Effect of selenium doping on the superconductivity of $Nb_2Pd(S_{1-x}Se_x)_5$

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We study the isovalent substitution effect by partially introducing Se on the S site in the newly discovered superconductor Nb_2PdS_5 ($T_c \sim 6$ K) whose upper critical field is found to be far above its Pauli paramagnetic limit. In this $Nb_2Pd(S_{1-x}Se_x)_5$ ($0 \leqslant x \leqslant 0.8$) system, superconductivity is systematically suppressed by the Se concentration and ultimately disappears when $x \geqslant 0.5$, after which a semiconductinglike ground state emerges. In spite of the considerably reduced T_c with Se doping, the ratio of the upper critical field H_{c2} to T_c remains unaffected. Moreover, the size of the heat capacity jump at T_c is smaller than that expected for a BCS superconductor, implying that a strong-coupling theory cannot be the origin of this large upper critical field. In addition, the low-lying quasiparticle excitations are consistent with a nodeless gap opening over the Fermi surface. These results combined impose severe constraints on any theory of exotic superconductivity in this system.

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A superconductor with a remarkably large upper critical field relative to its T_c always attracts sustained interest from both experimental and theoretical communities.[1–4] As a notable example, a very high H_{c2} observed in the iron pnictide $LaFeAsO_{0.89}F_{0.11}$ was effectively ascribed to a two-band effect.[5] Theoretically, a magnetic field destroys superconductivity by two distinct mechanisms: the *orbital* effect and the Pauli paramagnetic pair-breaking effect.[6] In the former, the vortices penetrate into the superconductor and the associated supercurrent increases the kinetic energy of the system. When this kinetic energy gain exceeds the condensation energy, the normal state recovers. In parallel, Cooper pairs may also be broken by Zeeman splitting produced by the magnetic field coupling to the electronic spins in a spin-singlet superconductor. In weak-coupling BCS theory, this Pauli limiting field H_p is $\sim 1.84\, T_c$.[7] However, a growing number of superconductors are found to have H_{c2} significantly higher than the Pauli limit.[8–10] The excess of H_{c2} beyond the Pauli limit has been accounted for by different theories such as strong spin-orbit coupling, strong-coupling modes, multiband effects, or even spin-*triplet* pairing.

Very recently, a new transition metal-chalcogenide-based compound $Nb_2Pd_{0.81}S_5$ was discovered to be superconducting below $T_c \sim 6.6$ K.[11] This superconductivity was found to be *unconventional* in the sense that its upper critical field, for field applied along the crystallographic b axis, was reported to surpass the Pauli paramagnetic limit by a factor of 3 as $T \to 0$ K. It was also suggested that this superconductivity may be in proximity to a magnetic instability. This very high upper critical field was tentatively ascribed to the multiband effect or spin-triplet pairing.[11,12] While both represent the likelihood for the enhanced H_{c2}, the experimental data are far from conclusive. Whether spin-orbit coupling or strong electron-boson coupling play a prominent role here, since both of which can also elevate H_{c2}, remains to be seen. In addition, its superconducting gap symmetry, which may also provide valuable information on the pairing character (e.g., the possibility of triplet pairing), has not yet been determined.

With these questions in mind, we study the effect of Se doping in this $Nb_2Pd(S_{1-x}Se_x)_5$ system. With the partial substitution of Se for S, the lattice parameters (and the unit cell volume) increase monotonically with Se content, indicating that a negative chemical pressure is induced. Meanwhile, the superconductivity is gradually suppressed and finally disappears around $x = 0.5$, above which the ground state is semiconductinglike. While T_c is rather sensitive to Se doping, the reduced upper critical field, H_{c2}/T_c, is seen to be robust against impurities. Furthermore, the quasiparticle excitations are indicative of a fully gapped superconducting order parameter with weak-coupling character. Collectively, these findings shed important light on the nature of the observed superconductivity.

