Spurious second transition in the heavy-fermion superconductor CePt$_3$Si

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Specific heat studies have shown a distinct second transition at $T \approx 0.48$ K in some nominally single-phase samples of the heavy Fermion superconductor CePt$_3$Si, $T_c=0.75$ K, which in the current work is also seen as structure in penetration depth measurements. The double transition structure is accentuated by a Ce deficiency in Ce$_{1-x}$Pt$_3$Si, becoming reproducible for $x \geq 2\%$. Electron microprobe, x-ray diffraction, and metallography studies of these Ce-deficient samples show only a minor amount of second phase which, by secondary electron backscattering, is similar in composition to Ce$_2$Pt$_{15}$Si$_7$. This compound is an antiferromagnet with a peak in C/T at 0.4 K with a magnitude of 22000 mJ (Ce-mol K^2)$^{-1}$. Thus, in the complexity of a the Ce-Pt-Si ternary phase diagram, the cause for the occasionally observed structure in the specific heat below the superconducting transition is a few tenths of a percent mass loss of Ce during arc-melting or annealing of the sample.

I. INTRODUCTION

Bauer *et al.*[1] recently discovered heavy Fermion superconductivity, $T_c=0.75$ K, coexisting with antiferromagnetism, $T_N=2.2$ K, in CePt$_3$Si, which occurs in a tetragonal structure without a center of inversion symmetry. Both the coexistence of magnetism with superconductivity as well as the non-centro-symmetric structure implied[1] the possibility of non-BCS superconductivity. Various theoretical discussions as to the possibility of spin triplet superconductivity,[2] or a mixture[3] of spin singlet and spin triplet pairing, have enlivened the study[4] of superconductivity in CePt$_3$Si.

While investigating[5] the response of the superconductivity and magnetism to small stoichiometry variations around 1:3:1 in CePt$_3$Si, we found a double transition in the specific heat (superconductivity at 0.75 K and a second transition at 0.48 K) in unannealed Ce$_{0.97}$Pt$_3$Si quite reminiscent of the double superconducting transitions[6] in UBe$_{13}$ doped with between 2% and 5% Th, and with a significantly larger specific heat anomaly ΔC at the lower transition than the indications found[7] in some samples of nominally stoichiometric CePt$_3$Si. A slight excess of Si, which has been found[8] to enhance ΔC at T_c in CePt$_3$Si, was also found to enhance the second transition. Samples were characterized by measurements of x-ray diffraction, metallography, electron microprobe analysis, specific heat down to 0.35 K, and penetration depth measurements down to 0.08 K.

II. EXPERIMENTAL

Samples of Ce$_{0.97}$Pt$_3$Si, Ce$_{0.97}$Pt$_3$Si$_{1.02}$, Ce$_{0.965}$Pt$_3$Si$_{1.02}$, and Ce$_{0.95}$Pt$_3$Si$_{1.02}$ were prepared by arc-melting together stoichiometric amounts of high purity Ce from Ames Lab,

99.98% pure Pt from Colonial Metals, and 99.9999% pure Si from Johnson Matthey Aesar. The stated nominal stoichiometries were accurate to ±0.002, e.g., the Pt stoichiometry was kept between Pt$_{2.998}$ and Pt$_{3.002}$. Mass losses during arc melting were less than 0.02% in total.

X-ray diffraction powder patterns were measured on all samples. Two small second phase lines, one on each side of the CePt$_3$Si [002] line at $2\Theta=32.9°$, became present for the Ce$_{0.95}$Pt$_3$Si$_{1.02}$ sample. Metallography indicated approximately 0.5%–1% second phase in the sample of Ce$_{0.95}$Pt$_3$Si$_{1.02}$ while secondary electron back scattering results in the JEOL Superprobe 733 electron microprobe apparatus were consistent with 2%–3% of a second phase. Electron microprobe of the Ce$_{0.95}$Pt$_3$Si$_{1.02}$ sample indicated that the *actual* Ce deficiency in the majority, CePt$_3$Si tetragonal phase was approximately 2/3 of the nominal deficiency (i.e., Ce$_{0.97}$ instead of the nominal Ce$_{0.95}$), which is consistent with the composition of the second phase (discussed below).

Specific heat was measured using established techniques[9] down to 0.35 K. Penetration depth measurements[10] were performed[11] utilizing a 21 MHz tunnel diode oscillator with a noise level of 2 parts in 10^9 and low drift in a magnetically shielded Oxford Kelvinox 25 dilution refrigerator.

