

Interplay between Fe 3*d* and Ce 4*f* magnetism and Kondo interaction in CeFeAs_{1-x}P_xO probed by ⁷⁵As and ³¹P NMR

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A detailed ³¹P (I=1/2) and ⁷⁵As (I=3/2) NMR study on polycrystalline CeFeAs_{1-x}P_xO alloys is presented. The magnetism of CeFeAsO changes drastically upon P substitution on the As site. CeFePO is a heavy fermion system without long range order whereas CeFeAsO exhibits a Fe-3*d* SDW type of ordering accompanied by a structural transition from tetragonal (*TT*) to orthorhombic (*OT*) structure. Furthermore Ce-4*f*¹ orders antiferromagnetically (AFM) at low temperature. At the critical concentration where the Fe-magnetism is diminished the Ce-Ce interaction changes to a ferromagnetic (FM) type of ordering. Three representative samples of the CeFeAs_{1-x}P_xO (*x*=0.05, 0.3 and 0.9) series are systematically investigated. 1) For the *x*=0.05 alloy a drastic change of the line width at 130 K indicates the AFM-SDW type of ordering of Fe and the structural change from *TT* to *OT* phase. The line width roughly measures the internal field in the ordered state and the transition is most likely first order. The small and nearly constant shift from ³¹P and ⁷⁵As NMR suggests the presence of competing hyperfine interactions between the nuclear spins and the 4*f* and 3*d* ions of Ce and Fe. 2) For the *x*=0.3 alloy, the evolution of the Fe-SDW type of order takes place at around 70 K corroborating the results of bulk measurement and μ SR. Here we found evidence for phase separation of paramagnetic and magnetic SDW phases. 3) In contrast to the heavy fermion CeFePO for the *x*=0.9 alloy a phase transition is found at 2 K. The field-dependent NMR shift gives evidence of FM ordering. Above the ordering the spin lattice relaxation rate ³¹(1/T₁) shows unconventional, non-Korringa like behaviour which indicates a complex interplay of Kondo and FM fluctuations.

PACS numbers:

I. INTRODUCTION:

The rare earth transition metal pnictides *RTPnO* (*R*: rare earth, *T*: transition metal, *Pn*: P or As) attracted considerable attention because of the startling discovery of superconductivity (SC) in the *RFeAsO*_{1-x}F_x series of compounds at elevated temperatures above 50 K that are surpassed only in the cuprate superconductors [1–7]. In CeFeAsO, antiferromagnetic (AFM) ordering is achieved by the Ce moments at 3.7 K whereas the high-temperature region is dominated by the 3*d* magnetism of Fe which culminates in a SDW type of AFM order of Fe at ~145 K. Interestingly, there is a structural transition from a tetragonal (*TT*) to an orthorhombic (*OT*) phase at ~150 K. Neutron scattering and muon spin relaxation μ SR experiments suggest that there is a sizeable inter-layer coupling in CeFeAsO [12, 14, 15]. Recent studies of CeRuPO and CeOsPO [8–10], on the other hand, indicate that CeRuPO is a rare example of a ferromagnetic (FM) Kondo lattice showing FM order of Ce at *T*_C=15 K and a Kondo energy scale of about *T*_K ≈ 10 K. In contrast, CeOsPO shows AFM order at *T*_N=4.5 K. However, recent studies of the Fe derivative CeFePO suggest that this is a heavy fermion metal close to a FM instability in which the magnetism is dominated by the 4*f* electrons [11].

The Fe 3*d* magnetism in these systems is very sensitive to the electronic environment. The interplay between SC and magnetism was vividly demonstrated by the electron doping studies in CeFeAsO_{1-x}F_x (*T*_c ≈ 41 K [16]) as well as in pressure studies on optimally doped CeFeAsO [17]. In this work we broaden investigations into electronic phenomena and the participation of electrons superconductivity and magnetism in the CeFeAsO system by substituting As in CeFeAsO by the smaller P ion. This approach seems especially attractive as it involves strong electronic correlations in heavy-fermion CeFePO. Theoretical work suggests that the Fe pnictide series where P is progressively substituted for As may present a route to magnetic quantum criticality [18]. In this context, the substitutional series CeFeAs_{1-x}P_xO appears to be especially attractive presenting a crossover from AFM fluctuations to FM fluctuations. This is already evidenced by the recent research work done by Luo. et. al [19]. Additional work [13], from which the phase diagram shown in Fig. 1 has been reproduced, illustrates the appealing standoff between cooperative (SDW, AFM, FM) and correlational (Kondo) phenomena in doped CeFeAs_{1-x}P_xO, which is the topic of this work. The primary macroscopic investigations of these alloys suggest that by increasing the P doping concentration the Fe-SDW type anomaly shifts to lower temperature and is completely suppressed at the critical concentration of *x*_c=0.35 [20]. Here, in addition, the nature of the Ce 4*f* magnetism changed from AFM to FM. Between *x*=0.35 to *x*=0.9 the ground state is governed by the long range Ce 4*f* based FM.

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Fe magnetism is absent beyond $x=0.35$. Above about $x \approx 0.9$ long range FM Ce order disappears and makes way to the Kondo interaction. This is in line with our earlier findings[11] which conveyed the heavy-fermion nature close to FM order in the $x=1$ system, CeFePO. In fact, the system appears to be partial to FM order as is demonstrated by appropriately small elemental substitution (As on the P site or Ru on the Fe site)[8]. In this paper we report ^{31}P ($I=1/2$) and ^{75}As ($I=3/2$) NMR studies on $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ with $x=0.05, 0.3$, and 0.9 (see Fig. 1) as a function of field and temperature. Whereas there is already an abundance of research reported on NMR work on $R\text{FePnO}$ type Fe pnictides involving various elements in the place of R , to our knowledge there exists at present only one paper concerning ^{75}As -NMR studies specifically on the CeFeAsO compound. Moreover, the present work involving ^{31}P -NMR provides an important advance on existing NMR studies by conspicuously addressing the role of the P-dopant in $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$. The rather complex $I = 3/2$ spectra did not enable clarification of the Fe AFM (SDW type) ordered state [24], -a topic which we sought to address in this work and hence this work involving ^{31}P -NMR provides an important advance on existing NMR studies. A very small P substitution ($x = 0.05$) in CeFeAsO affords the opportunity to probe ^{31}P as a favorable $I = 1/2$ nucleus with less complex spectra than those obtained in ^{75}As -NMR, yet without impacting severely on the magnetism in CeFeAsO. Besides, employing an $I = 1/2$ nucleus obviates the need to account for quadrupolar interactions.

