Evidence for Line Nodes in the Superconducting Energy Gap of Noncentrosymmetric $CePt_3Si$ from Magnetic Penetration Depth Measurements

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We report measurements of the magnetic penetration depth $\lambda(T)$ in high-quality $CePt_3Si$ samples down to 0.049 K. We observe a linear temperature dependence below $T \simeq 0.16T_c$, which is interpreted as evidence for line nodes in the energy gap of the low-temperature phase of this material. A kink in $\lambda(T)$ at about 0.53 K may be associated with the second superconducting transition recently reported. The results are discussed in terms of the symmetry of the superconducting order parameter.

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Most superconductors known to date are parity-conserving materials allowing the classification of their pairing states in spin singlets (even parity) or spin triplets (odd parity). The recently discovered heavy-fermion superconductor $CePt_3Si$ ($T_c = 0.75$ K) crystallizes in a tetragonal lattice with point group C_{4v} [1]. It has no spatial inversion symmetry, which implies that the spatial component of the wave function has no definite parity. To preserve the antisymmetry of the pairing, the same applies to the spin component. The direct implication of the parity violation is that the pairing symmetry should, in principle, be a mixture of spin-singlet and spin-triplet states. The symmetry analysis for the superconducting pairing state becomes more complicated. Recent theoretical arguments [2,3] indicate that such a mixture can be neglected under certain conditions; thus, the singlet and triplet pairing states can be considered separately as if parity is conserved.

In $CePt_3Si$ the upper critical field H_{c2} exceeds the paramagnetic limiting field [1], which readily points out to the occurrence of spin-triplet pairing in this material. This leads to a conflict because spin-triplet channels are known to be forbidden in the absence of inversion symmetry [4]. Frigeri *et al.* [2] showed, however, that spin-triplet states are not completely suppressed in the absence of an inversion center. Considering the spin-orbit coupling (SOC) to be weak, they suggested the p wave (odd parity) $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_y - \hat{\mathbf{y}}k_x$ as the possible pairing state. The gap structure for this state has point nodes. Further theoretical support for an odd-parity state was given by Samokhin *et al.* [3], who showed that SOC in $CePt_3Si$ is strong and that this fact, along with the absence of inversion symmetry, always yields an odd-parity order parameter with line nodes for one-dimensional irreducible representations (IRs). In recent work, Sergienko and Curnoe [5] proposed a model for noncentrosymmetric superconductors with strong SOC in which the temperature dependence of the thermodynamic properties would be governed by an even-parity function. Such a function would transform according to the IRs of the point group. In this scenario, $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_y - \hat{\mathbf{y}}k_x$ corresponds to an isotropic and fully gapped even function. As a consequence, these controversial discussions do not allow a definite conclusion on the symmetry and parity of the gap function in $CePt_3Si$ from a theoretical perspective.

The parity conservation issues and the splitting of the spin degeneracy in the electronic energy bands by the SOC are of high relevance in unconventional superconductivity, and this is why $CePt_3Si$ has gained so much interest. Of primary importance is thus the study of its pairing symmetry which has been even further complicated with the recent observation of a second superconducting transition [6,7]. To our knowledge, no experimental indication of the structure of the superconducting gap—or the symmetry of the pairing state—of $CePt_3Si$ has yet been provided.

Here we report measurements of the magnetic penetration depth $\lambda(T)$ in $CePt_3Si$, an electrodynamic property that has proven to be a fundamental probe of the energy gap structure of unconventional superconductors. We carried out measurements in polycrystalline and powder $CePt_3Si$ samples down to 0.049 K, a temperature which is well within the low-temperature limit $T \approx 0.2T_c$. The data exhibit a linear temperature dependence below $T \simeq 0.16T_c$, which is interpreted as the first strong evidence for line nodes in the gap structure of the superconducting pairing state of $CePt_3Si$.

