

Interplay between Co 3*d* and Ce 4*f* magnetism in CeCoAsO

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We have investigated the ground-state properties of polycrystalline CeCoAsO by means of magnetization, specific heat, and solid-state NMR. Susceptibility and specific-heat measurements suggest a ferromagnetic order at about, $T_C=75$ K. No further transitions are found down to 0.5 K. At 6.5 K a complex Schottky type of anomaly shows up in the specific-heat results. The interplay between Ce 4*f* and Co 3*d* magnetism being responsible for that anomaly is discussed. Furthermore ^{75}As -NMR investigations have been performed to probe the magnetism on a microscopic scale. As-NMR spectra are analyzed in terms of first and second-order quadrupolar interaction. The anisotropic shift component K_{ab} and K_c could be derived from the ^{75}As powder spectra. Towards lower temperature a strong shift anisotropy was found. Nonetheless K_{iso} tracks the bulk susceptibility down to $T=50$ K very well. Furthermore the presence of weak correlations among the Ce ions in the ferromagnetic state is discussed. The observed increase in C/T towards lower temperatures supports this interpretation.

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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 recent discovery of superconductivity with a transition temperatures T_C up to 50 K in the $R\text{FeAsO}_{1-x}\text{F}_x$ series of compounds being the highest T_C 's except for cuprate systems.¹⁻⁶ While the main studies on these materials are devoted to the superconducting materials, the nonsuperconducting members of these family stays mostly unexplored. Nevertheless studying these compounds may provide information to understand also the superconducting state. Recent studies of CeRuPO and CeOsPO (Refs. 7-9) indicate dissimilar types of magnetic ordering. CeRuPO is a rare example for ferromagnetic (FM) Kondo system showing a FM order at $T_C=15$ K and a Kondo energy scale of about $T_K \approx 10$ K. CeOsPO exhibits an antiferromagnetic (AFM) order at $T_N=4.5$ K. The recent studies of the relative CeFePO suggest that this is a heavy Fermion metal with strong correlation of the 4*f* electrons close to a magnetic instability.¹⁰ On the other hand in CeFeAsO, a complex interplay of Ce 4*f* and Fe 3*d* magnetism is found. Here, Ce orders antiferromagnetically at $T_N \approx 3.8$ K whereas the high-temperature regime is dominated by the 3*d* magnetism of Fe.^{11,12} There is a structural transition from tetragonal to orthorhombic at ≈ 151 K followed by spin-density wave (SDW)-type AFM order of Fe at ~ 145 K. Moreover Ce magnetism is not affected strongly by the presence of the Fe moments. Furthermore, neutron scattering, muon spin-relaxation experiments and recent analysis of $\chi(T)$, $C(T)$ suggest that there is a sizeable interlayer coupling in CeFeAsO.¹²⁻¹⁵ Therefore, the pure CeFeAsO system have already proven to be a rich reservoir of exotic phenomena.

Apart from isoelectronic substitution on CeTPnO with Fe, Ru, and Os chemically also the $T=\text{Co}$ series form. Results on LaCoAsO and LaCoPO were reported to exhibit ferromagnetic order of Co moment with Curie temperatures T_C of

about $T_C=50$ K and $T_C=60$ K, respectively. In contrast to Fe, where the 3*d* magnetism depends on the Pnictide (P, As), Co stays magnetic in both the P and As series. In LaCoAsO, Co saturation moments of 0.3-0.5 μ_B per Co (Refs. 16-18) are found. It has been proposed that spin fluctuations play an important role in the magnetic behavior of LaCoAsO,^{16,18} as well as the magnetic and superconducting properties of the iron-based superconductors. Last year we reported the detailed physical properties of CeCoPO and discussed about the interplay between 3*d* magnetic moments of Co and 4*f* electrons of Ce.¹⁹ This system, similar to LaCoPO, the Co 3*d* electrons order ferromagnetically. However, here the Ce ions are on the border to magnetic order and an enhanced Sommerfeld coefficient, $\gamma \sim 200$ mJ/mol K² was found. In CeTPnO the substitution of P by As change the magnetism drastically. It is already evident in the case of CeFeAsO.²⁰⁻²² Therefore it is natural to investigate the physical and microscopic properties of CeCoAsO compound. In this report we present the physical properties of polycrystalline CeCoAsO using susceptibility $\chi(T)$ and specific-heat $C(T)$ measurements. Additionally, we discuss the preliminary microscopic results as seen by ^{75}As -NMR study.

