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Localized-to-itinerant transition preceding antiferromagnetic quantum critical point and gapless superconductivity in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$

Shinji Kawasaki^{1✉}, Toshihide Oka¹, Akira Sorime¹, Yuji Kogame¹, Kazuhiro Uemoto¹, Kazuaki Matano¹, Jing Guo², Shu Cai², Liling Sun², John L. Sarrao³, Joe D. Thompson³ & Guo-qing Zheng^{1,2✉}

A fundamental problem posed from the study of correlated electron compounds, of which heavy-fermion systems are prototypes, is the need to understand the physics of states near a quantum critical point (QCP). At a QCP, magnetic order is suppressed continuously to zero temperature and unconventional superconductivity often appears. Here, we report pressure (P)-dependent ^{115}In nuclear quadrupole resonance (NQR) measurements on heavy-fermion antiferromagnet $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$. These experiments reveal an antiferromagnetic (AF) QCP at $P_c^{\text{AF}} = 1.2$ GPa where a dome of superconductivity reaches a maximum transition temperature T_c . Preceding P_c^{AF} , however, the NQR frequency ν_Q undergoes an abrupt increase at $P_c^* = 0.8$ GPa in the zero-temperature limit, indicating a change from localized to itinerant character of cerium's f -electron and associated small-to-large change in the Fermi surface. At P_c^{AF} where T_c is optimized, there is an unusually large fraction of gapless excitations well below T_c that implicates spin-singlet, odd-frequency pairing symmetry.

¹Department of Physics, Okayama University, Okayama 700-8530, Japan. ²Institute of Physics, Chinese Academy of Sciences, Beijing National Laboratory for Condensed Matter Physics, Beijing 100190, China. ³Los Alamos National Laboratory, Los Alamos, NM 87545, USA. ✉email: kawasaki@science.okayama-u.ac.jp; gqzheng123@gmail.com

Understanding non-Fermi liquid behaviors^{1,2} due to a zero-temperature magnetic transition, a QCP, and the unconventional superconductivity that emerges around it is one of the central issues in condensed matter physics. These phenomena are widely seen in strongly correlated electron systems such as heavy fermion systems¹, cuprates³, and iron pnictides^{4,5}. In cuprates, iron pnictides, or other compounds containing 3d transition-metal elements⁶, the quantum phase transition is described by itinerant spin-density wave (SDW) theories, where the QCP is due to an instability of the underlying large Fermi surfaces^{7–10}. Cerium(Ce)-based heavy fermion systems are understood based on the Kondo lattice model in which localized Ce 4f electron spins at high temperatures are screened below a characteristic temperature T_K by the conduction electrons¹¹. At high temperatures, the f electron spins are localized, and thus, the Fermi surface is small. With decreasing temperature, 4f electrons couple with the conduction electrons through Kondo hybridization, and the Fermi-surface volume gradually increases with decreasing temperature^{12,13}. In addition to the Kondo effect, there also is a long-range Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction that is the indirect exchange interaction among weakly screened, nearly localized 4f electrons. If the RKKY interaction overcomes the Kondo effect, f spins order antiferromagnetically below the Néel temperature T_N . By tuning a nonthermal control parameter such as pressure and/or chemical substitution, T_N can be suppressed completely to zero, and T_K increases as the parameter increases¹¹. A crossover from the small (localized) to the large (itinerant) Fermi surfaces will occur well below T_K in the Kondo lattice¹⁴. Depending on the relative balance between Kondo hybridization and the RKKY interaction, magnetic order may be of the SDW-type or the RKKY-type antiferromagnetic (AF) order that is mediated by itinerant electrons of a small Fermi surface. Quantum criticality of the latter type of magnetic order is predicted theoretically to be qualitatively different from SDW criticality and involves a breakdown of Kondo screening and a transition from small-to-large Fermi surfaces at the QCP^{10,15,16}. In practice, it can be difficult experimentally to distinguish unambiguously between these two scenarios, though distinctions have been inferred from combinations of thermodynamic, transport and inelastic neutron scattering measurements¹⁷. Unfortunately, it has not been possible to perform neutron scattering experiments under high pressure conditions, the “cleanest” tuning parameter that does not introduce additional disorder or break symmetry, to shed light on the nature of criticality in Kondo lattice systems. In contrast, pressure-dependent nuclear quadrupole resonance (NQR) measurements, which probe the dynamic spin susceptibility as well as the influence of Kondo hybridization, are straightforward, even at very low temperatures, and, as we show, can be used as differentiating probe of quantum criticality.

The AF superconductor $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ ^{18,19} is a good candidate to investigate this issue. CeRhIn_5 has a small Fermi surface²⁰, orders antiferromagnetically below $T_N = 3.8$ K, and exhibits pressure-induced superconductivity above $P = 1.6$ GPa at the transition temperature $T_c = 2.1$ K²¹. T_c increases to 2.3 K at 2.35 GPa where, in the limit of zero temperature, there is a magnetic–nonmagnetic transition^{22,23} accompanied by a change from small-to-large Fermi surface²⁰. The superconducting-gap symmetry is consistent with d-wave symmetry^{24,25}. On the other hand, CeIrIn_5 has a large Fermi surface²⁶, and also shows d-wave superconductivity below $T_c = 0.4$ K^{27–29}, which increases to 0.8 K at $P = 2.1$ GPa³⁰. The alloyed compound $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ orders antiferromagnetically below $T_N = 3.0$ K at $P = 0$ ³¹ and becomes superconducting below $T_c = 0.9$ K^{18,19,32}. $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is closer to an AF QCP than CeRhIn_5 , suggesting that Ir substitution for Rh acts a positive chemical pressure. This suggestion can be

understood by appreciating that underlying the evolution of ground states in the $\text{CeRh}_{1-x}\text{Ir}_x\text{In}_5$ series is a systematic change in orbital anisotropy of the Γ_7^2 crystal-electric field ground state wave function that produces progressively stronger hybridization with increasing x ³³.

Here, we report the results of ¹¹⁵In-NQR measurements on $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ under pressure, crystal structure analysis and a first-principle calculation of NQR frequency ν_Q (see “Methods” for details). From the temperature dependence of the nuclear spin-lattice relaxation rate ($1/T_1$), we find that the AF QCP is at $P_c^{\text{AF}} = 1.2$ GPa, where $T_c(P)$ reaches its maximum. From the pressure dependence of ν_Q , we find a localized-to-itinerant transition at $P_c^* = 0.8$ GPa before the AF QCP appears. Superconductivity is not only optimized at the AF QCP but also is realized with a remarkable proliferation of residual gapless excitations. Our results suggest that the large Fermi surface and AF instabilities in the presence of “impurity” scattering trigger unconventional gapless superconductivity in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$.

