CeFePO: A Heavy Fermion Metal with Ferromagnetic Correlations

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The ground state properties of CeFePO, a homologue of the new high temperature superconductors RFePnO$_{1-x}$F$_x$, were studied by means of susceptibility, specific heat, resistivity, and NMR measurements on polycrystals. All the results demonstrate that this compound is a magnetically nonordered heavy fermion metal with a Kondo temperature $T_K \sim 10$ K, a Sommerfeld coefficient $\gamma = 700$ mJ/mol K^2, and a mass enhancement factor of the order of 50. Analysis of the susceptibility data and of the spin relaxation time indicates that the strong electronic correlation effects originate from the Ce-4f electrons rather than from Fe-3d electrons. An enhanced Sommerfeld-Wilson ratio $R = 5.5$ as well as a Korringa product $S_0/T_1TK^2 \simeq 0.065$ well below 1 indicate the presence of ferromagnetic correlations. Therefore, CeFePO appears to be on the nonmagnetic side of a ferromagnetic instability.

The compounds RTPnO (R: rare earth, T: transition metal, Pn: P or As) have started to attract considerable attention because of the recent discovery of superconductivity with a transition temperature T_c exceeding 50 K in the RFeAsO$_{1-x}$F$_x$ series [1–4], being the highest T_c except for cuprate systems. This high T_c superconducting state appears to be of unconventional nature and related to the disappearance of an Fe-based spin density wave. While recent reports focus on the importance of electronic correlation effects due to 3d electrons close to a magnetic state, the homologous compounds with $R =$ Ce are attractive candidates for 4f-electron induced strong correlation effects. Thus last year, we presented a detailed study of the properties of CeRuPO and CeOsPO [5–7] and demonstrated that the former one is a rare example for a ferromagnetic (FM) Kondo lattice with a FM Ce ordering temperature $T_C = 15$ K and a Kondo temperature $T_K \sim 10$ K, while the latter one shows antiferromagnetic (AFM) order of stable trivalent Ce below $T_N = 4.5$ K. More recently, superconductivity at 41 K was also reported in CeFeAsO$_{1-x}$F$_x$ [4], but the relevance of 4f correlations could not yet be analyzed because of the very limited amount of experimental data. In this Letter we present a complete study of the basic physical properties of CeFePO using susceptibility $\chi(T)$, specific heat $C(T)$, and resistivity $\rho(T)$ measurements as well as NMR as a local probe. The analysis of our results indicates that CeFePO is a magnetically nonordered heavy fermion metal with strong 4f-based electronic correlations and FM fluctuations, while Fe correlations seem to be of minor importance. After submission of this Letter, a very precise investigation of LaFePO was reported by McQueen *et. al.* [8]. These authors conclude that LaFePO is a nonmagnetic metal with only weak exchange enhancement from spin fluctuations.

Polycrystalline samples were synthesized using a Sn-flux method in evacuated quartz tubes as described in [5,9]. Several powder x-ray diffraction patterns recorded on a Stoe diffractometer in transmission mode using monochromated Cu-K_α radiation ($\lambda = 1.5406$ Å) confirmed the $P4/nmm$ structure type and the formation of single phase CeFePO. The lattice parameters $a = 3.919(3)$ Å and $c = 8.330(5)$ Å refined by simple least squares fitting were found to be in good agreement with the reported structure data [10]. Susceptibility measurements were performed in a commercial Quantum Design (QD) magnetic property measurement system (MPMS). $\rho(T)$ was determined down to 0.4 K using a standard ac four-probe geometry in a QD physical property measurement system (PPMS). The PPMS was also used to measure $C(T)$ with a standard heat-pulse relaxation technique. NMR measurements are carried out by monitoring the spin-echo intensity as a function of applied field at a fixed frequency (12.1, 27, 76.4, and 130 MHz). Shift values are calculated from the resonance field H^* by $K = (H_L - H^*)/H^*$ whereas the Larmor field H_L is given by using H$_3$PO$_4$ with $^{31}K = 0$ as a reference compound. Relaxation rates $^{31}(1/T_1)(T)$ are determined by using the saturation recovery method.