II. EXPERIMENTAL

Polycrystalline $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ samples were synthesized using a Sn flux method in evacuated quartz tubes as described in Ref [12, 13] (where x denotes the nominal phosphorous content). The phosphorus concentration was confirmed by EDX analysis. X-ray powder diffraction showed only tiny foreign phases and the determined lattice spacings allowed for an estimation of the P concentration by using Vegard's rule. For NMR measurements, the powder samples were fixed in paraffin to ensure a crystallographically random orientation and to prevent signal reduction due to the skin-depth effect. ^{31}P and ^{75}As NMR measurements were performed with a standard pulsed NMR spectrometer (Tecmag) at the frequency 75 MHz (^{31}P -NMR) and 48 MHz (^{75}As -NMR) as a function of temperature. The field-sweep NMR spectra were obtained by integrating the echo in the time domain and plotting the resulting intensity as a function of the field. Shift values are calculated from the resonance field H^* by $K(T) = (H_L - H^*)/H^*$ whereas the Larmor field H_L is given by using H_3PO_3 (^{31}P -NMR) and GaAs (^{75}As -NMR) as reference compounds. Spin-lattice relaxation time (T_1) measurements were carried out by the standard saturation recovery method. On the As rich side of the phase diagram the very short T_1 lifetimes

turned out too short to be measured, but no such difficulty was encountered at the P-rich side ($x = 0.9$). We profited from this fact by additionally conducting field-dependent ^{31}P -NMR in the $x = 0.9$ sample in order to probe the low-temperature Ce-based FM order.

III. RESULTS

In this paper NMR results on the ^{31}P and ^{75}As nuclei on three different $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ samples are presented. The first one ($x = 0.05$) is close to the undoped end-point compound CeFeAsO. The midpoint concentration ($x = 0.3$) is located at the border where Fe magnetism is suppressed. The P-rich composition ($x = 0.9$) was chosen close to the heavy-fermion metal CeFePO as well as to enable detection of the FM order. Therefore, the three samples represent appropriate regions of interest on the complex phase diagram of this alloy system. In the following section on ^{31}P and ^{75}As NMR results are discussed in the context of magnetic and structural transitions in the As-rich sample in particular, and the Kondo interaction competing with the RKKY interaction in the As-poor samples.

A. ^{31}P and ^{75}As NMR for $x=0.05$: the SDW transition region

Figure 2 shows the ^{31}P field sweep NMR spectra at different temperatures. At high temperature a single narrow line is observed, as expected for a TT system. On lowering the temperature the overall features of the spectra remain largely invariant down to 132 K. No significant shift is observed down to this temperature. With further lowering of temperature to 130 K, a weak signal-to-noise ratio develops because of enormous line broadening in the ^{31}P NMR spectra. As a result we are unable to resolve ^{31}P NMR spectra. This is ascribed to SDW-type AFM ordering that develops abruptly between 132 and 130 K, resulting in a reduction in T_1 . Nevertheless, towards lower temperatures at around 5 K the ^{31}P NMR line re-emerged as a half-square like line shape.

The Full Width at Half Maximum (FWHM) of powder spectra in the AFM ordered state provides an rough estimate of the prevailing internal field of the system as sensed by the nuclei being probed [21–23].

The horizontal double arrows in Fig. 2 show the internal field at FWHM. Approaching the ordered phase from the paramagnetic state evidently produces a rather drastic change of the internal field. Although the overall spectra are hardly shifted with respect to field upon lowering the temperature. This is in contrast to ^{31}P NMR finding for the pure CeFePO system [11]. The temperature-independent shift found for the sample $x = 0.05$ indicates a cancelling out of hyperfine field contributions originating from Ce and Fe at the P-site. Furthermore, the cancellation could also be come by between the moments

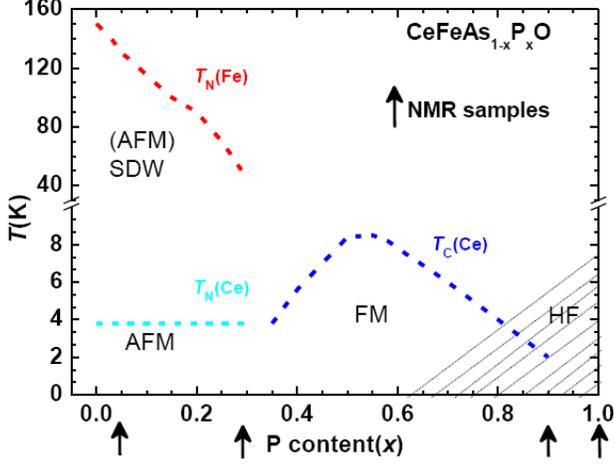


FIG. 1: Schematic phase diagram based on the Refs. [13, 19, 20, 47]. NMR samples are marked by \uparrow .

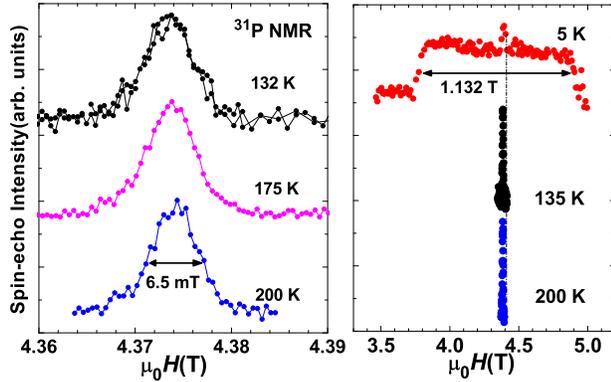


FIG. 2: ^{31}P field sweep NMR spectra for $x = 0.05$ at a selection of temperatures above the SDW transition (left) and well inside the ordered region at 5 K (right, expanded x-axis).

of the Fe-sublattice themselves with P either occupying symmetric positions in the magnetic lattice or random positions in an incommensurate SDW. The vertical line in the right-hand side panel of Fig. 2 shows the position of the Larmor field.