The polycrystalline sample ($T_c = 0.75$ K) of $CePt_3Si$ used in the present measurements was prepared by argon arc melting, and subsequently heat treated under high vacuum at 870 °C for three weeks to substantially increase its quality [1]. In order to discard possible effects from inhomogeneities and intergrain coupling in this sample, a second was obtained by grounding a piece of the mother sample in a mortar, sedimenting the resulting powder in alcohol and then casting it in Stycast 1266 epoxy. This second sample has $T_c = 0.66$ K as measured from the onset of the diamagnetic behavior in the penetration depth data. A scanning electron microscopic analysis carried out on both samples revealed that the polycrystalline one grew in a compact, layerlike pattern, whereas the powder consisted of grains with lognormal-distributed sizes having a medium size of about 2 μm. We also measured high-purity samples of polycrystalline cadmium and aluminum (not reported) for comparison. It is important to mention here that the low-temperature dependence of $\lambda(T)$ does not seem to be affected by the sample type (single crystal, polycrystal, etc.) measured, as long as the sample is of high quality and purity. Such a statement is supported by measurements in high-quality polycrystalline/powder samples of other superconducting materials, which have yielded the same low-temperature behavior of $\lambda(T)$ as measured in single crystals [8–12].

Penetration depth measurements were performed utilizing a 9.5 MHz tunnel diode oscillator with a noise level of less than 0.5 part in 10^9 and a very low drift. The magnitude of the ac field was estimated to be 5 mOe. The internal vacuum can of the dilution refrigerator employed to get low temperatures is surrounded by a layer of CRYOPERM 10 shield which reduced the dc field at the sample to around 1 mOe. This field is more than 3 orders of magnitude lower than $H_{c1}(0) = 6.5$ Oe (obtained from $H_c(0) =$ 260 Oe [6] and $\kappa = 140$ [1]); thus the possibility of vortex contributions to the measured $\lambda(T)$ is negligible. The samples were mounted, using a small amount of vacuum grease, on a small single crystal sapphire rod. The other end of the rod has a strong thermal connection to the mixing chamber of the dilution refrigerator. The sample temperature was measured with a calibrated RuO_2 thermometer located close to the sample.

A change in the penetration depth causes a variation in the susceptibility of the sample and, hence, in the sample-coil inductance which in turn shifts the measured frequency of the oscillator from a reference value $f(T) - f(T_{\rm min}) = G[\chi(T) - \chi(T_{\rm min})]$. Here $T_{\rm min}$ is the lowest temperature of the experiment and χ a function of λ. The G factor depends on the empty-coil frequency and on the sample and coil geometry, and is determined by measuring a sample of known behavior and of the same dimensions as the test sample. Since for polycrystals and powders the effective geometry and, hence, the demagnetizing factor is somewhat unknown, the determination of G for this sample type is not reliable. However, for the present study what matters is the high accuracy in the temperature variation of λ obtained from the measured $\chi(T)$. For the powder sample, the susceptibility χ was related to λ through $\chi = \frac{3}{2} \times \langle 1 - \frac{3\lambda}{r} \coth\frac{r}{\lambda} + \frac{3\lambda^2}{r^2} \rangle$. Here r is the radius of a grain and $\langle \cdots \rangle$ denotes an average defined by $\langle x \rangle \equiv \int x r^3 g(r) dr / \int r^3 g(r) dr$, $g(r)$ being the grain-size distribution.

Figure 1 shows $\Delta\lambda(T)/\Delta\lambda_0$ in the measured temperature range below T_c for the $CePt_3Si$ and Cd samples. Here $\Delta\lambda(T) = \lambda(T) - \lambda(T_{\rm min})$ and $\Delta\lambda_0$ is the total penetration depth shift. Strikingly broad transitions are observed in both $CePt_3Si$ samples, the transition of the powder being wider than that of the polycrystal. Usually a broad transition in nonsingle crystal samples is associated to intergrain or proximity effects, but such effects are not expected to be relevant in the present case because of the very small measuring magnetic fields (about 5 mOe) [8]. Moreover, in the crushed powder samples the intrinsic behavior was expected to be more pronounced and the transition less broad because of the larger interspace and weaker links between particles [8]. The response or susceptibility of the system is a function of $\lambda(T)/a$, where a is the relevant dimension of the sample. In the powder the mean a is 2 μm. One of the characteristic lengths in a superconductor is the zero temperature penetration depth $\lambda(0)$ which is equal to 1.1 μm in $CePt_3Si$ [1]. Since the relevant dimension is comparable to a characteristic length [$\lambda(0)/a$ of the order of 1], finite size effects certainly influence the observed superconductivity parameters in the powder sample. Such effects in superconductors are known to cause reduction of T_c and broadening of the transition [13], both observed in the powder data.