We start by briefly presenting the results of $\chi(T)$ of CeFePO. Below 350 K, $\chi(T)$ of CeFePO increases with decreasing temperature following a Curie-Weiss law down to 100 K [Fig. 3 inset (b)]. The effective moment $\mu_{\mathrm{eff}} = 2.56 \ \mu_B$, being almost identical to the expected value $\mu_{\mathrm{eff}} = 2.54 \ \mu_B$ for a free trivalent Ce ion, and the moderate Weiss temperature $\theta_W = -52$ K indicate a nearly stable trivalent Ce state and the absence of a significant contribution of a paramagnetic Fe moment in this temperature range. Below 100 K, $\chi(T)$ deviates from the Curie-Weiss law, increasing stronger with decreasing temperature than expected, which is attributed to crystal electric field effects. Below 10 K, the measured bulk susceptibility becomes strongly field dependent, showing a pronounced increase for low fields $\mu_0H < 1$ T, while for larger fields $\chi(T)$ levels off at a constant value $\chi_0 = 660 \times 10^{-9}$ m^3/mol. While such a field dependence is usually

attributed to paramagnetic defects or impurities, the NMR results suggest this to be an intrinsic property of CeFePO (see below). No anomaly corresponding to magnetic order could be resolved at any field. Thus, a preliminary analysis of these susceptibility data suggests a paramagnetic Kondo lattice. This conclusion is confirmed by the results of the specific heat measurements, plotted as C^{4f}/T vs T in Fig. 1. The $4f$ contribution C^{4f} to the specific heat was obtained by subtracting the reported specific heat data of LaFePO [8]. Below 10 K, C^{4f}/T increases logarithmically down to 1 K, where it levels off at a constant value $\gamma = 700$ mJ/mol K^2. No anomaly indicating a phase transition can be resolved above 0.4 K. Application of a small magnetic field $\mu_0 H < 1$ T does not change $C^{4f}(T)$, while a larger field leads to a smooth decrease of C^{4f}/T at low temperatures. The former result confirms the absence of long-range magnetic order, while the latter one is incompatible with spin-glass-type behavior. Therefore, the large C^{4f}/T value at low T has to be attributed to heavy fermions and γ corresponds to a strongly enhanced Sommerfeld coefficient in the electronic (heavy-fermion-based) specific heat. Comparing this with the Sommerfeld coefficient of the nonmagnetic LaFePO ($\gamma = 12.5$ mJ/mol K^2) [8], one estimates a low-temperature enhancement factor of the order of 50 for the heavy quasiparticles in CeFePO. The magnetic entropy $S(T)$ was calculated by integrating the measured $C^{4f}(T)/T$ over T for $T < 10$ K. The entropy $S(T)$ reaches $0.5R \ln 2$ at 5 K, indicating a Kondo temperature $T_K \sim 10$ K. The absolute values of $C(T)$, its temperature dependence as well as the deduced Kondo temperature are very close to those of the archetypical heavy fermion metal CeCu$_2$Si$_2$ [11]. The temperature dependence of the electrical resistivity $\rho(T)$ shown in inset (a) of Fig. 1 presents the typical behavior of a Kondo lattice system and thus confirms the above conclusion. Below 300 K, $\rho(T)$ decreases almost linearly, before dropping rapidly below 30 K due to the onset of coherent Kondo scattering. Below $T = 1$ K [see inset (b) of Fig. 1], $\rho(T)$ follows a $\rho \propto T^2$ dependence indicating the formation of a Landau-Fermi liquid ground state in agreement with the specific heat data.

However, the absolute value of $\rho(T)$ is rather high; very likely, this is not intrinsic of CeFePO but due to the granularity of the polycrystalline sample.