III. RESULTS AND DISCUSSION

Figure 1 shows the low temperature specific heat for the published data[1] for CePt$_3$Si and the present work's results for Ce$_{0.97}$Pt$_3$Si, Ce$_{0.97}$Pt$_3$Si$_{1.02}$ and Ce$_{0.965}$Pt$_3$Si$_{1.02}$. The lower transition in the specific heat for Ce$_{0.97}$Pt$_3$Si is clearly sharpened and increased in size by the addition of Si. This lower transition seems *a priori* quite large to be associated with a second phase, particularly since at these small Ce deficien-
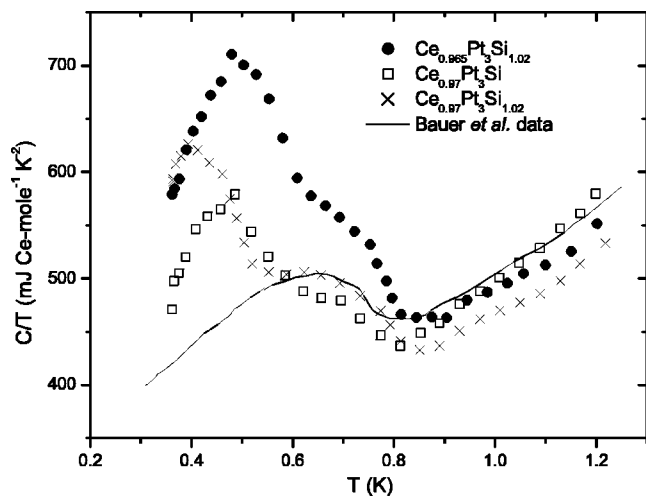
FIG. 1. The specific heat divided by temperature of CePt$_3$Si[1], Ce$_{0.97}$Pt$_3$Si, Ce$_{0.97}$Pt$_3$Si$_{1.02}$, and Ce$_{0.965}$Pt$_3$Si$_{1.02}$ vs. temperature. Note how the slight excess of Si sharpens and increases ΔC for both the upper and lower transitions in Ce$_{0.97}$Pt$_3$Si$_{1.02}$.
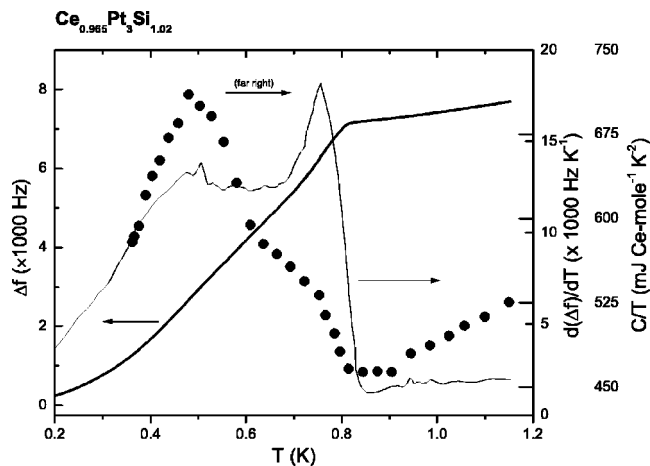

FIG. 2. The penetration depth, λ, proportional to the resonant frequency shift, vs. temperature using the left ordinate and the derivative of these data with respect to temperature using the right ordinate are displayed together with the specific heat of Ce$_{0.965}$Pt$_3$Si$_{1.02}$ from Fig. 1 vs. temperature.

cies the x-ray powder diffraction patterns indicate essentially no second phase.

In order to investigate the magnetic nature of the lower, second transition, which is difficult due to its being embedded in the superconductivity of the upper transition, penetration depth measurements were taken in the Ce$_{0.965}$Pt$_3$Si$_{1.02}$ sample and, together with the specific heat divided by temperature for the same composition, are shown in Fig. 2. In order to accentuate the structure seen in the penetration depth data, the first derivative is also plotted. Clearly, the specific heat anomaly at the lower transition corresponds to the structure seen in the penetration depth, λ, proportional to the measured shift in resonant frequency. The structure in the penetration depth could either[12] be due to superconductivity (where the penetration depth data are consistent with a drop in the superfluid density at 0.5 K due to the opening of a superconducting gap) or to a strong antiferromagnetic transition. In the latter case, the effect could come just from the susceptibility, χ, via $\lambda = \lambda(0)/(1 + 4\pi\chi)^{0.5}$, where $\lambda(0)$ is the trend without a transition. For an antiferromagnetic transition, χ would peak at T_{Neel}, and then fall at lower temperature, which would create a dip in the overall λ vs. T curve.

Electron microprobe secondary electron back scattering analysis of the second phase was performed in the Ce$_{0.95}$Pt$_3$Si$_{1.02}$ sample (which displays a specific heat anomaly, not shown, at the second transition about 25% larger than that shown for Ce$_{0.965}$Pt$_3$Si$_{1.02}$ in Figs. 1 and 2) due to the need to be able to reliably find regions of second phase to analyze. The results were taken using approximately a 2 μ wide beam in ten separate locations where the contrast in the backscattering picture indicated second phase. The composition, in atomic %, of the second phase was found to be, rather than the 20%/60%/20% of the 1:3:1 nominal stoichiometry, 8.8% Ce/61.2% Pt/30.0% Si. Converted to an integer amount of Ce, this would correspond to Ce$_2$Pt$_{13.9}$Si$_{6.8}$ or approximately Ce$_2$Pt$_{14}$Si$_7$. This composition is reminiscent of Ce$_2$Pt$_{15}$Si$_7$, inferred[13] to be magnetically ordered below 2 K using susceptibility measurements down to that tempera-

