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$Pr_4Fe_2As_2Te_{1-x}O_4$: A layered FeAs-based superconductor

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We report crystal growth at high pressure, structure determination, and magnetic and transport studies of an oxypnictide superconductor $Pr_4Fe_2As_2Te_{1-x}O_4$. Its structure resembles the known 1111 phase except for the considerably larger c lattice constant and intercalated tellurium atoms and it crystallizes in a tetragonal lattice [$a = 4.0165(2)$ Å, $c = 29.8572(16)$ Å, and space group $I4/mmm$ (no. 139)]. The electrical resistivity $\rho(T)$ and magnetization measurement show a transition at $T_c \approx 25$ K. The lower (H_{c1}) and upper (H_{c2}) critical fields are 2 mT and 6.5 T, respectively. The Ginzburg-Landau parameter of $\kappa \approx 80$ places this compound in the family of strong type-II superconductors.

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The layered d-metal pnictide and pnictide oxides (oxypnictides) have been intensively studied in recent years (see the review article[1] and references therein). This family consists of anti-fluorite-type M_2P_2 (M is a transition metal and P a pnictogen) layers alternating for some representatives with fluorite-type L_2O_2 layers (where L is a lanthanide). There are more than ten known structural types of this kind.[2,3] Some of them reveal superconductivity with a critical temperature T_c up to 58.1 K.[4]

The "new generation of high-T_c materials"[5] provides a broad research area because of the huge variability in chemical composition with a potential to form new structural types.[1,3,6] Some of these compounds, like SmFeAs(O,F), due to the optimal combination of high isotropic critical current densities and the relatively high T_c, could be considered as materials which meet requirements for possible applications.[7]

Here we report on another compound of the layered d-metal oxypnictide superconductors, $Pr_4Fe_2As_2Te_{1-x}O_4$, its crystal structure and basic physical properties such as T_c, dc resistivity, lower and upper critical fields, and Ginzburg-Landau parameters. For its synthesis a mixture of chemicals PrAs, PrTe, and FeO in molar proportion 0.9:0.1:1 was thoroughly ground in a malachite mortar and pressed into a pellet inside a glovebox in argon gas. The pellet was annealed at 1050 °C for 7 days in an Al_2O_3 crucible in a sealed quartz ampoule filled with Ar gas (≈0.2 atm). After that it was quenched in cold water. This precursor was used for crystal growth at high pressure (3 GPa) in NaCl/KCl flux employing a high-pressure cubic anvil system. The temperature was raised to 1500 °C in 1 h and then kept constant for 60 h, followed by cooling (45 °C/h) to 1050 °C and cooling in 1 h to room temperature. The flux was dissolved in water. The crystals of platelike shape were selected from the remaining mixture.

Single-crystal x-ray diffraction was performed on a Bruker diffractometer equipped with a CCD detector. Data reduction and multiscan absorption correction were done using APEX2 (Ref. 8) and SAINT (Ref. 9) software. The crystal structure was determined by a direct method and refined on F^2, employing the programs SHELXS-97 (Ref. 10) and SHELXL-97 (Ref. 11). The lattice parameters were determined as $a = 4.0165(2)$ Å and $c = 29.8572(16)$ Å, space group $I4/mmm$ (no. 139), and $Z = 2$. The structure was refined on the base of 2778 reflections, of which 670 were independent. The final anisotropic full-matrix least-squares refinement on F^2 with 19 variables converged at $R_1 = 3.74\%$ for the observed data. As the displacement parameter of the Te atom was found to be larger than for other atoms, it was assumed that this position was not fully occupied. The final refinement was performed with the occupation parameter for Te as a free variable. Details of the structure are shown in Table I. The composition of the samples was determined by means of energy-dispersive x-ray (EDX) analysis. The final composition obtained by structure refinement is $Pr_4Fe_2As_2Te_{0.88}O_4$ and agrees with the data from the EDX analysis. Analogous to other oxypnictides, the phase is called "42214."

The structure consists of alternating anti-fluorite-type Fe_2As_2 and fluorite-type Pr_2O_2 layers in the c direction separated by tellurium atoms (Fig. 1). It has a close resemblance to the 1111 structure. The lattice constants a and b are slightly larger (by ≈0.04 Å) while c is considerably larger (by ≈21.3 Å). The pnictogen height[12] and As-Fe-As angle (the α angle according to Lee *et al.*[13]), which are highly correlated with T_c, are 1.332(3) Å and 112.94(5)°, respectively.