II. EXPERIMENTAL

Samples are prepared by solid-state reaction technique. The starting materials that are taken for the preparation of parent CeCoAsO are Ce and As chips, and Co, Co₃O₄ powders. First, CeAs was prepared by taking stoichiometric amounts of Ce and As in 1:1 ratio, pressed into pellets and sealed in evacuated quartz tube. With repeated heat treatment, attaining a maximum temperature of 900 °C, and grinding inside a glove box filled with inert Ar gas, single phase CeAs were obtained. CeAs were then mixed thoroughly with Co₃O₄ and Co powder in stoichiometry and pressed into pellets. The pellets were wrapped with Ta foil

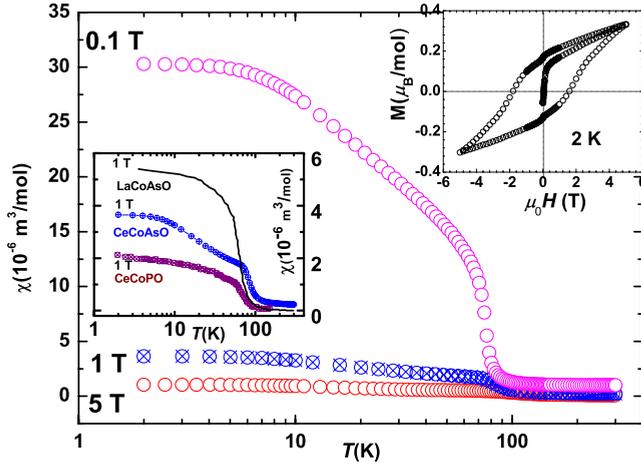


FIG. 1. (Color online) Temperature dependence of the susceptibility of CeCoAsO at different fields. The right inset shows the magnetization at 2 K and the left inset shows a comparison of the susceptibility for CeCoPO (data taken from Ref. 19), CeCoAsO, and LaCoAsO (data taken from Ref. 17) at 1 T.

and sealed in an evacuated quartz tube. They were then annealed at 1100–1150 °C for 40–45 hours to obtain the final CeCoAsO samples. X-ray powder-diffraction revealed a single phase sample with no foreign phases. Susceptibility $\chi(T)$ measurements were performed in a commercial Quantum Design (QD) magnetic property measurement system. Specific heat $C(T)$, measurements were performed in a QD physical property measurement system. For the NMR measurements, polycrystalline powder was fixed in the paraffin to ensure a random orientation. ^{75}As -NMR measurements were performed with a standard pulsed NMR spectrometer (Tecmag) at the frequency 48 MHz 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 GaAs (^{75}As NMR) as reference compound with $^{75}\text{K} \approx 0$.²³

III. RESULTS

A. Magnetization and specific-heat study

Figure 1 shows the susceptibility of CeCoAsO as a function of temperature at different fields as indicated. Above 200 K, the susceptibility follows the Curie Weiss behavior with an effective moment $\mu_{\text{eff}} = 2.74 \mu_B$. This value is higher than the value of $\mu_{\text{eff}}^{\text{Ce}} = 2.54 \mu_B$, expected for a free Ce^{3+} ion. This is because of the contribution of Co to the effective moment of $\mu_{\text{eff}} = \sqrt{\mu^{(\text{Co})2} + \mu^{(\text{Ce})2}}$. For the Co ions we calculate an effective moment of $\mu_{\text{eff}}^{\text{Co}} = 1.03 \mu_B$. Our results are in good agreement with findings from Ohta and Yoshimura *et al.*¹⁸ A sharp increase in the susceptibility is observed at around 75 K. Here, a strong-field dependence of the susceptibility typical for a FM system is evidenced. In the inset of Fig. 1 the magnetization $M(H)$ of CeCoAsO up to 5 T at 2 K is shown. A large hysteresis typical for hard ferromagnets is observed. A large hysteresis was also found for CeCoPO

