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Phys. Rev. B **98**, 014517 — Published 24 July 2018

DOI: [10.1103/PhysRevB.98.014517](https://doi.org/10.1103/PhysRevB.98.014517)

# Suppression of the magnetic order in CeFeAsO: non-equivalence of hydrostatic and in-plane chemical pressure

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(Dated: July 11, 2018)

We present a detailed investigation of the electronic properties of CeFeAsO under in-plane chemical (As by P substitution) and hydrostatic pressure by means of in-house and synchrotron Mössbauer spectroscopy. The Fe magnetism is suppressed due to both pressures and no magnetic order was observed above a P-substitution level of 40 % or 5.2 GPa hydrostatic pressure. We compared both pressures and found that the isovalent As by P substitution change the crystallographic and electronic properties differently than hydrostatic pressure.

PACS numbers: 74.70.Xa, 76.75.+i, 76.80.+y, 74.62.Dh

## I. INTRODUCTION

The parent compounds of the 122 and 1111 families of the iron-based superconductors show spin density wave (SDW) order below the magnetic transition temperature  $T_N$ .<sup>1,2</sup> By changing a non-temperature control parameter the SDW order can be suppressed. These control parameters can be classified in the following way: i) electron doping (Fe→Co,<sup>3,4</sup> O→F<sup>5</sup>), ii) hole doping (Ca→Na,<sup>6</sup> Ba→K<sup>7</sup>), iii) isovalent substitution (As→P<sup>8-10</sup>), and iv) external pressure.<sup>11-13</sup> Both electron and hole doping change the amount of conduction electrons. The nominal valence electron count remains constant in the case of isovalent substitution and external pressure.

The isovalent substitution of a larger by a smaller atom, e. g. As → P or La → Pr → Nd → Sm, results in chemical pressure. The resulting question is: what are the differences between chemical and hydrostatic pressure? It was shown that both methods of achieving pressures result in a similar suppression of the magnetic order.<sup>11,13-24</sup> The chemical substitution can be applied either in the FeAs-plane (in-plane) or in the rare earth-O plane (out-of-plane). Studies in the isostructural compound LaCoPO have shown that isovalent out-of-plane substitution (La substituted by Pr, Nd, and Sm) and hydrostatic pressure equally change the magnetic properties of the system.<sup>22-24</sup> Complementary we will focus on in-plane chemical substitution: As by P.

The CeFeAsO system is of particular interest due to the interaction of the Fe 3d and Ce 4f electrons. CeFeAsO shows spin density wave order of the Fe 3d electrons below  $\sim 145$  K and antiferromagnetic order of the

Ce 4f electrons below  $\sim 3.7$  GPa.<sup>25</sup> A strong Ce-Fe coupling at temperatures much higher than the Ce magnetic ordering temperature was found.<sup>26</sup> Upon P substitution the Fe magnetic order is suppressed and no Fe magnetic order was observed for  $x \geq 37$  %.<sup>25,27</sup> In contrast, the Ce magnetic ordering temperature remains constant for  $x < 30$  %.<sup>25</sup> For  $x \geq 30$  % the Ce magnetic order changes from antiferromagnetic to ferromagnetic.<sup>25</sup> Superconductivity was observed for  $x \sim 30$  %.<sup>25</sup> Resistivity measurements have shown the absence of superconductivity in CeFeAsO up to 50 GPa.<sup>28</sup> The application of hydrostatic pressure on P substituted samples indicated that hydrostatic pressure and P substitution change the electronic structure differently.<sup>29</sup> However, to resolve the microscopic changes in the magnetic structure a local probe is needed.

We studied the electronic hyperfine parameters as a function of P substitution and hydrostatic pressure in CeFeAsO by means of in-house and synchrotron Mössbauer spectroscopy as well as x-ray diffraction. A quantitatively different behavior for P substitution and hydrostatic pressure was found.

The work is organized in the following way: the experimental details will be presented in Sec. II and the obtained results in Sec. III and IV. The discussion of our results is given in Sec. V followed by a summary and conclusion in Sec. VI.

## II. EXPERIMENTAL DETAILS

Powder samples of CeFeAs<sub>1-x</sub>P<sub>x</sub>O with  $x = 0, 5, 15, 22, 30, 35, 40, 90,$  and 100 % were investigated by in-

house Mössbauer spectroscopy at the Institute of Solid State and Material Physics, TU Dresden, Germany. The P-substitution level  $x$  is given in nominal values.<sup>30</sup> Mössbauer spectra were recorded at temperatures between 1.8 and 305 K using a CryoVac Konti IT cryostat in standard transmission geometry. As a  $\gamma$  source  $^{57}\text{Co}$  in a rhodium matrix was used with an emission line width (HWHM) of 0.135(5) mm/s. Isomer shifts are given with respect to  $\alpha$ -Fe at room temperature. Powder samples were homogeneously distributed in thin polyamide PA6.6 sample holders of 13 mm diameter. The sample synthesis of the  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  powder is described elsewhere.<sup>30</sup> The in-house Mössbauer spectra were analyzed using the Mössfit software.<sup>31</sup>

Single crystals of  $\text{CeFeAsO}$  were investigated via time-domain synchrotron Mössbauer spectroscopy (SMS), also known as nuclear forward scattering, at the beamline 3ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory, USA. The experiments were performed in the hybrid operation mode which allows the high precision measurement of hyperfine interactions by offering a time window for data collection of 1.5  $\mu\text{s}$ . The incident beam was linearly polarized. The single crystals were enriched to an abundance of 10 %  $^{57}\text{Fe}$ . They were grown similar to  $\text{LaFeAsO}$ <sup>32</sup> and characterized by energy-dispersive x-ray spectroscopy and x-ray diffraction (XRD). SMS spectra were recorded at temperatures between 10 and 150 K and at pressures between 0.5 and 14 GPa using a special He-flow miniature cryostat and a diamond anvil cell.<sup>33,34</sup> For pressures up to 6 GPa diamond anvils with 800  $\mu\text{m}$  culet size and for higher pressures diamond anvils with 500  $\mu\text{m}$  culet size were used. Pressures were changed at low temperatures through a gas membrane. The pressure was measured *in situ* by an online ruby system. A Re gasket was pre-indentated to a thickness of 80  $\mu\text{m}$  (140  $\mu\text{m}$ ) and a 250  $\mu\text{m}$  (400  $\mu\text{m}$ ) hole was electro-sparked to act as the sample chamber for the 500  $\mu\text{m}$  (800  $\mu\text{m}$ ) diamond anvils. As the pressure transmitting medium Ne and a 4:1 mixture of Methanol and Ethanol were used to ensure hydrostaticity. The uncertainty in the pressure determination is 0.1 GPa if not stated otherwise. Single crystals of  $50 \times 50 \times 45 \mu\text{m}^3$  and  $130 \times 130 \times 25 \mu\text{m}^3$  for the 500  $\mu\text{m}$  and 800  $\mu\text{m}$  diamond anvils were used, respectively. The single crystals were aligned with the crystallographic  $ab$ -axis perpendicular to the incident beam. The beam size was  $10 \times 15 \mu\text{m}^2$  (FWHM). The SMS spectra were analyzed using the CONUSS software.<sup>35</sup> Both Mössfit and CONUSS exactly diagonalize the hyperfine Hamiltonian taking into account both electric and magnetic hyperfine interactions. For the former the transmission integral formalism and for the latter the thin absorber approximation was used. XRD experiments were conducted at the 13BM-C beamline of the APS using  $\text{CeFeAsO}$ -powder at room temperature.<sup>36</sup> X-rays with a wavelength of 0.434  $\text{\AA}$ , a Re gasket as described earlier and Daphne oil 7575 as the pressure transmitting medium were used. The x-ray diffraction patterns were