The magnetic properties in the superconducting state were investigated by dc magnetization (M) measurements with a Quantum Design magnetic properties measurement system (MPMS) equipped with a 7 T superconducting magnet. A set of six single crystals was studied in a magnetic field oriented parallel to the c axis. The crystals have a typical dimension of $\sim 80 \times 40 \times 5\ \mu m^3$ and the total volume used in magnetization measurements was $\sim 95 \times 10^{-9}$ cm^3. They were characterized by $M(T)$ measurements at low (1 and 5 mT) and high fields up to 3 T. These measurements allowed extraction of the lower and upper critical fields, H_{c1} and H_{c2}, respectively. Furthermore, field sweeps at constant temperature were used to estimate the shielding effect and to evaluate the maximum volume fraction of the superconducting phase.

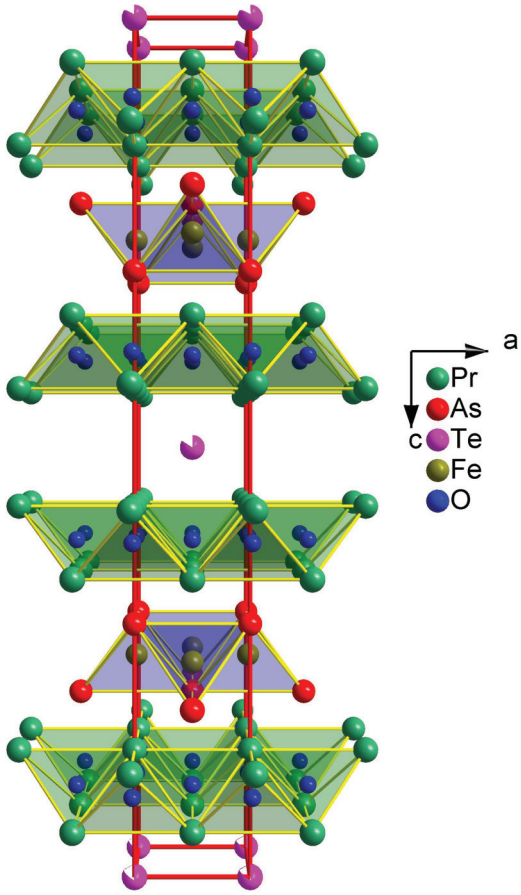

FIG. 1. (Color online) Crystal structure fragment of $Pr_4Fe_2As_2Te_{1-x}O_4$. Blue and green polyhedra indicate $FeAs_4$ and PrO_4 tetrahedra, respectively. The unit cell is outlined in red.

Figure 2(a) shows the results obtained for six single crystals of $Pr_4Fe_2As_2Te_{1-x}O_4$ upon heating the zero-field-cooled (ZFC) state (the virgin state) and upon cooling in a field (FC state). For a 1 mT field, a single-step transition to the superconducting state was observed. This transition broadens with increasing field, as shown in Fig. 2(a) for a 5 mT field. Such broadening of the transition suggests a small value of H_{c1}

TABLE I. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters [Å^2 × 10^3] for $Pr_4Fe_2As_2Te_{1-x}O_4$. Space group is $I4/mmm$, $a = 4.0165(2)$ Å, and $c = 29.8572(16)$ Å.

Atom	Site	x	y	z	U_{iso}[a]	$U_{11} = U_{22}$	U_{33}
Pr_1	4*e*	1/2	1/2	0.0684(1)	9(1)	8(1)	11(1)
Pr_2	4*e*	0	0	0.1480(1)	9(1)	9(1)	10(1)
As_3	4*e*	1/2	1/2	0.2054(1)	12(1)	13(1)	10(1)
Te_4	2*a*	0	0	0	16(1)	18(1)	12(1)
Fe_5	4*d*	1/2	0	1/4	11(1)	10(1)	12(1)
O_6	8*g*	1/2	0	0.1073(2)	10(1)	10(2)	12(2)

[a]U_{iso} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form $-2\pi^2(h^2a^2U_{11} + \cdots + 2hka^*b^*U_{12})$. For symmetry reasons $U_{23} = U_{13} = U_{12} = 0$.