whereas for other $R\text{CoAsO}$ no such large hysteresis was found.¹⁸ In the left inset of Fig. 1 we compare the susceptibility results of CeCoAsO with that of LaCoAsO and CeCoPO at 1 T. It should be mentioned that for CeCoAsO at smaller fields no peak could be resolved which is in contrast to CeCoPO.¹⁹ The temperature dependence of the susceptibility is quiet similar for CeCoAsO and CeCoPO whereas there is a pronounced difference to that of LaCoAsO. In LaCoAsO there is no influence of $4f$ magnetism. Therefore the magnetization curve looks like a simple textbook ferromagnet. It has to be mentioned that we took the data for LaCoAsO from Ref. 17. For this set of data $\chi(\text{LaCoAsO}) > \chi(\text{CeCoAsO})$ is found in the FM state but surprisingly the data by Ohta *et al.*¹⁸ shows smaller values (at same field) suggesting $\chi(\text{LaCoAsO}) < \chi(\text{CeCoAsO})$. Nonetheless our results for CeCoAsO are in perfect agreement with findings in Ref. 18. The different behavior for CeCoPO and CeCoAsO indicate that the Ce $4f$ creates a significant change in the overall magnetic behavior. This unusual behavior of the susceptibility indicates an intricate magnetic structure with strong polarization of the itinerant Co moments on the more localized Ce moments. Such effects are also known from $4f$ -ion $\text{Fe}_4\text{Sb}_{12}$ skutterudites. Here $\text{EuFe}_4\text{Sb}_{12}$ shows similar magnetization curves.²⁴ One approach could be to describe CeCoAsO in the framework of a classical ferrimagnet such as $R\text{Co}_5$ with $R = \text{Y, Ce, Pr, \dots}$.²⁵ Magnetization in these system is governed by the two subsystems of the $4f$ and $3d$ moments and their intermolecular and intramolecular interactions. Because of the antiferromagnetic coupling of the rare-earth spins with the Co spin for light rare-earth ions such as Ce, usually an ferromagnetic alignment of the Ce $4f$ moment and the Co $3d$ moments is expected²⁵ in the ordered state. This would imply $\chi(\text{CeCoAsO}) < \chi(\text{LaCoAsO})$. Unfortunately because of inconsistent literature for LaCoAsO data we have no prove for that. To summarize the magnetization section it should be note that besides the high-temperature ordering at $T_C = 75$ K for CeCoPO and $T_C = 75$ K for CeCoAsO no further transitions are evident from magnetization measurements. This is in contrast to other $R\text{CoAsO}$ system with $R = \text{Gd, Sm, or Nd}$, where the rare-earth moments orders antiferromagnetically at low temperature.^{18,26} The temperature and field dependence of the specific heat $C(T)$ of CeCoAsO is shown in Fig. 2. Towards high temperatures $C(T)$ converges nicely to the classical Dulong Petit limit of ~ 100 J/mol-K. By lowering the temperature a broad anomaly at $T_C \sim 75$ K is visible on the top of the phonon dominated specific heat. We have estimated the background using the third order polynomial from 65 to 85 K, excluding the temperature range near the peak at 75 K. Then the background was subtracted from the data to obtain specific heat. In the left inset we have shown the $C(T)/T$ vs T plot after subtracting the background. It is worthwhile to mention that at the same temperature (75 K) the susceptibility increases sharply. Therefore, this anomaly is being due to the ferromagnetic ordering of Co. At around 6.5 K an additional broad anomaly in the $C(T)$ shows up. The right inset shows the $C(T)/T$ vs T plots. In this inset both anomalies are rather pronounced. To understand the origin of the low-temperature anomaly we have investigated the field-dependent specific heat in the temperature range 1.8–15