Figure 3 shows the ^{75}As field sweep NMR spectra at different temperatures (top part of the left panel). The central transition of the ^{75}As NMR spectra shows a pronounced second-order quadrupolar splitting indicating relatively large quadrupole interaction. The full ^{75}As NMR spectrum at 150 K as well as the central part of the 132 K spectrum are shown at the lower panel. Arrows indicate the location of satellite transitions. The

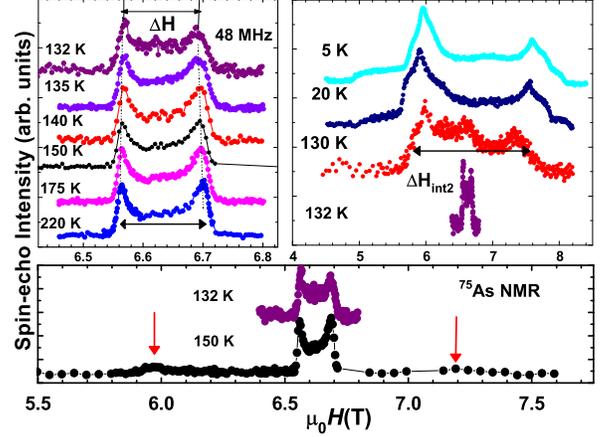


FIG. 3: ^{75}As field sweep NMR spectra at different temperatures for $x=0.05$. The upper left panel shows the central transition with pronounced second-order quadrupolar splitted ^{75}As NMR spectra above the SDW transition. Lower panel shows the ^{75}As spectra at 150 K and 132 K. Upper right panel shows the ^{75}As spectra close to (132 and 130 K) and below (20 and 5 K) the SDW transition.

upper right-hand panel provides a comparison of the spectra above and below the SDW transition. Typical powder response with strong quadrupole coupling is evident. The NMR response evolves insidiously with temperature down to 132 K. Further cooling, however, results in strong broadening of the resonant line and consequently considerable losses in the signal-to-noise ratio. Similar ^{75}As NMR spectra were also reported for NdFeAsO [28] in which the line profiles were explained in terms of the asymmetry parameter η (here $\eta = (V_{xx} - V_{yy})/V_{zz}$, and V_{xx} , V_{yy} and V_{zz} represent the electric field gradients for three principle axes). Interestingly, except for the weak resonance near 6.6 T at $T = 130$ K, the nature of the line shape remains invariant down to low temperatures.

The resonance at 6.6 T, originating at high temperatures and thus clearly a feature of the paramagnetic phase, can be found down to 130 K. Below this temperature the line broadening signals SDW type of ordering, and one concludes that in a narrow temperature window below SDW ordering the paramagnetic phase and SDW-ordered phase may co-exist.

The splitting ΔH_Q of the central NMR resonance due to second-order quadrupolar interaction is given by [29, 30];

$$\Delta H_Q = \frac{\nu_Q^2}{48\gamma_N^2 H} (25 - 22\eta + \eta^2), \quad (1)$$

where γ_N and ν_Q represents the gyromagnetic ratio of ^{75}As (7.292 MHz/10 kOe) and nuclear quadrupolar

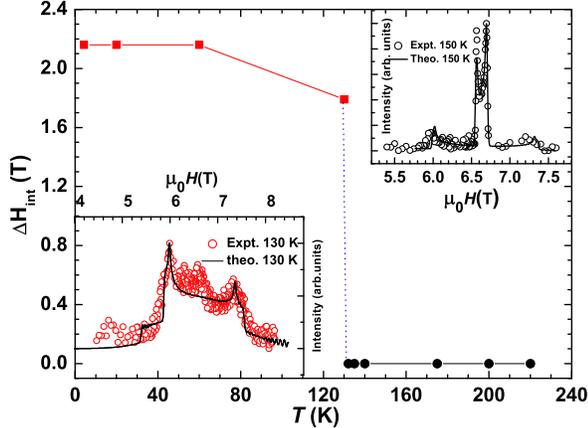


FIG. 4: Temperature dependence of the FWHM of the ^{75}As NMR spectra below (red square) and above (closed circle) the SDW transition temperature. Right-hand inset shows the 150 K ^{75}As spectra together with the theoretical simulation. Left-hand inset shows the 130 K ^{75}As spectra together with the theoretical simulation.

splitting frequency, respectively. ΔH_Q depends on ν_Q^2 , $1/H$ and η . ΔH_Q amounts to be 0.132 T above the SDW transition. This is shown in the Fig. 3 (top part of the left-hand panel).

The insets of Fig. 4 show ^{75}As NMR spectra at 150 K and at 130 K together with the theoretical simulation. Simulation has been done considering the standard 2nd order perturbation effect of quadrupolar interaction incorporating the Knight-shift powder pattern. Furthermore we have introduced Gaussian line broadening effects [26, 27]. At 150 K and 130 K the spectra are fitted reasonably well, taking into account the second-order quadrupolar perturbation contribution. The parameters obtained for 150 K are $\nu_Q = 9.57 \pm 0.2$ MHz and $\eta = 0.03$. These values are close to findings for other members of the paramagnetic pnictide family [24, 25, 28]. For 130 K the parameters obtained are different, viz. $\nu_Q = 11.00 \pm 0.4$ MHz and $\eta = 0.1 \pm 0.02$. This change reflects the change of magnitude and direction of the electric field gradient due to the structural phase transition. Using Eqn. 1, $\nu_Q = 9.56$ MHz is obtained, which is very close to the value obtained from a simulation of the entire ^{75}As spectrum above the SDW transition.