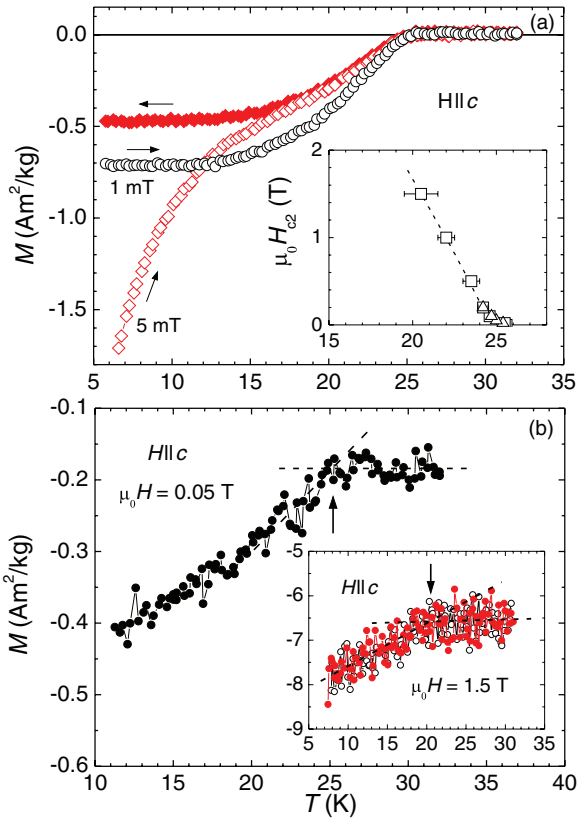

FIG. 2. (Color online) (a) Magnetization versus temperature at low magnetic fields, obtained upon heating from the zero-field-cooled superconducting state (open symbols) and upon cooling in a field from the normal state (closed diamonds), for a set of six single crystals of the $Pr_4Fe_2As_2Te_{1-x}O_4$ compound. The magnetic field is oriented parallel to the c axis of the crystals. The inset shows the upper critical field versus temperature as obtained from the magnetization measurements at higher fields. Results for two series of experiments with different sample mounting are shown (squares and triangles). (b) Magnetization versus temperature at fields of 0.05 and 1.5 T (the inset), for the same set of single crystals as in (a). The H_{c2} values have been taken at the points where the dashed lines cross, as marked by arrows. The inset shows the results obtained for two temperature runs (closed and open symbols). The diamagnetic signal from the sample holder has not been subtracted.

and reveals relatively weak pinning for the sample investigated. This conclusion is consistent with the $M(T)$ results obtained for the FC state, which show a large diamagnetic signal.

At higher applied fields, the superconducting signal decreases; however, it was possible to observe a clear transition to the superconducting state at fields up to 1.5 T. Figure 2(b) shows how the upper critical field was determined from the magnetization measurements. The inset of Fig. 2(a) shows the $H_{c2}(T)$ dependence in the vicinity of the critical temperature $T_c \approx 25.5$ K. For the slope $dH_{c2}/dT \approx -0.35$ T/K, the zero-temperature upper critical field $\mu_0 H_{c2}(0) \approx 6.5$ T has been estimated in the frame of Werthamer-Helfand-Hohenberg theory, assuming no appreciable Pauli paramagnetic limiting.[14] This $H_{c2}(0)$ is rather low compared with those obtained for other FeAs-based superconductors with a similar T_c.

The lower critical field H_{c1} was taken as the first penetration field obtained from the initial $M(H)$ measurements after correction for the demagnetizing effect, for the crystals in a virgin state. The roughly estimated $\mu_0 H_{c1}(5\,\mathrm{K}) \approx 2$ mT and the extrapolated $\mu_0 H_{c2}(0) \approx 6.5$ T were used to evaluate the Ginzburg-Landau parameter $\kappa \approx 80$ from the formula $H_{c2}/H_{c1} = 2\kappa^2/\ln\kappa$. Then the coherence length $\xi \approx 7$ nm was derived from the formula $\mu_0 H_{c2} = \phi_0/2\pi\xi^2$, and finally the penetration depth of $\lambda = \kappa\xi \approx 560$ nm could be obtained.

The shielding effect of the set of six single crystals was estimated from the slope of the $M(H)$ virgin curve obtained at 5 K. The demagnetizing factor was determined from the crystal shape to be $D \approx 0.9$ and the shielding effect was calculated to amount to $(95 \pm 5)\%$. This perfect shielding gives a maximum volume fraction of the superconducting phase of $f \approx 0.95$ (± 0.05) and thus indicates bulk superconducting properties of the $Pr_4Fe_2As_2Te_{1-x}O_4$ compound. Considering the $M(T)$ results obtained at low temperatures and 1 mT field [see Fig. 2(a)], a shielding effect of about 60% ($f \approx 0.6$) may be estimated. This apparently inconsistent result can be fully understood if we bear in mind that due to the demagnetizing factor ($D \approx 0.9$), for the 1 mT applied field, an effective magnetic field of 10 mT appears at the crystal edges. This field is much higher than H_{c1}, and thus the crystals remain in the mixed state.