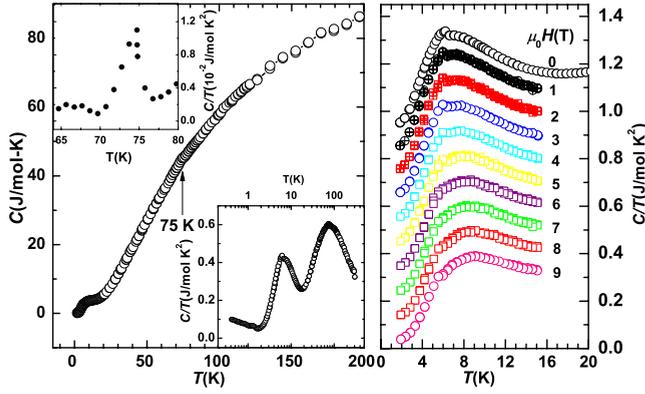


FIG. 2. (Color online) (Left panel) Temperature dependence of the specific heat of CeCoAsO. The right inset shows the specific heat plotted as C/T on a logarithmic temperature scale. The left inset shows the behavior of transition after subtracting the background. Right panel shows the specific heat plotted as C/T vs T at different field in the temperature range 1.8–20 K (note that 0.1 J/mol-K² was added as an offset in the C/T plot on the right).

K and in the field range 0–9 T. The right panel of Fig. 2 shows the C/T vs T plot at different fields (curves are shifted on y axis by 0.1 J/mol-K²). It seems that the effect of field on $C(T)$ is very small. Nonetheless, the broad maxima is shifted insignificantly towards higher temperatures with increasing field. The preliminary analysis of the specific heat reveal that this broad anomaly at low temperature is not due to the ordering of Ce. Rather this is reminiscent of Schottky-type anomaly. This might be attributed to the level splitting Crystal Electric Field (CEF) ground state of Ce by the polarization field of Co. For Ce³⁺ ion is, in a tetragonal environment, $J=5/2$ splits into three doublets. No further degeneracy can be removed by the CEF. However, these levels can be further split by the exchange field of the moments and/or the internal field of the 3d and 4f moments.^{13,14,27–31}

Below 1.8 K, C/T increases logarithmically and tends to saturate at further low temperature at $\gamma \sim 200$ mJ/mol-K². This enhancement might indicate the presence of strong correlations between the Ce ions in the Co-dominated ferromagnetic ground state.

Furthermore, at zero field we have estimated the entropy gain by integrating the 4f part to the specific heat C_{4f}/T in the temperature range 1.8–15 K. For the estimation of the entropy gain we have subtracted the phonon contribution by using reference compound data of LaCoAsO in the temperature range 1.8–15 K after Sefat *et al.*¹⁷ However, the contribution of LaCoAsO to the specific heat is small below 15 K. The estimated entropy gain for CeCoAsO at 15 K is 75% of $R \ln 2$. This supports the scenario based on the splitting of the CEF doublet ground state.

B. ⁷⁵As NMR

Figure 3 shows the field sweep ⁷⁵As-NMR spectra at different temperatures. Because ⁷⁵As is a $I=3/2$ nuclei, the quadrupole interaction should be taken into account for the interpretation of the spectra. The main effects are (I) first-order interaction, occurrence of pronounced satellite peaks

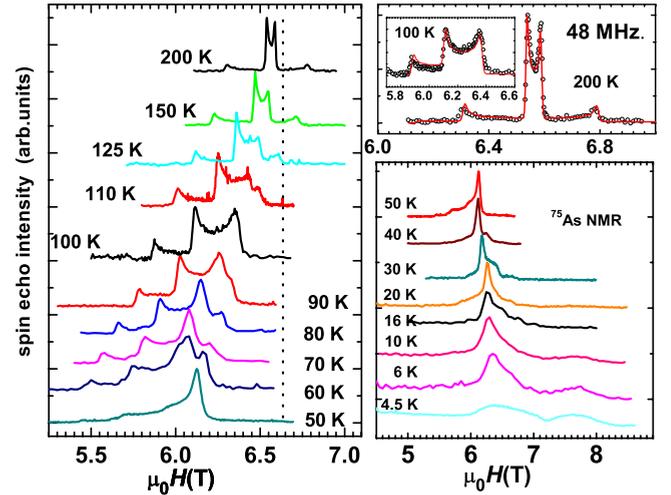


FIG. 3. (Color online) Temperature dependence of the ⁷⁵As field sweep NMR spectra at 48 MHz down to 50 K (left panel). Dotted line indicates the Larmor field estimated from the reference compound GaAs with ⁷⁵K_{ab} ≈ 0²³. ⁷⁵As spectra below 50 K (right, bottom). ⁷⁵As spectra at 200 and 100 K together with the theoretical simulation (solid line) (right, top).

