transition temperature also displays a very anisotropic response to uniaxial stress\cite{6}, similar to the effect seen in CePd\textsubscript{2}Si\textsubscript{2}\cite{7}. This is reminiscent of the strong sensitivity of \(T_c\) to the ratio of tetragonal lattice parameters \(c/a\) seen in the CeM\textsubscript{In\textsubscript{5}} (M = Co, Rh, Ir) and PuM\textsubscript{Ga\textsubscript{5}} (M = Co, Rh) compounds \cite{8}.

If we accept that superconductivity at high pressure in CeCu\textsubscript{2}Si\textsubscript{2} is mediated by valence fluctuations, does it have any uniquely identifying features? More specifically, is there any way to recognize such a compound without an exhaustive pressure investigation such as reported in \cite{5}? Since CeCu\textsubscript{2}Si\textsubscript{2} is so far the only firm example of this phenomenon, it is hard to say what is a characteristic feature of valence fluctuation (VF) mediated superconductivity, and what is unique to CeCu\textsubscript{2}Si\textsubscript{2}. We have investigated the resistivity \(\rho\) and specific heat (by ac calorimetry) of CeCu\textsubscript{2}Si\textsubscript{2} in a hydrostatic helium pressure medium, along with further resistivity measurements on a variety of samples in a quasi-hydrostatic steatite medium. By providing some detailed results we can perhaps provide some clues that might be used to recognize VF mediated superconductivity elsewhere.

In Figure 1 the resistance of CeCu\textsubscript{2}Si\textsubscript{2} below 1 K and up to 6.5 GPa in hydrostatic conditions is shown. The width of the resistive superconducting transition varies strongly with pressure. It is sharp at the lowest pressure, where \(T_c\) is close to its ambient pressure value. However, when \(T_c\) increases sharply around 2–3 GPa, the transition width becomes very broad, of the same order as \(T_c\) itself. Close to the maximum of the transition temperature, the transition sharpens again, though never becoming as sharp as at ambient pressure. It should be noted that the maximum \(T_c\) does not coincide with the narrowest transition in the high pressure region.

The very broad transition at 1.76 GPa was investigated in some detail, and it was shown that the upper part of the resistance drop could be suppressed by increasing the measurement current, leading to a sharp transition with a width close to the ambient pressure value. The \(R = 0\) point could be suppressed more rapidly with a magnetic field than the upper part. Along with the observation that the specific heat jump coincided with the point at which the resistance vanished, these indicated the presence of filamentary superconductivity with a characteristic temperature much higher than that of the majority of the sample.

The exact details of the superconducting transition vary substantially between samples and with pressure conditions (see \cite{9} for further examples). However these broad resistive transitions appear to be a universal feature of CeCu\textsubscript{2}Si\textsubscript{2} at high pressure, regardless of the pressure conditions. Let us recall that even for the highest \(T_c^\text{onset}\) measured in a single crystal, at 2.4 K, a tail of 1% of the normal state resistivity remained well below 2 K, vanishing only at 1.5 K (see \cite{10}). We can note, however, that the pressure dependence of \(T_c^{P=0}\) is remarkably well reproduced between many different samples when normalised to its value at \(P=0\), while \(T_c^\text{onset}\) displays much more scatter. The status of the superconductivity of CeCu\textsubscript{2}Si\textsubscript{2} between \(T_c^\text{onset}\) and \(T_c^{P=0}\) remains mysterious.

The recently discovered HF superconductor CeNiGe\textsubscript{3} \cite{11} displays similarly broad transition widths, along with a large increase in residual resistivity, and is probably the most likely candidate for valence fluctuation mediated superconductivity in another compound. The CeM\textsubscript{In\textsubscript{5}} systems have also been shown to have a fairly large pressure dependence of their resistive transition widths, though perhaps not to the same extent. The relative position of the magnetic and valence instability pressures \(P_c\) and \(P_v\) may play an important role in the presence or otherwise of VF mediated superconductivity in other Ce-based HF compounds. CeCu\textsubscript{2}(Ge, Si)\textsubscript{2} remains the only case in which it is clear that \(P_c \ll P_v\).