Polycrystalline samples of $Nb_2Pd(S_{1-x}Se_x)_5$ with nominal Se content of $x = 0$, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.6, and 0.8 were grown by a solid-state reaction method.[11] The starting materials of Nb(99.99%), Pd(99.9%), and S/Se(99.99%) powders were mixed thoroughly in the ratio of 2:1:7.2 in the glove box filled with Ar gas. The excess amount of S/Se is necessary to compensate the high vapor pressure of S/Se during the reaction. The pelletized mixtures were loaded into an evacuated quartz tube which was slowly heated to 825°C and kept at this temperature for 48 hours before being quenched to room temperature. The structure of the polycrystalline samples was characterized by powder x-ray diffraction (XRD) at room temperature using a Rigaku diffractometer with Cu $K\alpha$ radiation and a graphite monochromator. Lattice parameters were obtained by Rietveld refinements. The resistivity of each sample was measured with a standard four-probe technique, and the specific heat was measured by a long relaxation method using a commercial Quantum Design PPMS-9 system.

Figure 1 (left panel): displays the powder XRD patterns of a series of $Nb_2Pd(S_{1-x}Se_x)_5$ samples. The main XRD peaks of these samples can be well indexed based on a monoclinic cell structure with the $C2/m$ space group. Extra minor peaks, marked by the asterisks in the figure, are still detectable. Indeed, the isostructural Nb_2PdSe_5 compound

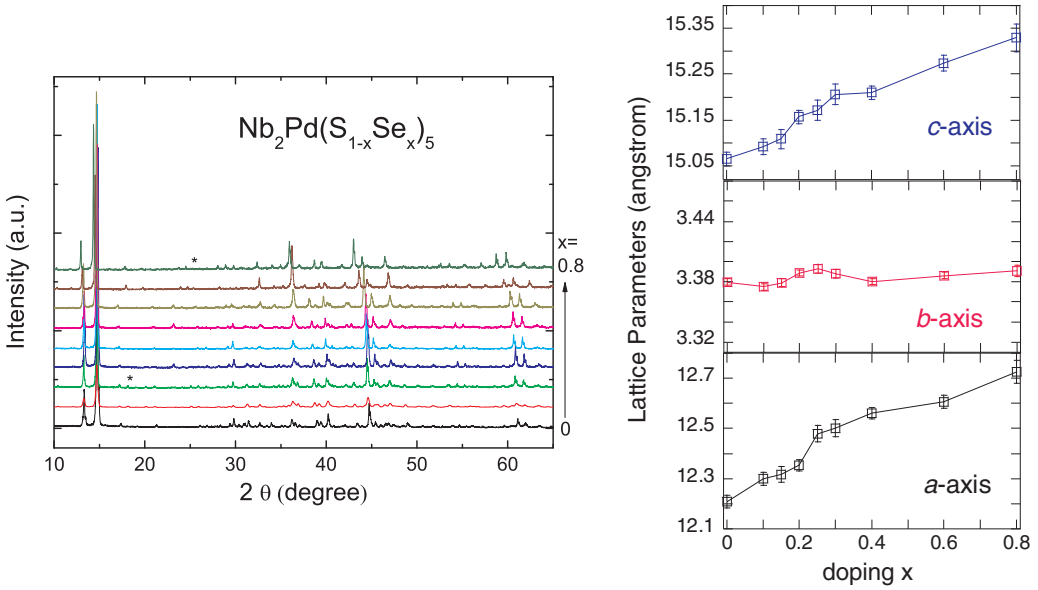

FIG. 1. (Color online) Left panel: The powder XRD patterns for a series of $Nb_2Pd(S_{1-x}Se_x)_5$ samples studied in the paper. The asterisks mark the possible impurity phases. Right panel: The lattice parameters as a function of nominal Se content extracted by using Rietveld analysis.