analyzed using GSAS-II.<sup>37</sup> The numerical results of our XRD study are recorded in the supplement together with the numerical values of chosen diagrams.<sup>38</sup>

### III. X-RAY DIFFRACTION RESULTS

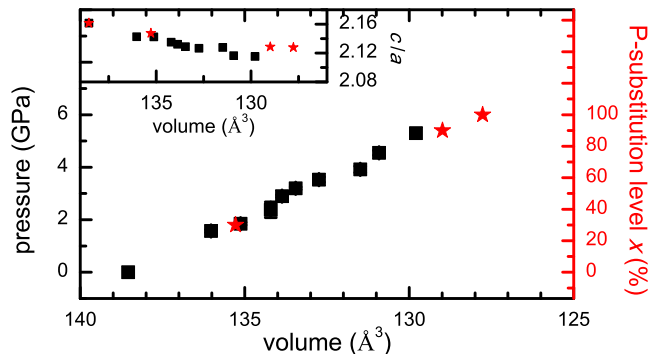


FIG. 1. Unit cell volume at room temperature as a function of applied pressure  $p$  (black square) and the P-substitution level  $x$  (red star, taken from Ref.<sup>39</sup>). 100 % P-substitution ( $\text{CeFeAsO} \rightarrow \text{CeFePO}$ ) reduces the unit cell volume similar to the application of 6 GPa hydrostatic pressure.

To compare the structural effects of P substitution and external pressure XRD measurements up to 5.3 GPa at room temperature using a  $\text{CeFeAsO}$  powder sample were performed. The unit cell volumes of the by Mössbauer spectroscopy investigated P-substitution levels as well as at the applied pressure points are summarized in Tab. I. The resulting unit cell volumes and  $c/a$  ratios are shown in Fig. 1 together with published data on  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  for comparison.<sup>39</sup> At room temperature and ambient pressure  $\text{CeFeAsO}$  crystallizes in a tetragonal structure with the space group  $P4/nmm$ .<sup>40</sup> No indications for structural transitions up to 5.3 GPa and that the  $c/a$  ratio is more reduced in the case of hydrostatic pressure than upon P substitution were found. By comparing the unit cell volumes it was found that 100 % P-substitution ( $\text{CeFeAsO} \rightarrow \text{CeFePO}$ ) has the same effect as the application of 6 GPa hydrostatic pressure.

Atomic distances and block sizes are shown in Fig. 2. The Ce-O-Ce as well as the As-Fe-As block size are pressure independent. Both the Fe-As and Ce-As distances are reduced with increasing hydrostatic pressure. Therefore the reduction in the unit cell volume is achieved by reducing the distance between the Ce-O-Ce and As-Fe-As blocks. In contrast the unit cell compression due to the P-substitution is caused by a compression of the As-Fe-As layer.<sup>27</sup>

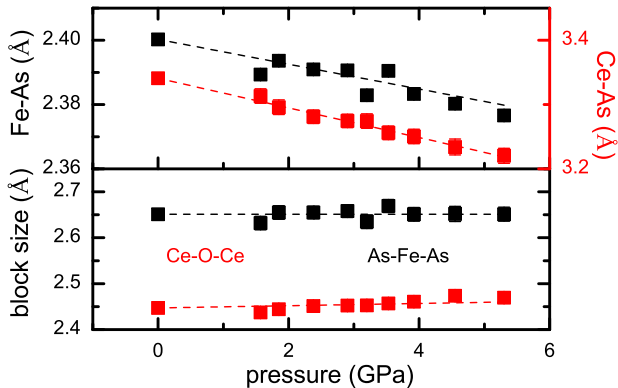


FIG. 2. Atomic distances and block sizes for CeFeAsO as a function of pressure.

TABLE I. Unit cell volume of the investigated P-substitution levels  $x$  (left two columns) and for the hydrostatic pressures  $p$  (right two columns). The volumes were calculated by extrapolating the data from Fig. 1.

$x$ / %	$V$ / $\text{\AA}^3$	$p$ / GPa	$V$ / $\text{\AA}^3$
0	138.46	0.8	137.1328
5	138.00	2.4	134.48
15	136.92	2.8	133.81
22	136.17	3.1	133.32
30	135.31	3.6	132.49
35	134.77	4	131.82
40	134.23	4.5	130.99
90	128.85	5.2	129.83
100	127.77		

#### IV. MÖSSBAUER SPECTROSCOPY RESULTS

Mössbauer spectra of  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  in the paramagnetic and magnetically ordered phase are shown in Fig. 3. In the paramagnetic phase an asymmetric doublet structure is observed which is most pronounced for  $x \leq 30$  %. For powder samples one would expect a symmetric spectrum as the angle between the incident  $\gamma$  and the principal axis of the electric field gradient (EFG) is averaged out. The asymmetric paramagnetic spectra indicate that the samples consists of tiny polycrystalline platelets instead of powder in accordance with the plate-like crystal habit. As a consequence the angle between the incident  $\gamma$  and the principal axis of the EFG is not averaged out resulting in an asymmetric doublet. The magnetically ordered phase is characterized by a sextet structure for  $x \leq 22$  % while for  $x = 30$  and 35 % a broadening and a symmetrization of the spectra was observed.

