Pairing symmetry in two distinct superconducting states of $CeCu_2Si_2$

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We report that the two distinct superconducting phases of $CeCu_2Si_2$ with a slightly different T_c revealed an opposite pressure dependence of T_c and quite a different normal state at low temperatures; a strongly T-dependent C_p/T peaking around 0.6 K for the high-T_c phase as contrasted with a very weak T dependence for the other. The superconducting C_p, however, exhibited a quadratic T dependence above 0.2 K and below $\sim$0.1 K in both phases. We herein speculate that these two superconducting states might be due to a different pairing mechanism or symmetry.

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Ever since the discovery of the first heavy-electron superconductor $CeCu_2Si_2$,[1] various types of superconducting f-electron systems like UPt_3, UBe_{13},[2] UPd_2Al_3,[3] and $CeCoIn_5$ (Ref. 4) have become known. It has been furthermore disclosed that antiferromagnets like $CePd_2Si_2$ (Ref. 5) and even a ferromagnet like UGe_2 (Ref. 6) exhibit superconductivity under pressure at fairly low temperatures. These experimental findings have naturally generated a great deal of theoretical interest and investigations concerning superconducting pairing mechanism in such f-electron systems subjected to a supposedly strong Coulomb repulsion.[7,8] Although any successful interpretation has unfortunately not been put forward for most of them due to both experimental and theoretical difficulties, UPt_3 has recently been claimed as an odd-parity superconductor from a Knight shift study.[9]

$CeCu_2Si_2$ is not an exception either and the true nature of the earliest heavy-electron superconductor has not been clarified yet despite of enormous efforts, particularly made by Steglich's group since the discovery.[10] There still remain many unsolved problems about this compound. In order to clarify how the superconducting phase emerges by changing the composition we have reinvestigated the compound by preparing homogeneous polycrystalline samples at many different compositions, and recently reported that there exist two distinct superconducting states with only a slightly different T_c (0.6 and 0.7 K) located side by side in the homogeneity range.[11,12] A more careful reanalysis of their low-temperature data has strongly implied that these two superconducting states may belong to different symmetries of a superconducting pairing state which are derived from a quite dissimilar normal state. The normal states have been revealed upon destroying the superconductivity by sufficiently strong magnetic fields of about 2.5 T. The low-T_c phase with a slightly excess copper demonstrated an almost temperature-independent $C_p/T(\equiv\gamma)$, while the high-T_c phase closer to the stoichiometric composition demonstrated a strongly T-dependent γ peaking around 0.55 K. It is interesting to note here that each of these superconducting states seems to keep its identity without merging in spite of the small difference in the condensation energy or T_c and the intimate proximity of the composition (only at most 0.25 at. % apart). This fact may be due to a microscopic origin like an abrupt change of the Fermi surface. It is a very rare case in which two different superconducting phases appear side by side in the supposedly uniform homogeneity field of the identical crystal structure of a tetragonal $ThCr_2Si_2$ type. It must be further noted that the high-T_c superconducting phase is derived from a normal state located in a region of antiferromagnetic instability, where the weak magnetism in the copper-poor region fades away on moving into the copper-rich region. A superconductivity similar to the one recently discovered under pressure in the vicinity of the antiferromagnetic quantum critical point[5] (QCP) might be realized at the normal pressure in the present compound $CeCu_2Si_2$. Based on these observations we herein argue that a spin-fluctuation-mediated d-wave state may be realized in these phases or at least in the high-T_c phase, as theoretically predicted near an antiferromagnetic instability.[8]

In this paper, we present detailed experimental results pertinent to these superconducting phases by referring to only a few samples of each group as listed in Table I. More results on the other polycrystalline samples in the rest of the homogeneity field of $CeCu_2Si_2$ will be published elsewhere.[13]

Polycrystalline samples prepared by levitation melting were employed in the present study and the details of preparation will be given elsewhere. We merely remark here that the superconducting samples located very close each other in the homogeneity field have almost identical lattice parameters, $a=4.096\pm0.003$ Å and $c=9.911\pm0.006$ Å,[12] being thereby crystallographically undistinguishable within the present experimental precision, as can be seen in Table I. It should also be noted that the nominal compositions of samples used in this study fall within 0.5 at. % from the stoichiometry and that the boundary of the two groups runs approximately along the 39.6 Si at. % line (see Figs. 1 in Refs. 11 and 12). The specific heat was measured by a quasiadiabatic heat pulse method in a ^{3}He cryostat and a dilution refrigerator for the range of 0.15 and 25 K, the magnetic susceptibility between 2 and 400 K in 3 kOe with a commercial superconducting quantum interference device magnetometer and the electrical resistivity between 0.03 and 300 K with a dc four terminal method.