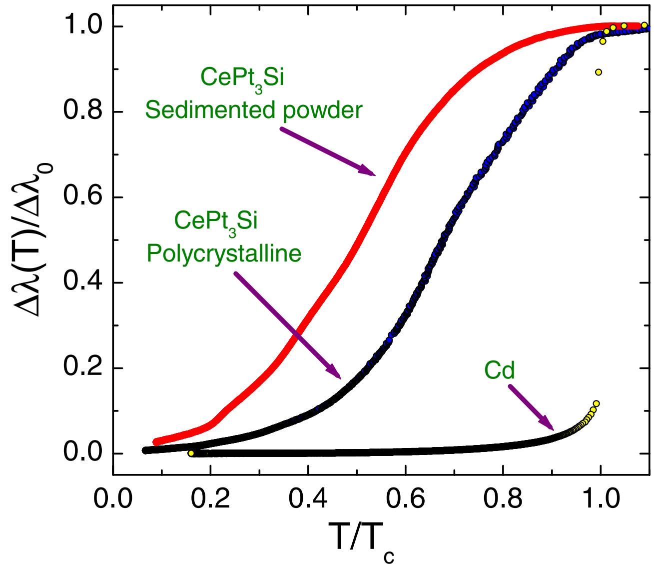

FIG. 1 (color online). The normalized $\Delta\lambda(T)$ vs T/T_c for both samples of $CePt_3Si$ and for conventional superconducting cadmium.

The polycrystalline sample data have an inflection point or kink around 0.53 K which is near to the temperature of the second superconducting transition ($T_{c2} = 0.55$ K) recently reported in $CePt_3Si$ [6,7]. This change of behavior at about 0.53 K is not observed in the powder sample, but here it could be masked by other effects. Measurements of the penetration depth or the ac magnetic susceptibility in polycrystals and single crystals of UPt_3 [12], an antiferromagnetic heavy-fermion superconductor with double transition, depict kinks at the second transition temperature and overall similar T behaviors as that found here for $CePt_3Si$. The kink at 0.53 K in the polycrystalline data of Fig. 1 might thus be associated to the second superconducting transition of $CePt_3Si$ (see below for further discussion).

Figure 2(a) shows $\Delta\lambda(T)$ against T/T_c for a polycrystalline sample of $CePt_3Si$ and, for comparison, a Cd sample up to $0.6T_c$. Cadmium ($T_c = 0.52$ K) is a fully gapped spin-singlet s-wave superconductor for which all thermodynamic and transport properties follow an exponential temperature behavior. This T dependence is indeed observed in the Cd data of Fig. 2(a). The inset in this figure displays the same data of $CePt_3Si$ for $T \leq 0.2T_c$. The powder sample has the same qualitative low-temperature behavior as the polycrystal but, because of possible surface damage during the crushing, displays stronger field penetration as suggested by the larger slope $\Delta\lambda(T)/\Delta T$ [see Fig. 2(b)]. It can be clearly seen in Fig. 2 that $\Delta\lambda(T) \propto T$ below $T \simeq 0.16T_c$ in the $CePt_3Si$ samples.