SMS spectra in the paramagnetic and magnetically ordered phase for various pressures are shown in Fig. 4. In the paramagnetic phase no oscillations in the time spectra were observed up to pressures of 14 GPa. The magnetically ordered phase is characterized by many oscillations with additional wiggles due to the angle between

the magnetic hyperfine field and the incident  $\gamma$  beam.

#### A. Electric field gradient

In the principal axis system, the EFG is fully determined by its  $z$  component  $V_{zz}$  and the asymmetry parameter  $\eta$ . The latter is zero due to the tetragonal symmetry of the crystallographic structure in the paramagnetic phase. In the magnetically ordered phase no non-zero  $\eta$  was observed which is consistent with the absence of an orthorhombic distortion.<sup>25</sup> Neutron scattering experiments report an orthorhombicity of 0.5 % for CeFeAsO which is suppressed due to P substitution.<sup>27</sup> However, the changes in the EFG due to the orthorhombic distortion are below the resolution limit of our method.

In Mössbauer spectroscopy an energy shift, the so-called quadrupole splitting  $QS$ , due to the interaction of the Fe nucleus with an EFG rather than  $V_{zz}$  itself is measured. From the  $QS$  the electric field gradient  $V_{zz}$  at the Fe nucleus can be deduced. Here both  $QS$  in mm/s and  $V_{zz}$  in  $\text{V}/\text{\AA}^2$  are provided. The conversion factor is  $1 \text{ V}/\text{\AA}^2 = 0.0167 \text{ mm/s}$  which corresponds to a nuclear quadrupole moment of Fe of 160 mb.<sup>41,42</sup> At this point we want to emphasize that in the paramagnetic phase only the absolute value of  $V_{zz}$  is obtained. However, it was shown that in the LaFeAsO-based compounds  $V_{zz}$  is positive.<sup>43,44</sup> In the magnetic phase a positive  $V_{zz}$  value was obtained and thus we are confident that this is also the case in the paramagnetic phase of the CeFeAsO series.

Experimentally determined  $V_{zz}$  values at various temperature regions between 2 and room temperature are shown in Fig. 5. At room temperature  $V_{zz}$  is close to zero for CeFeAsO indicating a nearly spherical electron distribution around the Fe nucleus.  $V_{zz}$  shows a parabolic behavior as a function of  $x$  with a maximum at intermediate  $x$ . The  $V_{zz}$  values of CeFeAsO and CeFePO are equal to formerly reported data.<sup>45,46</sup>

For  $x \leq 22$  %,  $V_{zz}$  increases by  $\approx 2\text{V}/\text{\AA}^2$  between room temperature and the onset temperature of the magnetic order,  $T_N^{\text{onset}}$ . This increase of  $V_{zz}$  inside the paramagnetic phase as a function of temperature is likely a steric effect such as a change in the  $c/a$  ratio or the anion height.

At  $T_N^{\text{onset}}$ , which we define as the highest temperature with a non-zero magnetic volume fraction,  $V_{zz}$  jumps from 2(1)  $\text{V}/\text{\AA}^2$  to 7(1)  $\text{V}/\text{\AA}^2$  for  $x = 0$  and 5 % and from 12.0(5)  $\text{V}/\text{\AA}^2$  to 14.0(5)  $\text{V}/\text{\AA}^2$  for  $x = 15$  and 22 %, respectively. This indicates a change of the electron distribution and hence of  $V_{zz}$  due to the magnetic phase transition.

In the magnetically ordered phase  $V_{zz}$  remains constant within error bars down to lowest measured temperatures. The increase in  $V_{zz}$  at the magnetic phase transition is suppressed similar to the reduction of  $T_N^{\text{onset}}$  and the magnetic hyperfine field as a function of  $x$ . No influ-

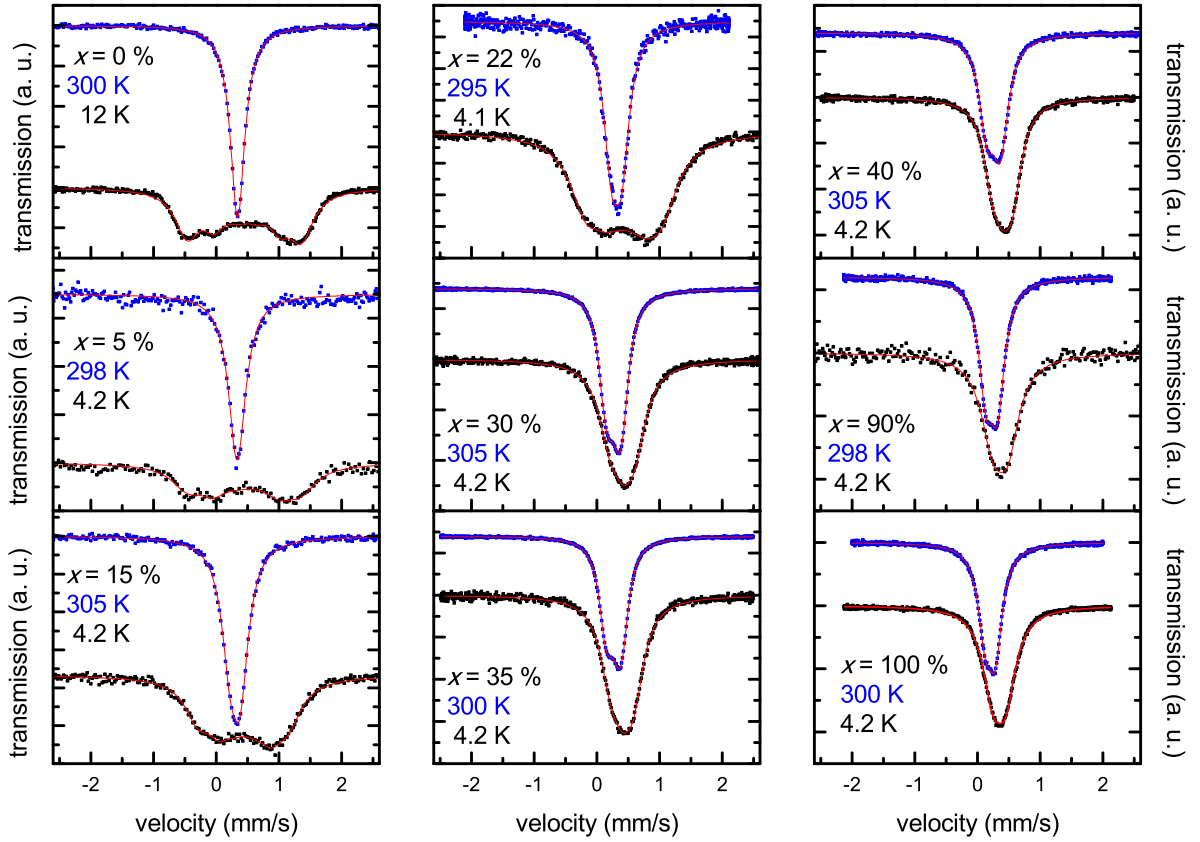


FIG. 3. Mössbauer spectra of  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  in the paramagnetic and magnetically ordered phase. The solid red lines are theoretically calculated spectra. See text for details.

