Anisotropy of the pressure derivatives of the specific heat and the density of electron states in the heavy-fermion system $CeCu_2Si_2$

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Through an analysis of experimental data of Lang *et al.* [Phys. Scripta **39**, 135 (1991)] on the thermal expansion of a $CeCu_2Si_2$ single crystal, it is shown that the pressure derivatives of the jump in the specific heat at the superconducting transition and of the effective density of electron states are strongly anisotropic. The results of the analysis are compared with experiments by Bleckwedel and Eichler [Solid State Commun. **56**, 693 (1985)] on the pressure dependence of the specific heat in a polycrystalline $CeCu_2Si_2$ sample.

We have previously[1] used Landau's theory of phase transitions to analyze experimental data on the thermal anomalies in the thermal expansion and elastic moduli of a $YBa_2Cu_3O_7$ single crystal near its superconducting transition. An analysis of this sort, which also applies to a multicomponent order parameter, reveals numerous important properties of superconductors. In particular, it reveals the anomalies of these materials which stem from the crystallographic anisotropy.

In the present letter we follow the approach of Ref. 1 to analyze experiments on the thermal expansion of a perfect $CeCu_2Si_2$ single crystal.[2] This is a heavy-fermion system in which a superconductivity arises below $T_c \simeq 0.63$ K. We wish to stress that the large anomalies in the thermal expansion and elasticity are unique to heavy-fermion systems. We then compare the results of this analysis with the experimental data of Ref. 3, which was a study of the pressure dependence of the specific heat in this system.

According to Ref. 2, when the tetragonal $CeCu_2Si_2$ single crystal goes superconducting, one observes a pronounced anisotropy in the jumps in the coefficients of thermal expansion, $\delta\beta_a(T_c) \simeq +1.74\times10^{-6}$ K^{-1} and $\delta\beta_c(T_c) \simeq -2.8\times10^{-6}$ K^{-1}, along the crystallographic a and c axes, respectively. Working from this circumstance, and using the thermodynamic Ehrenfest relation

$$\delta\beta_i(T_c) = \frac{\delta C}{T_c}\frac{dT_c}{dp_i}, \quad i=a,c, \tag{1}$$

where δC is the jump in the specific heat (per unit volume) at $T=T_c$, Lang *et al.*[2] concluded that there was a pronounced anisotropy in the derivatives dT_c/dp_i. These are the derivatives of the superconducting transition temperature with respect to the

components p_i of the pressure tensor $\hat{p}$ along the a and c axes. Lang *et al.* derived the following estimates for these derivatives: $dT_c/dp_a \simeq +8$ mK/kbar and $dT_c/dp_c \simeq -12.5$ mK/kbar.

In addition, experimental data found in Ref. 2 demonstrate yet another anomaly in the thermal expansion coefficients $\beta_i(T)$--one which has yet to be explained. Specifically, at the transition to the superconducting state the slope of the temperature dependence of the coefficients, $\beta_i(T)$, changes. This change in slope corresponds to jumps in the temperature derivative $\delta(d\beta_i/dT)$ below and above T_c. According to Fig. 2 in Ref. 2, for the $CeCu_2Si_2$ single crystal there is a pronounced anisotropy of these jumps: $\delta(d\beta_a/dT) \simeq +1.1\times 10^{-5}\ \mathrm{K}^{-2}$ and $\delta(d\beta_c/dT) \simeq -5.3\times 10^{-6}\ \mathrm{K}^{-2}$ for the a and c axes, respectively. We showed in Ref. 1 that a change in the slope of the temperature dependence of the thermal expansion coefficients, $\beta_i(T)$, at the transition to the superconducting state was due to the superconducting order parameter $\Delta(T)$ below T_c and was proportional to $\Delta^2(T)$ near the transition. For the jumps in the temperature derivatives $\delta(d\beta_i/dT)$ at the superconducting transition, we derived[1] a thermodynamic relation similar to (1):

$$\delta\left(\frac{d\beta_i}{dT}\right) = -\frac{\delta C}{T_c}\frac{d\ln(\alpha^2/b)}{dp_i}, \quad i=a,c. \tag{2}$$

Here α and b are parameters of a Landau expansion of the density of the thermodynamic potential Φ near the superconducting transition:

$$\Phi(T,\Delta,\hat{p}) = \Phi_0(T,\hat{p}) + (1/2)\alpha(\hat{p})[T - T_c(\hat{p})]\Delta^2 + (1/4)b(\hat{p})\Delta^4, \tag{3}$$

where $\Phi_0(T,\hat{p})$ corresponds to the normal state of the metal. Using the experimental data of Ref. 2 for the jump in the specific heat, $\delta C_{\mathrm{mol}} \simeq 0.71$ J/(K · mole), and the molar volume, $V_{\mathrm{mol}} \simeq 50.3$ cm^3, and also using the values given above for T_c and the jumps in the derivatives $\delta(d\beta_i/dT)$, we find the following pressure derivatives with the help of (2):

$$\frac{d\ln(\alpha^2/b)}{dp_a} \simeq -4.9\times 10^{-2}\ \mathrm{kbar}^{-1}, \quad \frac{d\ln(a^2/b)}{dp_c} \simeq +2.4\times 10^{-2}\ \mathrm{kbar}^{-1}. \tag{4}$$