Results

The hyperfine coupling constant at the In(1) site. The hyperfine coupling between nuclear and electronic spins relates the measured $1/T_1$ to the underlying dynamical spin susceptibility as discussed in “Methods”. Figure 1 shows the pressure–temperature phase diagram of the $\text{CeRh}_{1-x}\text{Ir}_x\text{In}_5$ system. If substituting Ir for Rh acts as a positive chemical pressure, we would expect the hyperfine coupling constant [¹¹⁵A(1)] at the In(1) site (Fig. 2a) of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ to be smaller than that of the host material CeRhIn_5 because ¹¹⁵A(1) = 25 kOe μ_B^{-1} in CeRhIn_5 decreases with increasing pressure but becomes constant at ¹¹⁵A(1) ~ 7 kOe μ_B^{-1} above $P = 1$ GPa. Such a pressure-dependent ¹¹⁵A(1) will affect the information inferred from $1/T_1$ ³⁴ and, therefore, it is important to determine ¹¹⁵A(1) for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ before proceeding to details of its T_1 results under pressure. Figure 2b shows the frequency-swept ¹¹⁵In-nuclear magnetic resonance (NMR) spectra at a constant field. The spectrum is consistent with previously reported spectra of CeRhIn_5 ³⁴. From these data, we establish the temperature dependence of the ¹¹⁵In(1)-NMR center line plotted in Fig. 2c. With these results, we calculate (Methods) the temperature dependence of the Knight shift ¹¹⁵K(1)_c (%) and compare it to dc susceptibility χ_c (emu mol^{−1}) in Fig. 2d. As clearly shown

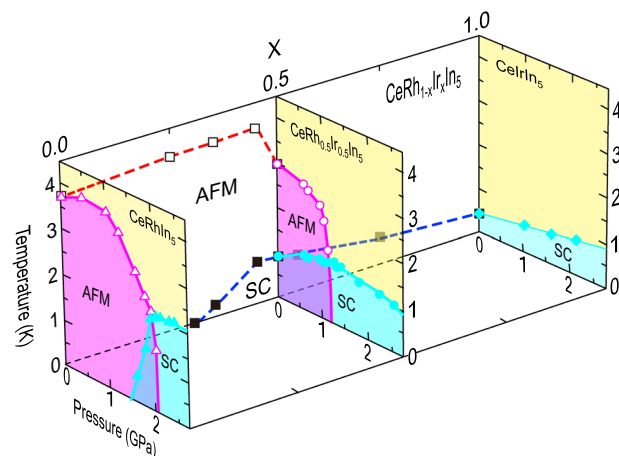


Fig. 1 Phase diagram of $\text{CeRh}_{1-x}\text{Ir}_x\text{In}_5$. x and pressure dependence of the Neel temperature T_N (open squares, triangles, and circles) and the superconducting transition temperature T_c (solid squares, triangles, circles, and diamonds) for $\text{CeRh}_{1-x}\text{Ir}_x\text{In}_5$ ($P = 0$)¹⁹, CeRhIn_5 ^{21–23}, and CeIrIn_5 ³⁰ under pressure. AFM and SC indicate antiferromagnetic metal and superconductivity, respectively.

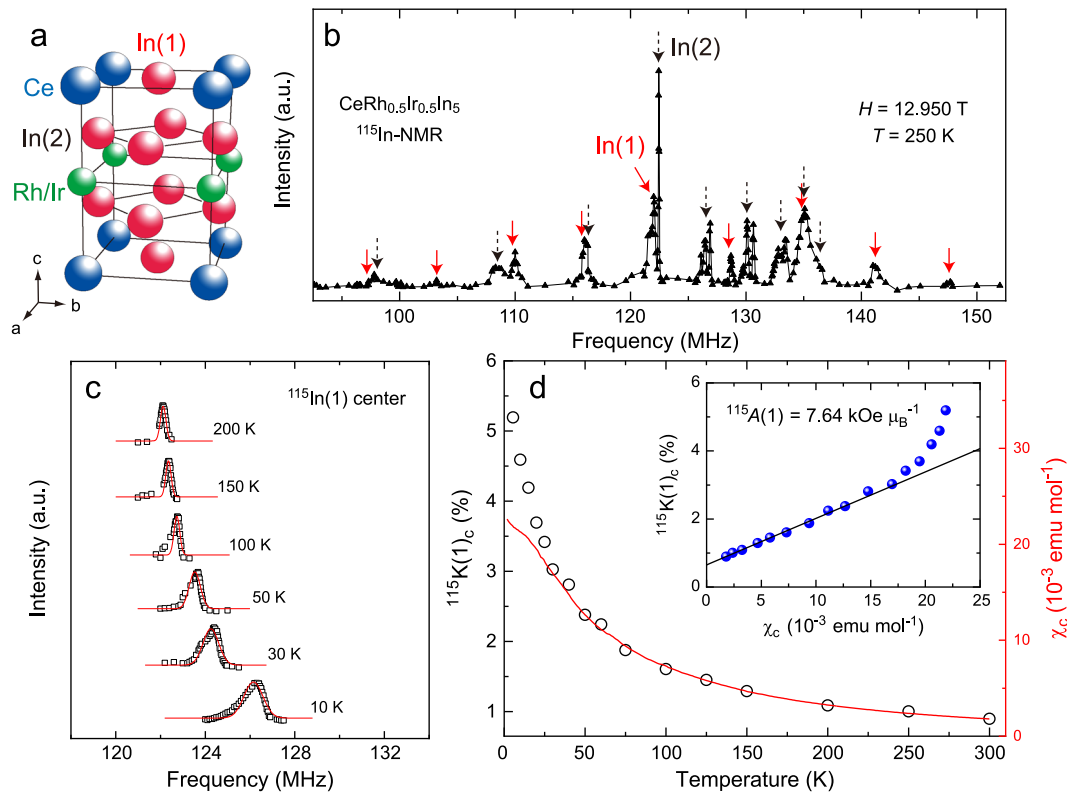


Fig. 2 Hyperfine coupling constant. **a** Crystal structure of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$. **b** Frequency-swept ^{115}In -nuclear magnetic resonance (NMR) spectra of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$. Solid [dotted] arrows indicate In(1)[In(2)] resonance peaks, respectively. **c** Temperature dependence of the ^{115}In (1)-NMR center line. The curves are Gaussian fits. **d** Temperature dependence of the Knight shift $^{115}K(1)_c$ (open circles) and dc susceptibility χ_c (solid curve). The inset shows $^{115}K(1)_c$ vs. χ_c . The solid straight line is a fit to the data above $T = 30$ K, which yields the hyperfine coupling constant $^{115}A(1) = 7.64 \text{ kOe } \mu_B^{-1}$. Error bars are smaller than the size of the data points.

in the figure, the relation $K(T) \propto ^{115}A(1)\chi(T)$ holds above $T = 30$ K. A breakdown of this linear relationship at low temperature is common in heavy electron systems³⁵, but a previous In-NMR study suggested that $^{115}A(1)$ is temperature-independent in CeIrIn_5 in such temperature regime³⁶. In the inset of Fig. 2d, we plot $^{115}K(1)_c$ vs. χ_c and obtain the hyperfine coupling constant as $^{115}A(1) = 7.64 \text{ kOe } \mu_B^{-1}$. This closely corresponds to the value of $^{115}A(1)$ in CeRhIn_5 under a pressure of 1 GPa (Supplementary Note 1 and Supplementary Fig. 1), and thus, it substantiates the suggestion that Ir substitution with $x = 0.5$ (chemical pressure) is equivalent to the application of a physical pressure greater than $P = 1$ GPa to CeRhIn_5 . Therefore, we reasonably can ignore any significant pressure dependence of $^{115}A(1)$ in inferring the pressure evolution of physical properties from $1/T_1$ in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$.