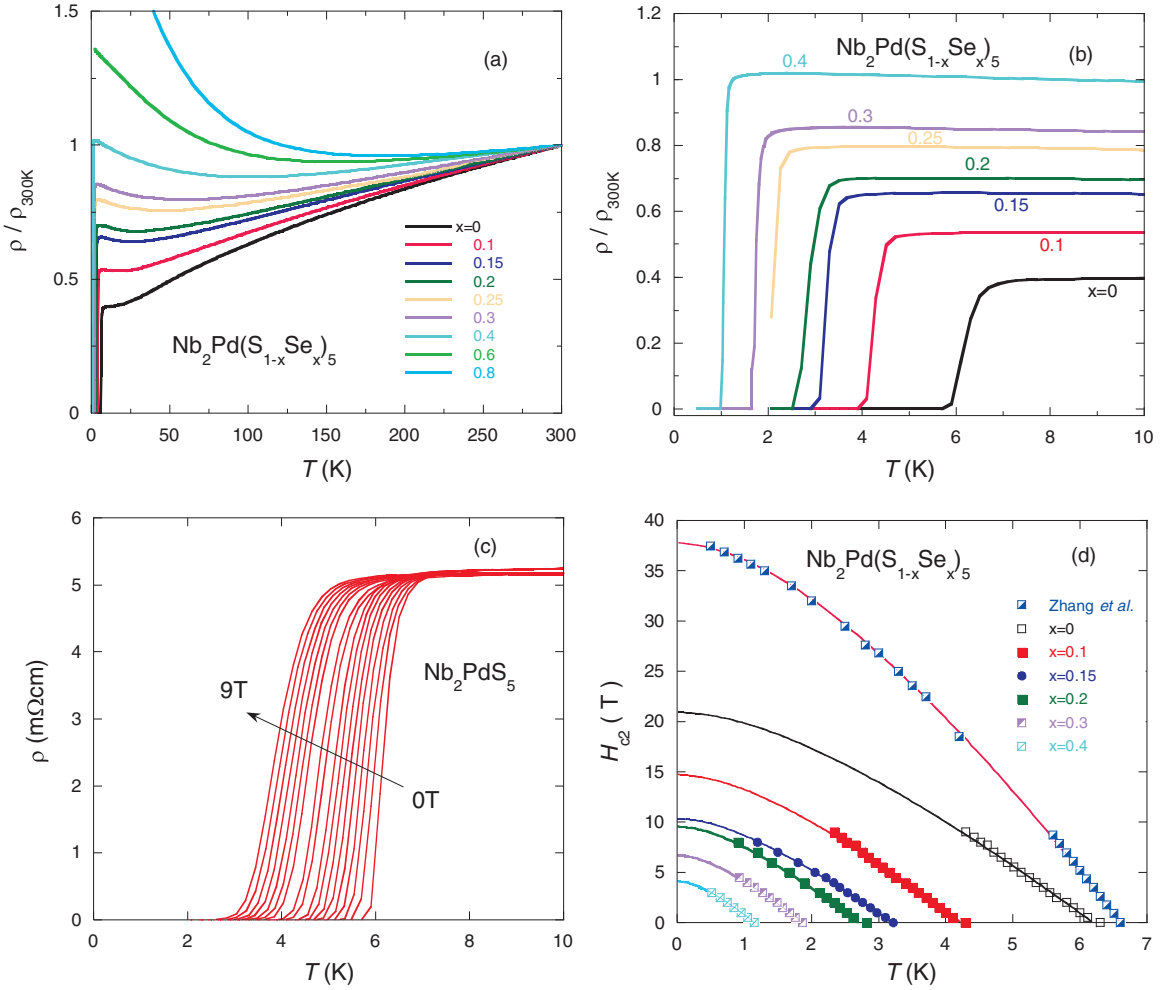

FIG. 2. (Color online) (a) Temperature dependence of the zero-field resistivity of $Nb_2Pd(S_{1-x}Se_x)_5$ ($0 \leqslant x \leqslant 0.8$). All curves are renormalized to their individual 300-K values for clarity. (b) shows the enlarged plot for the low temperature superconducting transition. (c) The fixed-field temperature sweeps below T_c for Nb_2PdS_5 as an example. (d) The resultant H_{c2} extracted using the criterion of 90% of normal-state resistivity. The data by Zhang *et al*. on $Nb_2Pd_{0.81}S_5$ single crystal ($H \parallel b$) were also incorporated for comparison. The solid lines represent the corresponding WHH fitting.

has been reported in previous literature.[13] Note that all x-ray diffractions for doped samples shift systematically to lower 2θ angles with increasing Se concentration, implying that Se atoms are incorporated into the lattice and lead to expansion of the lattice parameters. Figure 1 (right panel): shows how the extracted lattice parameters vary with Se content. Both the c axis and the a axis increase monotonically with increasing Se content, while the b axis shows less doping dependence. Overall, these results indicate that the Se atoms are successfully doped into the system.