($3/2 \leftrightarrow 1/2, -1/2 \leftrightarrow -3/2$), (II) second-order interactions, splitting of the central $-1/2 \leftrightarrow 1/2$ transition. At high temperature the second-order quadrupolar splitting central transition along with the two first-order satellite transitions are observed and the spectra could be nicely simulated (Fig. 3, right, top). Initially, with lowering of temperature down to 50 K, the whole spectra is shifted towards the low-field side with considerable line broadening and develops large anisotropy. However, below 50 K the whole spectra shifts towards the high-field side with further gradual line broadening. The line broadening of the spectra become enormous below 15 K. It is clear from Fig. 3 that the NMR spectra become more and more complex by lowering the temperature and the simulation of this broad spectra, at low temperature, is rather complicated. Nevertheless, with considerable effort it is possible to identify the singularities of these spectra down to 20 K. Therefore, estimation of the shift is possible by fitting the singularity of the spectra down to 20 K. During the compilation of this paper we realize that similar analysis has been performed for LaCoAsO.³³ In Fig. 3 (Lower right panel) below 10 K a considerable background intensity is perceived in the low-field side. This background signal is the combination of the ⁵⁹Co spectra and the ⁷⁵As-NMR spectra. We already measured some ⁵⁹Co-NMR spectra. The estimated ν_Q value from ⁷⁵As-NMR spectra at high temperature is 3.6 MHz. This value is similar to that of LaCoAsO system³³ and somewhat smaller than that was found for the CeFeAsO system.²² While lowering the temperature ν_Q monotonically increases and down to 20 K no drastic changes could be detected. This rules out a sudden structural change in this compound. From the simulation of the spectra, we have estimated the shift components ⁷⁵K_{ab} and ⁷⁵K_c corresponding to $H \perp c$ and $H \parallel c$ direction, respectively.

Figure 4 shows the variation in ⁷⁵K_{ab}, ⁷⁵K_c, and ⁷⁵K_{iso} as a function of temperature. ⁷⁵K_{iso} was estimated using the equation ${}^{75}\text{K}_{\text{iso}} = \frac{2}{3} {}^{75}\text{K}_{\text{ab}} + \frac{1}{3} {}^{75}\text{K}_{\text{c}}$. From Fig. 4 it is evident that

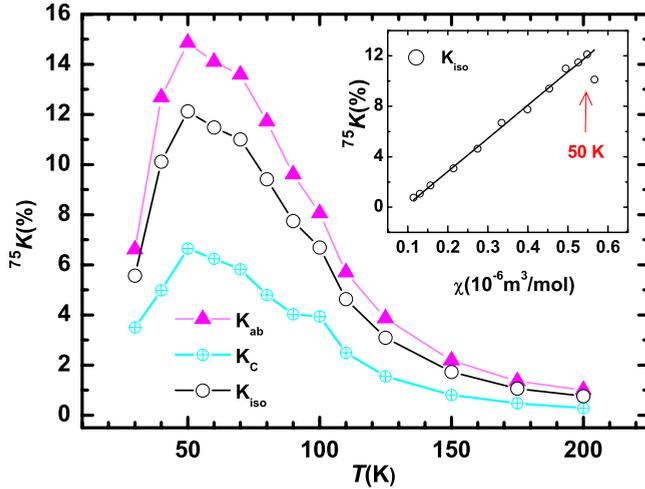


FIG. 4. (Color online) Temperature dependence of the $^{75}\text{K}_{\text{ab}}$, $^{75}\text{K}_{\text{c}}$, and $^{75}\text{K}_{\text{iso}}$. Inset shows the plots of $^{75}\text{K}_{\text{iso}}$ against the bulk susceptibility χ measured at 5 T.