ence of the Ce magnetic order on  $V_{zz}$  has been observed similar to the unsubstituted compound.<sup>45</sup> For  $x \geq 30\%$   $V_{zz}$  increases upon cooling and saturates below 100 K.

The SMS spectra in the paramagnetic phase show no oscillations up to 330 ns. This gives an upper boundary for the absolute value of the quadrupole splitting of  $\sim 0.1$  mm/s ( $6 \text{ V}/\text{\AA}^2$ ). Analyzing the spectra gives a value of  $< 0.01$  mm/s ( $0.6 \text{ V}/\text{\AA}^2$ ) at 1 GPa which is similar to the  $V_{zz}$  values within error bars at ambient conditions. By increasing the external pressure,  $V_{zz}$  increases to  $0.08(1)$  mm/s at 7 GPa and  $0.11(1)$  mm/s at 14 GPa with both values obtained at 15 K.

In the magnetically ordered phase, the quadrupole splitting jumps to  $0.08(2)$  mm/s ( $4.8(1.2) \text{ V}/\text{\AA}^2$ ) and stays constant within error bars down to lowest temperatures.

### B. Magnetic order

The temperature dependence of the magnetic volume fraction for  $x \leq 22\%$  and applied pressures of  $p \leq 5.2$  GPa is shown in Fig. 6.

$T_N^{\text{onset}}$  decreases with increasing  $x$  and  $p$ . The phase transition region, which can be defined as the temperature difference between  $T_N^{\text{onset}}$  and  $T_N^{100\%}$  (the highest temperature with a magnetic volume fraction of 100%) increases from  $\approx 10$  K for  $x \leq 5\%$  to  $60(10)$  K for  $x = 15$  and  $22\%$ . For  $x = 30$  and  $35\%$  no magnetic volume fraction was extracted as the obtained magnetic hyperfine fields are too small to distinguish between a) a smaller hyperfine field and 100% magnetic volume fraction or b) a slightly larger hyperfine field and a magnetic volume fraction of  $< 100\%$ , in particular as  $V_{zz}$  shows no measurable difference between the paramagnetic and magnetically ordered phase (in contrast to  $x \leq 22\%$ ). As a consequence, the magnetic volume fraction was set to 100% in the magnetically ordered phase. This may influence the analysis close to the phase transition temperature but the low-temperature behavior and therefore the saturated magnetic hyperfine field is unaffected.

$T_N^{\text{onset}}$  is reduced as a function of the applied pressure consistent with reported results from electrical resistivity measurements.<sup>28</sup> The phase transition region between  $T_N^{\text{onset}}$  and  $T_N^{100\%}$  stays constant up to an applied pressure of at least 4.5 GPa. For an applied pressure of 5.2 GPa a magnetic volume fraction of  $24(1)\%$  was found