A T-linear dependence of the penetration depth in the low-temperature region is expected for clean, local superconductors with line nodes in the gap function. Assuming a spherical Fermi surface (as it has been done in other studies [2,3]), it is found [1] that both the mean free path $l = 800$ Å and $\lambda(0) = 11000$ Å are larger than the coherence length $\xi_0 = 81$ Å, implying that $CePt_3Si$ is a clean, local superconductor. Hence, the experimental penetration depth results point out to the existence of line nodes in the structure of the superconducting pairing state and, therefore, to unconventional superconductivity in $CePt_3Si$. Nuclear spin-lattice relaxation rate $1/T_1$ measurements in $CePt_3Si$ [14] did not find a T^3 law as expected for line nodes. We argue that it may be due to the fact that such measurements were performed *above* the low-temperature regime. On the other hand, our results rule out any association of the small peak observed just below T_c in $1/T_1T$ with the presence of an isotropic (even- or odd-parity) gap function, for which the low T dependence of $\Delta\lambda(T)$ is exponential.

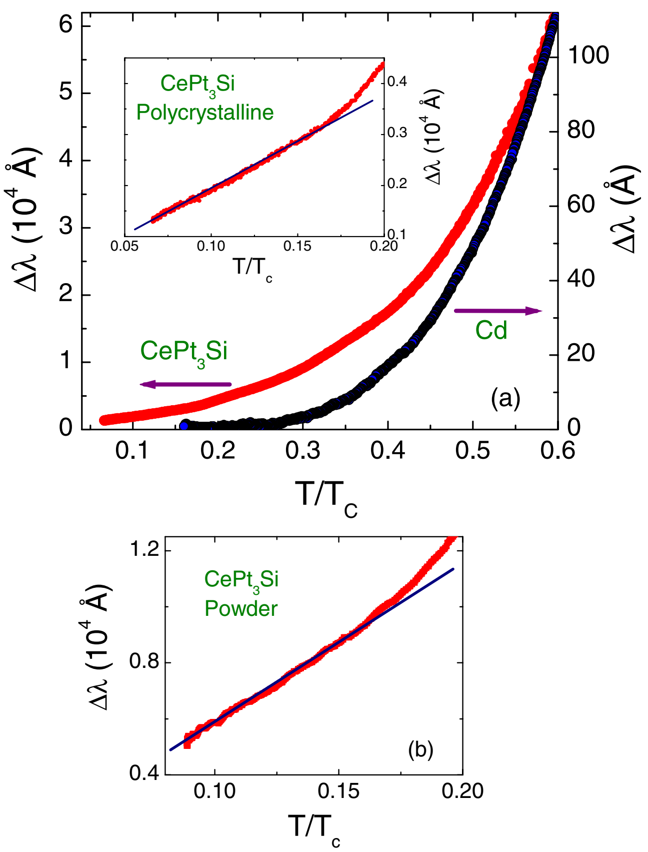

FIG. 2 (color online). (a) $\Delta\lambda(T)$ against T/T_c for a polycrystalline sample of $CePt_3Si$ in the low-temperature region. For comparison, data of Cd (an isotropic gapped spin-singlet superconductor) are also presented. Note the difference in the vertical scales. The inset shows the linear temperature behavior of $\lambda(T)$ in the $CePt_3Si$ sample below $T \simeq 0.16T_c$. (b) $\Delta\lambda(T)$ against T/T_c for the sedimented powder sample. Solid lines are visual guides.

Some of the theories proposed [3,5] for $CePt_3Si$ allow, without specifying a particular state, for the existence of line nodes in the pairing state. This is consistent with the penetration depth data presented here. The $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_y - \hat{\mathbf{y}}k_x$ pairing model [2] with no line nodes is not supported by the $\lambda(T)$ data. However, unlike in other unconventional superconductors, a partial knowledge of the structure of the energy gap in this material does not seem to be sufficient even to discern the parity—whether it is singlet or triplet—of the pairing state, based on the theoretical scenarios suggested so far for the noncentrosymmetric $CePt_3Si$ [2,3,5].

An additional constraint, apart from the lack of an inversion center and the paramagnetic limiting, on the possible symmetry of the pairing state is the existence of a second superconducting transition. The appearance of two superconducting phase transitions is normally a consequence of the breakdown of the crystal point group or time-reversal symmetry. To date there is no experimental evidence for broken time-reversal symmetry in $CePt_3Si$, leading to a lowering of the point group symmetry as the origin of the second transition. The splitting of the superconducting transition will then discard a "pure" state, like a d-wave state, as the pairing symmetry.