$^{75}\text{K}_{\text{ab}}$ and $^{75}\text{K}_{\text{c}}$ increases with decreasing temperature presenting a strong anisotropy. At high temperature the anisotropy is small whereas with decreasing the temperature the anisotropy is enhanced considerably. If we compare $^{75}\text{K}_{\text{ab}}$ and $^{75}\text{K}_{\text{c}}$ at 50 K, it is seen that anisotropy of the transferred field is really important here and $^{75}\text{K}_{\text{ab}}$ is 2.5 times larger than $^{75}\text{K}_{\text{c}}$.

From Fig. 4 it is seen that $^{75}\text{K}_{\text{ab}}$, $^{75}\text{K}_{\text{c}}$, and $^{75}\text{K}_{\text{iso}}$ increases with decreasing temperature following the bulk susceptibility down to the temperature 50 K. However, with further lowering the temperature down to 30 K shift is decreasing with temperature leaving a maxima at around 50 K. This maxima traced back the results of susceptibility and specific-heat study. Which indicates the ferromagnetic Co ordering take place at T_{c} 75 K. It is worthwhile to mention that the bulk susceptibility is constantly increasing with decreasing the temperature. It is well established that NMR shift probes the local susceptibility, therefore it is normally not influenced by the small amount of the impurity. There are two possibilities for the decrease in the shift. First, the system have small amount of impurities which is not tracked by the x-ray diffraction measurement and makes the increase in susceptibility. Second, there are polarization effects on the Ce ions by the internal magnetic field of the Co magnetism. Which in turn changes the transferred hyperfine field below 50 K. The former one is unlikely because of the well-matched magnetization result of CeCoPO and LaCoAsO.^{18,19} Therefore, the later scenario is more likely. Below 50 K the decrement of the shift reveals that the ferromagnetically ordered Co moment polarizes the Ce moment. Which eventually makes the magnetic structure complicated and changes the hyperfine field in this system. NMR probes the magnetism on a microscopic scale. As NMR gives the local hyperfine field arising from the 4f Ce and the 3d Co ions. Usually for the itinerant 3d ions the negative core polarization is the dominant exchange mechanism whereas for localized Ce moments the strong conduction-electron polarization contribution (Fermi contact interaction) becomes important. Sometimes both fields cancel out each other leading to $K=0$ condition but

often the Fermi contact interaction is more than one order of magnitude larger.³⁴ Therefore the total shift could be composed as $K=K_{4f}+K_{3d}$. Furthermore K_{4f} couples strongly on the effective Ce 4f moment. The effective moment is reduced because of CEF splitting which results in a reduction in K_{4f} . This might explain the shift maximum observed.

For an estimation of the hyperfine coupling constant $^{75}\text{K}_{\text{iso}}$ is plotted as a function of the bulk susceptibility χ in the inset of Fig. 4. For this we have used the susceptibility measured at 5 T. We assume that $\chi=\chi_{\text{iso}}$, meaning that there is no alignment or the texture in the CeCoAsO sample. From the inset it is seen that $^{75}\text{K}_{\text{iso}}$ is nicely following the bulk susceptibility in the temperature range 200–50 K. From the linear curve we have estimated the hyperfine coupling constants at the ^{75}As site, $^{75}\text{A}_{\text{iso}}\approx 18 \text{ kOe}/\mu_{\text{B}}$. The estimated $^{31}\text{A}_{\text{iso}}$ for the CeCoPO and LaCoAsO is around $14 \text{ kOe}/\mu_{\text{B}}$ and $24.8 \text{ kOe}/\mu_{\text{B}}$, respectively.^{33,35} Therefore for CeCoAsO the value of hyperfine coupling constants is higher than that of CeCoPO system which could be interpreted as being due to a weaker 3d-4f polarization in CeCoAsO.

Below 15 K the additional line broadening shows up in the spectra. Such a broadening can not be explained by the impurities or disorder. As a first approach this line broadening traced back the specific-heat anomaly at 6.5 K and increase in C/T below 1.8 K. This broadening is also typical for the onset of correlation. However, for this system at present with the available data it is not settled whether this is the result of complicated magnetic structure or it is due to the correlation. For another 4f-3d pnictide NdCoAsO very recently McGurie *et al.*²⁶ proposed from neutron-scattering multiple phase transitions at low temperature.