Pressure dependence of T_N and T_c . Figure 3a and b shows the temperature dependence of $1/T_1$. The magnitude of $1/T_1$ for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is much greater than that for the nonmagnetic reference material $\text{La}(\text{Rh},\text{Ir})\text{In}_5$ ³⁷, due to f electron spin correlations, that are reflected in the dynamical susceptibility χ'' to which $1/T_1$ is proportional. At $P = 0$, $1/T_1$ exhibits a small peak at $T_N = 3.0$ K and decreases below $T_c = 0.9$ K¹⁹. As shown in Fig. 3a and the inset, $T_N(P)$ can be identified up to $P = 1.12$ GPa but disappears above $P_c^{\text{AF}} = 1.2$ GPa. A superconducting transition is observed at all pressures, as evidenced by an abrupt reduction of $1/T_1$ below $T = T_c(P)$. T_c increases with increasing pressure and exhibits a maximum $T_c^{\text{max}} = 1.4$ K around $P_c^{\text{AF}} = 1.2$ GPa and then decreases with further increase of P ; T_c^{max} is 1.6 times higher than $T_c = 0.9$ K at $P = 0$.

Pressure dependence of the Kondo hybridization. To probe the character of f electrons as a function of pressure, we use the In(1) ^{115}In -NQR frequency ν_Q . In general, ν_Q is determined by the surrounding lattice and on-site electrons with the latter being dominant in strongly correlated electron systems³⁸; in the current case the latter reflects f - c hybridization that generates an electric field gradient (EFG) at the In(1)-site, as was found in previous ^{115}In -NQR and NMR studies on CeIn_3 ³⁹ and CeRhIn_5 ³⁴ under pressure. Figure 4a–c shows the pressure dependence of the In(1) NQR spectrum and ν_Q (see Supplementary Note 2 and Supplementary Fig. 2 for detail). In general, ν_Q is expected to increase smoothly with decreasing volume³⁹; however, this is not the case here. At $T = 4.2$ K, ν_Q weakly increases up to $P = 1.24$ GPa but jumps at $P^* = 1.35$ GPa above which the slope $d\nu_Q/dP$ increases by more than a factor of three. The same trend is also found at lower temperatures where we see that P^* decreases as T is reduced. We denote the midpoint of the ν_Q jump in the P - T plane as $(P^*, T^*) = (1.35 \text{ GPa}, 4.2 \text{ K})$, $(1.13 \text{ GPa}, 1.6 \text{ K})$, and $(0.90 \text{ GPa}, 0.3 \text{ K})$, respectively. The same result is also found in the In(2) site. Figure 4d, e shows the temperature dependence of the In(2) NQR spectrum and its peak position together with In(1) ν_Q at $P = 1.12$ GPa. As found in the In(1) site, the In(2) ν_Q increases below $T^* = 1.5$ K. In a previous study on CeRhIn_5 , a similar change of EFG was found in the In(2) site at $P^* = 1.75$ GPa, although detailed pressure dependence for the In(1) site with a high accuracy was not conducted³⁴.

We consider the origin for the ν_Q jump. Figure 5a shows results of X-ray diffraction measurements that give the pressure dependence of a - and c -axis lengths; the lattice parameters decrease smoothly with increasing pressure to $P = 4$ GPa, without

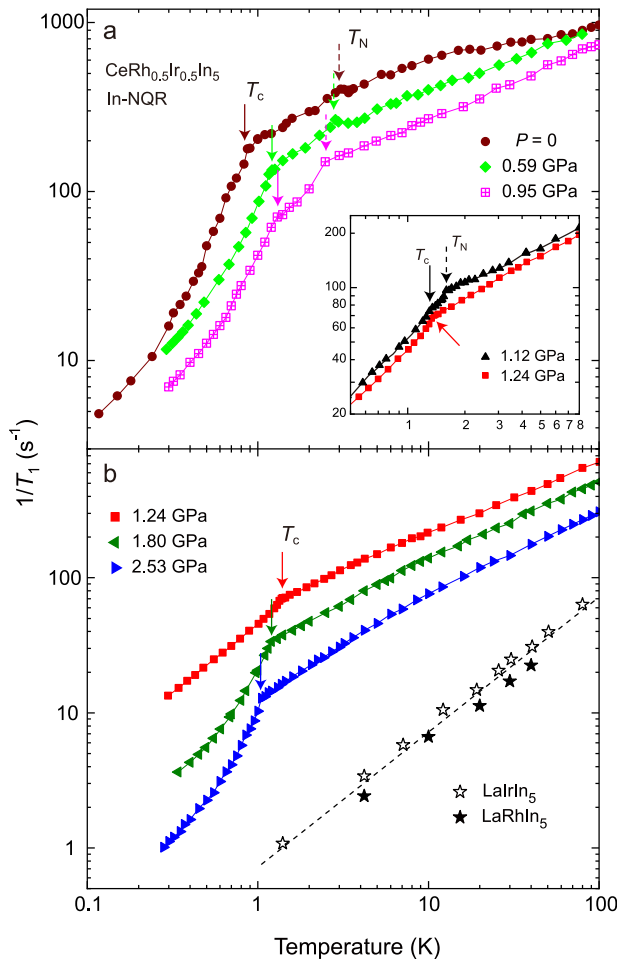


Fig. 3 Antiferromagnetism and superconductivity under pressure.