If we assume that ν_Q is roughly inversely proportional to the unit-cell volume associated with the structural change which is at most 5%, the change in ν_Q gives a spectral broadening of at most 0.02 T at half the maximum intensity at 6.6 T [21]. It should be borne in mind that in this system the structural change does not accompany any unit-cell volume change, and therefore the structural change itself cannot be responsible for such a large line-broadening at 130 K. The change in the

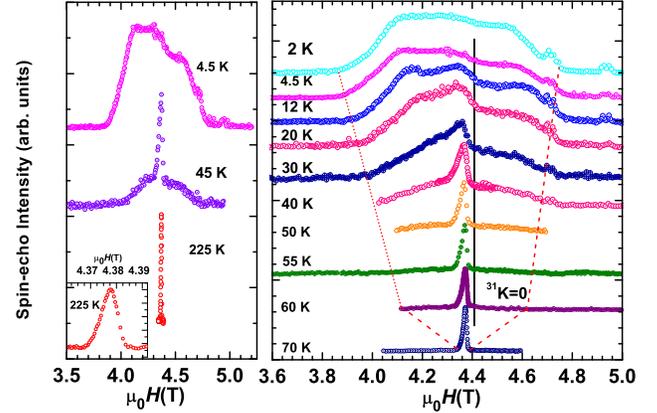


FIG. 5: ^{31}P field sweep NMR spectra at different temperatures for $x = 0.3$. The solid vertical line indicates the position of the Larmor field, and the evolution of the SDW ordering is indicated by the dotted line.

ν_Q value from 150 K to 130 K is only around 1.43 MHz, which is rather unlikely to produce a change of the line width (in terms of field) by more than an order of magnitude. The changes in the internal field and the ν_Q and η values at 130 K indicate that the SDW-type Fe AFM ordering and the structural transition from TT phase to OT phase occur near-simultaneously. On the other hand, for the parent compound CeFeAsO the available results suggest that the structural and AFM Fe ordering take place at two distinctly different temperatures 150 K and 145 K, respectively.

As already discussed, the spectral width is an indication of the distribution of the internal field (ΔH_{int}) at the P or As site. Fig. 4 (main panel) shows the variation of the internal field across the magnetic phase transition. A negligibly small internal field persists from 220 K down to 132 K, but increases abruptly upon cooling through 130 K. It is evident that the internal field is nearly fully developed as soon as ordering sets in and very little growth in the internal field takes place upon cooling from 130 K to 5 K. The discontinuous tendency of the magnetic internal field at 130 K indicates that the SDW transition is likely to be first-order.

B. ^{31}P and ^{75}As NMR for $x=0.3$: the critical region

A typical set of ^{31}P field sweep NMR spectra is shown in Fig. 5 at different temperatures. (Left panel) Fig. 5 shows the ^{31}P field sweep NMR spectra at three different temperatures. Right-hand panel shows the temperature variation of ^{31}P field sweep NMR spectra in the temperature range 70 – 2 K. The NMR spectra change considerably over this temperature range. The

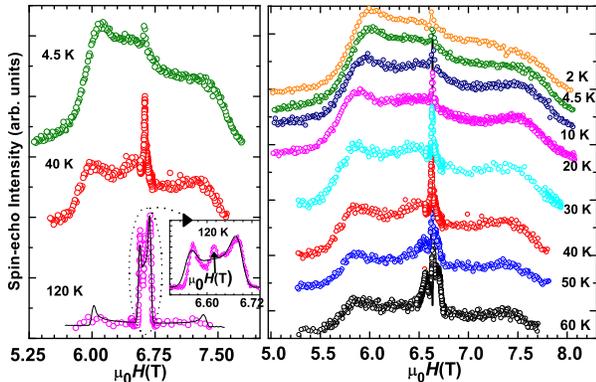


FIG. 6: ^{75}As field sweep NMR spectra at different temperatures for $x = 0.3$. Vertical line (inset) indicates the position of the Larmor field.

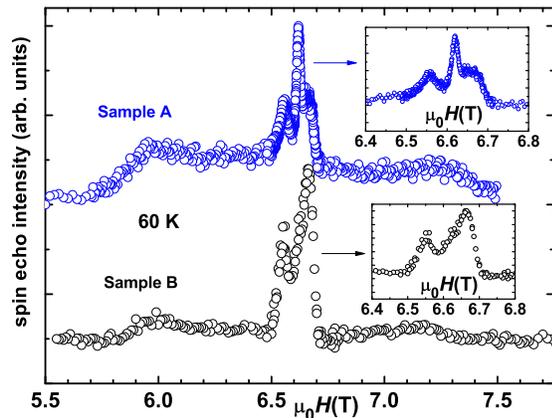


FIG. 7: ^{75}As field sweep NMR spectra at 60 K for $x=0.3$ for two different batches. Inset shows the quadrupolar splitted central transition for two batches.

vertical line indicates the position of Larmor field. At high temperatures (inset in left-hand panel) a narrow, single anisotropic line is observed as expected for a TT structure. A moderate anisotropy develops together with line broadening as the temperature is lowered, and at the same time there is an overall shift of the resonance towards lower fields.

The overall line shape is not changed remarkably down to the temperature 70 K. However, with further lowering of temperature at around 60 K, all of a sudden a structure develops. This is more evident below 50 K. The line consists of a superposition of a smeared anisotropic broadened background and a narrow single line (At 4.35T). Moreover, the smeared anisotropic broadened background is gaining intensity and anisotropy upon lowering the temperature down to 2 K, whereas the intensity of the single narrow line (At

4.35T) is fading out. And it is hardly traceable below 20 K. The small signal observed at around 4.75 T and 4.95 T, are due to the presence of small amount Sn impurity, corresponding to the NMR signals of ^{119}Sn and ^{117}Sn isotopes, respectively. As the sample is prepared by Sn-flux method, therefore it is likely to be the presence of small amount of impurity in the sample.

The change of line shape in the ^{31}P NMR spectra at around 60 K is evidently due to a modified SDW-type of Fe AFM ordering, although the effects of the structural transition from the TT phase to OT phase cannot be excluded. However this is unlikely as because synchrotron XRD measurements do not suggest any structural transition. The effective width of the broadened line is about 0.6 T, which might be used a first estimation of the internal field of the Fe ordered moment sensed by the P nuclei. The red dotted lines in Fig. 5 are guides to the eye and track the evolution of the internal field towards low temperatures. At 60 K and below, the presence of a narrow central peak along with the smeared broadened background suggest co-existence of the paramagnetic and SDW type AFM ordered phases.