IV. DISCUSSION AND SUMMARY

Our findings on CeCoAsO yield several interesting phenomena which shall now be discussed. The presented results point to a FM ordering of Co ions at $T_{\text{c}}=75 \text{ K}$ similar to FM order in the P-homologue.¹⁹ Similar to CeCoPO unusual but more S-like shaped $\chi(T)$ curves below T_{c} are observed. This is in contrast to LaCoPO and LaCoAsO where $\chi(T)$ behave like textbook ferromagnets. For CeCoPO and CeCoAsO a complex interplay of Co 3d moments with more localized Ce 4f moments has to be considered. More into detail: Co 3d ions order ferromagnetically at $T_{\text{c}}=75 \text{ K}$ and the resulting internal field transferred to the Ce site partially polarizes the Ce 4f ions. Due to thermal excitation the polarization is getting stronger towards lower temperatures leading to an S-like shape of $\chi(T)$. Moreover, in the specific heat an additional broad anomaly at around 6.5 K shows up, which is different to CeCoPO system. This low-temperature Schottky anomaly indicates a complex level splitting of the ground state of the rare-earth moment by the internal field.

In order to get a deeper microscopic insight of this system we have performed ^{75}As -NMR investigations. The NMR shift is increasing with decreasing the temperature following the susceptibility down to 50 K. The shift is decreased with lowering the temperature further resulting in a broad maxima at 50 K. This indicates that there is a change in hyperfine field below 50 K. Furthermore, in the ^{75}As -NMR spectra the

additional line broadening below 15 K, traced back the specific-heat anomaly at 6.5 K. Such broadening effects are typical for the onset of correlations. But also a reconstruction of hyperfine fields because of CEF splitting could be a possible explanation. To fully understand the low-temperature magnetism it deserves further investigation specially with microscopic tool, for instance neutron scattering and/or μ SR.

Furthermore based on the presented results doping studies on CeCoAsO might be fruitful in the context of superconductivity. The superconducting state of the doped RFeAsO systems are suggested to be unconventional nature. One key point to get the superconductivity in the CeFeAsO system is to suppress the Fe magnetism by changing the carrier concentration. One approach would be to substitute F in place of O, or substitute As by P or Fe by small concentration of Co. In all cases for the specific doping concentration one would get superconductivity.^{4,36,37} Therefore still it is not settled the nature of the carrier concentration required for this CeFeAsO based superconductor. Apart from the Fe-based pnictides, superconductivity was also found in LaNiPO and LaNiAsO. Furthermore in the 122 relative Ba(Fe,Co)₂As₂ T_C 's up to 22 K are found.⁵⁹ ⁵⁹Co-NMR investigations clearly reveals that Co is nonmagnetic.^{32,38} The absence of superconductivity in CeCo(As/P)O is not surprising considering the fact that here Co carries a moment and long-range order is observed. Furthermore in these system there is a complex interplay between the Ce 4f and 3d magnetism playing a crucial role to

control the magnetism. It is worthy to mention, as far as 3d magnetism is concern, there is a major difference between the CeCoAsO to that of CeFeAsO. For CeFeAsO, Fe magnetism can be tuned easily replacing As by P and SDW type transition diminished whereas for CeCoAsO, Co magnetism stays rigid with that and SDW transition is absent. However, still there is a possibility to suppress the Co magnetism either by doping or pressure, because an ordering temperature of around 70 K is rather low for Co ordering. Therefore further research has to answer the question whether the superconductivity appears in this system after the suppression of the Co magnetism. Which will eventually opens up the opportunity to understand the nature of coupling between the 4f and itinerant electrons in the RTPnO systems. And NMR/NQR would be the valuable tool to probe the magnetism and superconductivity.

In summary we presented magnetization, specific heat and ⁷⁵As-NMR investigations on polycrystalline CeCoAsO. The magnetization and specific-heat data reveal that in this system Co orders ferromagnetically at 75 K. Moreover specific heat study shows a Schottky anomaly at low temperature at around 6.5 K, which is likely due to the level splitting of the ground state of rare-earth moment by the internal field. Furthermore the analysis of the ⁷⁵As-NMR spectra clearly demonstrate the strong shift anisotropy towards lower temperature. Moreover the breakdown of the K vs χ linearity below 50 K might be the signature of CEF interaction.

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