Figure 2(a) presents zero-field resistivity $\rho(T)$ curves from room temperature to the lowest temperature studied for all samples, renormalized to their individual 300-K values for clarity. For the parent compound Nb_2PdS_5, $\rho(T)$ is metallic upon cooling from room temperature and becomes superconducting below $T_c \sim 6.3$ K. Upon Se doping, a well-defined resistivity upturn develops in the normal state at $T_{\min}$, which shifts to higher temperature with increasing Se content. Meanwhile, T_c is gradually suppressed by Se concentration and finally disappears as $x \geqslant 0.5$. Interestingly, the resistivity upturn cannot be fitted to a gaplike excitation of $\rho = \rho_0 \exp(E_g/k_B T)$ nor a variable-range hopping model.[14,15] The residual resistivity ratio is systematically reduced by Se doping. Hence, it appears more likely that this resistivity upturn results from a disorder-induced localization effect. A closeup view for the superconducting transition is given in Fig. 2(b).

The magnetotransport of the superconducting samples, as exemplified for the parent compound Nb_2PdS_5 shown in Fig. 2(c), was studied by fixed-field temperature sweeps. The as-determined $H_{c2}(T)$, using the criterion of 90% of normal state values, is summarized in Fig. 2(d). The H_{c2} for a field aligned along the b axis of a $Nb_2Pd_{0.81}S_5$ single crystal is also incorporated in the figure for comparison. As noted in the figure, while the H_{c2} is significantly reduced in our polycrystal compared with its single-crystal profile, consistent with its highly anisotropic Fermi surface, it still exceeds the Pauli limit by a factor of ~2. Similar to data for single crystals of $Nb_2Pd_{0.81}S_5$, we also satisfactorily fitted our