We first display in Fig. 1 the thermal variation of the electrical resistivity for several samples of the two groups. Although the absolute values are not very reliable because of residual microcracks inherent in these annealed polycrystalline samples, we notice the following differences in the variation of the $\rho(T)$ for the two groups: (1) The temperature

TABLE I. Polycrystalline samples employed in this study.

	Sample number	Composition (at. %)[a]			Lattice parameters (Å)		T_c (K)[b]		$\Delta C_p/\gamma T_c$@T_c
		Ce :	Cu :	Si	a	c	from ρ	from C_p	
High-T_c group	#41	20	40	40	4.0973	9.9118	0.65	~0.65[c]	~0.31[c]
	#38	20	40.375	39.625	4.0948	9.9035	0.68	0.66	0.83
	#52	20.25	39.875	39.875	4.0985	9.9177	0.71	0.67	0.74
	#57	20.25	40	39.75	4.0934	9.9158	0.73	0.67	0.89
Low-T_c group	#50	20.25	40.25	39.5	4.0973	9.9053	0.61	0.59	1.27
	#54	20.208	40.416	39.375	4.0987	9.9040	0.64	0.59	1.35
	#70	20.125	40.5	39.375	4.0998	9.9140	0.63	0.58	1.16

[a]Compositions are nominal values.
[b]Each determined as a midpoint of resistive or specific-heat transition.
[c]No sharp anomaly in C_p/T was found at T_c for the stoichiometric sample.

corresponding to the low-temperature local maximum diminishes from about 25 K for the high-T_c group (#41, 52, and 57) to somewhat below 20 K for the low-T_c group (#50, 54, and 70). (2) This local maximum is a little bit larger for the low-T_c group. (3) The high-temperature local maximum around 100 K, which is believed to be due to the crystalline electric field (CEF) splitting is negligible for the low-T_c group. These facts may implicate some important physical significance somehow related to the Kondo effect in the present system.[10] If the local maximum around 20 K scales with the Kondo temperature T_k, T_k for the low-T_c group must be lower than that for the other.

The typical residual resistivity ρ_0 for each group was found to be $\leqslant 20\ \mu\Omega$ cm for the high-T_c samples and $\sim 100\ \mu\Omega$ cm for the low-T_c samples. This trend is consistent with the reported one.[10] Although all these samples contained microcracks and the absolute values may not very rigorously be compared,[11] the high-T_c samples have a much smaller ρ_0 than the low-T_c samples, in contrary to the reported positive correlation between T_c and ρ_0.[14] The large ρ_0 of the low-T_c samples may be due to the lower T_k, as hinted above. The normal-state resistivity $\rho(T)$ data below about 4 K were fitted with either ρ_0+AT^2 or $\rho_0+\alpha T$ and found that the former is more appropriate for the temperature range of 0.04 and ~ 2 K, though the linear T dependence is found at intermediate temperatures between 0.7 and ~ 2.5 K for the low-T_c group and between ~ 1.5 and ~ 3.5 K for the high-T_c group. A fractional power between 1 and 2 is thereby found in a very narrow range around 1.5 K, which is often referred to as evidence of the non-Fermi-liquid regime in the literature. We are not sure whether such an argument is very meaningful or not and we simply remark here that the samples we studied are rather Fermi-liquid-like in this sense. More details of this account will be reported elsewhere.[13]

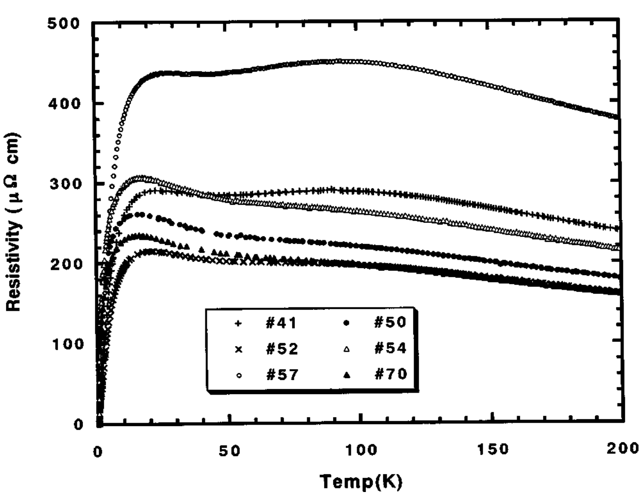

FIG. 1. Electrical resistivity of high-T_c (#41, 52, and 57) and low-T_c group (#50, 54, and 70). Note the slightly larger hump below 20 K for the latter, while the broad one around 100 K is larger for the former.