Temperature dependence of the In(1)-nuclear quadrupole resonance (NQR) nuclear spin-lattice relaxation rate $1/T_1$ (a) below and (b) above the antiferromagnetic (AF) quantum critical point P_c^{AF} . (Inset) Data for $P = 1.12$ and 1.24 GPa just around the Neel temperature T_N and the superconducting transition temperature T_c . The dotted (solid) arrows indicate $T_N(T_c)$, while the dashed line for $\text{La}(\text{Ir,Rh})\text{In}_5$ indicates $1/T_1T = \text{constant}$. Data at $P = 0$ ¹⁹ and for $\text{La}(\text{Ir,Rh})\text{In}_5$ are obtained from ref. ³⁷. Error bars are smaller than the size of the data points.

any signature of a structural transition. From these data, we calculate the EFG using the first-principles Hiroshima Linear-Augmented-Plane-Wave (HiLAPW) codes⁴⁰. As expected, the calculated ν_Q^{HiLAPW} increases monotonically with applied pressure (Fig. 5b). This and the lack of any anomaly in $1/T_1$ at (P^*, T^*) rule out a change in lattice contribution to ν_Q as the origin of the ν_Q jump. Furthermore, Fig. 5b compares the pressure dependence of ν_Q^{HiLAPW} for $\text{CeRh}(\text{Ir})\text{In}_5$ and $\text{LaRh}(\text{Ir})\text{In}_5$. ν_Q^{HiLAPW} for $\text{CeRh}(\text{Ir})\text{In}_5$ is uniformly greater than that for $\text{LaRh}(\text{Ir})\text{In}_5$, because $\text{CeRh}(\text{Ir})\text{In}_5$ has the additional EFG from hybridized f electrons, unlike nonmagnetic $\text{LaRh}(\text{Ir})\text{In}_5$. This result is consistent with previous band calculations^{41,42}.

We conclude from these results that the jump in $\nu_Q(P)$ at (P^*, T^*) is due to a pronounced increase in Kondo hybridization at (P^*, T^*) and that the larger $d\nu_Q/dP$ above (P^*, T^*) reflects that increased hybridization. Because increased Kondo hybridization transfers f spectral weight from localized to itinerant degrees of freedom, and hence an increase in Fermi surface volume, the pronounced jump in ν_Q signals the experimental observation of a small (localized) to large (itinerant) Fermi surface. As the

principal axis of the EFG at the In(2) site is perpendicular to that of the In(1) site, the ν_Q change at both sites suggests that the entire Fermi-surface volume changes at (P^*, T^*) .

Determination of the AF QCP. The temperature dependence of T_1 just above $T \geq T_c(P)$ can be described by the self-consistent renormalization (SCR) theory for spin fluctuations around an AF QCP⁴³. A three-dimensional AF spin fluctuation model is applicable also to the low temperature thermopower S/T around the pressure-induced AF QCP of $\text{CeRh}_{0.58}\text{Ir}_{0.42}\text{In}_5$ ⁴⁴. Near an AF QCP, the SCR model predicts $1/T_1T \propto \sqrt{\chi_Q(T)} = 1/\sqrt{T + \theta}$ ⁴³, where $\chi_Q(T)$ is the Curie-Weiss staggered susceptibility and θ is a measure of the distance to the AF QCP. At the QCP, $\theta = 0$ and $\chi_Q(T)$ diverges toward 0 K. $1/T_1T$ can be represented by the sum of magnetic and small nonmagnetic contributions as $1/T_1T = 1/(T_1T)_{\text{AF}} + 1/(T_1T)_{\text{lattice}}$. For the lattice term, we use the mean value of $1/T_1T$ from reference materials LaRhIn_5 and LaIrIn_5 (Fig. 3b), which gives $1/(T_1T)_{\text{lattice}} = 1.44 \text{ (s}^{-1} \text{K}^{-1})$.

Figure 6a, b are plots of $1/T_1T$ vs. T for the AF phase below $P = 1.12$ GPa and for the paramagnetic phase above $P = 1.24$ GPa, respectively. The solid curves in Fig. 6b are least-squares fits to $1/T_1T = a/(T + \theta)^{0.5} + 1.44$ just above $T_c(P)$, with a and θ as parameters. Approaching the AF QCP from $P = 2.53$ GPa, θ decreases with decreasing pressure, as can be seen in Fig. 6b. The pressure dependences of θ , T_N , and T_c are plotted in Fig. 6c. From a linear fit of $\theta(P)$, the AF QCP ($\theta = 0$ K) for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is obtained at $P_c^{\text{AF}} = 1.2$ GPa, where the highest T_c is realized. The present results clearly indicate that spin fluctuations play a significant role for superconductivity in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$.

Unconventional superconductivity at P_c^{AF} . As seen in Fig. 6a, b, there is a strong pressure dependence of the magnitude of $1/T_1T$ at the lowest temperatures of these measurements. To place these results in perspective, we normalize $1/T_1T$ by its value at T_c , $1/T_1T(T_c)$, and plot the ratio in Figs. 7a, b as a function of reduced temperature $T/T_c(P)$. Deep in the superconducting state, this ratio is clearly largest at $P = 1.12$ GPa near P_c^{AF} and depends only weakly on temperature below T_c . This result contrasts with expectations for a fully gapped, e.g., s -wave, superconductor where $1/T_1$ should decrease exponentially to a very small value well below T_c and for a clean d -wave superconductor where $1/T_1$ decreases as T^3 . In $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ at $P = 1.12$ GPa there must be a substantial fraction of low-lying excitations in the normal state that remains ungapped below T_c . Namely, $[T_1T(T = 0.3\text{K})]^{-0.5}/[T_1T(T_c)]^{-0.5} = N(E_F)^{\text{residual}}/N(E_F)^{\text{normal}}$ is the relative density of state (DOS) at $T = 0.3$ K, which is consistent with the fraction of ungapped quasiparticle DOS in the superconducting state.

To obtain the relative DOS, for simplicity we assume that T_1 below T_c is predominantly determined by itinerant quasiparticles. Previously, an analysis within the context of two-fluid phenomenological theory has deduced that the $4f$ local moments also contribute to relaxation^{45,46}. Nonetheless, as shown in Supplementary Note 3 and Supplementary Figs. 3 and 4, such a model reproduces essentially the same result as we obtained here.

Phase diagram. Figure 8a shows the pressure dependence of T_N and T^* inferred from In(1) NQR, together with T_c on the P - T plane. T^* inferred from In(2) NQR at $P = 1.12$ GPa coincides with the result obtained from In(1). T^* extrapolates to zero at $P_c^* = 0.8$ GPa, which is distinctly smaller than $P_c^{\text{AF}} = 1.2$ GPa. In CeRhIn_5 ($x = 0$), a similar result was suggested with $P_c^* = 1.75$ GPa³⁴ and $P_c^{\text{AF}} = 2.1$ GPa⁴⁷. Comparison of these critical