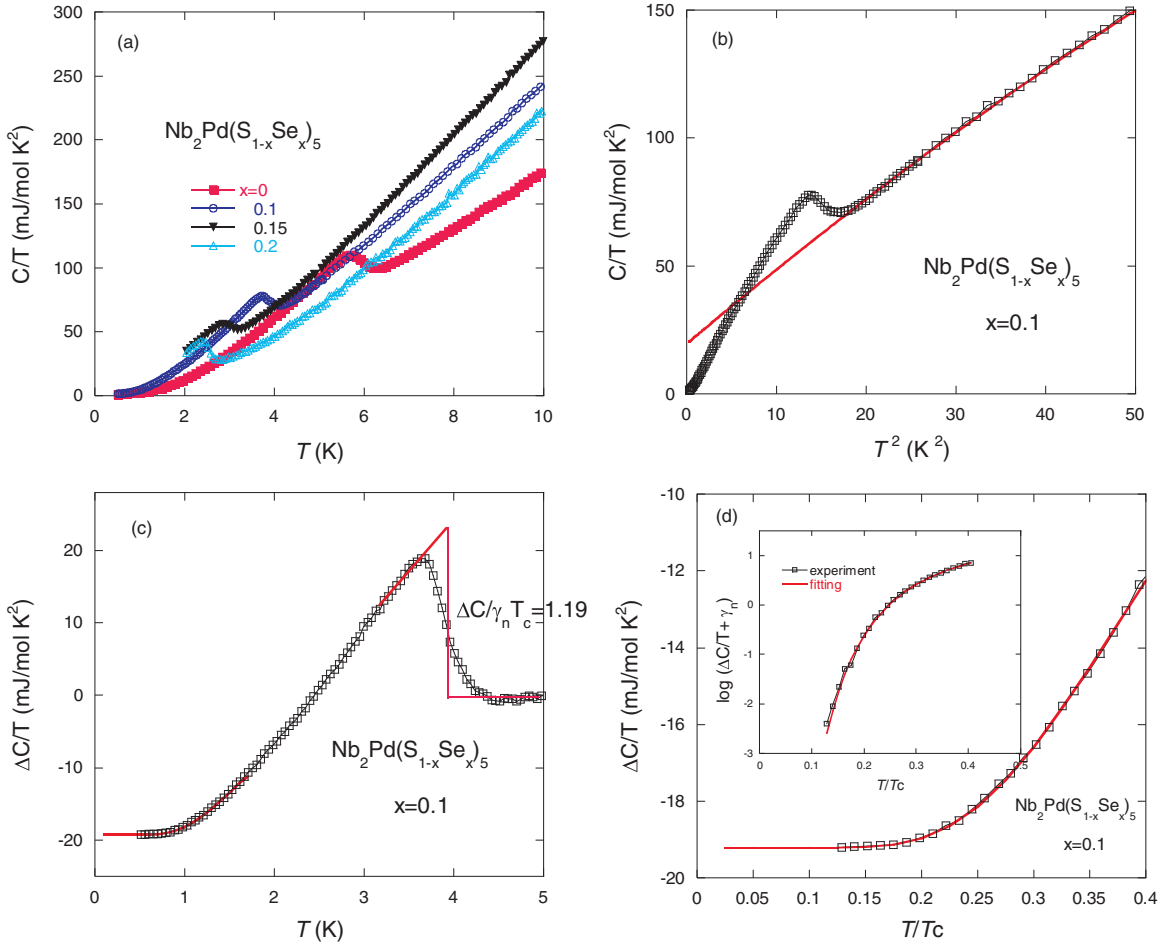

FIG. 3. (Color online) (a) Heat capacity anomalies associated with T_c for various dopings. (b) The plot of C/T vs T^2 for $Nb_2Pd(S_{1-x}Se_x)_5$ ($x = 0.1$) as a demonstration. The red line stands for the fit to its normal-state heat capacity as $C_n/T = \gamma_n + \beta_n T^2 + \alpha_n T^4$ above T_c and the extrapolation to low temperatures, giving $\gamma_n = 19.2$ mJ/mol K^2, $\beta_n = 2.97$ mJ/mol K^4, and $\alpha_n = -0.00738$ mJ/mol K^6. (c) $\Delta C/T$ [$=(C - C_n)/T$] as a function of temperature. The normalized heat capacity jump at T_c, $\Delta C/\gamma_n T_c$, using the entropy-conserving construction, is equal to ~1.2 for the $x = 0.1$ sample. (d) The blowup of the low-temperature data. The red line is the fit to $\Delta C/T \sim bT^{-5/2}\exp(-\Delta_g/k_B T) - \gamma_n$, with $b = 3683$ mJ K$^{0.5}$/mol, $\Delta_g = 2k_B T_c$, and $\gamma_n = 19.2$ mJ/mol K^2. The inset is the same data plotted on logarithmic scale (Ref. 23).

experimental data with the Werthamer-Helfand-Hohenberg (WHH) model.[16,17] This is depicted by the color-coded solid lines in Fig. 2(d).

Figure 3 presents the detailed calorimetric study of our samples. As seen in Fig. 3(a), a clear heat capacity anomaly associated with the superconducting transition is observed at ~6 K for the parent compound. This anomaly is seen to move to lower temperature with Se doping. As an example, in Fig. 3(b), the anomaly for the $x = 0.1$ sample is isolated by subtracting the normal-state heat capacity which was fitted by $C_n/T = \gamma_n + \beta_n T^2 + \alpha_n T^4$ (the first term represents the electronic contribution, while the remaining terms represent the phonon contribution) above T_c and extrapolated to low temperatures, as shown by the red curve.[18–21] It is noted that the normal state by this procedure has an ~7% excess of entropy compared to that of the superconducting state below T_c. Here, it is worth noting that the intercept of C/T vs T^2 as $T \to 0$ K goes to zero, which indicates that the fraction of nonsuperconducting sample is indeed very small.[22] The resultant ΔC, normalized to T, is plotted in Fig. 3(c).

From Fig. 3(c), it is seen that the size of the heat capacity jump in our polycrystal samples is much higher than that reported in single-crystal samples.[11] Importantly, the value of the normalized jump, $\Delta C/\gamma_n T_c \sim 1.2$, is considerably smaller than the weak-coupling BCS value of 1.43. The value of this normalized jump is seen to vary slightly with different doping levels x, being the largest at a value of ~1.2. The small $\Delta C/\gamma_n T_c$ would seem to rule out a strong-coupling origin of the observed superconductivity,[24,25] which was reported to be responsible for the significantly enhanced H_{c2} in the heavy-fermion superconductor $CeCoIn_5$.[8] As stated above, however, there is an ~7% entropy difference between our extracted normal state and the superconducting state. Therefore the intrinsic $\Delta C/\gamma_n T_c$ might be slightly larger than 1.2 and close to the BCS value of 1.43. On the other hand, the small amount of (nonsuperconducting) disorder phase may also lead to slightly larger $\Delta C/\gamma_n T_c$ value. Moreover, we note that in the textbook example of a two-gap superconductor MgB_2, the normalized $\Delta C/\gamma_n T_c$ is also smaller than 1.43.[26,27] In this respect, it would be very interesting to see if the superconducting order parameter of the $Nb_2Pd(S_{1-x}Se_x)_5$ system is of two-gap character as well.