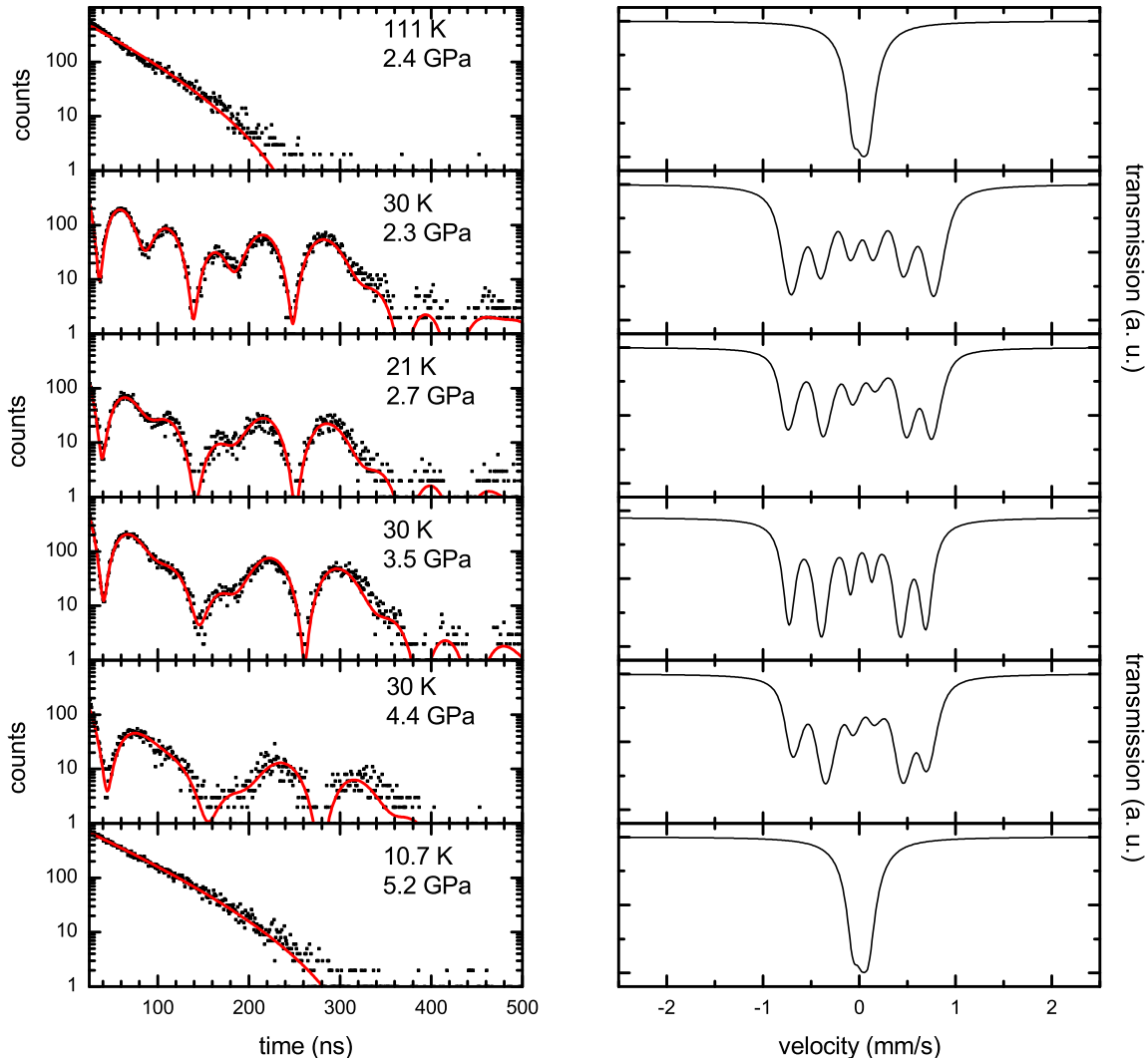


FIG. 4. Synchrotron Mössbauer spectroscopy spectra of CeFeAsO in the paramagnetic and magnetically ordered phase for various pressures (left column). The solid red lines are theoretical spectra. The corresponding spectra of the fit in the energy domain are shown in the right column for clarity. The energy domain spectra were theoretically calculated using the hyperfine parameters extracted from the time domain measurements.

while for 5.1 GPa a pure paramagnetic signal at lowest measured temperature was observed. Note that the given pressure values are determined at the ruby position with an uncertainty in the pressure determination of 0.1 GPa.

The temperature dependence of the magnetic hyperfine field,  $B_{\text{hf}}(T)$ , as a function of  $x$  and  $p$  is shown in Fig. 7.  $B_{\text{hf}}(T)$  was analyzed using an order parameter fit of the form

$$B_{\text{hf}}(T) = B_{\text{hf}}(T = 0) \left[ 1 - \left( \frac{T}{T_N} \right)^\alpha \right]^\beta \quad (1)$$

at temperatures above the magnetic Ce ordering. The

results are shown in Tab. II.

Both the onset of the magnetic order as well as the saturated magnetic hyperfine field at lowest temperatures are continuously suppressed as a function of  $x$ . For  $x = 40\%$  no magnetic order was observed which is consistent with results from other methods.<sup>25,27,47</sup> For  $x = 5\%$  an increase of the magnetic hyperfine field from 5.40(2) above 4 K to 5.95(8) T below 4 K is observed due to the antiferromagnetic ordering of the Ce 4*f* electrons.<sup>25</sup> This transferred magnetic hyperfine field was also observed in the unsubstituted compound CeFeAsO where an increase by 0.9 T was measured.<sup>26,45,48</sup> Increasing  $x$  to 15% or above leads to a full suppression of this transfer.

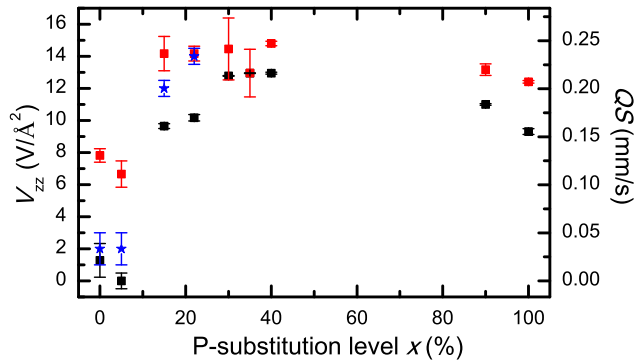


FIG. 5.  $V_{zz}$  as a function of the P-substitution level  $x$  at room temperature (black), at  $\sim 4$  K (red), and at  $T_N^{\text{onset}}$  (blue) in  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ . At room temperature  $V_{zz}$  is close to zero for  $\text{CeFeAsO}$  indicating a nearly spherical electron distribution around the Fe nucleus.  $V_{zz}$  shows a parabolic behavior as a function of  $x$  with a maximum at intermediate  $x$ . The increase from room temperature to  $\sim 4$  K is largest for  $x \leq 5\%$  and decreases with increased  $x$ . In contrast, for pressures  $\leq 4.5$  GPa  $V_{zz}$  remains constant within error bars with values of  $\sim 0$  in the paramagnetic phase and  $4.8(1.2)$   $\text{V}/\text{\AA}^2$  ( $0.08(2)$  mm/s) in the magnetically ordered phase.

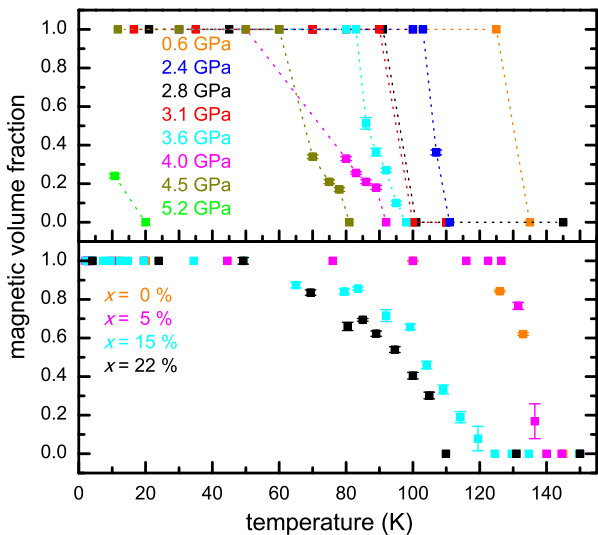


FIG. 6. Magnetic volume fraction in  $\text{CeFeAsO}$  as a function of the applied pressure  $p$  (top) and of the P-substitution level  $x$  (bottom). The onset temperature of the magnetic phase transition is suppressed with increasing  $x$  and  $p$ . The phase transition region broadens for higher  $x$  whereas it remains sharp for increasing pressure.

TABLE II. Exponents  $\alpha$  and  $\beta$  obtained by analyzing the temperature dependence of the magnetic hyperfine field applying Eq. 1 to temperatures above the Ce magnetic order. To determine the critical exponent  $\beta_c = \beta(\alpha = 1)$ , Eq. 1 was applied in the vicinity of the phase transition and with  $\alpha = 1$ .