The derivatives in (4) are strongly anisotropic. Their absolute values are comparable in magnitude to the anisotropic pressure derivatives of the logarithm of the superconducting transition temperature, $d\ln T_c/dp_a \simeq 1.3\times 10^{-2}\ \mathrm{kbar}^{-1}$ and $d\ln T_c/dp_c \simeq -2.0\times 10^{-2}\ \mathrm{kbar}^{-1}$. Working from these results and the fact that the ratio (α^2/b) determines the jump in the specific heat, $\delta C = (\alpha^2/2b)T_c$, we can thus predict a pronounced anisotropy in the pressure derivatives of the jump in the specific heat given by[1]

$$\frac{d\ln\delta C}{dp_i} = \frac{d\ln(\alpha^2/b)}{dp_i} + \frac{d\ln T_c}{dp_i}, \quad i=a,c. \tag{5}$$

Specifically, we find the pronounced anisotropy

$$\frac{d\ln\delta C}{dp_a} \simeq -3.6\times 10^{-2}\ \mathrm{kbar}^{-1}, \quad \frac{d\ln\delta C}{dp_c} \simeq +0.4\times 10^{-2}\ \mathrm{kbar}^{-1}. \tag{6}$$

Let us analyze some experimental data on the thermal expansion of a $CeCu_2Si_2$ single crystal[2] in its normal state. We assume that at low temperatures, $T \leqslant 1$ K, corresponding to the experiments of Ref. 2, the thermal expansion is dominated by the electron component:[4]

$$\beta_i^e(T) = -\gamma T \frac{d \ln \gamma}{dp_i}, \quad i=a,c, \tag{7}$$

where γ is the coefficient in the electron specific heat, $C_e(T) = \gamma T$. For $CeCu_2Si_2$ this coefficient is 0.78 J/(K^2 · mole), according to Fig. 1 in Ref. 2. The basis for this suggestion is the temperature dependence of the coefficients $\beta_i^e(T)$ which was measured in Ref. 2 at $T \leqslant 1$ K and in a magnetic field $H=3$ T, which destroys the superconductivity. Under these conditions, according to Fig. 2 of Ref. 2, the temperature dependence $\beta_i^e(T)$ is linear for the c axis, while for the a axis there is a slight deviation from the linear law in (7). Using these experimental data along with (7), we find the following estimates of the anisotropic pressure derivatives along the a and c axes of the logarithm of the coefficient γ :

$$\frac{d \ln \gamma}{dp_a} \simeq -2.0 \times 10^{-2} \text{ kbar}^{-1}, \quad \frac{d \ln \gamma}{dp_c} \simeq -0.6 \times 10^{-2} \text{ kbar}^{-1}. \tag{8}$$

The derivatives in (8) indicate (first) that the specific heat of the $CeCu_2Si_2$ single crystal in its normal state is an anisotropic function of the pressure. Second, since we have $\gamma = \pi^2 N^*(\epsilon_f)/3$, where $N^*(\epsilon_f)$ is the effective density of electron states at the Fermi level ϵ_f, and when we take into account (for example) the electron–phonon coupling and spin fluctuations, we find that the derivatives in (8) yield estimates of the anisotropic pressure derivatives of the effective density of electron states, which is generally not equal to the actual density of states, $N(\epsilon_f)$:

$$\frac{d \ln N^*}{dp_a} \simeq -2.0 \times 10^{-2} \text{ kbar}^{-1}, \quad \frac{d \ln N^*}{dp_c} \simeq -0.6 \times 10^{-2} \text{ kbar}^{-1}. \tag{9}$$

If we use the BCS model to determine the ratio $\alpha^2/b = [8\pi^2/7\zeta(3)]N(\epsilon_f)$, where $N(\epsilon_f)$ is the density of states of the quasiparticles responsible for the superconducting properties, and if we use $\zeta(3) \simeq 1.20$, then the general thermodynamic results for the derivatives in (4) are simultaneously BCS-model estimates of the anisotropic pressure derivatives of $N(\epsilon_f)$ in this case:

$$\left(\frac{d \ln N}{dp_a}\right)_{\text{BCS}} \simeq -4.9 \times 10^{-2} \text{ kbar}^{-1}, \quad \left(\frac{d \ln N}{dp_c}\right)_{\text{BCS}} \simeq +2.4 \times 10^{-2} \text{ kbar}^{-1}.$$

