Competitive Coexistence of Superconductivity with Antiferromagnetism in CeRhIn$_5$

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We carried out ac magnetic susceptibility measurements under pressures P on the heavy fermion antiferromagnet CeRhIn$_5$. We report bulk superconductivity (SC) at ambient pressure with a transition temperature $T_c \simeq 90$ mK. The degraded SC in a powdered or polished sample was restored by annealing, showing that the SC state is sensitive to inhomogeneity. In a coexistence region of the SC with antiferromagnetism (AF), we find that $T_c(P)^n T_N(P)^{1-n} = \text{const}$ where T_N indicates a Néel temperature and n denotes a ratio of electronic specific heat coefficients below and above T_N, indicating the competition of the SC and the AF for states at the Fermi surface.

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The interplay between magnetism and superconductivity has been an interesting topic in solid-state physics. The ground states of these long-range ordered states should be antagonistic because of the competitive nature between superconducting screening and internal fields generated by magnetic orderings. However, when magnetism and superconductivity are, respectively, carried by deeply seated $4f$ electrons and by outermost electrons such as s, p, and d electrons, like RRh$_4$B$_4$ where R denotes rare earth elements, antiferromagnetism (AF) readily coexists with type II superconductivity (SC) [1]. In contrast to these materials, some Ce-based heavy fermion compounds exhibit an unusual coexistence of AF and SC at ambient pressure or high pressures [2,3], in which both AF and SC are believed to arise from $4f$ electrons. A magnetic mediation of the pairing mechanism has been argued for these novel compounds [2]; however, there are still many unsolved questions in this unique group of materials to be further clarified.

Recent discovery of the pressure-induced superconductor CeRhIn$_5$ provides a good opportunity to study the correlation between AF and SC: At ambient pressure, CeRhIn$_5$ orders antiferromagnetically with a staggered magnetic moment $0.8\mu_B$/Ce below a Néel temperature $T_N = 3.8$ K [4,5]. As the pressure increases, T_N slightly increases and passes through a maximum at around $P \sim$ 7–8 kbar, and then it is considered to be sharply depressed to zero in the vicinity of a characteristic pressure $P_c \sim$ 18.5 kbar [6]. At pressures above P_c, a purely SC state appears with a high SC transition temperature $T_c \simeq 2.2$ K. Nuclear quadrupole resonance experiments under pressure suggested the microscopic coexistence of AF and SC in a range of 16.3–17.5 kbar as well as the gapless nature of the SC in a low-lying excitation spectrum [7], which may be explained by odd-frequency superconductivity [8]. Measurements of specific heat indicated the spin-density-wave nature of antiferromagnetism, which opens a gap over part of Fermi surfaces [9]. A de Haas–van Alphen (dHvA) experiment indicated that $4f$ electrons in CeRhIn$_5$ are well localized at ambient pressure and fully delocalized above 24 kbar [10].

To date, a number of different temperature (T) vs pressure (P) phase diagrams have been sketched for CeRhIn$_5$ based on different measurements [6,11,12]. It is commonly accepted that the SC appears only under pressure. This implies that the coexistence of AF and SC in the narrow pressure range between $\sim$16 kbar and P_c could be due to extrinsic origins, such as the pressure inhomogeneity, because the SC state above P_c can be mixed into the AF state due to the pressure gradient within a sample, as is often observed in a high pressure experiment. Very recently specific heat measurements did detect a tiny anomaly of the SC transition below P_c [13,14], but the calorimetry measurements were only made at $T \geq 0.35$ K. In fact, it seems very difficult to detect any anomaly at much lower temperatures due to the large contribution from a nuclear Schottky anomaly. Hence, the existence of the bulk SC in a lower T-P region is not yet clear. Furthermore, there remains a fundamental problem of how the unconventional SC correlates with the AF order; whether the long-range AF order enhances the SC or destroys it.