The inverse magnetic susceptibility was fairly well fitted above about 150 K with a Curie-Weiss law. We found the effective moment in the range of $2.58\pm0.02\ \mu_B$/Ce ion and the Weiss temperature in the range of 105 ± 12 K. The obtained effective moment well corresponds to the theoretical value for a trivalent Ce ion assuring that the Ce ions in these samples are paramagnetic at high temperatures. The susceptibility exceeds the extrapolated values from the Curie-Weiss law at lower temperatures, the low-T_c group slightly more than the high-T_c group.

The specific heat of several superconducting samples is plotted as $C_p/T(=\gamma)$ versus T in Fig. 2, where the characteristic features of the two groups clearly manifest themselves. We note here that any corrections have not been made for all the C_p data presented in this paper. The peaks for the high-T_c group are slightly rounded and broader and the jumps at T_c, ΔC_p are smaller, compared with those for the low-T_c group. The parameter $\Delta C_p/\gamma T_c$ then amounts to 1.35 at $T_c^{C_p}=0.59$ K for #54 and 0.89 at $T_c^{C_p}=0.67$ K for #57 (see Table I for the rest). It is very important to remember here that all the C_p/T curves for the superconducting phase appear to extrapolate themselves toward 0 K, guaranteeing thereby that these samples of both groups are clean and fully superconducting. It is further noted that the specific heat of both groups follows a quadratic power law T^2 above about 0.2 K and below about 0.1 K, as shown in the inset. The quadratic T-dependence may indicate line nodes of zeros in

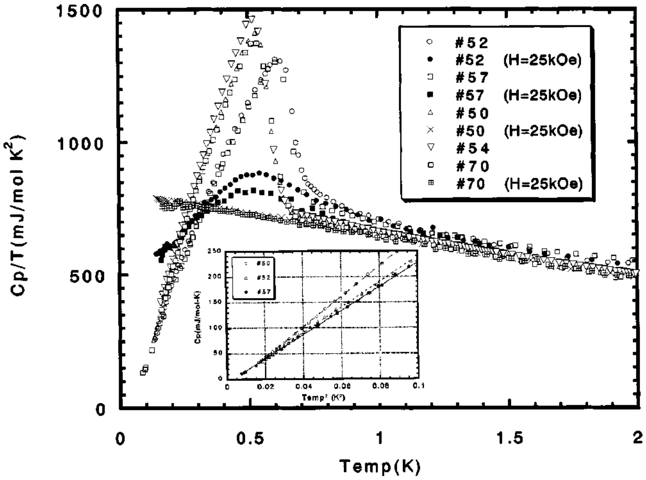

FIG. 2. C_p/T vs T in $H=0$ and 25 kOe for several samples of two superconducting groups. The inset displays C_p vs T in a log-log plot for high-T_c (#38, 52, and 57) and low-T_c (#50 and 54) groups.

the energy gap and an even-parity state if spin-orbit interaction is present, for both superconducting states.[15]

We further note here about Fig. 2 that the normal state revealed by applying 25 kOe exhibits quite a different T-dependent γ below about 1 K, as shown for the high-T_c (#52 and 57) and low-T_c (#50 and 70) groups. As the concentration of copper, x, is increased from about 38 at. % in the field of homogeneity, a peak in C_p/T appears around 0.55 K beyond $x=39$ at. % as reported earlier[11] and it seems to converge to that of the high-T_c #57, which is the nearest sample only 0.25 at. % apart from the low-T_c #50. This broad peak of γ for the former around 0.55 K is much reminiscent of a magnetic short-range order, but whatever magnetic state it could be, the present superconducting C_p/T curves for #52 and #57 vanishing towards 0 K assert that the strongly T-dependent normal state entirely condenses into a superconducting state. On the other hand, the present result suggests that the weakly T-dependent normal state γ of the low-T_c group may not be due to the loss of coherence, as previously assumed for a similar T dependence in diluted systems.[16] It could not, however, satisfactorily be fitted either with the paramagnon model[17] or the impurity Kondo model with $T_\mathrm{k}\sim 7$ K (Ref. 18) or the spin fluctuation model for the QCP limit of Moriya and Takimoto,[19] although each of these models in some degree simulates the experimental C_p/T curve.