In order to get a deeper insight into the many-body phenomena in this compound, we used ^{31}P-NMR as a microscopic local probe. A typical set of spectra at different temperatures is shown in Fig. 2 for a NMR frequency of 76.4 MHz (corresponding to 4.47 T). One single narrow ^{31}P-NMR line as expected from the crystal structure was found at room temperature (right-hand panel of Fig. 2). It develops strong anisotropy towards lower temperatures (left-hand panel of Fig. 2). The shape is characteristic of a powder pattern from a spin $I = 1/2$ nucleus in a tetragonal symmetry. The broadened ^{31}P-NMR lines could be simulated consistently at all temperatures with shift-tensor components $K_{ab}(T)$ and $K_c(T)$ corresponding to the $H \perp c$ and $H \parallel c$ directions, respectively (inset in Fig. 2). The relative shift values $^{31}K_{ab}(T)$ and $^{31}K_c(T)$ are both positive, in contrast to the results obtained for CeRuPO and CeOsPO [5]. While $^{31}K_c(T)$ is almost independent of T, $^{31}K_{ab}(T)$ increases strongly with decreasing temperatures (Fig. 3). Above 15 K, $^{31}K_{iso} = (2K_{ab}/3) + (K_c/3)$ tracks the bulk susceptibility $\chi(T)$ obtained by MPMS measurements at 5 T [inset (a)]. Below 10 K, the line shape of the spectra becomes field dependent. While at high fields ($\mu_0 H > 7$ T) the line shape observed at higher temperatures is maintained down to 2 K, reducing the field below 4 T leads to a strong broadening of the contribution related to $H \perp c$ and to a shift of its maximum to lower K values. In contrast, the contribution connected with $H \parallel c$ is not affected. Since foreign phases or impurities usually do not contribute to the NMR signal [12], and since impurities would not show such an anisotropic behavior, this broadening cannot be explained by disorder or impurities. Such a broadening is typical for the onset of short-range ferromagnetic correlations. These correlations are likely to be
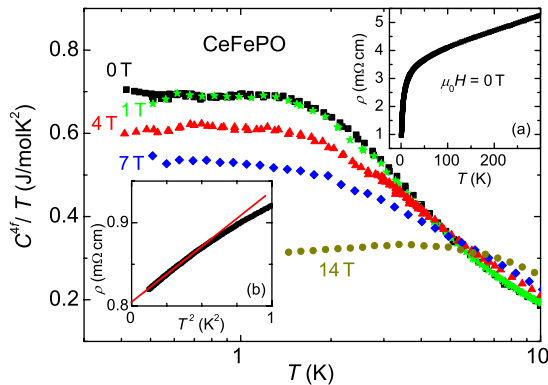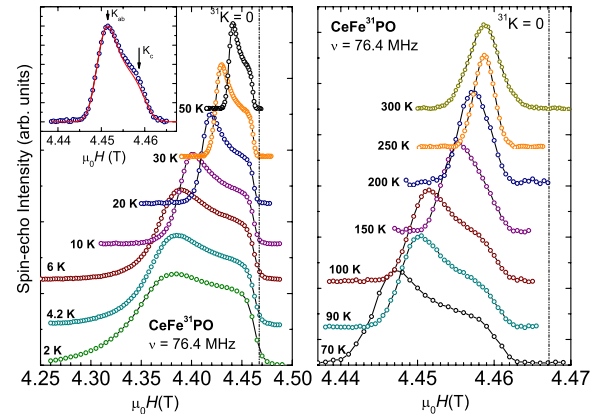

FIG. 1 (color online). $4f$ increment to the specific heat of CeFePO plotted as C^{4f}/T vs T in different magnetic fields. Inset (a) shows $\rho(T)$ and (b) $\rho(T^2)$.

FIG. 2 (color online). ^{31}P field-sweep NMR spectra at $\nu = 76.4$ MHz and different temperatures. Vertical dashed lines indicate the Larmor field obtained from a reference compound. Inset shows a typical powder spectrum, together with the simulation at $T = 50$ K (arrows indicate resonance fields H^* for the $H \perp c$ and $H \parallel c$ direction).
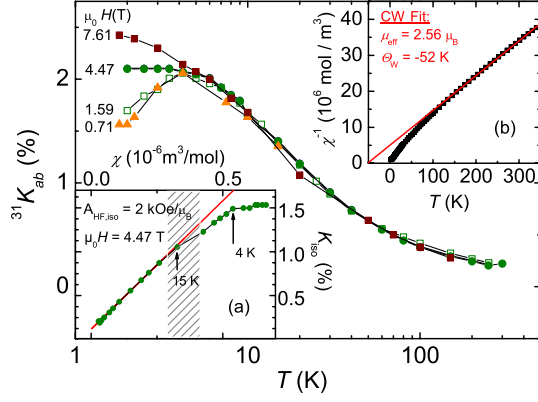
FIG. 3 (color online). Shift component $^{31}K_{ab}$ as a function of temperature in different magnetic fields as indicated [Field values were calculated from NMR frequency using $(^{31}\gamma_{\mathrm{NMR}}/2\pi) = 17.10$ MHz/T]. Inset (a) shows the isotropic shift $^{31}K_{\mathrm{iso}} = (2K_{ab}/3) + (K_c/3)$ versus isotropic (bulk) susceptibility from MPMS measurements (5 T). Inset (b) shows $\chi^{-1}(T)$, solid line corresponds to a Curie-Weiss (CW) fit.

responsible for the field dependent low T increase in $\chi(T)$, too. Since only the component $H \perp c$ is affected in the NMR spectra, only the basal-plane components of the magnetic moments start to be ferromagnetic correlated. This strong anisotropy supports that these correlations originate from the Ce moments. A fit of the whole spectra still leads to a reasonably well defined K_{ab} value, but the resulting K is now field dependent. At high fields, K_{ab} increases down to the lowest T, while at low fields it shows a clear maximum. This specific field dependence appears to indicate that CeFePO is close to a ferromagnetic instability.

