Drastic change in transport of entropy with quadrupolar ordering in PrFe$_4$P$_{12}$

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The antiferroquadrupolar ordering of PrFe$_4$P$_{12}$ is explored by probing thermal and thermoelectric transport. The lattice thermal conductivity drastically increases with the ordering, as a consequence of a large drop in carrier concentration and a strong electron-phonon coupling. The low level of carrier density in the ordered state is confirmed by the anomalously large values of the Seebeck and Nernst coefficients. The results are reminiscent of URu$_2$Si$_2$ and suggest that both belong to the same class of partial metal-insulator transitions. The magnitude of the Nernst coefficient, larger than in any other metal, indicates a new route for Ettingshausen cooling at Kelvin temperatures.

In Pr intermetallics, the Kondo coupling between $f$-electrons and conduction electrons, the core of heavy-fermion phenomena, presents unique features associated with the double occupancy of the $4f$ orbital. In particular, the filled Skutterudites of the Pr$_2$T$_4$P$_{12}$ family (where Tr stands for Fe, Ru or Os and Pn stands for P, As or Sb) have become a growing subject of investigation. The diversity of electronic instabilities associated with this particular structure (including superconducting, insulating, and metallic phases) is intriguing. The extreme sensitivity of the ground state to small variations suggests a subtle interplay between the orbital degrees of freedom, the crystal electric field and the incomplete hybridization between $f$ electrons and the conduction band.

In this context, the case of PrFe$_4$P$_{12}$ deserves particular attention. This system is host to a phase transition at 6.5 K with sharp signatures in all macroscopic properties. Contrary to what was initially assumed, it does not correspond to an antiferromagnetic (AFM) ordering. In the ordered state, no magnetic Bragg peak is detected by neutron scattering and no internal field is seen by muon spin relaxation measurements. Moreover, nuclear specific heat data rule out any ordered magnetic moment on the Pr site. All these experiments converge to establish the non-magnetic nature of this phase transition. An alternative order parameter, namely an antiferroquadrupolar (AFQ) one has emerged as the most plausible candidate for the ordered state. This scenario would explain both the field-induced staggered magnetic moment and the superlattice reflection resolved by X-ray diffraction. Both of them correspond to the same wave-vector $Q = [1,0,0]$ which, according to the band calculations, is a possible nesting vector of the Fermi surface. The AFQ scenario is also compatible with the magnetization data.

In this Letter, we report on a study of thermal and thermoelectric transport in PrFe$_4$P$_{12}$, which documents a decimation of the Fermi surface with the ordering. According to our analysis, most carriers disappear at the transition, paving the way for an enhanced mean-free-path of both phonons and the residual quasi-particles. Thus, the ordered state of PrFe$_4$P$_{12}$ emerges as a heavy-fermion semi-metal. Such a radical interplay between itinerant electrons and the loss of orbital degrees of freedom contrasts with typical cases of AFQ ordering, such as CeB$_6$ or DyB$_2$C$_2$. It is reminiscent of what was observed in the case of the hidden-order transition in URu$_2$Si$_2$ and provides useful input for the ongoing debate on the identity of hidden order there.

Single crystals of PrFe$_4$P$_{12}$ were grown by a tin-flux method described elsewhere. Nernst effect, thermopower and thermal conductivity were measured using a one-heater-two-thermometer set-up which allowed us to measure all transport coefficients of the sample in the same conditions. For temperatures above 1.5 K a set-up with cernox thermometers in a $^4$He cryostat was used. The data were complemented with subkelvin measurements using another set-up with RuO$_2$ thermometers in a dilution refrigerator. The magnetic field, $H$ was applied perpendicular to the [applied] heat-current ($J_Q$) and the [measured] electric-field ($E$) vectors. For sample no.1 (which had a residual resistivity of $\rho_0 = 23 \mu\Omega$cm), the configuration was $H \parallel [1,1,0]; J_Q \parallel E_x \parallel [0,0,1]$ and $E_y \parallel [1,1,0]$. For sample no.2 ($\rho_0 = 32 \mu\Omega$cm), it was $H \parallel [0,0,1]; J_Q \parallel E_x \parallel [1,1,0]$ and $E_y \parallel [1,1,0]$. Hence, Nernst signal ($N = E_y/E_{\parallel}$) and Seebeck coefficient ($S = E_x/E_{\parallel}$) were measured in adiabatic conditions.