It would not be unreasonable at all to expect that the superconducting states developed from these two dissimilar normal states may utterly differ in nature despite the minute difference in composition and T_c, and might even belong to a different pairing symmetry.[20] We have seen the clearly different specific heat anomaly at T_c in Fig. 2. Further evidence of the fact that these two superconducting phases really differ in nature has recently been obtained from a high-pressure experiment in which an opposite sign of dT_c/dp has been found, as displayed in Fig. 3.[21] We merely note here that the pressure dependence of the high-T_c, #38 sample seems to be consistent with that reported before.[14]

It is interesting to note that a Monte Carlo simulation on

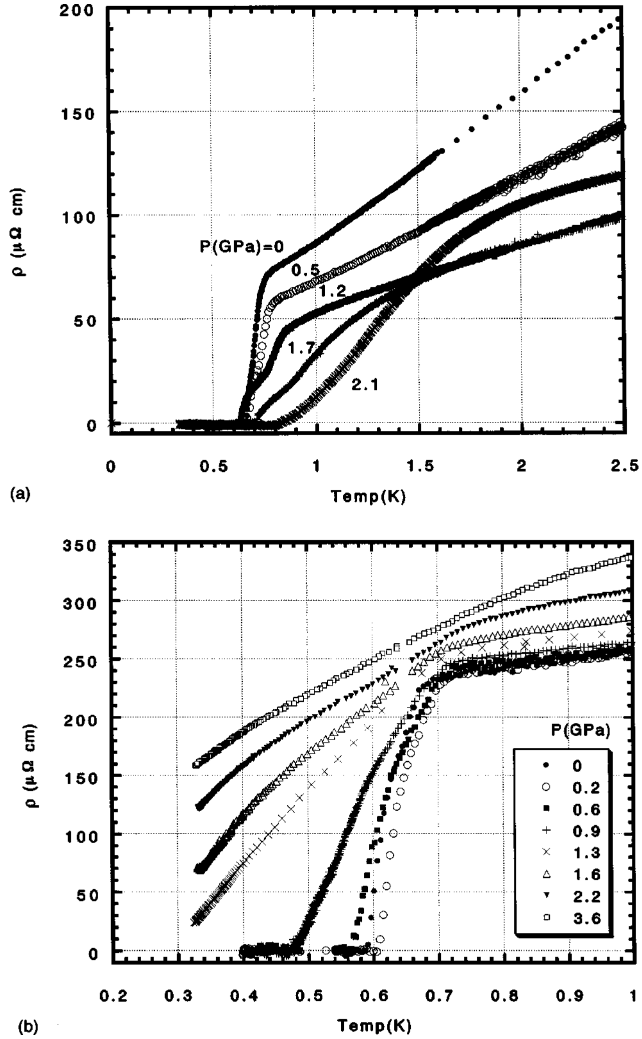

FIG. 3. The variation of T_c as a function of P for #38 (high-T_c) (a) and #50 (low-T_c) (b), showing the opposite sign of pressure effect.

the Hubbard model has revealed that an effective nearest neighbor attraction in the limit of large on-site electron-electron repulsion leads to enhancement of singlet d-wave pairing correlations.[8] By taking account of the fact that the high-T_c superconductivity of the present system emerges near the antiferromagnetic instability, we argue that such an even-parity pairing may be realized in the high-T_c group. It also seems to be consistent with the quadratic T dependence of the specific heat of the superconducting state, if the spin-orbit effect is important, as noted above (see the inset of Fig. 2).[15]

In Fig. 4 the magnetic-field dependence of $\rho(T)$ is shown for #52 of the high-T_c group and #54 of low-T_c group, from which upper critical field curves, $H_{c2}(T)$ were deduced by defining the mid-point as a superconducting transition in each field. It is evident that the resistive behaviors in magnetic fields at low temperatures below about $T_c/3$ are quite contrasting for the two groups, as already noted before.[11] This difference may suggest that superconducting parts in the sample retreat quite differently in external magnetic fields with T. The increasing resistance with decreasing T in #54