Considering the transition splitting, an analysis of superconductivity in $CePt_3Si$ can be performed within a model based on a *single* primary order parameter belonging to a two-dimensional irreducible representation of the group symmetry of the normal state [15]. The order parameter in this model is a two-component vector $\Delta(\mathbf{k}) = \eta_1\phi_1(\mathbf{k}) + \eta_2\phi_2(\mathbf{k})$ coupled to a symmetry breaking field. Such a model has been applied to UPt_3 [16]. As an example of a possible candidate for the pairing state of $CePt_3Si$, let us take $E_g(1, 1)$, which is one of the three states of the spin-singlet two-dimensional E_g representation [5]. The orbital order parameter would have the form $\Delta(\mathbf{k}) = \eta_1 k_z k_x + \eta_2 k_z k_y$. In the high temperature phase (HTP), $(\eta_1, \eta_2) = (1, 0)$ or $(0, 1)$, and in the low-temperature phase (LTP), $\eta = (1, 1)$. In other words, the gap symmetry would be $k_z k_x$ (or $k_z k_y$) for the HTP and $k_z(k_x + k_y)$ for the LTP. Both pairing states have equatorial line nodes as well as point nodes. In this example, $\Delta\lambda(T) \propto T$, which corre-

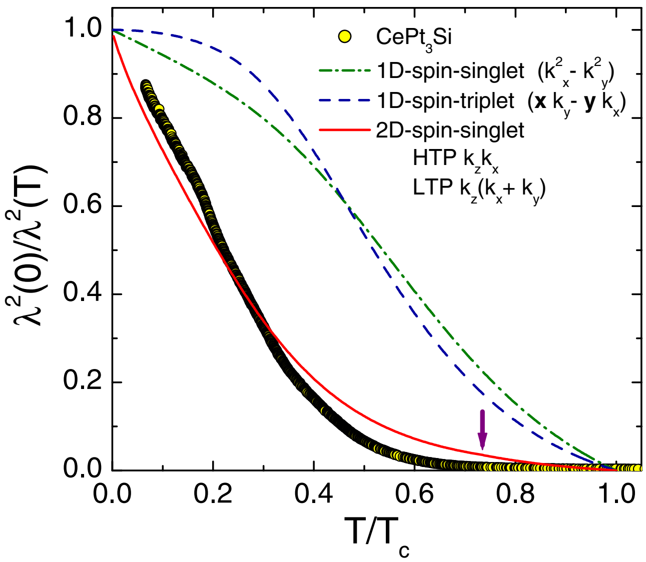

FIG. 3 (color online). (a) Results of the numerical evaluations of the models discussed in the text and $[\lambda(0)/\lambda(T)]^2$ for the polycrystalline $CePt_3Si$ sample. The arrow indicates the point where the T behavior of the superfluid density should have a crossover from the HTP to LTP.

sponds to the low T behavior of $\lambda(T)$ in the low-temperature phase, would be a consequence of the pairing symmetry $k_z(k_x + k_y)$.

In order to gain further insight into the symmetry problem, we carried out some numerical evaluations and compared them to the experimental data. They were performed using the superfluid density expression for a superconductor

$$\frac{\lambda^2(0)}{\lambda^2(T)} = \left[1 + 2\left\langle \int_0^\infty d\epsilon \frac{\partial f}{\partial E_k} \right\rangle\right]. \qquad (1)$$