Figure 6 shows the ^{75}As field sweep NMR spectra for the $x = 0.3$ compound at different temperatures. In the inset of the left panel, the central part of the ^{75}As spectra at 120 K is shown. The right-hand panel shows a series of ^{75}As spectra in the low-temperature range, and a number of interesting features are noted. At high temperature the spectra reveal typical second-order quadrupole splitting. For a single-phase As position, we would expect a second order split central line as observed for the system $x = 0.05$. However, for $x = 0.3$ shown in Fig. 6, a relatively sharp narrow line along with the second-order split central line, at around 6.625 T, is also observed. This is indicated by the black arrow in the inset of Fig. 6 (left-hand panel). This resonance may conceivably originate from a tiny amount of As-rich impurity phase. To investigate this conjecture, we have compared these results (labeled sample A) with a second batch of sample material (sample B) believed to be of superior analytical quality. Figure 7 shows an overlay of the ^{75}As Field sweep NMR spectra taken at 60 K for two samples. Inset of Fig. 7 shows the central transition on a magnified scale. It is seen that the sharp narrow line at 6.625 T is absent in spectrum of sample B, and confirms the presence of As impurity content in sample A. Moreover, an impurity of this nature may itself contribute finite line broadening in the ^{75}As NMR spectrum. Hence, we refrain from extracting further detailed information from Fig. 6, aside from noting that the quadrupolar split central transition suffers loss of intensity towards low temperatures and eventually disappears below 20 K.

C. ^{31}P and ^{75}As NMR for $x=0.9$: the Kondo region

A typical set of ^{31}P field sweep NMR spectra at different temperatures is shown in Fig. 8. One single narrow ^{31}P -NMR line as expected from the crystal structure was found at 200 K (right-hand panel of Fig. 8). The line develops strong asymmetry and increased line-width towards lower temperature (left-hand panel of Fig. 8) at 75 MHz. Furthermore and in contrast to the other samples in this study the line shifts strongly with temperature. With increasing the frequency, onset of line broadening commences already at high temperatures. The shape is characteristic of a powder pattern from a spin $I = 1/2$ nucleus in a TT symmetry. The ^{31}P spectra 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 of the Fig. 8). Similar to CeFePO $^{31}K_{ab}$ shows a strong temperature dependence whereas K_c is almost temperature independent. Figure 10 shows the variation of $^{31}K_{ab}(T)$ with temperature for CeFePO [11] and CeFeAs $_{0.1}\text{P}_{0.9}\text{O}$. Above 30 K $^{31}K_{ab}$ for the $x = 0.9$ sample resembles the $^{31}K_{ab}$ for the $x = 1$ sample. It shows CW-like $4f^1$ Ce magnetism. Here, a larger shift value indicates a large hyperfine field at the P site. However, below 30 K $^{31}K_{ab}$ for the $x = 0.9$ sample deviates significantly towards lower temperature. The inset shows the field dependence of $^{31}K_{ab}(T)$. Here, below 10 K a strong field dependence of the residual shift for $T \rightarrow 0$ is observed. $^{31}K_{ab}(T)$ is decreasing with increasing frequency (field). This indicates a FM ordered ground state. For a FM system, the magnitude of the susceptibility should decrease with increasing the field due to progressive saturation of the magnetization. As shift is following the susceptibility, the specific field dependence could be the indication that the system is FM ordered. Furthermore, line broadening could be the indication of onset of electronic correlations. This broadening towards lower temperature could also be associated with the Kondo effect.

Figure 9 shows the ^{75}As field sweep NMR spectra at different temperatures. The obtained spectra are typical powder patterns with strong quadrupole coupling. With decreasing temperature the entire spectra are shifted towards lower fields. Moreover, the spectra become more anisotropic at lower temperature similar to the case of ^{31}P spectra. All of the ^{75}As spectra fit consistently in the whole temperature range and enable estimation of $^{75}K_{ab}$ and $^{75}K_c$. The arrows indicate the satellite transitions. The obtained fit parameter is $\nu_Q = 9.27 \pm 0.20$ MHz. Lower inset of Fig. 10 shows $^{75}K(T)$ as a function of temperature. Similar to the $^{31}K(T)$, highly anisotropic behaviour in $^{75}K(T)$ is observed. Here $^{75}K_{ab}$ is increased upon lowering the temperature, whereas $^{75}K_c$ remains almost independent of temperature. Similar values of $^{75}K_{ab}$ and $^{31}K_{ab}$ indicate that the hyperfine field is similar on the As and P sites.

In this subsection we present ^{31}P spin-lattice relaxation ($^{31}(1/T_1)$) data on CeFeAs $_{0.1}\text{P}_{0.9}\text{O}$. T_1 measure-

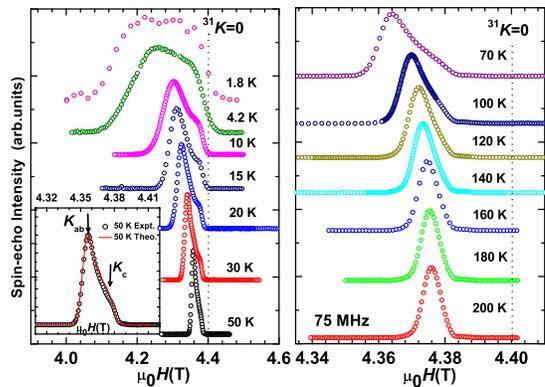


FIG. 8: ^{31}P field sweep NMR spectra for $x = 0.9$ at different temperatures. The vertical dashed line indicates the Larmor field obtained from the reference compound. The inset shows a representative powder spectrum, together with the simulation at $T = 50$ K (arrows indicate the resonance fields corresponding to the shift values of $^{31}K_{ab}$ and $^{31}K_c$ for the field direction $H \perp c$ and $H \parallel c$, respectively).