Fig. 1 presents the results of thermal conductivity ($\kappa$) measurements. As seen in the upper panel, the onset of ordering is marked by a steep increase in $\kappa/T$. This enhancement is diminished by the application of a magnetic field which leads to a gradual suppression of the ordering. The effect of ordering on lattice and electronic thermal conductivities can be probed by checking the temperature dependence of the Lorenz number ($L = \frac{\rho_0}{\kappa}$). The lower panel presents the temperature dependence of $L/L_0$ (where $L_0 = 2.44 \times 10^{-8}$ $V^2/K^2$). Its magnitude at $T_Q$ ($\sim 5$ K) quantifies the dominance of the lattice contribution to heat transport. The transition is accompanied by a drastic enhancement in $L/L_0$ which reaches a peak.
value of 18 and then decreases to yield unity in the zero-temperature limit, in agreement with the Wiedemann-Franz (WF) law. If electrons were the only heat carriers, then $L/L_0 < 1$ at finite temperatures and its magnitude would decrease with magnetic ordering. Indeed, the presence of magnetic fluctuations above $T_N$ tends to amplify the relative weight of large-$q$ scattering and to rectify the excess in thermal resistivity produced by the presence of small-$q$ inelastic scattering\cite{18}. The unusual enhancement of $L/L_0$ observed here is reminiscent of (but more dramatic than) what was observed in URu$_2$Si$_2$\cite{16} and could be safely attributed to an increase in the lattice heat transport. We put aside the unlikely hypothesis of a supplementary heat transport by exotic excitations in the ordered state. Indeed, in sharp contrast to what is reported here, heat transport in CeB$_6$ is not affected by AFQ ordering \cite{19}.

The relative weights of electronic, $\kappa_e$ and phononic, $\kappa_{ph}$ contributions to heat transport can be estimated assuming that $\kappa_e$ follows the WF law even at finite temperatures. Since $\rho e^2/\kappa^2$ can become as low as $0.4L_0$ in presence of inelastic scattering, this procedure would only indicate the qualitative trend. As seen in the inset of the upper panel, both components of heat transport are affected by the ordering. While $\kappa_{ph}/T$ displays a steady enhancement of one order of magnitude, $\kappa_e/T$ increases significantly after an initial decrease. This can be understood in a picture similar to the one proposed for URu$_2$Si$_2$\cite{16}. The opening of a gap at the onset of ordering destroys most of the Fermi surface. The associated drop in the density of itinerant electrons leads to a decrease in the phonon scattering and an enhancement of the lattice thermal conductivity. The behavior of $\kappa_e/T$ reflects the combination of a decrease, induced by the drop in the carrier number, and an increase due to the rise in the mean-free-path of the surviving quasiparticles as a consequence of the restricted phase space in the ordered state. Thus, the analysis of thermal conductivity underlines the strength of the electron-phonon coupling in PrFe$_4$P$_{12}$ and points to a large decrease in the carrier density with ordering. Fig. 2 presents the data on the Seebeck coefficient. In agreement with the earli-
est study\textsuperscript{[2]} the absolute value of thermopower, \(S\), was found to increase in the ordered state and attain a large peak (-113 \(\mu\)V/K). By continuing the zero-field measurements down to 0.18 K, a shoulder-like feature around 1 K in \(S(T)\) is also resolved. The application of the magnetic field leads to a gradual suppression of the enhancement in \(S\). The lower panel, which presents the same data as \(S(T)\) vs. temperature, reveals a non-monotonic \(S/T\) at zero field which extrapolates to \(-56 \pm 8\mu\)V/K² at zero temperature. Its absolute value is comparable to the largest \(S/T\) ever reported (+50\(\mu\)V/K² in CeNiSn\textsuperscript{[20]}). In many correlated metals, the absolute value of the dimensionless ratio \(q = \frac{S}{T} \frac{N_{\text{Av}}}{\gamma}\) (\(\gamma\) is the electronic specific heat, \(e\) the elementary charge and \(N_{\text{Av}}\), the Avogadro number) is of the order of unity\textsuperscript{[21]}. Miyake and Kohno have argued that, in the zero-temperature limit, for both Born and unitary limits of scattering, \(S/T\) becomes inversely proportional to the renormalized Fermi Energy and this leads to the observed correlation\textsuperscript{[22]}. Let us recall that when the carrier density is much lower than one itinerant electron per formula unit, a proportionally larger \(|q|\) is expected\textsuperscript{[22]}. For example, in the case of CeNiSn, \(q \approx 107\) is compatible with the very low level of carrier density \((<0.01\text{e}^-/\text{f.u.})\) in this heavy-fermion semi-metal. The relative magnitudes of \(S/T\) and \(\gamma\) is compatible with the low level of carrier density in the ordered state of PrFe\(_4\)P\(_{12}\). At zero-field, \(S/T\) and \(\gamma\approx0.1\) J/(K²mol)\textsuperscript{[2]} yield \(q \approx -58 \pm 10\). At \(B = 5.5\) T, by linearly extrapolating the low-temperature data to \(T=0\), one obtains \(S/T \approx +8 \pm 2\mu\)V/K², and this together with \(\gamma\) (estimated to be \(\approx 1.3\) J/(K²mol) for this orientation\textsuperscript{[23]}, yield \(q \approx 0.6 \pm 0.2\). This simple argument indicates that the high-field state is an ordinary HF metal, and the ordered state is a dilute (with \(~0.02\) carriers per f.u.) liquid of heavy quasi-particles, i.e. a heavy-fermion semi-metal.