Here $\langle \cdots \rangle$ represents an angular average over the Fermi surface and f is the Fermi function. The total energy $E(k) = \sqrt{\epsilon^2 + |\Delta(T,k)|^2}$, where ϵ is the single-particle energy measured from the Fermi surface and k the wave vector. We assumed a spherical Fermi surface and used the standard gap interpolation formula of $\Delta(T)$ for a polar state with $\Delta C/C_n = 0.25$, as obtained in Ref. [1]. The results are presented in Fig. 3 where numerical data for the spin-singlet, d-wave type, $k_x^2 - k_y^2$, the spin-triplet, p-wave type, $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_y - \hat{\mathbf{y}}k_x$, and the spin-singlet two-dimensional $E_g(1,1)$ state are compared to the experimental data. The arrow in the plot indicates the point where the second transition should take place, and where an inflection point or kink must occur signaling the crossover from the HTP to LTP pairing states. The kink is hardly visible in the numerical data, in part because we took the reasonable guess that the gaps are of equal magnitudes. The inflection point observed in $\Delta\lambda(T)$ in Fig. 1 is not resolved in the superfluid density data of Fig. 3. A clear disagreement is seen in Fig. 3 between the experimental data and the one-dimensional (d- or p-wave) gap models. The data qualitatively follow the two-dimensional $k_z(k_x + k_y)$ model which inherently allows a second superconducting transition.

Even though the parity and symmetry of the gap function is not clear to date, we emphasize that $\Delta\lambda(T) \sim T$ will definitely reflect the symmetry of the low-temperature phase of $CePt_3Si$, independently of whether $\Delta\lambda(T)$ shows any indication of the second superconducting transition just below the first one.

In summary, we reported on magnetic penetration depth measurements on $CePt_3Si$ samples. Regardless of the pairing state multiplicity, the data require the existence of line nodes in the superconducting gap structure.

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[1] E. Bauer, G. Hilscher, H. Michor, C. Paul, E. W. Scheidt, A. Gribanov, Y. Seropegin, H. Noël, M. Sigrist, and P. Rogl, Phys. Rev. Lett. **92**, 027003 (2004).
[2] P. A. Frigeri, D. F. Agterberg, A. Koga, and M. Sigrist, Phys. Rev. Lett. **92**, 097001 (2004).
[3] K. V. Samokhin, E. S. Zijlstra, and S. K. Bose, Phys. Rev. B **69**, 094514 (2004).
[4] P. W. Anderson, Phys. Rev. B **30**, 4000 (1984).
[5] I. A. Sergienko and S. H. Curnoe, Phys. Rev. B **70**, 214510 (2004).
[6] E. W. Scheidt *et al.* (to be published).
[7] G. R. Stewart *et al.*, Two Superconducting Transitions in Heavy Fermion $CePt_3Si$, APS March Meeting, Los Angeles, CA, 2005, Abstract No. B39.00003 (unpublished).
[8] R. B. Goldfarb, M. Lelental, and C. A. Thompson, in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, edited by R. A. Hein (Plenum, New York, 1991), p. 49.
[9] T. Xiang, C. Panagopoulos, and J. R. Cooper, Int. J. Mod. Phys. B **12**, 1007 (1998).
[10] R. Prozorov, A. Snezhko, T. He, and R. J. Cava, Phys. Rev. B **68**, 180502(R) (2003).
[11] F. Manzano, A. Carrington, N. E. Hussey, S. Lee, A. Yamamoto, and S. Tajima, Phys. Rev. Lett. **88**, 047002 (2002).
[12] P. J. C. Signore, B. Andraka, M. W. Meisel, S. E. Brown, Z. Fisk, A. L. Giorgi, J. L. Smith, F. Gross-Alltag, E. A. Schuberth, and A. A. Menovsky, Phys. Rev. B **52**, 4446 (1995).
[13] W. H. Li, C. C. Yang, F. C. Tsao, and K. C. Lee, Phys. Rev. B **68**, 184507 (2003).
[14] M. Yogi, Y. Kitaoka, S. Hashimoto, T. Yasuda, R. Settai, T. D. Matsuda, Y. Haga, Y. Ōnuki, P. Rogl, and E. Bauer, Phys. Rev. Lett. **93**, 027003 (2004).
[15] V. P. Mineev and K. V. Samokhin, *Introduction to Unconventional Superconductivity* (Gordon and Breach, New York, 1999).
[16] J. A. Sauls, Adv. Phys. **43**, 113 (1994).