Measurements of magnetization versus temperature have also been performed for an individual single crystal. These experiments were done with an MPMS with enhanced sensitivity (MPMS-XL). Although the signal-to-noise level was lower than for the collection of six single crystals, the findings were identical, with a critical temperature around 25 K (Fig. 3).

The electrical resistivity (ρ) as a function of temperature was measured on a single crystal using a standard four-probe method in a van der Pauw geometry. Because of the small size of the crystal ($<100\ \mu$m), the platinum contacts were attached by focused ion beam (Fig. 4). The contact resistance was less than 100 Ω, and the measuring current was 100 μA. No heating effect was observed on the resistivity. The superconducting

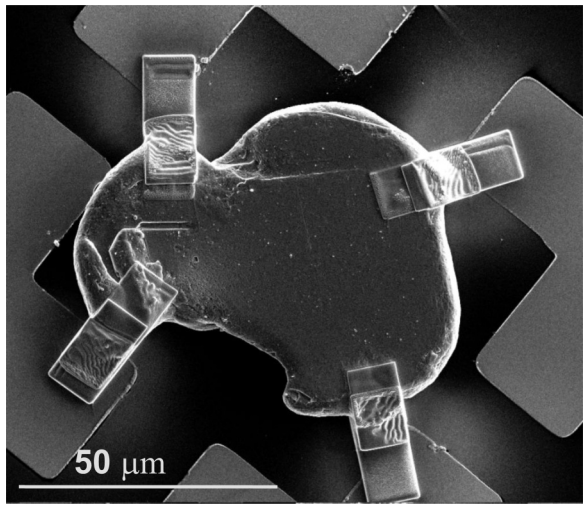

FIG. 4. Single crystal of $Pr_4Fe_2As_2Te_{0.88(1)}O_4$ contacted for resistivity measurements.

transition temperature is reliably $T_c \approx 25$ K (Fig. 5). The value of $\rho(300\ \mathrm{K}) \approx 2$ mΩ cm is 5–10 times higher than for a typical, optimally doped pnictide superconductor. The ρ-T curve corroborates the notion that the sample is underdoped, and very likely some disorder is present in the structure. This disorder might be at the origin of the mild upturn of ρ below 70 K before reaching T_c.

In conclusion, the superconducting compound $Pr_4Fe_2As_2Te_{1-x}O_4$ was synthesized, with T_c of 25 K, and bulk superconductivity was confirmed by dc magnetization measurements. The superconducting state is characterized by the GL parameters $\xi \approx 7$ nm, $\lambda \approx 560$ nm, and $\kappa \approx 80$, and thus this compound should be classified as a strong type-II superconductor.

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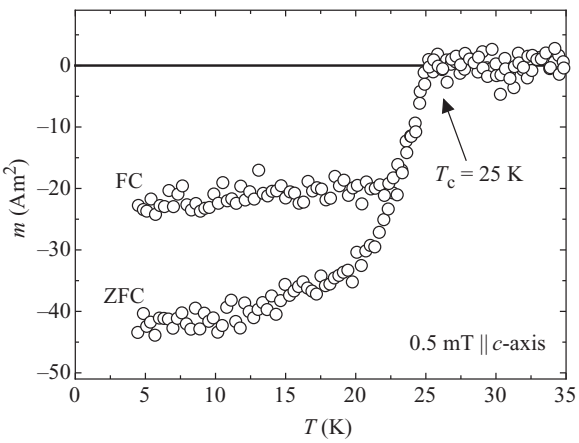

FIG. 3. Temperature dependence of the magnetic moment for $Pr_4Fe_2As_2Te_{0.88(1)}O_4$ single crystal in an applied magnetic field of 0.5 mT along the c axis.

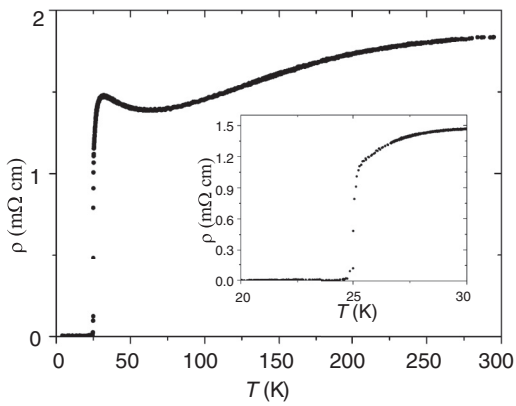

FIG. 5. Temperature dependence of the electrical resistivity for $Pr_4Fe_2As_2Te_{1-x}O_4$ single crystal. Inset shows $\rho(T)$ around the superconducting transition.

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