Fig. 3 displays the temperature dependence of the Nernst coefficient, \(\nu\), which becomes very large in the ordered state, in particular below \(T_x \approx 2.8\) K and reaches a maximum, \(\nu_{\text{max}}\), around \(T \approx 1.5\) K, which is \(51 \pm 3\mu\)V/KT in sample 1 and \(38 \pm 2\mu\)V/KT in sample 2. Since \(\nu_{\text{max}}^1/\nu_{\text{max}}^2 \sim \rho_0^1/\rho_0^2 \sim 1.3\), \(\nu_{\text{max}}\) appears to inversely scale with \(\rho_0\). These numbers are one order of magnitude larger than what was found in URu\(_2\)Si\(_2\)\textsuperscript{[17]} or in CeCoIn\(_5\)\textsuperscript{[24]}, which are host to Nernst coefficients of exceptionally large magnitudes. The lower panel of the same figure presents the field dependence of the Nernst signal and shows that the destruction of the order by the magnetic field leads to the suppression of \(N\) down to negligibly low values. The giant Nernst signal is indeed a property of the ordered state of PrFe\(_4\)P\(_{12}\).

How can quasi-particles of a non-magnetic metal produce a Nernst signal of such a magnitude? This question brings us to the following relation in the Boltzmann picture\textsuperscript{[15, 25, 26]}:

\[
N = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\partial \tan \theta_H}{\partial \epsilon} \epsilon_F \tag{1}
\]

In other words, the Nernst signal tracks the energy dependence of the tangent of the Hall angle \((\tan \theta_H = \frac{\rho_{xy}}{\rho_{xx}})\) at the Fermi level. Since in a first approximation, this energy derivative is just proportional to \(\frac{\tan \theta_H}{\epsilon_F}\), a combination of a large Hall angle and a small Fermi energy can lead to a very large Nernst signal. Comparing the temperature dependence of \(N/T\) and \(\tan \theta_H\) in Fig. 4 reveals the relevance of this picture to PrFe\(_4\)P\(_{12}\). The two quantities display a striking correlation. Ordering is associated with a jump in \(\tan \theta_H\) which increases by two orders of magnitude and a (much smaller) increase in \(N/T\). Another distinct increase in both quantities is also visible at \(T_x \approx 2.8\) K. The unprecedented magnitude of the Nernst coefficient in the ordered state of PrFe\(_4\)P\(_{12}\) is thus concomitant with a large value of \(\tan \theta_H\). Quantitatively, according to the approximation derived from eq. 1, the low-temperature magnitudes of \(N/T\) and \(\tan \theta_H\) yield \(\epsilon_F \sim 7\) K, comparable to the width of the Kondo resonance (8.7 K) estimated by specific heat\textsuperscript{[26]}.