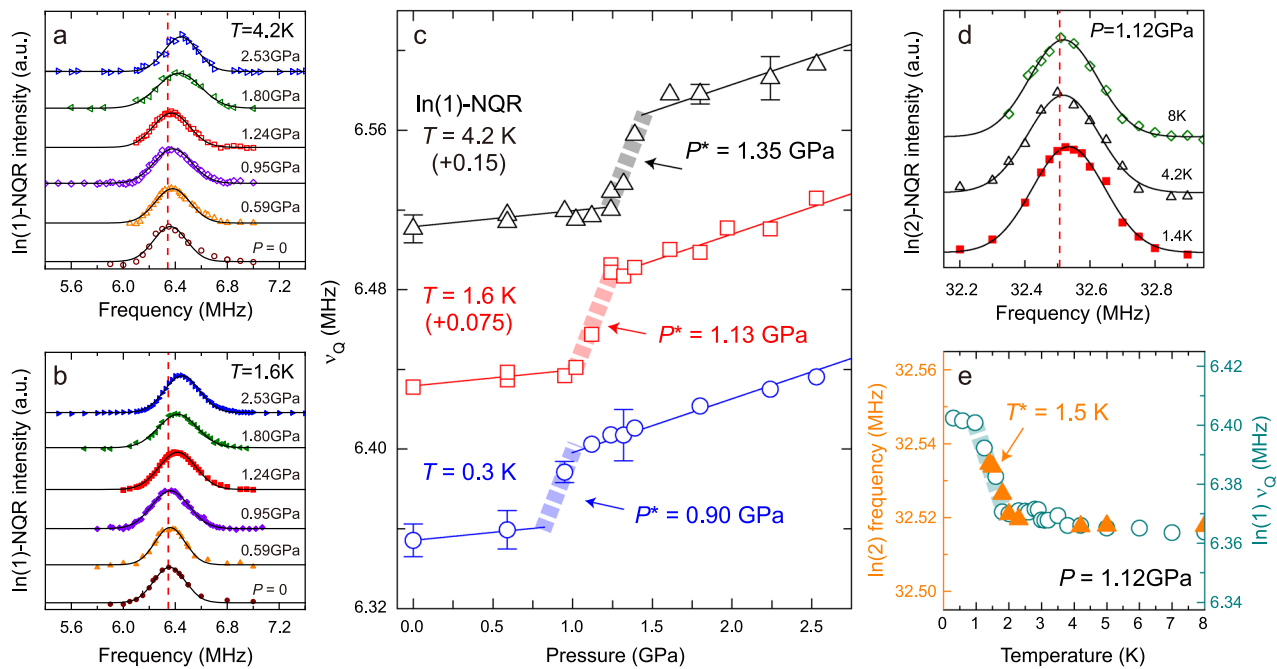


Fig. 4 Localized to itinerant transition. Pressure dependence of the In(1) ^{115}In -nuclear quadrupole resonance (NQR) spectrum ($\pm 1/2 \leftrightarrow \pm 3/2$ transition line) at $T = 4.2\text{ K}$ (a) and 1.6 K (b). The curves are Gaussian fits. The dotted vertical lines indicate the peak positions at $P = 0$. c Pressure dependence of the NQR frequency (ν_Q) obtained at $T = 0.3, 1.6$, and 4.2 K . For clarity, the vertical axis for $T = 1.6$ and 4.2 K are offset by the amount shown in the parenthesis. Solid arrows indicate localized-to-itinerant transition pressure (P^*) which is defined from the midpoint of ν_Q jump. Solid straight lines are fits to the data which yield the slope $d\nu_Q/dP = 0.008$ (0.027) below (above) P^* . Error bars represent the uncertainty in estimating ν_Q . d Temperature dependence of the In(2) ^{115}In -NQR spectrum ($\pm 3/2 \leftrightarrow \pm 5/2$ transition line) at $P = 1.12\text{ GPa}$. The curves are Gaussian fits. Vertical line indicates the peak position at $T = 8\text{ K}$. e Temperature dependence of the peak position of the In(2) spectrum (solid triangles) and In(1) ν_Q (open circles) at $P = 1.12\text{ GPa}$. Solid arrow indicates localized-to-itinerant transition temperature T^* which is defined from the midpoint of ν_Q jump. The dashed line serves as visual guide. Error bars are smaller than the size of the data points except for those in (c).

pressure values shows that Ir substitution with $x = 0.5$ (chemical pressure) is effectively equivalent to the application of a physical pressure of about $P = 1\text{ GPa}$ to CeRhIn_5 . This conclusion is consistent with that drawn from our measurement of the hyperfine coupling presented earlier (Supplementary Note 1 and Supplementary Fig. 1). We emphasize again that, in the pressure regions we are interested for CeRhIn_5 and $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$, ^{115}A (1) is constant, and thus changes in physical properties are not related to a changing hyperfine coupling but to the quantum criticality.

As shown in Fig. 8b, in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$, remarkably, the fraction of ungapped excitations strongly depends on pressure, reaching a maximum at the AF QCP. In the coexistent state at $P = 0$ ¹⁹, this fraction is 50%, but increases to 96% at P_c^{AF} and then decreases to 55% with the increasing pressure at $P = 2.53\text{ GPa}$. The highest T_c around the AF QCP of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is realized unexpectedly with the largest fraction of gapless excitations. The present observation is completely different from that for CeRhIn_5 under pressure; in CeRhIn_5 , the relative fraction of gapless excitations (88%) in the coexistent state is rapidly suppressed to almost zero as it approaches the QCP⁴⁷.

Discussion

From the phase diagram shown in Fig. 8, it is clear that the localized to itinerant transition ($T^*(P)$) does not occur exactly at the AF QCP; in the limit of zero temperature, P_c^* precedes P_c^{AF} . One possibility would be that the Fermi-surface change across the $T^*(P)$ boundary marks a line of abrupt changes of the Ce valence that terminates near $T = 0$ in a critical end point. A model that considers this possibility, however, appears to exclude the $T^*(P)$ boundary from extending into the AF state^{48,49}, contrary to our

results. In contrast, a breakdown of the Kondo effect gives rise to a small-to large Fermi surface change across $T^*(P)$ ⁵⁰. This idea leads to a $T = 0$ phase diagram^{16,51} similar to the results of Fig. 8. Associated with the Kondo breakdown and development of a large Fermi surface, soft charge fluctuations can emerge without a change in formal valence of Ce ions⁵². Within experimental uncertainty of $\pm 1.5\%$, there is no detectable difference between CeRhIn_5 and CeIrIn_5 at 10 K in their spectroscopically determined Ce valence⁵³, even though their Fermi volumes differ—a result that, together with the phase diagram of Fig. 8, supports a Kondo breakdown interpretation as do thermopower measurements on $\text{CeRh}_{0.58}\text{Ir}_{0.42}\text{In}_5$ ⁴⁴. Notably, the T^* boundary has no notable effect on the evolution of $T_c(P)$. In passing, we mention a possibility of a more general case, a Lifshitz transition. Watanabe and Ogata⁵⁴, and Kuramoto et al.⁵⁵ pointed out that, even though the Kondo screening remains, a competition between the Kondo effect and the RKKY interaction can lead to a topological Fermi surface transition (Lifshitz transition) below the AF QCP^{54,55}, which is also consistent with our observation.

The large $1/T_1T$ below T_c at pressures near the AF QCP (Figs. 6 and 7) is quite remarkable, and its temperature independence implies a large DOS that remains ungapped in the superconducting state even though this is the pressure range where T_c is a maximum. Such an anomalously high value of ungapped DOS in the superconducting state has never been found in other QCP materials such as high T_c cuprates⁵⁶ and the iron-pnictide superconductors^{5,57}, even though magnetic fluctuations are also strong around their QCP. For the Ce115 family, no significant gapless excitations have been observed so far around a QCP⁵⁸.