$p$ / GPa	$x$ / %	$\alpha$	$\beta$	$\beta_c$
0.6				0.09(4)
2.4		3.0(2)	0.18(1)	0.17(1)
2.8		2.3(1)	0.18(1)	0.14(1)
3.1		2(1)	0.17(6)	0.12(1)
3.6		1.8(2)	0.15(1)	0.12(1)
4.0		3.3(4)	0.42(6)	0.13(3)
4.5		1.2(6)	0.18(8)	0.13(4)
0		2.6(2)	0.25(1)	0.17(1)
5		1.7(2)	0.02(1)	0.14(1)
15		0.6(4)	0.09(3)	0.10(1)
22		0.7(6)	0.09(5)	0.10(3)

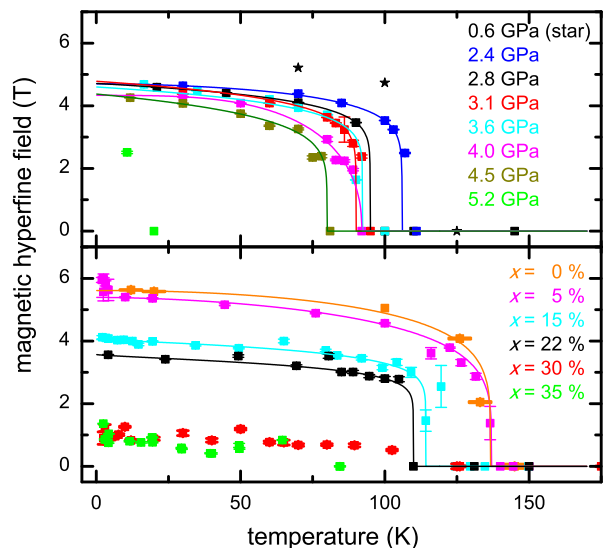


FIG. 7. Temperature dependence of the magnetic hyperfine field as a function of  $p$  (top) and  $x$  (bottom) in  $\text{CeFeAsO}$ . Lines are calculated with Eq. 1.

The saturated magnetic hyperfine field is suppressed with increasing applied pressure (Fig. 11). Between 0 and 4.5 GPa the saturated magnetic hyperfine field is reduced by  $\sim 24\%$  followed by an abrupt suppression to zero. Between 5.2 and 14 GPa no magnetic order was found down to 16 K.

The azimuth angle  $\theta$  between the principal axis of the EFG, which is parallel to the crystallographic  $c$ -axis, and the magnetic hyperfine field at lowest observed temperatures is shown in Fig. 8 as a function of  $x$  and  $p$ . For  $\text{CeFeAsO}$  at ambient conditions an angle of  $\theta = 90^\circ$  was obtained. Therefore, the Fe magnetic moments are lo-

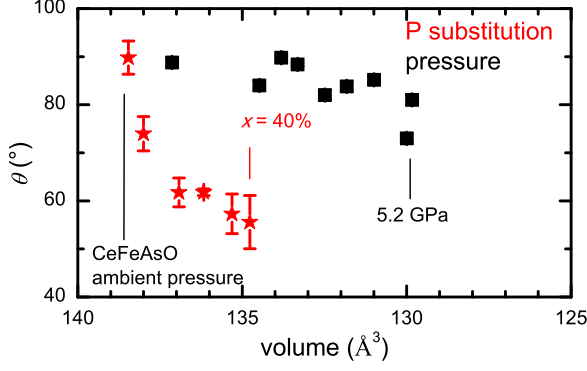


FIG. 8. Azimuth angle  $\theta$  between the principal axis of the EFG and the Fe magnetic hyperfine field as a function of the P-substitution level  $x$  (red star) and hydrostatic pressure (black square). For the conversion between volume,  $x$ , and  $p$  see Tab. I.

cated in the crystallographic  $ab$ -plane consistent with neutron scattering experiments.<sup>49</sup> Upon the application of pressure a small tilting of  $10^\circ$  out of the crystallographic  $ab$ -plane at 4.5 GPa is observed. In contrast,  $\theta$  decreases to  $56(6)^\circ$  as a result of P substitution.

### C. Isomer and chemical shift in $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$

The temperature dependence of the isomer shift,  $\delta(T)$ , for selected P-substitution levels is shown in Fig. 9.  $\delta(T)$  is given by

$$\delta(T) = \delta_c + \delta_R(T), \quad (2)$$

where  $\delta_c$  denotes the temperature-independent chemical shift.  $\delta_R(T)$  is the temperature-dependent contribution due to the second-order Doppler shift and was analyzed in the Debye approximation:

$$\delta_R(T) = -\frac{9}{16} \frac{k_B}{M_{\text{Fe}} c} \times \left[ \theta_M + 8T \left( \frac{T}{\theta_M} \right)^3 \int_0^{\theta_M/T} \frac{x^3}{e^x - 1} dx \right] \quad (3)$$

with  $M_{\text{Fe}}$  being the mass of the resonant  $^{57}\text{Fe}$  nucleus and  $\theta_M$  denotes the Mössbauer temperature.  $\theta_M$  can be interpreted as the Debye temperature of the Fe nucleus. By fixing  $M_{\text{Fe}}$  to its nuclear value of 56.93 a.u.,  $\theta_M$  and  $\delta_c$  were calculated. The obtained results are shown in Tab. III.

An increase of  $\theta_M$  from CeFeAsO to CeFePO upon As $\rightarrow$ P substitution was found while  $\delta_c$  decreases.

TABLE III. Mössbauer temperature  $\theta_M$  and chemical shift  $\delta_c$  obtained by applying Eq. 2 to the temperature dependence of the isomer shift in  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ .

$x$ / %	$\theta_M$ / K	$\delta_c$ / mm/s
0	381(32)	0.680(7)
	377(5) <sup>50</sup>	
5	445(53)	0.68(1)
15	342(26)	0.642(6)
22	401(13)	0.661(3)
30	385(5)	0.620(1)
35	360(5)	0.614(1)
40	401(12)	0.613(3)
90	438(23)	0.582(6)
100	448(31) <sup>46</sup>	0.55 <sup>46</sup>

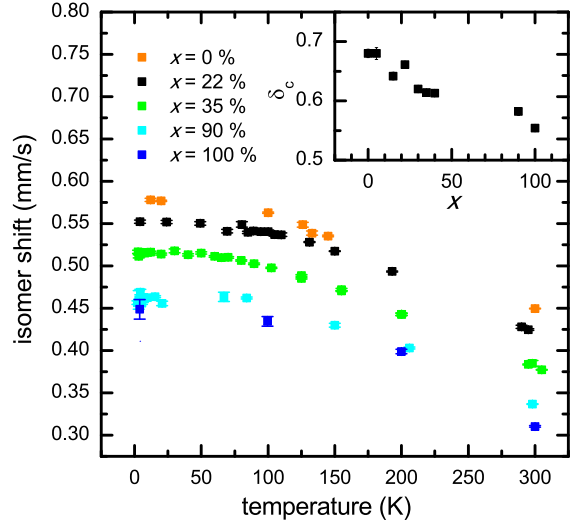


FIG. 9. Temperature dependence of the isomer shift of  $x = 0, 22, 35, 90,$  and  $100\%$  ( $x = 5, 15,$  and  $40\%$  are omitted for the sake of clarity). In the inset the chemical shift  $\delta_c$  in mm/s as a function of  $x$  in % is shown.