To resolve these problems in this unique system, we attempted to grow a high quality single crystal of CeRhIn$_5$ and make a more systematic measurement. Here we report experimental results of ac magnetic susceptibility $\chi(T)$. According to these measurements, we have constructed a new T-P phase diagram. One of our new findings is the observation of SC at ambient pressure with $T_c \simeq 90$ mK that continues smoothly to the high pressure SC state. This shows that the coexistence of SC and AF is intrinsic but not caused by the pressure inhomogeneity, because there is no pressure gradient at all at ambient pressure. In our new T-P phase diagram, T_c rises steeply above 10–11 kbar whereas the Néel temperature shows a steep decrease in nearly the same pressure region, which may lead us to speculate the competitive nature of the coexistence. Interestingly, these ordering temperatures were found to correlate with each another via the relationship ${T_c}^n {T_N}^{1-n} = T_{c0}$ with P ($<P_c$) as an implicit parameter, where T_{c0} is a (hypothetical) SC transition temperature in the absence of the AF order and $n \equiv \gamma_0/\gamma_n$, with γ_0 and γ_n denoting an electronic specific heat coefficient in the

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AF and paramagnetic state, respectively. This finding gives a strongly supporting evidence for the competition of SC and AF for states at the Fermi surface, as theoretically discussed by Bilbro and McMillan for the competition of SC and charge density waves [15]. We believe that these results provide important information for establishing a theory to understand the SC in this heavy fermion compound and its interrelation with the magnetic order.

Single crystals of $\mathrm{CeRhIn_5}$ were grown from an In flux [6]. No traces of secondary phase were detected from the powder x-ray diffraction. The high quality of the samples is confirmed by a sharp SC transition shown below. The ac magnetic susceptibility was measured by a Hartshorn bridge method in a modulation field of 0.1 Oe and ~100 Hz in the temperature range of 0.06–1.2 K using a ^{3}He-^{4}He dilution refrigerator up to pressures of about 12 kbar, and in the temperature range of 0.35–8 K using a ^{3}He cryostat up to about 24 kbar. The demagnetization field effect was not corrected throughout this investigation. The pressure was generated by a clamped pressure cell, with Daphne oil 7373 as the pressure transmitting medium. The pressure value was calibrated with Pb manometers. In all measurements, the pressure gradient was estimated to be less than 0.2 kbar.

Figure 1 shows the typical T dependence of the real part of ac magnetic susceptibility $\chi'(T)$ under selected pressures. In all measurements, the superconducting transition temperature T_c was defined by a temperature at which the sample was observed to reach 90% of the full shielding effect in the $\chi'(T)$ curve. At ambient pressure we clearly observe the appearance of SC diamagnetism below $T_c \simeq 90$ mK. When the pressure is raised up to 17.1 kbar, T_c increases monotonically and the diamagnetic signal becomes broader. (One may notice that an additional structure occurs at high pressures above ~10 kbar, a two-step-like feature in $\chi'(T)$ and a double peak structure in $\chi''(T)$ (not shown here). It is tentatively attributed to the inhomogeneity of the pressure distribution; however, the possibility of a second phase transition, like that observed in $\mathrm{(U, Th)Be_{13}}$ [16], could not be excluded: we need a further investigation. Interestingly, in the vicinity of P_c (~18.5 kbar), the transition begins to sharpen abruptly; the transition width ΔT_c was estimated to be about 100 mK. Further increase of the pressure results in a small increase of T_c with a rate of $dT_c/dP \sim 0.04$ K/kbar, consistent with a previously reported value [11,17]. Note that the transition width becomes very sharp, $\Delta T_c \sim 10$ mK, at 23.5 kbar. The broadening effects in the intermediate P region were also observed from the previous pressure studies but the origin is not clear yet [11]. Here we note that this broadening effect appears to be prominent between ~10 kbar and P_c. Since the pressure dependence of T_c is large in this pressure region [see Fig. 2(a)], the broadening effect is probably ascribed to the pressure gradient in the sample, although it was estimated to be at most 0.2 kbar.