Figure 2 shows the superconducting transition in CeCu\textsubscript{2}Si\textsubscript{2} as detected by ac calorimetry in a helium pressure medium. Details of the experimental technique, along with some discussion its limitations can be found in Ref. \cite{5}. It should be noted that the curves shown almost certainly contain a substantial minority contribution from the pressure medium and diamond anvils, so precise quantitative comparisons are diffi-

![Figure 1](image-url)
conducting transitions are shown both at ambient pressure and close to $P_c$ of two polycrystalline CeCu$_2$Si$_2$ samples prepared by Ishikawa. Note the large increase in residual resistivity under pressure combined with a nearly complete resistive transition.

At 4.34 GPa, the normal state resistivity at $T_c$, has more than doubled in sample #50, and increased substantially in sample #57\textsuperscript{1}, and the resistive transition is nearly (though not totally) complete in both. Similar behaviour has been seen in single crystalline CeCu$_2$Si$_2$ samples [14]. Comparing the temperature dependence of the normal state, it seems that the enhancement of the impurity scattering is reduced as temperature increases, and the two samples show very similar behaviour approaching room temperature.

The results discussed in the previous section indicated that there exists another temperature dependent contribution to the resistivity in addition to the usual electron-electron, phonon, and magnetic scattering terms. This is the VF enhanced impurity scattering.

According to the theoretical prediction [12], the residual resistivity $\rho_0$ at $T = 0$ is given by

$$\rho_0 = B n_{\text{imp}} |u(0)|^2 \ln \left| \frac{\partial n_f}{\partial f} \right| / N_F + \rho_{0 \text{unit}}^\text{unit},$$  \hspace{1cm} (1)$$

where the coefficient $B$ is determined by the host metal band structure, $n_{\text{imp}}$ is the concentration of impurities with moderate scattering potential $u(q)$ coming from disorder other than Ce ions, $N_F$ is the density of states of quasiparticles around the Fermi level, and the last term represents the residual resistivity due to unitary

\textsuperscript{1} The resistivity of #57 under pressure has been slightly corrected for experimental difficulties (a small constant contact resistance was subtracted) – see [6] for further explanation.
The temperature dependence of the normal state resistivity at low temperature and high pressure has two contributions, with positive and negative slopes – $AT^n$ quasiparticle scattering, and a temperature dependent impurity term. Only at 7.20 GPa is the negative slope of the latter visible in this sample.

scattering mainly arising from any deficit or defect of the Ce ions (likely to be small in the samples reported). The term $(−∂n_f/∂φ_f)$ is a measure of the rate of valence change with pressure (which acts through the $f$-level $ε_f$, and is maximum at the valence instability pressure $P_v$).

The temperature dependence of the enhanced impurity scattering has not so far been predicted, and progress on this front would be very useful, in order to better analyse any non-Fermi liquid exponents in the quasiparticle scattering. According to Fig. 3, there should be a term with negative temperature dependence, reminiscent of the Kondo impurity term, and indeed such behaviour has been attributed to scattering from remaining Ce$^{3+}$ ‘impurities’ in the intermediate valence regime [15].

Figure 4 illustrates how a negative slope of $\rho(T)$ can occur due to the competition between the quasiparticle and impurity scattering at high pressure, in another sample of CeCu$_2$Si$_2$. At the pressures shown, superconductivity is being suppressed, and the $A$ coefficient of the quasiparticle scattering $AT^n$ is rapidly falling, indicating the transition from a heavy fermion to valence fluctuating regime. Only at 7.20 GPa is there a clear minimum in the resistivity, around 6 K. At lower pressure, the $A$ coefficient was large enough to mask the impurity contribution, while at still higher pressure, the enhancement of the residual resistivity is reduced as the system moves away from the valence instability. One very puzzling observation in some samples was a further change in the sign of the slope as $T \rightarrow 0$, giving a maximum around 4 K, which persists in a magnetic field large enough to suppress any trace of superconductivity [16].

In summary, we have shown some unexplained features of the high pressure superconducting and normal state of CeCu$_2$Si$_2$ around the valence instability, with the aim that these might be better explained theoretically, and also as possible signposts for critical valence fluctuations in other compounds.

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