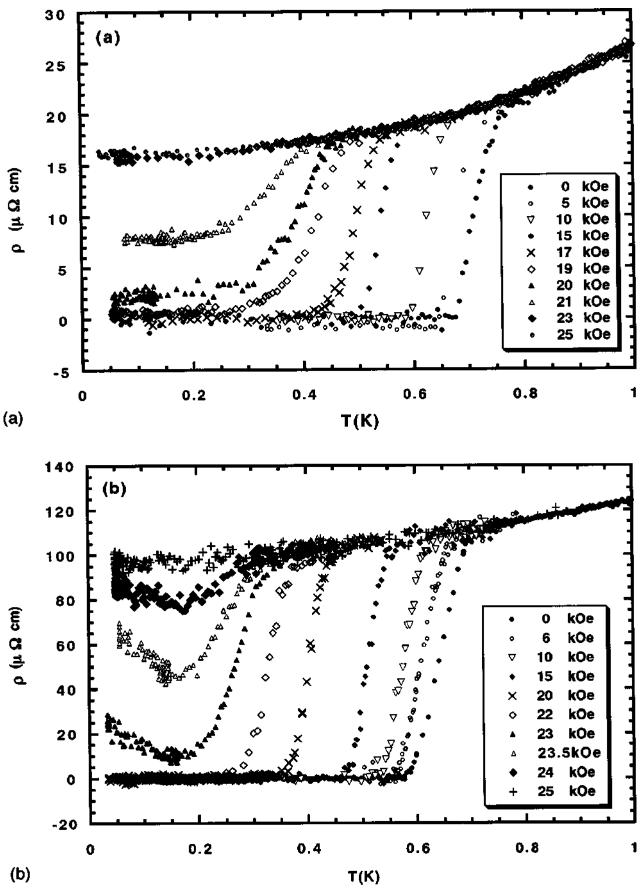

FIG. 4. Resistive superconducting transition of #52 (high-T_c) (a) and #54 (low-T_c) (b) in several external magnetic fields. Note the different behavior at lowest temperatures.

indicates rapidly subsiding superconducting parts with decreasing T, implying a re-entrant behavior.[22] On the other hand, the destruction of superconductivity rapidly proceeds with the field but not with T for #52. Accordingly we found a very similar $H_{c2}(T)$ curve for #52 and #54, except for the re-entrant curve exhibited by #54.[12] It is very important to further investigate whether this different behavior in external magnetic fields may reflect the difference in the pairing symmetry or not. In fact, structures of vortex lattice in superconductors with an unconventional symmetry have intensively been studied by theorists.[15]

It is finally remarked that no evidence of multiple phase transitions was found in any properties in the external magnetic field investigated in the present study. We thereby think the possibility of multicomponent order parameter for the case of $CeCu_2Si_2$ unlikely, contrasting with the case of UPt_3 or $U_{1-x}Th_xBe_{13}$.[15]

In summary we have confirmed that the fundamentally antiferromagnetic non-superconducting state evolves into the high-T_c and then another low-T_c superconducting state with the increasing copper concentration in the homogeneity field of $CeCu_2Si_2$. This general trend is consistent with the one previously reported by Steglich's group.[10] In the present study we have further characterized two superconducting phases with slightly different T_c's situated side by side (only at most 0.25 at. % apart) in the homogeneity field. They exhibit quite different normal states and opposite signs of the pressure dependence dT_c/dp, although the specific heat in the superconducting state follows a quadratic T dependence rather than a cubic one for both phases. We speculate from these facts whether the two superconducting states belong to different pairing symmetries of even parities, and probably belong to the high-T_c phase as d-wave states which appear near the region of an antiferromagnetic instability. It is a little puzzling that the low-T_c phase, possessing a much larger ρ_0, exhibits a sharper and larger anomaly of C_p, i.e. a more ideal bulk superconducting transition at T_c than the high-T_c phase. Disorder apparently benefits the superconductivity rather than degrades it. It is also the low-T_c phase that exhibits a re-entrant behavior in external magnetic fields. These facts may suggest the possibility of an interesting superconductivity in this phase. In any case, it is very amazing that such two different superconducting states emerge in a supposedly uniform and crystallographically undistinguishable homogeneity field. We merely propose here that a magnetic interaction, whatever it could be, may play a decisive role in determining the pairing mechanism or symmetry. It may result, for instance, from a change of the Fermi surface and/or the CEF effect with the copper concentration, which are known by now to strongly influence the f-electron states.[15] In fact, we have already remarked in the discussion of the $\rho(T)$ curves some features indicating a noticeable difference in the Kondo effect and the CEF effect for the two superconducting phases.[20] The present case would without doubt provide us with a good opportunity for our better understanding of the superconductivity in heavy f-electron systems.