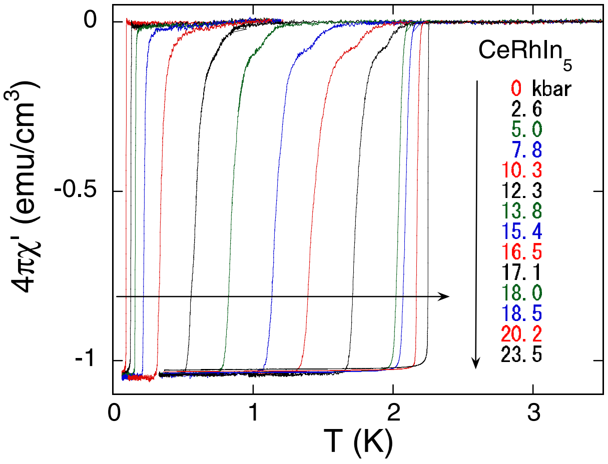

FIG. 1 (color online). Temperature dependence of the real part of ac magnetic susceptibility $\chi'(T)$ for $\mathrm{CeRhIn_5}$ (sample A) at selected pressures. Although the demagnetization effect is not corrected, it is understood that a P-independent saturation value of $-4\pi\chi'(T)$ below T_c corresponds to the full shielding effect, because the superconductivity above P_c (~18.5 kbar) is established to be of the bulk origin.

The results of ac magnetic susceptibility measurements on several samples studied here are summarized in Fig. 2(a), a T-P phase diagram. The SC transition temperature T_c was defined as mentioned above. The Néel temperature T_N was deduced from a $\chi''(T)$ curve as shown in Fig. 2(b), which exhibits an anomaly in its slope at T_N, with an error of ±50 mK. Note that this definition of T_N gives a value consistent with a previously reported one [4,11]. The most striking feature of the P dependence of T_c is that T_c starts to rise steeply at a pressure of about 10 kbar after a gradual increase. Note that in the same P region, T_N exhibits a steep decrease. We also notice that there seems to be a break in the slope of the $T_c(P)$ curve at around P_c. Tentatively we ascribe these observations to the interplay between the SC and the AF. This unique pressure dependence of T_c and T_N is quite different from that of other pressure-induced HF superconductors.

For a comparison, we plot T_c deduced from ac calorimetry measurements reported by Knebel *et al.* (denoted by open circles) [13] and Park *et al.* [14] (crosses); the difference between the two groups could be partially attributed to the quality of sample. It is worth noting that those specific heat results, especially the data by Park *et al.*, are in good agreement with our ac magnetic susceptibility result (at higher pressures).

Next we argue the competition between SC and AF. The specific heat measurement seems to indicate that the AF order produces a gap on the part of the Fermi surface [9]. This implies that there will be fewer remaining low energy degrees of freedom to participate in the formation of SC. The restoration of the missing region of the Fermi surface can be made by the application of pressure. As a consequence, the density of states available for SC at a Fermi energy E_F will be increased with P, which possibly results

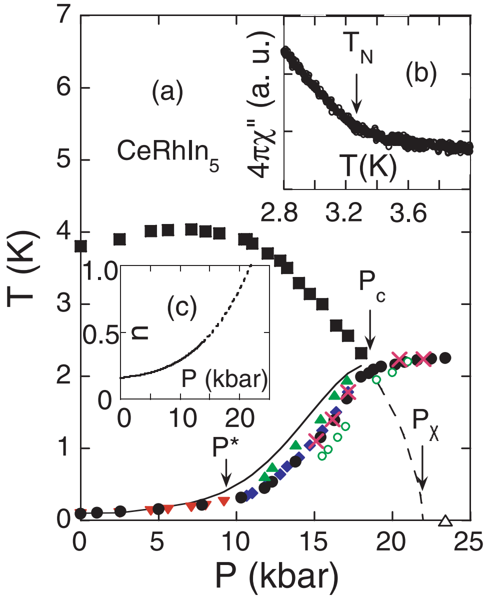

FIG. 2 (color online). (a) Temperature-pressure phase diagram of CeRhIn$_5$. Filled symbols are obtained from the present measurements for sample A (circles and triangles; triangles denoting the first SC transition in the intermediate P region), sample B (inverted triangles), and sample C (diamonds and squares). The solid line represents the superconducting transition temperatures calculated from the relation ${T_c}^n {T_N}^{1-n} = T_{c0}$; the broken line represents the speculated AF ordering temperatures (see text). An open triangle is deduced from dHvA experiments [10]. Open circles and crosses are taken from ac calorimetry measurements by Knebel *et al.* [13], and Park *et al.* [14], respectively. (b) Temperature dependence of the imaginary part of ac magnetic susceptibility $\chi''(T)$ at 14 kbar. The arrow indicates the AF transition temperature T_N. (c) Pressure dependence of the ratio n deduced from the specific heat measurements of Ref. [17]. The broken line indicates an extrapolation, corresponding to that of the γ coefficient estimated by Fisher *et al.* (see Fig. 6 in Ref. [17]). Here we assumed that n does not change drastically at P_c and $\gamma_n = 420$ mJ/mol K^2 [6] at all pressures.