ture. The ternary Ce-Pt-Si phase diagram has been reevaluated[14,15] following the earlier work,[13] with the conclusion that the correct single phase stoichiometry is actually Ce$_3$Pt$_{23}$Si$_{11}$ (or equivalently Ce$_2$Pt$_{15.3}$Si$_{7.3}$). Since only incomplete[16] characterization of the low-temperature properties of Ce$_3$Pt$_{23}$Si$_{11}$ (and only[13] χ down to 2 K for Ce$_2$Pt$_{15}$Si$_7$) exists, we prepared a sample of Ce$_3$Pt$_{23}$Si$_{11}$ and measured its
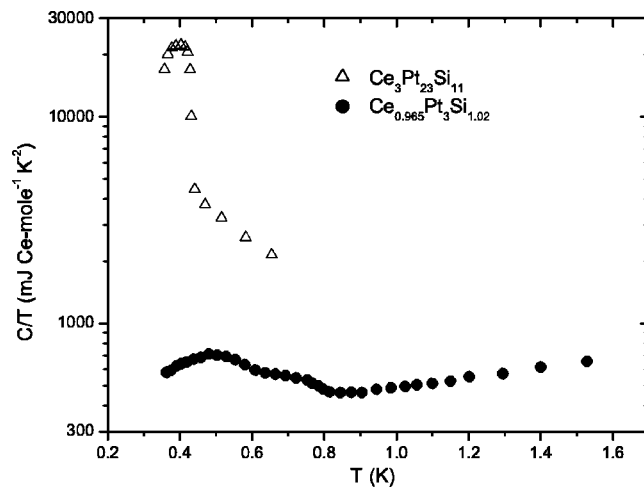

FIG. 3. The semilog plot of the specific heat divided by temperature vs. temperature of Ce$_3$Pt$_{23}$Si$_{11}$ and Ce$_{0.965}$Pt$_3$Si$_{1.02}$ for comparison. The peak in C/T occurs at approximately 0.41 K for Ce$_3$Pt$_{23}$Si$_{11}$ and at 0.48 K for the Ce-deficient sample of CePt$_3$Si. This difference may be due to differences in stoichiometry affecting the ordering temperature (see also the shift of the lower transition between Ce$_{0.97}$Pt$_3$Si and Ce$_{0.97}$Pt$_3$Si$_{1.02}$ in Fig. 1). Certainly, the electron microprobe analysis of the second phase in our material is slightly different (equivalent to Ce$_3$Pt$_{21}$Si$_{10}$) than 3:23:11. Another example of variation of the peak temperature can be inferred from a recent work (Ref. 16) where three data points below 0.43 K for C/T of Ce$_3$Pt$_{23}$Si$_{11}$ revealed no peak down to their lowest temperature of measurement, 0.37 K, with C/T (0.37 K) approximately 8% larger than our measured value of C_{max}/T at 0.41 K.

x-ray diffraction pattern, its magnetic susceptibility, and its low temperature specific heat, shown in Fig. 3.

The result is that the sample has a very large anomaly in C/T at 0.41 K due presumably[12,13] to an antiferromagnetic transition, with C/T at the maximum equal to approximately 22000 mJ (Ce-mol $K^2)^{-1}$. As well, the second phase x-ray lines seen in $Ce_{0.95}Pt_3Si_{1.02}$ and discussed above correspond exactly to the measured positions and intensities for lines in $Ce_3Pt_{23}Si_{11}$.

IV. CONCLUSIONS

In conclusion, the penetration depth anomaly at around 0.5 K shown in Fig. 2, as well as the specific heat anomalies at the same temperature shown for Ce deficient samples of $CePt_3Si$, appear to be due to a second phase of $Ce_3Pt_{23}Si_{11}$, which is rather close in composition to the electron microprobe measured composition for the second phase present in our $Ce_{0.95}Pt_3Si_{1.02}$ sample. The enhancement of the second transition in $Ce_{0.965}Pt_3Si_{1.02}$ vs. $Ce_{0.97}Pt_3Si$ is likely caused by both the increased deficiency in Ce and the slight excess of Si increasing the amount of second phase present. Even for the $Ce_{0.97}Pt_3Si$ sample, with 3% Ce deficiency and no Si excess, the second anomaly in C is already larger than the upper, superconducting anomaly.

Thus, a visible (e.g., $\approx 10\% - 15\%$ of the upper anomaly) second anomaly can occur in the specific heat of nominally $CePt_3Si$ due to less than 0.05% second phase of $Ce_3Pt_{23}Si_{11}$, clearly undetectably small by x-ray diffraction, metallography, or even microprobe techniques. Based on the results in the present work, such an amount of $Ce_3Pt_{23}Si_{11}$ second phase could be caused by less than a 0.5% Ce deficiency, either through losses caused during preparation or during annealing to sharpen the transition.

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