In general, gapless excitations are expected from impurity scattering in d -wave superconductors^{59–62}. Though there are no

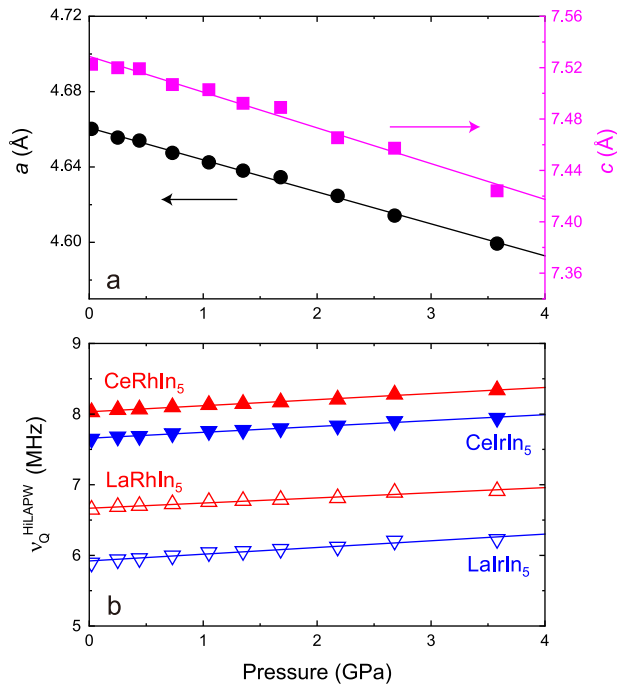


Fig. 5 Lattice parameters and band calculation. **a** Pressure dependence of a - and c -axis lengths for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ at room temperature. **b** Pressure dependence of the nuclear quadrupole resonance frequency ν_Q^{HILAPW} obtained from band calculations [Hiroshima Linear-Augmented-Plane-Wave (HiLAPW) code] for $\text{CeRh}(\text{Ir})\text{In}_5$ and $\text{LaRh}(\text{Ir})\text{In}_5$. $\text{LaRh}(\text{Ir})\text{In}_5$ corresponds to the $4f$ -localized model of $\text{CeRh}(\text{Ir})\text{In}_5$. Both are calculated with the same lattice constant. Error bars are smaller than the size of the data points.

intentionally added impurities in our crystal, the random replacement of 50 % Rh by Ir results in a broadening of the $\text{In}(1)$ NQR line by a factor of ~ 5 compared to CeIrIn_5 ^{19,27}. Such randomness increases the resistivity at 4 K (just above T_N) from $\sim 4 \mu\Omega\text{cm}$ in CeRhIn_5 to over $20 \mu\Omega\text{cm}$ in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ ³². Quantum critical fluctuations can further enhance that scattering⁶¹ to make part of a multi-sheeted Fermi surface gapless⁶³. Such scattering concomitantly leads to pair breaking, resulting in a large reduction of T_c ^{59–64}, which is inconsistent with our observations. The relative DOS at the pressure-induced QCP is almost zero in CeRhIn_5 ⁴⁷ but is enhanced to 96% in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ at P_c^{AF} . If we assume that the symmetry of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is also d -wave, T_c should be reduced to zero with such a significant residual DOS at E_F ⁶⁵. In contrast to this expectation, the maximum $T_c = 1.4$ K for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ remains at 61% of $T_c = 2.3$ K for CeRhIn_5 at their respective QCPs. Hence, the present results suggest that superconductivity near P_c^{AF} in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ is more exotic than d -wave.

Model calculations of superconductivity in a two-dimensional Kondo lattice show that near an AF QCP d - and p -wave spin-singlet superconducting states are nearly degenerate, with an odd frequency p -wave spin-singlet state being favored when entering the large Fermi surfaces region to take advantage of the nesting condition with the vector $\mathbf{Q} = (\pi, \pi)$ ⁶⁶. A p -orbital wave function with spin-singlet pairing symmetry satisfies Fermi statistics in the odd-frequency channel^{67–70}, and this odd-frequency pairing is more robust against nonmagnetic impurity scattering than even-frequency pairing⁷¹. Indeed, for a scattering strength that kills d -wave superconductivity completely, spin-singlet odd-frequency pairing will survive with a T_c that is approximately 60% of that in the absence of scattering⁷¹. Motivated by these theoretical results,

we suggest that odd-frequency spin-singlet pairing is realized in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ in the vicinity of its critical pressures. Its robust T_c in the presence of substantial disorder scattering that gives rise to a large residual density of states at P_c^{AF} where quantum critical fluctuations are strongest and the presence of a nearby change from small-to large Fermi surface at P_c^* are fully consistent with our proposal. We stress that the unique aspect of both strong fluctuations and large Fermi surface is not shared by the end members, CeIrIn_5 or CeRhIn_5 . Knight shift and experiments that directly probe the gap symmetry will be useful to test this possibility.

In summary, we reported systematic ^{115}In -NQR measurements on the heavy fermion AF superconductor $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ under pressure and find that an AF QCP is located at $P_c^{\text{AF}} = 1.2$ GPa, at which $T_c(P)$ reaches its maximum. The pressure and temperature dependence of ν_Q reveal a pronounced increase in hybridization that signals a change from small-to large Fermi surface in the limit of zero temperature at $P_c^* = 0.8$ GPa which is notably lower than P_c^{AF} . Thus, our work sheds new light on the quantum phase transition in f -electron systems. There is a strong enhancement of the quasiparticle DOS in the superconducting state around P_c^{AF} where the Fermi surface is large. The robustness of T_c under these conditions can be understood if the superconductivity is odd-frequency p -wave spin singlet. Traditionally, Hall coefficient and quantum oscillation experiments have been used to probe the Fermi surface change. Our work demonstrates that the NQR frequency can be used as a powerful tool to examine the change in Fermi surface volume for heavy electron systems. In particular, the NQR technique does not require single crystals and is not limited by sample quality or pressure, and thus will open a new venue to understand strongly correlated electron superconductivity.

Methods

Samples. Single crystals of $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ were grown from an In flux as reported in a previous study¹⁸. All experiments were performed with the same batch of crystals used in the previous NQR study¹⁹. As documented in detail in ref. ¹⁹, there is no phase separation into Rh-rich and Ir-rich parts even in the coarsely crushed powder. In fact, no excess peaks in the NMR/NQR spectrum are found and the spectrum can be reproduced by a Gaussian function. Moreover, T_1 is of single component, which also indicates that Ir is randomly distributed. For NMR Knight shift measurements, two single crystals, sized 2 mm—4 mm—0.5 mm and 2 mm—3 mm—0.4 mm, were used. For NQR measurements, the crystals were moderately crushed into grains to allow RF pulses to penetrate easily into the samples. Small and thin single-crystal platelets cleaved from an as-grown ingot were used for X-ray and dc-susceptibility measurements.