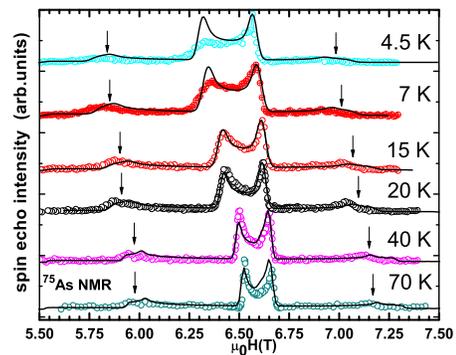


FIG. 9: ^{75}As field sweep NMR spectra for $x = 0.9$ at different temperatures along with a simulation (see text). Arrows indicate the position of the satellite transitions.

ments were performed at different temperatures at a frequency of 75 MHz at the $H \perp c$ position of the anisotropic NMR line (left arrow in the inset of Fig. 8). $^{31}(1/T_1)$ was obtained by fitting the nuclear magnetization ($m(t)$) recovery with a standard single exponential function, for a $I = 1/2$ nucleus:

$$m(0) - m(t) = m(0) \exp(-t/T_1) \quad (2)$$

Figure 11 shows the temperature dependence of $^{31}(1/T_1)$ for the $x = 0.9$ sample together with the pure system CeFePO[11]. At high temperatures $^{31}(1/T_1)$ of both samples are found to merge whereas towards lower temperatures a strong increase with decreasing temperature was found. At around 10 K, $^{31}(1/T_1)$ decreases to form a broad maximum. With further cooling at 2 K $^{31}(1/T_1)$ is sharply decreased by an order of magnitude. The sharp decrease of $^{31}(1/T_1)$ indicates the system undergoes a FM transition at about 2 K, consistent with bulk measure-

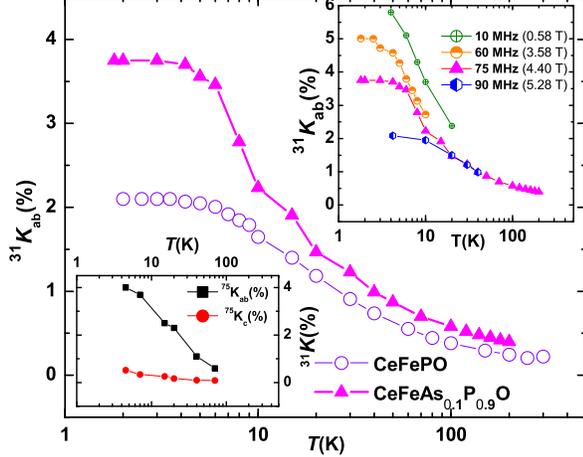


FIG. 10: Shift component $^{31}K_{ab}$ as a function of temperature for CeFePO at 76 MHz (data taken from [11]) and for the CeFeAs_{0.1}P_{0.9}O at 75 MHz. Upper inset shows $^{31}K_{ab}$ at different frequencies (fields). Lower inset shows $^{75}K_{ab}$ and $^{75}K_c$ as a function of temperature at 48 MHz.

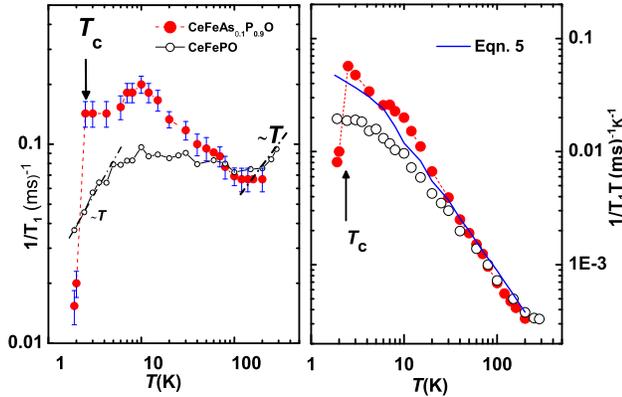


FIG. 11: $^{31}(1/T_1)$ as a function of temperature for CeFePO (data taken from [11]) and CeFeAs_{0.1}P_{0.9}O (left). $^{31}(1/TT_1)$ together with the calculated values (solid line) plotted as function of temperature (right-hand panel).

ments.

The comparison of $^{31}(1/T_1)$ with the parent compound CeFePO is noteworthy. In contrast to CeFePO, in CeFeAs_{0.1}P_{0.9}O the plateau-like region in $^{31}(1/T_1)$ is absent and long-range FM order is observed. Crossover from a strong Kondo type of interaction to AFM order has been studied by NMR as a local probe in a

number of cases. Good examples are systems such as CeCu₂(Si/Ge)₂ [36, 37] and Ce(Ru/Rh)₂Si₂ [38, 39]. On the other hand, systems where doping induces a crossover from a Kondo type of interaction to long-range FM order are rare. A distribution of Kondo temperatures or Kondo disorder is likely to exist in proximity to FM order. One example is CeRu₂(Si,Ge)₂ where the stoichiometric Si compound is a heavy fermion and the Ge end compound a $T_c = 7.5$ K ferromagnet. For CeRu₂(Si_{1-x}Ge_x)₂ the phase diagram is rather complex and a complex AFM type of phase was found between the Kondo and the FM region ($0.06 \leq x \leq 0.65$) [40]. Another example is the ^{29}Si NMR study in CeSi_x where FM order shows up below $x = 1.83$ whereas Kondo interaction typifies the behaviour above $x = 1.82$ (≤ 2). Here $^{29}(1/T_1)$ also shows a strong increase in the vicinity of the FM order [46]. For CeFeAs_{0.1}P_{0.9}O we do not have evidence for an AFM type of ordering, judging by field-dependent NMR investigations. Here, the Kondo interaction probably competes with FM clusters on a short time scale. The competition of Kondo and FM type interactions therefore could be responsible for the non-Korringa like behavior of CeFeAs_{0.1}P_{0.9}O.

Furthermore, it should be mentioned that due to the strong field dependence of the ferromagnetism a strong field dependence of $^{31}(1/T_1)$ could be expected. Therefore a detailed study of $(1/T_1)$ as a function of field is required to address this problem quantitatively. This topic is not the main concern of this paper. We would like to add that in a μSR study the magnetic volume fraction was found to start increasing from 10 K, i.e. well above T_c , which is consistent with our NMR findings [44]. Brüning *et al.* compared NMR results of CeFePO with those of LaRuPO, LaFeAsO_{1-x}F_x and CeCu₂Si₂ to show that the $1/T_1$ is dominated by the 4f-electron contribution [11, 31–33]. In their analysis, they mentioned that a similar temperature dependence of the relaxation rate were found for the compounds CeFePO and CeCu₂Si₂ and concluded a similar spin fluctuation relaxation mechanism in both compounds. Furthermore, the strong correlation effects in CeFePO originate from the Ce-4f electrons rather than the from the Fe-3d electrons.