The pronounced difference between these derivatives and the values in (9), found from an analysis of experiments on the thermal expansion of a $CeCu_2Si_2$ single crystal in its normal state, indicates a substantial difference in the densities of electron states N and N^*. This result means that, although for the measured jump in the specific heat we have a ratio[2] $(\delta C/\gamma T_c)_{\text{exp}} \simeq 1.48$, which is close to the value of 1.43 predicted by the BCS model, the prediction of that model for the anisotropic pressure derivatives $d\ln\delta C/dp_i = d\ln\gamma/dp_i + d\ln T_c/dp_i$ contradicts the results of our thermodynamic analysis of the experimental data. This conclusion may be taken as one more piece of

evidence against the validity of the BCS model for describing the superconducting state in $CeCu_2Si_2$. This circumstance calls to mind another circumstance which constitutes evidence against the validity of the BCS model for $CeCu_2Si_2$: The temperature dependence of the specific heat in the superconducting state is not exponential at low temperatures ($T \ll T_c$), according to the observations of Ref. 2.

It is interesting to compare the results of our general thermodynamic analysis for the derivatives in (6) and (9) with experimental data on the dependence of the specific heat of a polycrystalline $CeCu_2Si_2$ sample on the hydrostatic pressure p_h.[3] Using (6) and (9), we correspondingly write

$$\left(\frac{d\ln N^*}{dp_h}\right)_{\text{cal}} = 2\frac{d\ln N^*}{dp_a} + \frac{d\ln N^*}{dp_c} \simeq -4.6\times 10^{-2}\ \text{kbar}^{-1}, \tag{10}$$

$$\left(\frac{d\ln \delta C}{dp_h}\right) \simeq -6.8\times 10^{-2}\ \text{kbar}^{-1}. \tag{11}$$

We must stress that the "hydrostatic" pressure derivatives which we have found, (10) and (11), are an order of magnitude greater than the pressure derivative of the logarithm of the superconducting transition temperature found in Ref. 2: $d\ln T_c/dp_h \simeq 0.5\times 10^{-2}$ kbar^{-1}. We can also compare (10) with the pressure derivative of the effective density of electron states found from measurements of the pressure dependence of γ (the coefficient in the electron specific heat) in the normal phase. The data for a polycrystalline $CeCu_2Si_2$ sample in Fig. 2 of Ref. 3 thus yield $(d\ln\gamma/dp_h)_{\text{exp}} = (d\ln N^*/dp_h)_{\text{exp}} \simeq 6.4\times 10^{-2}$ kbar^{-1}. This figure is close to the value which we found [see (10)]. Using the value $B = 1.2\times 10^3$ kbar for the bulk modulus,[2] we can also write, for comparison, values of the dimensionless derivative of the logarithm of the density of electron states with respect to the logarithm of the volume: $(d\ln N^*/d\ln V)_{\text{cal}} \simeq 55$ and $(d\ln N^*/d\ln V)_{\text{exp}} \simeq 70$.[3] These values of the electron Grüneisen parameter for the heavy-fermion system $CeCu_2Si_2$ are one or two orders of magnitude larger than those in ordinary metals.[5] We run into a more complex situation when we try to compare our value of the pressure derivative in (11) with the experimental dependence[3] of the jump in the specific heat on the hydrostatic pressure, $\delta C(p_h)$. According to Fig. 3 of Ref. 3, this dependence is very nonmonotonic. At low pressures, $p_h \leqslant 3$ kbar, there is an increase in $\delta C(p_h)$ with increasing pressure. As one explanation for this increase, Bleckwedel and Eichler[3] cited the defectiveness of the $CeCu_2Si_2$ polycrystalline sample which they studied and the possibility that the volume of the superconducting phase might vary with the pressure. Evidence that the sample studied in Ref. 3 was poorer in superconducting properties than the single crystal used in the experiments of Ref. 2 comes from a measurement[3] of the jump in the specific heat at $p_h = 0$, which amounts to 33% of the value of δC found for the single crystal in Ref. 2. At high pressures, $3 < p_h \leqslant 6$ kbar, there is a decrease in the jump $\delta C(p_h)$ with increasing pressure according to Ref. 3. The derivative corresponding to Fig. 3 of that paper, $(d\ln\delta C/dp_h)_{\text{exp}} \simeq -1.0\times 10^{-1}$ kbar^{-1}, is consistent with the value calculated here, (11).

On the basis of this discussion we can say, in particular, that the anisotropic pressure derivatives of the jump in the specific heat and the effective density of electron

states in the $CeCu_2Si_2$ single crystal which we have found through an analysis of experiments on thermal expansion do not contradict independent measurements of the behavior of these properties as a function of the hydrostatic pressure. It also follows from our discussion that it would be worthwhile to use some good single-crystal samples for an experimental test of the anisotropic pressure dependence predicted here for the jump in the specific heat at the superconducting transition.

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