## V. DISCUSSION

To reveal the differences in the electronic structure between hydrostatic pressure and P substitution, following Ref.<sup>51</sup>, the obtained electronic hyperfine parameters as a function of the unit cell volume are compared. The relation between the unit cell volume and  $x$  and  $p$  is shown in Fig. 1.

In the paramagnetic phase CeFeAsO has a  $V_{zz}$  of close to zero indicating a nearly spherical charge distribution around the Fe nucleus while CeFePO has a  $V_{zz}$  of  $9.3(2) \text{ V/\AA}^2$  indicating a deviation from a spherical charge distribution. This is consistent with reported results from neutron scattering experiments.<sup>27</sup> They found a continuous reduction of the size of the  $Pn\text{-Fe-P}n$  block, with  $Pn = \text{As/P}$ , as well as a continuous reduction of the  $\text{Fe-P}n$  distance. As a consequence the  $\text{Fe-P}n\text{-Fe}$  tetrahedra angle increases from  $\sim 112.2^\circ$  to  $\sim 114.6^\circ$  for  $x = 0$  and



43 %, respectively. Thus the angle continuously deviates from the ideal value of  $109.47^\circ$  with increasing  $x$ . This continuous change in the  $\text{FePn}$  block properties explains the increase in  $V_{zz}$  from  $\text{CeFeAsO}$  to  $\text{CeFePO}$  but cannot explain the maximum at intermediate  $x$ . We attribute this maximum to the disorder induced by the substitution which is expected to be strongest at  $x \sim 50$  %.

In contrast, the value of  $V_{zz}$  in the paramagnetic phase increases only slightly and monotonically as a function of hydrostatic pressure. This indicates a slight deviation from the spherical charge distribution around the Fe nucleus with increasing pressure. As it was shown in Fig. 2 the As-Fe-As layer remains robust against the application of hydrostatic pressure. Reported high temperature Fe-As-Fe angles for  $\text{CeFeAsO}$  are  $112.6(1)^\circ$ .<sup>49,52</sup> A minor reduction of the Fe-As-Fe angle to  $\sim 112.2^\circ$  at 5.3 GPa was observed. Due to the tetragonal symmetry a reduction of the Fe-As distance will not increase  $V_{zz}$ . The crystallographic parameters which are significantly changing in the investigated pressure region are the  $c/a$  ratio and the Ce-As distance and thus the As-Fe-As and Ce-O-Ce block distance. However, both crystallographic parameters are expected to have only a minor influence on  $V_{zz}$ , in contrast to the As-Fe-As block size in the P-substituted compound.<sup>27</sup> Eventually the only small increase of  $V_{zz}$  reflects the robustness of the As-Fe-As layer against hydrostatic pressure and the only minor changes in the Fe-As-Fe angle.

At the magnetic phase transition temperature  $V_{zz}$  abruptly increases and remains constant within error bars down to lowest temperatures. It was found that  $V_{zz}$  remains constant within error bars in the magnetic phase at all investigated pressures. The abrupt increase in  $V_{zz}$  at the magnetic phase transition is suppressed with increasing external pressure similar to the magnetic hyperfine field. For  $\text{CeFeAsO}$  a splitting in temperature between the structural and magnetic phase transition was reported.<sup>27,30</sup> No change in  $V_{zz}$  at the structural phase transition was observed. For comparison: in  $\text{FeSe}$ , where a tetragonal-to-orthorhombic phase transition without a coinciding magnetic order occurs, similarly no change in  $V_{zz}$  was observed.<sup>53</sup> This indicates that the magnetic phase transition causes a redistribution of the electronic charge and hence changes  $V_{zz}$  while the changes due to the structural phase transition are negligible. This result also explains why the abrupt increase of  $V_{zz}$  at the magnetic phase transition and the magnetic hyperfine field are equally suppressed.

$T_N^{\text{onset}}$  shows qualitatively similar behavior for increasing  $x$  and  $p$  and is shown in Fig. 10.  $T_N^{\text{onset}}$  is continuously reduced until  $x \sim 30$  % and  $p \sim 4.5$  GPa followed by a sharp suppression to zero at  $x \sim 40$  % and  $p \sim 5.2$  GPa. No magnetic order was observed at higher values. For the P substitution series it is consistent with neutron scattering experiments where no magnetic order was found at  $x \sim 37$  %.<sup>27</sup> The phase transition region  $\Delta T = T_N^{\text{onset}} - T_N^{100\%}$  increases with increased  $x$ . We at-

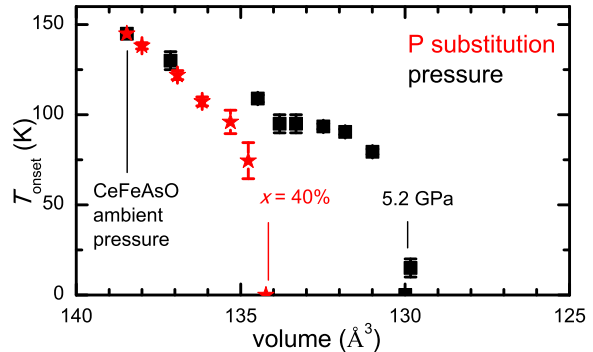


FIG. 10. Onset temperature of the Fe magnetic order as a function of hydrostatic pressure (black square) and P substitution (red star).  $T_N^{\text{onset}}$  is suppressed in a qualitatively similar way as a function of hydrostatic pressure and P substitution but more effective by the latter. For the conversion between volume,  $x$ , and  $p$  see Tab. I.

tribute this to the fact that the P substitution results in local P distributions and hence a distribution of magnetic ordering temperatures. In contrast  $\Delta T$  remains constant within error bars for all applied pressures. This supports that the increase in  $\Delta T$  is caused by the disorder due to the P substitution.