The phase transition in PrFe\(_4\)P\(_{12}\) is a case of partial or aborted metal-insulator transition (MIT), where
the Fermi surface (FS) is not completely wiped out. Band calculations have found that the main FS is a distorted cube with a strong nesting instability. Experimentally, de Haas van Alphen measurements detected in the ordered state (i.e. for $H < 5T$) a low-frequency branch corresponding to a FS occupying only 0.15 of the first Brillouin zone. This would yield a carrier density of 0.003 holes/f.u. which is compatible with the magnitude of the Hall coefficient at low temperatures (yielding 0.005 holes/f.u.), but significantly lower than the carrier density ($0.02 e^{-}/f.u.$) estimated from the magnitude of the thermomagnetic figure of merit ($\gamma$. This discrepancy points to the presence of other undetected pockets of FS in the ordered state as initially suggested by the contrast between the large value of $\gamma$ and the modest mass enhancement of the only FS detected by dHvA. The unobserved electron-like quasi-particles should be heavier with a shorter mean-free-path. These two assumptions are sufficient to explain why they have escaped detection by dHvA and why they dominate specific heat and thermopower but contribute little to the Hall effect. Assuming that the latter is entirely due to a single FS, one may write: $\tan \theta_H = \frac{R_B}{\sqrt{T}}$ (where $k_F$ and $\ell_c$ are respectively the Fermi wave-vector and the electronic mean-free-path and $\ell_B = \sqrt{\frac{e^2}{m^*}}$ is the magnetic length scale). The enhancement of $\tan \theta_H$ at $T_Q$ reflects combined effect of the shrinking of the Fermi surface and the increase in the mean-free-path. Taking for $k_F$ the average radius of the single FS seen by dHvA measurements, the magnitude of $\tan \theta_H$ at low temperatures implies $\ell_c \sim 4000 A$, compatible with the relatively easy observation of quantum oscillations at 3 T. Very recently, a complete MIT induced by pressure was observed in PrFe$_4$P$_{12}$. Remarkably, both the pressure-induced insulator and the ambient pressure AFQ are destroyed in presence of a magnetic field of comparable magnitude. However, X-ray diffraction measurements under pressure resolve a superlattice reflection present in the AFQ state and none in the pressure-induced insulator pointing to a different mechanism for the two transitions.

Both $N/T$ and $\tan \theta_H$ show a steep increase below $T_x (\sim 2.8 K)$. This temperature is marked by a minimum in $S/T$ (see Fig. 2), a broad shoulder-like feature in specific heat and a minimum in bulk magnetization close to this temperature. This energy scale was observed for both field orientations studied here and does not vary much with the magnetic field (see the inset in Fig. 4). It is too early to identify it as another phase transition in the ordered state since the feature in specific heat is just a broad shoulder.

A number of implications emerge. The consequences of ordering on transport properties in PrFe$_4$P$_{12}$ and in URu$_2$Si$_2$ are similar. In both cases, the transition leads to a drastic, yet incomplete, destruction of the FS. Moreover, according to our analysis, the exceptional magnitude of the Nernst coefficient is just a consequence of three independent factors: a low carrier density, a large mass enhancement and a long mean-free-path. Experiments on heavy-fermion semi-metals would tell if these are the only ingredients needed to produce a Nernst signal of such a magnitude, or there is any additional source specific to the exotic orders. An Ettingshausen cooler is conceivable when the thermomagnetic figure of merit ($Z/T = N^2/\ell$) is close to unity. For a metal, this requirement means $N \approx \sqrt{\ell} = 153 \mu V/K$. To the best of our knowledge, PrFe$_4$P$_{12}$ is the first case of a metal approaching this value at 1 K.

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