From the fluctuation dissipation theorem for a localized 4f-electron moment system the $1/T_1$ can be written as [34]

$$1/T_1 T \propto \gamma^2 \sum_{\mathbf{q}} A_{hf}^2(\mathbf{q}, w) \frac{\chi''(\mathbf{q}, w)}{w} \quad (3)$$

where A_{hf} is the effective hyperfine coupling and $\chi''(\mathbf{q}, w)$ is the absorptive part of dynamical spin susceptibility.

In a simplified picture with a small number of Ce neighbouring atoms, a situation which prevails in the present system (P/As is coupled to 4 Ce neighbors), one may neglect the \mathbf{q} dependent contribution. Under these circumstances, $1/(T_1 T)$ in a Kondo lattice should be dominated by the contribution of the 4f electrons, the latter which may be approximated as proportional to the ratio of the

static susceptibility $\chi(T)$ and the effective relaxation rate $\Gamma(T)$ of the 4f electrons,

$$(1/T_1T)_{4f} \propto \chi(T)/\Gamma(T) \quad (4)$$

[35, 36, 41, 42]. Further on for Kondo systems $\Gamma(T) \propto \sqrt{T}$ is valid for $T > T_K$ [43], where as for $T \ll T_K$ a constant value $\Gamma_0 \sim K_B T_K$ was found. We calculated the temperature dependence of

$$(1/T_1T)_{4f} = C^{31} K_{ab}(T)/\sqrt{T} \quad (5)$$

where C is a temperature-independent parameter. We added a small temperature-independent contribution $(1/T_1T)_{CE} = 0.0001(ms)^{-1}K^{-1}$ to account for the contribution of the conduction electrons at high temperature where the contribution of the 4f electrons becomes negligible. The solid line in Fig. 11 (right-hand) illustrates our calculation. The experimental data of $\text{CeFeAs}_{0.1}\text{P}_{0.9}\text{O}$ are adequately described by this approach. It seems obvious that the onset of Kondo interactions in this doped compound is similar to that in pure CeFePO . Additionally Fig. 11 shows that in the temperature range 40 – 2 K the magnitude of $^{31}(1/T_1T)$ is higher than what is the case in CeFePO , which is consistent with the magnetic susceptibility and Knight shift data. Furthermore it should be mentioned that the $^{31}(1/T_1)$ power law (eqn.5) observed here differs significantly from what was found for itinerant ferromagnets like ZrZn_2 , where $1/T_1T \sim \chi(T)$ is valid. This indicates that the system is not a typical Moriya-type ferromagnet.

In contrast to CeFePO , an additional long-range FM ordering of Ce takes place in the present As-doped system. The residual shift exhibits a strong field dependence which is characteristic of FM ordering at low temperature. This is consistent with $C_p(T)$ measurements where ordering at $T_c = 2$ K was found [47]. The line broadening in NMR data could be due to reduction of T_2 due to Kondo and/or FM interactions. To conclude, the P-rich $x = 0.9$ sample could be identified as a heavy Fermion system with a FM ground state. This presents a rather unique situation among correlated electron systems.

D. Comparison and discussion

After presenting the detailed NMR results for three P concentrations of $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$, we now compare and discuss our findings. Table I collects the important results obtained from the NMR study for three P concentrations. For $x=0.05$: AFM (Fe)+ structural transition at 130 K, with higher P content of $x=0.30$: AFM (Fe) ordering suppressed to 70 K and no structural transition, $x=0.90$: no AFM Fe ordering, no structural transition, FM ordering of Ce. In a recent study of Clarina de la Cruz *et. al.* it is claimed it is not possible to separate out the structural from the magnetic phase transition for $x \geq 0.05$ within experimental resolution [20]. The alloy system $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ becomes paramagnetic in the

TT structure, like CeFePO , above $x \approx 0.4$. However, bulk measurements suggest that above $x \approx 0.4$, Ce order FM. Furthermore according to Clarina de la Cruz *et. al.* for $x = 0.05$ two transitions (magnetic and structural) take place at around 140 K, whereas our NMR investigations describe a similar occurrence albeit at $T = 130$ K, -a result which is in line with the resistivity data shows the anomaly close to $T=130$ K [47]. The occurrence of both transitions (magnetic and structural) at the same temperature for the present system is in contrast to all other doping series where with increasing doping at the Fe/As site structural and magnetic transition is getting separated. Therefore present NMR results apart from confirming the magnetic and structural transitions, additionally provide insightful information. Here it should be noted that NMR results describe the drastic change of internal field due to Fe $3d$ ordered moment at $T=130$ K. Basically, this change of internal field is the consequence of a changing magnetic order parameter. Our data are supportive of the Fe-AFM SDW type transition to be first-order.

According to neutron scattering results for $x = 0.3$, the structural transition and Fe AFM ordering (T_N) take place at ≈ 85 K, which is relatively higher than the suggested result from bulk measurements ≈ 70 K. On the other hand, NMR investigations, in line with μSR results [44] described this phase transition consistent with the findings of bulk measurements. From the ^{31}P NMR study there is evidence for a phase separation in terms of paramagnetic and AFM-SDW type phases. This rules out the possibility of termination to a quantum critical point with increasing P concentration at the $x = 0.3$ region.

In the following paragraph, we present a comparison of the relative change in internal field upon P doping (0.05 \rightarrow 0.3) as estimated from the ^{31}P and ^{75}As NMR study. The field ratios are given by

$$\frac{(^{31}\Delta H_{\text{int}})_{0.05}}{(^{31}\Delta H_{\text{int}})_{0.3}} = \frac{1.132T}{0.6T} \simeq 1.9, \quad (6)$$

$$\frac{(^{75}\Delta H_{\text{int}})_{0.05}}{(^{75}\Delta H_{\text{int}})_{0.3}} = \frac{1.9T}{1.1T} \simeq 1.727 \quad . \quad (7)$$

On the other hand, a relative change of the Fe static ordered moment, moving from $x = 0.05$ to 0.3, has been reported from neutron scattering and is as follows,

$$\frac{(\mu_{Fe})_{0.05}}{(\mu_{Fe})_{0.3}} \implies \frac{0.8\mu_B}{0.4\mu_B} \simeq 2 \quad . \quad (8)$$

Therefore the relative change of Fe static ordered moment for the two P concentration values ($x = 0.05, 0.3$) and the relative change of the estimated internal field for the same P concentration are in close agreement.