NQR measurement. For NQR, the nuclear spin Hamiltonian can be expressed as, $\mathcal{H}_Q = (h\nu_Q/6)[3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)]$, where h is Planck's constant and $I = 9/2$ for the In nucleus is the nuclear spin; ν_Q and the asymmetry parameter η are defined as $\nu_Q = \frac{3eQV_{zz}}{2I(2I-1)\hbar}$ and, $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$, respectively, and Q and $V_{\alpha\beta}$ are the nuclear quadrupole moment and EFG tensor, respectively. In $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$, there are two inequivalent In sites, one in the CeIn [In(1)] layer and another in the (Rh,Ir) In₄ [In(2)] layer (see Fig. 2a). The principle axis of the EFG at the In(1) [In(2)] site is parallel [perpendicular] to the c -axis. The ^{115}In -NQR spectra for $\text{In}(1) \pm 1/2 \leftrightarrow \pm 3/2$ transition line (Supplementary Note 2 and Supplementary Fig. 2), $\pm 7/2 \leftrightarrow \pm 9/2$ transition line (Supplementary Fig. 5), the $\text{In}(2) \pm 3/2 \leftrightarrow \pm 5/2$ transition line and T_1 for the In(1) site ($\eta = 0$) (Supplementary Note 4 and Supplementary Figs. 6 and 7) were obtained as reported in an earlier study^{19,72}. Here, T_1 probes the dynamic spin susceptibility through the hyperfine coupling constant A_q as $1/T_1 \propto T \sum_{\mathbf{q}} |A_q|^2 \chi''(\mathbf{q}, \omega_0)/\omega_0$, where ω_0 is the NQR frequency⁷³ and \mathbf{q} is a wave vector for AF order and/or quantum critical fluctuation in $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$. Meanwhile, $1/T_1 \propto N(E_F)^2 k_B T$ holds in a Pauli paramagnetic metal, i.e., in a heavy Fermi liquid state (Korringa law). Here, $N(E_F)$ is the density of states at E_F .

A NiCrAl/BeCu piston-cylinder-type pressure-cell filled with Daphne (7474) oil was used. The T_c of Sn was measured to determine the pressure. Measurements below 1 K were performed using a ^3He refrigerator.

X-ray measurement. A diamond anvil cell filled with a $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ single crystal and Daphne oil were used for room temperature X-ray measurements under pressure; the pressure was determined by measuring the fluorescence of ruby. All measurements were made at zero-magnetic field.

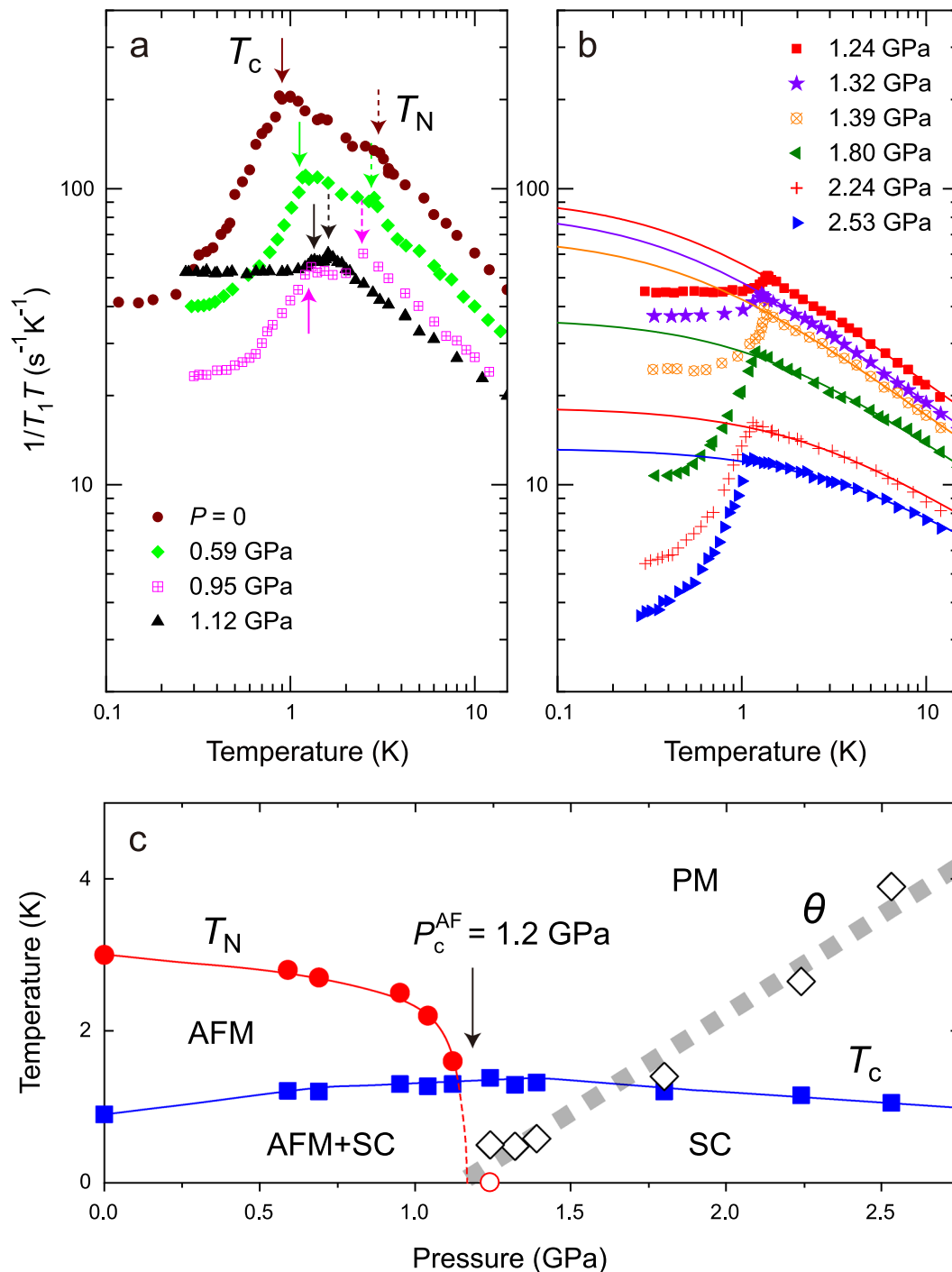


Fig. 6 Antiferromagnetic (AF) quantum critical point (P_c^{AF}). Temperature dependence of the nuclear spin-lattice relaxation rate divided by temperature $1/T_1 T$ below (a) and above (b) P_c^{AF} with the fitting curves (see text). The dotted (solid) arrows indicate the Neel temperature T_N (the superconducting transition temperature T_c). c Summary of pressure dependence of the characteristic temperature θ (see text), T_N , and T_c . The dotted straight line (filled diamonds) is a fit to the data which yields $P_c^{AF}(\theta=0) = 1.2$ GPa. PM and AFM indicate paramagnetic and antiferromagnetic metal, respectively. SC indicates superconductivity. Error bars are smaller than the size of the data points.