in an enhancement of T_c. With this assumption of a partial gapping of the Fermi surface, we can evaluate $T_c(P)$ using the following relation that was put forward firstly by Bilbro and McMillan [15] and confirmed experimentally by Lacoe *et al.* [18],

$$ {T_c}^n {T_N}^{1-n} = T_{c0}. \tag{1}$$

At ambient pressure, γ_0 and γ_n are estimated to be 56 and 420 mJ/K^2 mol [6,17], respectively. This leads to $n \equiv \gamma_0/\gamma_n \simeq 0.13$, from which one may estimate that about 87% of the density of states at the Fermi energy was removed below T_N, in other words, the number of states participating in the SC transition is only 13%. The ratio n under pressure was obtained using specific heat data reported by Fisher *et al.* [17]: As shown in Fig. 2(c), n seems to reach unity at a pressure of about 22 kbar. This implies that the AF order may disappear at this pressure, so that T_{c0} was estimated from an observed T_c value at 22 kbar to be 2.2 K. Then, we evaluated T_c via Eq. (1) [see a solid line in Fig. 2(a)]. Consequently, we find the good agreement between the calculated and experimental results of T_c. This is a quantitative description of the competitive coexistence of SC and AF at the Fermi surface in CeRhIn$_5$

Let us examine more closely the $n(P)$ curve in Fig. 2(c). As mentioned above, the AF order may survive up to about 22 kbar, which is referred to as P_X hereafter. This leads us to draw a speculative $T_N(P)$ curve denoted by a broken line in Fig. 2(a), although we could not detect any anomaly corresponding to the AF order in the ac magnetic susceptibility measurements above P_c because the SC screens out a signal from the AF. On the other hand, the dHvA measurement shows the occurrence of the breakup of the Fermi surface at 23–24 kbar [see an open triangle symbol in Fig. 2(a)] [10]. From these results, we infer that the AF order does not disappear drastically at P_c, but T_N is depressed to zero temperature at P_X. (Note that P_X is close to a pressure at which T_c shows a maximum.) The proceeding neutron scattering experiment should be helpful for clarifying this point.

In the above, we have assumed that the SC is intrinsic because of the following features that are suggestive of the bulk SC: a very sharp drop in $\chi'(T)$ at T_c, a saturation value of $-4\pi\chi'(T)$ corresponding to the full shielding effect (see caption in Fig. 1), and the vanishing magnitude of the imaginary part $\chi''(T)$ below T_c (see below). Further, we consider that the aforementioned relationship between T_c and T_N is not fortuitous but rather indicative of the intrinsic SC. However, it is also true that such a large diamagnetic signal is not necessarily a conclusive evidence of the bulk SC. Actually, Zapf *et al.* first reported the SC transition at ambient pressure, but they did not give a conclusion of whether the SC is bulk or filamentary, because the diamagnetism disappeared in a powdered sample [19]. Unfortunately, however, the base temperature of their measurement was ~90 mK for the powdered sample, in contrast to ~60 mK for a bulk single crystal. Therefore, we attempted to make a close examination of a sample dependence and an annealing effect with the same experimental conditions for all samples.

Figure 3(a) shows the T dependence of the real and imaginary parts of the ac magnetic susceptibility of CeRhIn$_5$ (sample A) in three types of states at ambient pressure. The as-grown sample (denoted as single) shows a very sharp SC transition at about 90 mK. Then, the bulk single crystal was powdered, and the SC shielding effect of this sample (denoted as powdered) was observed to be obviously degraded. To eliminate any deformation induced during powdered procedure, we annealed the powdered sample at 800 °C for 100 h, and we found that the annealing results in the remarkable improvement of the SC; the transition became much sharper with the SC volume fraction of about 70% at 58 mK. This result can be interpreted as indicating the bulk nature of the ambient pressure SC in CeRhIn$_5$.