Finally, we present spin-lattice-relaxation (T_1) data on CeFePO. T_1 measurements were performed as a function of temperature at two different frequencies, 27 and 76.4 MHz (corresponding to 1.59 and 4.47 T, respectively), at the $H \perp c$ position of the anisotropic NMR line (left arrow in the inset of Fig. 2). The nuclear magnetization recovery curves $M(t)$ could be fitted at any temperature and field with a standard single exponential function. $^{31}(1/T_1T)$ plotted in Fig. 4 increases monotonically over 2 orders of magnitude upon cooling down from 300 to 4 K. At lower temperatures, $^{31}(T_1T)^{-1}$ stays constant at about 20 (s K)$^{-1}$. Since NMR data on the reference compound LaFePO are presently not available, we note that the homologue LaRuPO has a $^{31}(T_1T)^{-1}$ value $\simeq 1$ (s K)$^{-1}$, more than 1 order of magnitude smaller than that of CeFePO. Even $1/T_1T$ of ^{75}As in doped LaFeAO$_{1-x}$F$_x$ [13,14] is smaller than that of ^{31}P in CeFePO indicating that the relaxation is dominated by the $4f$ contribution. No significant frequency or field dependence of T_1 could be detected in CeFePO, in contrast to the behavior of $K(T)$. In Kondo lattice systems, $1/T_1T$ is dominated by the contribution of the $4f$ electrons, which is within simple approximations proportional to the ratio of the static susceptibility $\chi(T)$ and the dynamical relaxation rate $\Gamma(T)$ of the $4f$
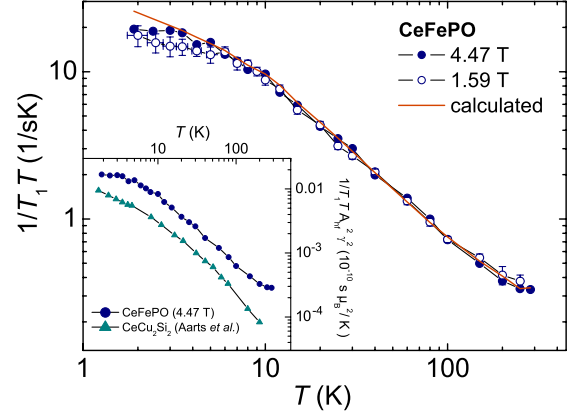

FIG. 4 (color online). $^{31}(1/T_1T)$ as a function of temperature for different fields as indicated. Solid line represents the calculation described in the main text. Inset shows the comparison with ^{29}Si-NMR ($I = 1/2$) results on CeCu$_2$Si$_2$ (data taken from Ref. [20]). $(1/T_1T)$ is normalized by $(A_{\mathrm{hf,iso}}\gamma_{\mathrm{NMR}})^2$.

electrons, $1/T_1T \propto \chi(T)/\Gamma(T)$ [15–18]. Further on, for a Kondo system one may expect $\Gamma \propto \sqrt{T}$ for $T > T_K$ [19], but merging into a constant value $\propto T_K$ at low T. Since for $T > 10$ K, $\chi(T)$ and $K(T)$ are proportional, we calculated the temperature dependence of $1/T_1T$ using $1/T_1T = aK(T)/\sqrt{T}$, where a is just a T-independent parameter to scale the whole curve to the absolute experimental values. We added a small T-independent contribution $(T_1T)^{-1} = 0.12$ (s K)$^{-1}$ to account for the contribution of the conduction electrons at high T, where the contribution of the $4f$ electrons is vanishing. The results of this calculation shown as the solid line in Fig. 4 agree very well with the data from 300 K down to 10 K, showing that the dynamical relaxation rate Γ indeed follows the expected $\sqrt{T}$ behavior. The deviation below 10 K is as expected, since $\Gamma(T)$ should merge in a constant value instead of decreasing further. Further on, we compare in the inset of Fig. 4 $^{31}(1/T_1T)$ of CeFePO with ^{29}Si-NMR ($I = 1/2$) results of the prototypical heavy fermion metal CeCu$_2$Si$_2$ [20] which has a similar Kondo scale. For CeCu$_2$Si$_2$ we specifically chose the NMR results on ^{29}Si in order to compare data of two nuclei with $I = 1/2$ and used the results of Aarts *et al.* [20], because these data were obtained at a field comparable to our measurements at 76.4 MHz (4.47 T). To account for different NMR nuclei and hyperfine couplings, $1/T_1T$ values are divided by $(A_{\mathrm{hf,iso}}\gamma_{\mathrm{NMR}})^2$. The comparison can then be performed on an absolute scale without having introduced model dependent parameters. Both curves share the same overall temperature dependence, but CeFePO shows larger absolute values. The very similar T dependences $\propto \chi(T)/\sqrt{T}$ found for CeFePO and CeCu$_2$Si$_2$ hint at similar spin-fluctuation relaxation mechanisms in both compounds and confirm that the strong correlation effects in CeFePO originate from the Ce-$4f$ electrons rather than from Fe-$3d$ electrons. Further on, since this similarity is observed on the same absolute temperature scale, it confirms comparable Kondo tempera-