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[1] F. Steglich, J. Aarts, C.D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[2] G.R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[3] C. Geibel, A. Böhm, R. Caspary, K. Gloos, A. Grauel, P. Hellmann, R. Modler, C. Schank, G. Weber, and F. Steglich, Physica B **186–188**, 188 (1993).

[4] C. Petrovic, P.G. Pagliuso, M.F. Hundley, R. Movshovich, J.L. Sarrao, J.D. Thompson, Z. Fisk, and P. Monthoux, J. Phys.: Condens. Matter **13**, L337 (2001).

[5] F.M. Grosche, S.R. Julian, N.D. Mathur, and G.G. Lonzarich, Physica B **223&224**, 50 (1996).

[6] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braith-

waite, and J. Flouquet, Nature (London) **406**, 587 (2000).

[7] R.M. Martin and J.W. Allen, J. Magn. Magn. Mater. **31–34**, 473 (1983); H. Razafimandimby, P. Fulde, and J. Keller, Z. Phys. B: Condens. Matter **54**, 111 (1984).

[8] J.E. Hirsch, Phys. Rev. Lett. **54**, 1317 (1985); D.J. Scalapino, E. Loh, and J.E. Hirsch, Phys. Rev. B **34**, 8190 (1986); S. Schmitt-Rink, K. Miyake, and C.M. Varma, Phys. Rev. Lett. **57**, 2575 (1986); K. Miyake, S. Schmitt-Rink, and C.M. Varma, Phys. Rev. B **34**, 6554 (1986).

[9] H. Tou, Y. Kitaoka, K. Asayama, N. Kimura, Y. Onuki, E. Yamamoto, and K. Maezawa, Phys. Rev. Lett. **77**, 1374 (1996).

[10] See for example, F. Steglich, P. Gegenwart, C. Geibel, P. Hinze, M. Lang, C. Langhammer, G. Sparn, T. Tayama, O. Trovarelli, N. Sato, T. Dahm, and G. Varelogiannis, in *More is Different*, edited by N. Phuan Ong and R.N. Bhatt (Princeton University Press, Princeton, 2001), p. 191.

[11] M. Ishikawa, N. Takeda, P. Ahmet, Y. Karaki, and H. Ishimoto, J. Phys.: Condens. Matter **13**, L25 (2001).

[12] M. Ishikawa, N. Takeda, P. Ahmet, Y. Karaki, H. Ishimoto, D. Huo, and J. Sakurai, J. Phys. Chem. Solids **63**, 1165 (2002).

[13] M. Ishikawa and N. Takeda (unpublished).

[14] D. Jaccard, H. Wilhelm, K. Alami-Yadri, and E. Vargoz, Physica B **259–261**, 1 (1999).

[15] See a review, M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991), and references therein.

[16] N. Grewe and F. Steglich, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier Science BV, Amsterdam, 1991), Vol. 14, Chap. 5, p. 364, and references therein.

[17] S. Doniach and S. Engelsberg, Phys. Rev. Lett. **17**, 750 (1966); N.F. Berk and J.R. Schrieffer, *ibid.* **17**, 433 (1966).

[18] V.T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[19] T. Moriya and T. Takimoto, J. Phys. Soc. Jpn. **64**, 960 (1995).

[20] If the local maximum in the $\rho(T)$ around 20 K as shown in Fig. 1 is interpreted as a Kondo peak, the Kondo temperature must be slightly higher for the high-T_c group. Although this is not inconsistent with the slightly higher T_c of the group, it appears to be very unlikely that such a difference in T_{k} explains that of T_c.

[21] M. Koeda, M. Hedo, Y. Uwatoko, N. Takeda, and M. Ishikawa (unpublished).

[22] W. Assmus, M. Herrmann, U. Rauchschwalbe, S. Riegel, W. Lieke, H. Spille, S. Horn, G. Weber, F. Steglich, and G. Cordier, Phys. Rev. Lett. **52**, 469 (1984).