EFG calculation. The EFG is calculated using the all electron full-potential linear augmented plane wave method implemented in the Hiroshima Linear-Augmented-Plane-Wave (HiLAPW) code with generalized gradient approximation including spin-orbit coupling⁴⁰.

Hyperfine coupling constant. To estimate the hyperfine coupling constant for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$, $^{115}\text{In}(1)$, we measure the $^{115}\text{In}(1)$ -NMR spectrum and dc susceptibility. For NMR, the nuclear spin Hamiltonian is expressed as $\mathcal{H} = -^{115}\gamma \hbar \mathbf{I} \cdot \mathbf{H}(1 + K) + \mathcal{H}_Q$, where the gyromagnetic ratio $^{115}\gamma = 9.3295 \text{ MHz T}^{-1}$, \mathbf{H} is the

external magnetic field, and K is the Knight shift. ^{115}In -NMR spectra have nine transitions from $I_z = (2m + 1)/2$ to $(2m - 1)/2$ where $m = -4, -3, -2, -1, 0, 1, 2, 3, 4$ for $\text{In}(1)$ and $\text{In}(2)$ sites, respectively, with K , ν_Q , and η as parameters. At ambient pressure, ν_Q and η at the $\text{In}(1)$ [$\text{In}(2)$] site are 6.35 MHz (17.37 MHz) and 0 (0.473), respectively¹⁹. The Knight shift for $\text{In}(1)$, $^{115}K(1)_c(T)$, was calculated from the peak in the $^{115}\text{In}(1)$ -NMR center line ($m = 0$) taken by sweeping the RF frequency at a fixed field $H = 12.950 \text{ T}$ and χ_c (emu mol⁻¹) is obtained by dc susceptibility measurements at $H = 3 \text{ T}$ using a superconducting quantum interference device with the vibrating sample magnetometer. The magnetic field H is fixed perpendicular to the CeIn layer (c -axis).

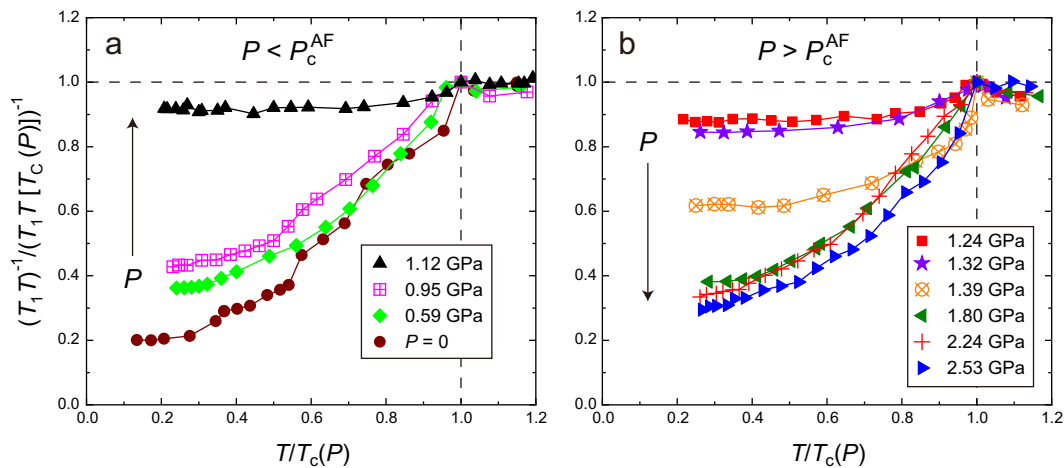


Fig. 7 Low-lying excitations in the superconducting state. Temperature dependence of the nuclear spin-lattice relaxation rate divided by temperature $1/T_1 T$ below (a) and above (b) the antiferromagnetic (AF) quantum critical point (P_c^{AF}). Data at $P = 0$ are obtained from the literature¹⁹. Horizontal and vertical axes are normalized by the superconducting transition temperature $T_C(P)$ and $1/T_1 T [T_C(P)]$, respectively. Error bars are smaller than the size of the data points.

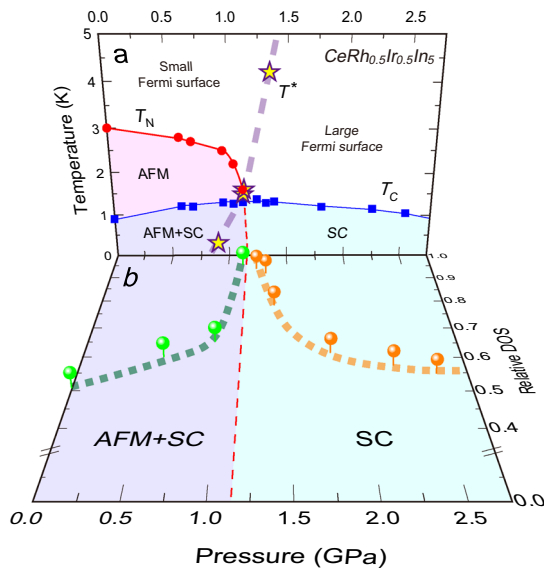


Fig. 8 Phase diagram. a Pressure-temperature phase diagram for $\text{CeRh}_{0.5}\text{Ir}_{0.5}\text{In}_5$ obtained at zero-magnetic field. The solid circles, squares, and stars indicate the Neel temperature T_N , the superconducting transition temperature T_C , and the localized-to-itinerant transition temperature T^* , respectively. The broken curve is a phase boundary separating small and large Fermi surfaces. b Pressure dependence of the relative density of states (DOS) on the $T = 0.3$ K plane. The dotted straight line indicates the antiferromagnetic (AF) quantum critical point ($P_c^{AF} = 1.2$ GPa). The solid and dashed curves serve as visual guides. AFM and SC indicate antiferromagnetic metal and superconductivity, respectively. Error bars are smaller than the size of the data points.

Data availability

The data that support the findings of this study are available on reasonable request. Correspondence and requests for materials should be addressed to G.-Q.Z.

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Author contributions

G.-Q.Z. planned the project. J.L.S. and J.D.T. synthesized the single crystal. S.K., T.O., A.S., Y.K., and K.U. performed NQR measurements. S.K. and Y.K. performed the NMR and susceptibility measurements. J.G., S.C., and L.L.S. performed the X-ray measurement. K.M. performed the band structure calculation. G.-Q.Z., S.K., and J.D.T. wrote the paper. All authors discussed the results and interpretation.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to S.K. or G.-q.Z.

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