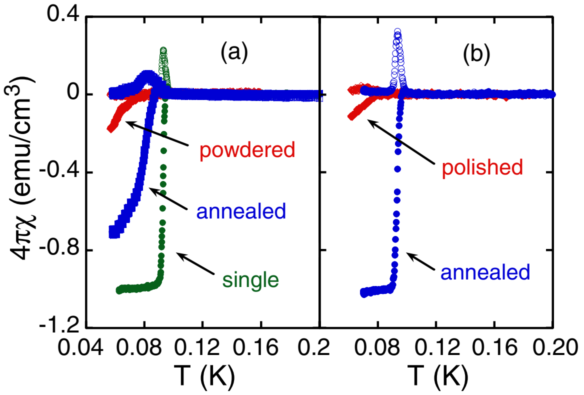

FIG. 3 (color online). (a) Temperature dependence of the ac magnetic susceptibility of CeRhIn$_5$ (sample A) at ambient pressure in the form of the bulk single crystal (circles), the powdered single crystal (diamonds), and the annealed powdered crystal (squares). Open (filled) symbols represent the imaginary (real) part. (b) Temperature dependence of the ac magnetic susceptibility of CeRhIn$_5$ (sample D) at ambient pressure for the polished sample (circles) and the annealed polished sample (diamonds). Open (filled) symbols represent the imaginary (real) part.

Furthermore, as shown in Fig. 2(a), it should be stressed that our T_c values coincide with those obtained from the specific heat experiment performed under pressure. This is a strong evidence that our ac susceptibility measurements observe the bulk SC, at least at higher pressures where the tiny anomaly was detected in the specific heat. (Note that an anomaly in the specific heat corresponding to the ambient pressure SC can be extremely small, because of the small value of $n \simeq 0.13$.)

Instead of the powdering, we polished a thin sample (with dimensions $2 \times 2 \times 0.1$ mm^3) using sandpaper, and we observed again the degraded SC [see a curve denoted as polished in Fig. 3(b)]. The polished sample was annealed at 750 °C for 100 h, and then the SC transition was found to become much sharper, $\Delta T_c \sim 5$ mK for $T_c \simeq 90$ mK. This result together with that in Fig. 3(a) indicates that the SC state at ambient pressure (and possibly at low pressures) is very sensitive to inhomogeneity in the sample, like observed in the P-induced SC of antiferromagnet CeIn$_3$ [2].

Finally, we estimate the SC upper critical magnetic field at ambient pressure. For an as-grown sample, we have $H_{c2}(T) \sim 10$ Oe at $T \simeq 69$ mK (not shown here), and a simple extrapolation to zero temperature gives $H_{c2}(0) \sim 90$ Oe. On the other hand, we evaluated a thermodynamic critical field to be $H_c(0) \sim 20$ Oe from $\gamma_0 = 56$ mJ/K^2 mol assuming the following equations; $H_c(0)^2/8\pi = N(0)|\Delta(0)|^2/2$ and $2|\Delta(0)|/k_B T_c = 3.5$. This yields a Ginzburg-Landau parameter $\kappa \sim 3$. [Note that these values are regarded as an upper and lower bound of $H_c(0)$ and κ, respectively.]

To summarize, we have made an intensive study of pressure effect on the correlation between antiferromagnetism and superconductivity in heavy fermion CeRhIn$_5$. We have found that the superconductivity occurs at ambient pressure with $T_c \simeq 90$ mK and continues to the high pressure SC state above the characteristic pressure P_c ($\sim$18.5 kbar). We emphasize that the degraded superconductivity in the powdered single crystal was remarkably restored by the annealing. This strongly suggests the bulk nature of the superconductivity, implying the intrinsic coexistence between superconductivity and antiferromagnetism. In particular, we wish to stress the finding of the correlation between $T_c(P)$ and $T_N(P)$, i.e., $T_c(P)^n T_N(P)^{1-n} = T_{c0}$ in the wide pressure region between ambient pressure and P_c. It is interpreted as indicating that the antiferromagnetism and superconductivity compete for stability: At low pressures Cooper pairs are formed only on part of the Fermi surface due to the gap formation by the antiferromagnetic order. As the pressure is raised, the density of states available for the superconductivity at E_F will be increased. We also pointed out that the SC state at ambient pressure (and possibly at low pressures) is very sensitive to inhomogeneity in the sample. Further work is still necessary to characterize this interesting superconducting state in the antiferromagnetically ordered phase.

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