tures in both compounds. The larger values of the normalized $1/T_1T$ in CeFePO perfectly agree with the higher susceptibility. For CeFePO, $\chi(2\,\text{K})$ saturates at $660 \times 10^{-9}\,\text{m}^3/\text{mol}$ in high fields whereas for CeCu$_2$Si$_2$ $\chi(2\,\text{K}) \approx 100 \times 10^{-9}\,\text{m}^3/\text{mol}$ was published [21]. Since both compounds have almost the same Sommerfeld coefficient in their electronic specific heat, a larger susceptibility implies an enhanced Sommerfeld-Wilson ratio $R = \chi/\gamma R_0$, $R_0 = \pi^2 k_B^2/(\mu_0 \mu_{\text{eff}}^2)$ in CeFePO. With $\mu_{\text{eff}} = 1.73 \mu_B$ corresponding to an average value $\mu_{\text{sat}} = 1\,\mu_B$ expected for a Ce^{3+} doublet ground state [22], we obtain $R = 5.5$, which highlights the presence of dominating FM correlations in CeFePO. This scenario is supported by the analysis of the Korringa product given by $T_1 T K^2 \equiv S_0 = \mu_{\text{eff}}^2/3\pi\hbar k_B \gamma_n^2$. Magnetic correlations modify this relation by introducing an enhancement factor $K(\alpha)$, given by $T_1 T K^2 = S_0/K(\alpha)$ where $K(\alpha) > 1$ and $0 < K(\alpha) < 1$ reflects the existence of AFM and FM correlations among the quasiparticles, respectively. For CeFePO, a value of $K(\alpha) \simeq 0.065$ is found at 2 K (4.47 T), in fact indicating strongly dominating FM correlations. A value $K(\alpha) \ll 1$ is also found in other heavy fermion metals with dominating FM correlations like YbRh$_2$Si$_2$ [23] and CeRu$_2$Si$_2$ [24]. In contrast, for CeCu$_2$Si$_2$ with dominating AFM correlations, $K(\alpha) > 1$ was determined [25].

To conclude, we prepared polycrystalline samples of CeFePO by a Sn-flux technique and determined its ground state properties by means of susceptibility, specific heat, electrical resistivity, and NMR measurements. $\chi(T)$ follows a Curie-Weiss law at high temperatures with an effective moment expected for free trivalent Ce^{3+} but levels off below 4 K at a constant, enhanced Pauli susceptibility $\chi_0 = 660 \times 10^{-9}\,\text{m}^3/\text{mol}$. $C^{4f}(T)/T$ increases logarithmically below 10 K and also saturates below 2 K at $\gamma = 700\,\text{mJ/K}^2\,\text{mol}$. The temperature dependence of $\rho(T)$ presents the typical behavior of a heavy fermion metal with a strong decrease when cooling down to below 30 K due to the onset of coherent Kondo scattering. In the NMR measurements, $1/T_1T$ increases roughly with $\chi(T)/\sqrt{T}$ upon cooling from 300 to 10 K, but saturates below 10 K at a strongly enhanced Korringa term. Thus, CeFePO presents the typical properties of a classical Ce-based heavy fermion metal. At low T, we observe the behavior expected for a Landau-Fermi liquid: a T-independent susceptibility χ_0, a T-independent $C(T)/T$, a T-independent $1/T_1T$, as well as a resistivity increment with T^2. None of the investigated properties give evidence for magnetic ordering above 0.4 K. Therefore, CeFePO may be classified as a paramagnetic heavy fermion metal. The absence of significant Fe contribution to the effective moment at elevated temperatures indicates that the magnetism in CeFePO is dominated by the Ce-$4f$ electrons. Thus, the observed strong electronic correlation effects originate from the Ce-$4f$ electrons rather than the Fe-$3d$ electrons. An enhanced Sommerfeld-Wilson ratio as well as a reduced Korringa product highlight the presence of dominat-

ing FM correlations. Therefore, CeFePO is likely to be located on the nonmagnetic side close to a FM instability.

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