VARIATION OF THE HEAVY FERMION GROUND STATE IN CeCu$_2$Si$_2$ CRYSTALS BY STOICHIOMETRY CONTROL

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To gain insight into the formation of the heavy Fermion state in CeCu$_2$Si$_2$, we have studied the relationship between the high temperature and low temperature physical properties. The single crystals are grown from metallic solvents, such as Sn, In or Ga. The low temperature susceptibility $\chi$ can be varied by factors of 5, and samples with smallest $\chi$ have the largest linear contribution $\gamma$ to the specific heat. This "anticorrelation" of $\chi$ and $\gamma$ is unexpected. The reduction of $\chi$ at low $T$ is mainly due to a temperature independent antiferromagnetic molecular-field type interaction $\chi^{-1}(T) = 1 + \beta T + \gamma$, and not due to interactions which become dominant below a characteristic temperature. Superconductivity occurs in small $\chi$ - large $\gamma$ samples.

1. Introduction

After the discovery of superconductivity in CeCu$_2$Si$_2$ [1], heavy Fermion superconductivity rapidly became one of the most interesting fields in solid state physics. The heavy Fermion state forms at low temperatures in a lattice of cerium or uranium ions that carry their full magnetic moments at high temperature [2,3]. The details of the heavy Fermion state are not quite clearly understood, and we found it helpful to study the relation between high and low temperature properties in single crystals of CeCu$_2$Si$_2$. Controlled chemical substitutions strongly influence the susceptibility and the specific heat. The observed "anticorrelation" between $\chi$ and $\gamma$ is discussed.

2. Crystal growth

Single crystals were grown from metallic solvents, such as Cu, Sn, In and Ga. As the nutrient-solvent ratio is varied, the amount of solvent atoms incorporated in the CeCu$_2$Si$_2$ lattice could be influenced. From steric considerations, the solvent atoms we used are most likely to occupy Cu sites. The most extensive studies involved crystals grown from Sn, and we found it necessary to introduce excess Cu to compensate for the formation of parasitically forming Cu–Sn compounds. In turn, the unit cell volume, the $c/a$ ratio as well as the physical properties could be systematically varied as a function of the Sn concentration in Ce(Cu, Sn)$_2$Si$_2$. A more complete account with numerical data will be given elsewhere [4].

3. Magnetic susceptibility at high and low temperatures

From the large number of crystals we studied, three are selected here to demonstrate the relation between the various physical properties. For brevity, the crystal grown from Cu solvent is labeled "A", the one from Sn with large Cu excess in the melt "B", and the one from In "C".

The magnetic susceptibility $\chi$ is anisotropic [5,6] as expected from the proposed CEF level scheme [7]. The differences among the various crystals is most pronounced at low temperatures where the susceptibilities vary by factors of 4–5. The origin of these differences, however, is not rooted in low temperature interactions. This is illustrated in fig. 1 where an overview of $\chi(T)$ is given for crystal A. The CEF-only susceptibility $\chi_0(T)$ is also shown [8]. The shape of the $\chi_0(T)$ and $\chi(T)$ curves are obviously very similar, and the vertical shift suggests a description in terms of a molecular field: $\chi^{-1}(T) = \chi_0^{-1}(T) + \lambda$. The molecular field parameter $\lambda$ is larger in the $a$-direction than in the $c$-direction. We
note in passing that the layer of Ce-atoms is parallel to the a-direction. The effective moment at the highest temperatures is within experimental accuracy of the one of the free Ce$^{3+}$ ion (2.54μ$_B$).

Next we compare the three crystals in fig. 2. To simplify the graph, only $\chi_a$ is shown, and the striking difference among the crystals is the value of $\chi_a$. In table 1 the molecular field parameters for the two crystallographic directions are compiled. It is interesting to note that $\lambda_a - \lambda_c$ is sample independent ((80 ± 2) mol/emu) despite the variation of $\lambda_a$ by a factor of about two, and is larger than the CEF-only value of 35 mol/emu.

At temperatures below 10 K, the susceptibility of A and B are very similar and small ($\chi_a = 6.2 \times 10^{-3}$ and $6.6 \times 10^{-3}$ emu/mol, respectively at 5 K), whereas $\chi_a$ is twice as large for C. Both A and B exhibit only a very slight increase of $\chi$ on further cooling to 1.3 K, but $\chi$ of sample C goes through a maximum at ≈ 3.6 K. We never found it necessary to subtract an "impurity" contribution from the raw susceptibility data since there is no $1/T$ contribution present, and no saturation of magnetic impurities was found in fields up to 50 kOe. The slight increase of $\chi$ below 10 K therefore appears to be an intrinsic property of CeCu$_2$Si$_2$, and we will return to this point later.

4. Specific heat measurements

The specific heat $c_p$ was measured from 0.3 K to 1.5 K for samples A and C, and to 12.5 K for sample B. The values of $c_p$ at 1.5 K range between 635 mJ/mol K$^2$ for A to 890 mJ/mol K$^2$ for B. To emphasize the electronic contribution to $c_p$, it is customary to plot $c_p/T$ vs. $T$. On such a plot, the temperature dependences are quite different for the three samples. For C the $c_p/T$ value extrapolates to 400 mJ/mol K$^2$, whereas $c_p/T$ increases on lowering $T$ to ≈ 700 mJ/mol K$^2$ for A and to ≈ 1100 mJ/mol K$^2$ for B. The maximum of $c_p/T$ for B at 0.8–0.9 K is noteworthy.

5. Discussion

The possibility to control the chemical composition of CeCu$_2$Si$_2$ single crystals offers an additional way to elucidate the origin of the heavy Fermion state. We find that an interaction of molecular-field type dominates the magnetic properties of CeCu$_2$Si$_2$ and the strength of this interaction is determining the low temperature susceptibility. The specific heat $c_p/T$ is larger for the samples with small $\chi_a$. It appears that $\chi$ and $\lambda$ are "anticorrelated". The ratio $\chi/\lambda$ is ≈ 1 for A, ≈ 0.65
for B and 2.6 for C. To calculate this ratio, we used the values of \( \frac{1}{4}(\chi + 2\chi_{\omega}) \) and \( c_p/T \) from an extrapolation \( T \to 0 \). It has been noted in the earliest work on CeCu_2Si_2 that for "good" samples the \( \chi/\lambda \) ratio is < 1. We suggest this is due to the uncertainty at which temperature \( c_p/T \) should be taken. In the case of our sample B and also in a recent study [9] the value of \( c_p/T \) goes though a maximum below 1 K, the origin of which has been ascribed [9] to the fact that coherence is developing between the Ce sites. The new structure in the lowest temperature excitation spectrum makes any choice of a \( c_p/T \) value arbitrary. Therefore, the "enhancement" of \( c_p/T \) over \( \chi \) in the "best" samples is not due to particular Fermi liquid parameters. Sample A shows diamagnetism in ac susceptibility measurements (0.5 K), but from the heat capacity data gapless superconductivity has to be inferred. It is noteworthy that \( \chi(T) \) and \( c_p/T \) monotonously increase toward \( T \to 0 \) and the \( \chi/\lambda \) ratio is close to 1. The occurrence of superconductivity is not necessarily tied to the formation of the coherent state below 1 K.

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