In the low-temperature limit, we uncovered another interesting feature of the observed superconductivity. In a superconductor with a gap node, one expects $C_{el} \sim T^2$ so $\Delta C/T \sim aT - \gamma_n$. Instead, a nodeless superconductor predicts $\Delta C/T \sim bT^{-5/2}\exp(-\Delta_g/k_B T) - \gamma_n$.[20,22] As clearly seen in Fig. 3(d), the electronic specific heat is dominated by the exponential dependence up to $T/T_c \sim 0.4$, which is better illustrated in the logarithmic plot in the inset, indicating a nodeless gap on the Fermi surface, similar to $Ta_2Pd_xS_5$ compound.[28] This seemingly precludes a d-wave gap or a simple $p_x(p_y)$ symmetry where node(s) are present, although complex order parameter structures such as $p_x + ip_y$ are still possible.

Finally, the resultant phase diagram is summarized in Fig. 4. Accompanied by an increase of resistivity minimum T_{min}, the superconducting transition T_c is systematically suppressed by Se doping in $Nb_2Pd(S_{1-x}Se_x)_5$, and ultimately disappears when $x \geqslant 0.5$, where the ground state is semiconductinglike,

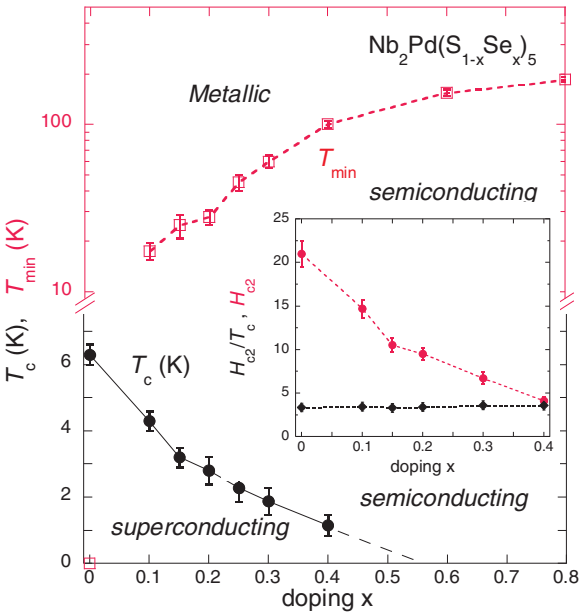

FIG. 4. (Color online) The phase diagram of T_c and resistivity minimum T_{min} as a function of doping level x. Note that the y axis is broken up for T_c and T_{min}, respectively. The inset shows the evolution of H_{c2} and H_{c2}/T_c as doping.

presumably induced by disorder effect. Intriguingly, as seen in the inset, while the upper critical field H_{c2} is significantly reduced by the doping, the normalized H_{c2}/T_c is rather robust against impurities, exceeding the Pauli limiting value of $1.84T_c$ by a factor of 2. The robustness of this large H_{c2} relative to T_c up to $x \sim 0.4$ seems at odds with the spin-triplet origin of the enormous H_{c2} observed in $Nb_2Pd_{0.81}S_5$, which should be sensitive to nonmagnetic impurity scattering. To firmly rule out the spin-triplet scenario, it would be a litmus test to study the Knight shift suppression below T_c.[29,30]

In summary, we study the isovalent doping effect, i.e., the partial substitution of Se for S, in the newly discovered superconducting Nb_2PdS_5 system. While T_c substantially decreases with Se doping, its high H_{c2} with respect to T_c, H_{c2}/T_c, is found to be immune to the Se impurities. Moreover, the heat capacity study reveals that the superconductivity is fully gapped, with relatively weak-coupling strength. Both of these findings seemingly argue against strong-coupling and spin-triplet pairing as the origin of the large H_{c2}. Alternatively, multiband effects or strong spin-orbit coupling, or even a subtle combination of the two, could be responsible for the large H_{c2}. Regarding the latter, it shall be very instructive to substitute heavier elements, such as Pt, for Pd to study the role of spin-orbit coupling in this exotic superconductor.

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