The magnitude of the estimated internal field (in our approach) from powder ^{31}P and ^{75}As spectra, in principle, may vary because for ^{75}As spectra, below the Fe-ordering, satellites may introduce additional line broadening. This makes the ^{75}As NMR spectra even more

complicated. Therefore it is not possible to isolate the effect of internal field to the central transition. As a result, the estimated internal field from the ^{31}P and ^{75}As NMR spectra may vary for a specific P concentration. Nonetheless, the relative change of internal field for two different P concentrations should be independent of the probed nuclei, which is indeed the case here.

For the $x = 0.05$ and 0.3 compositions an additional line broadening accompanies the Ce magnetism at low temperatures. Well below the Fe AFM transition the Fe ordered moment should saturate. Thus, this cannot produce any additional line broadening in the spectra. Therefore the additional broadening in ^{75}As spectra originates from the Ce magnetism for $x = 0.05$. A similar situation prevails in the case of the $x = 0.3$ sample.

By comparison, the magnetic transition at Fe-AFM ordering is rather sharp in the $x = 0.05$ case, compared to $x = 0.3$. The line shape changes rather drastically for the $x = 0.05$ sample, while a gradual evolution of line shape is observed in $x = 0.3$. The magnetic transition in the $x = 0.05$ system is likely to be first-order. For $x = 0.3$ the internal field does not affect the line shape as strongly compared to the $x = 0.05$ system. By contrast, it suddenly develops a distinct structure at full width of quarter maximum position at around 70 K, and the intensity develops with lowering temperature in a manner which suggests either that the ordered moment of Fe is still not fully saturated and/or that not all of the Fe moments participate in ordering just below 70 K. This leads to the conjecture that paramagnetic and ordered phases may co-exist in a presumably inhomogeneous distribution. The magnetic volume fraction of this compound just below the ordering temperature may be somewhat less than 1. Nonetheless, at sufficiently low temperatures a magnetic volume fraction of 1 is eventually achieved.

For $x = 0.9$ the TT phase persist throughout the entire temperature range. In contrast to the $x = 1$ sample a long range FM order is likely to be confirmed by ^{31}K measurements. Additionally, the $^{31}(1/T_1)$ results indicate a complex interplay of FM and Kondo type of fluctuations in the proximity of the long range FM order. To study the very interesting cross-over from Kondo to FM type of interaction more detail studies are required.

Next, we compare the three concentrations ($x = 0.05$, 0.3 , and 0.9) in the context of shift results. The magnitude of the shift was found to increase with increasing P concentration. For $x = 0.05$ a near temperature-independent shift is observed. For $x = 0.3$ the line position is shifted slightly with lowering the temperature indicating a small shift value. A cancellation of hyperfine fields at the P/As site may be responsible for a weakly temperature dependent shift. This is, in fact, very likely because the conduction electron polarization from the $4f^1$ ion produces a positive field whereas the core polarization from the $3d$ ion usually results in a negative hyperfine field. However, with increasing P concentration the effect of Fe $3d$ moments is reduced. This enhances the shift. Therefore it is clear that in the As rich side

of the $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ alloy the contributions of Ce- $4f$ and Fe- $3d$ magnetism are significant, whereas in the P rich side the Ce $4f$ magnetism dominates. Cancellation could also be possible to come by between the moments of the Fe-sublattice themselves with P/As either occupying symmetric positions in the magnetic lattice or random positions in an incommensurate SDW.

Comparing the ^{31}P NMR spectra for three different concentration at low temperature, a noticeable difference in the effective line width is observed close to 5 K. With increasing P concentration the line width decreases. This is consistent with the fact that contribution of Fe magnetism is lowered with increasing P concentration.

IV. SUMMARY AND CONCLUSION

To conclude, we have prepared polycrystalline samples of $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ by a Sn-flux technique. A systematic study of ^{31}P and ^{75}As NMR was conducted on the $x = 0.05$, 0.3 and 0.9 members of this series. 1). For the $\text{CeFeAs}_{0.95}\text{P}_{0.05}\text{O}$ compound a drastic change of the line width at 130 K indicates AFM ordering of Fe and the structural change from TT to OT. Associating linewidth with the internal field of the system, a large change of the internal field evidences AFM (SDW type) transition which is likely to be first-order. Small and nearly constant shift values are found in ^{31}P and ^{75}As NMR and ascribed to competing mechanism of the $4f$ and $3d$ magnetism of Ce and Fe respectively. Simulations of powder spectra are complex below the SDW transition because lineshapes are influenced by coinciding SDW-magnetic and structural phase transitions. 2). On the other hand, for the $\text{CeFeAs}_{0.7}\text{P}_{0.3}\text{O}$ compound the evolution of the Fe-SDW type order close to 70 K corroborates the results of bulk measurement and μSR . The complicated line shapes in spectra of this system do not permit unambiguous fitting to be performed. The line shape is, nonetheless, in evidence of a phase separation (paramagnetic and ordered phase) taking place. A considerable anisotropy develops upon cooling. 3). In contrast to CeFePO , in $\text{CeFeAs}_{0.1}\text{P}_{0.9}\text{O}$ additional magnetic ordering develops. Field-dependent shift results give the evidence of FM ordering. Above the ordering $^{31}(1/T_1)$ shows unconventional, non-Korringa like behaviour which indicates a complex interplay of Kondo and FM fluctuations.

The present system contributes valuable insights about incipient magnetic order in the presently intensively studied iron pnictide family of compounds, but warrants thorough investigations in its own right due to the unusual emergence of cooperative ferromagnetism within a Kondo lattice of local Ce moments that are generically coupled antiferromagnetically to the conduction electrons.

TABLE I: Comparison of results obtained from different P concentration.

	$x=0.05$	$x=0.3$	$x=0.9$
$T_N(Fe)$	130 K	70 K	No Fe ordering
$T_{N,C}(Ce)$	Additional line broadening	Additional line broadening	2 K (FM)
Structural transition	130 K (TT→OT) ^a	No transition	No Transition(TT)

^aTT-Tetragonal Phase, OT-Orthorhombic Phase.

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