The temperature dependence of the magnetic hyperfine field was analyzed using Eq. 1. A second-order phase transition in the magnetic hyperfine field for all investigated pressures and P-substitution levels was found consistent with published results for  $\text{CeFeAsO}$ .<sup>30</sup> A critical exponent  $\beta_c$  of  $0.17(1)$  was obtained in  $\text{CeFeAsO}$ . Both the application of pressure and P substitution result in a reduction of  $\beta_c$  in direction of the two-dimensional Ising universality class ( $\beta_c = 0.125$ ). This behavior indicates an increase of the two-dimensionality of the magnetic order. Published Mössbauer data suggest that the critical exponent of the magnetic hyperfine field is of similar value in  $\text{LaFeAsO}$  ( $0.2(1)$ ) and  $\text{PrFeAsO}$  ( $0.19(2)$ ).<sup>45</sup> A 2D Ising critical exponent was also found in  $\text{BaFe}_2\text{As}_2$ ,<sup>54,55</sup>  $\text{SrFe}_2\text{As}_2$ ,<sup>56</sup>  $\text{Ba}_{0.75}\text{Na}_{0.25}\text{Fe}_2\text{As}_2$ ,<sup>57</sup> and  $\text{Ca}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$ .<sup>6</sup> The reduction in  $\beta_c$  and therefore in the dimensionality due to chemical pressure was also observed in  $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$  where a crossover from three- to two-dimensional Ising behavior from 50 % to 30 % Na-substitution level was found.<sup>6</sup>

The low-temperature saturated magnetic hyperfine field (above the Ce ordering temperature) as a function of  $x$  and  $p$  is shown in Fig. 11. It is continuously reduced to zero with increasing  $x$ . This behavior as a function of  $x$  is similar to that of the Fe magnetic moment and orthorhombicity.<sup>27</sup> In contrast, the saturated magnetic hyperfine field is reduced by 24 % between 0 and 4.5 GPa followed by an abrupt suppression to zero above 5.2 GPa showing a behavior similar to  $T_N^{\text{onset}}$ .

It was shown that the Fe magnetic moment is propor-

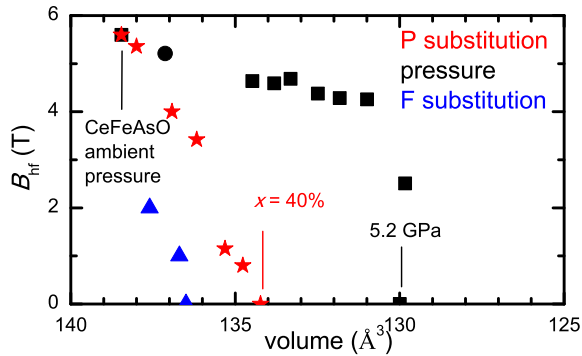


FIG. 11. Low-temperature saturated magnetic hyperfine field (above the Ce ordering temperature) as a function of hydrostatic pressure (black square) and P substitution (red star). The black circle data point was taken at 70 K and 0.6 GPa. P substitution results in a continuous suppression of the magnetic hyperfine field to zero at  $x = 40\%$ . In contrast, the application of hydrostatic pressure results in a reduction of the magnetic hyperfine field by 24 % at 4.5 GPa followed by an abrupt reduction to zero at 5.2 GPa. For the conversion between volume,  $x$ , and  $p$  see Tab. I.  $\text{CeFeAsO}_{1-y}\text{F}_y$  data (blue triangle) taken from Ref.<sup>58</sup>

tional to the Fe-As distance and vanishes for distances smaller than 2.36 Å.<sup>27,59,60</sup> The Fe magnetic moment is not directly accessible by Mössbauer spectroscopy which measures the magnetic hyperfine field. Theoretical calculations on  $\text{BaFe}_2\text{As}_2$  have shown that the conversion factor between the Fe magnetic moment and the magnetic hyperfine field changes with chemical substitution.<sup>61</sup> The changes in the conversion factor are severe for electron and hole doping but are below 3 % for P substitution.<sup>61</sup> Unfortunately no calculations for hydrostatic pressure were performed but it is more likely that the conversion factor exhibits only minor changes in the case of hydrostatic pressure.<sup>61</sup> Therefore the conversion factor between Fe magnetic moment and magnetic hyperfine field is treated as constant in our work. The saturated low-temperature magnetic hyperfine field as a function of the Fe-As distance is shown in Fig. 12.

At this point we want to emphasize that our XRD measurements were conducted at room temperature while the reported neutron scattering data was obtained at 1.8 to 8 K.<sup>27</sup> However, the Fe-As distance is nearly temperature independent with changes below 0.002 Å between room temperature<sup>52</sup> and 1.8 K<sup>49</sup> in  $\text{CeFeAsO}$  and therefore we assume that this also the case in the P-substituted compounds and under hydrostatic pressure.<sup>27</sup> The Fe-As distance continuously decreases below the threshold value 2.36 Å for  $x \sim 37\%$ .<sup>27</sup> The reduction of the magnetic hyperfine field as a function of applied hydrostatic pressure shows the qualitatively same behavior above 2.38 Å. This result supports that the Fe magnetic moment is somewhat proportional to the Fe- $Pn$  distance which determines the hybridization strength of the Fe 3d and

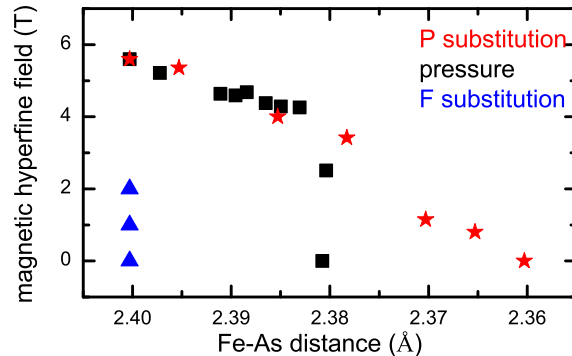


FIG. 12. Magnetic hyperfine field as a function of the Fe-As distance for hydrostatic pressure (black square), P substitution (red star), and F substitution (blue triangle). Fe-As distance as a function of the P-substitution level is taken from Ref.<sup>27</sup>. For the conversion between volume,  $x$ , and  $p$  see Tab. I.  $\text{CeFeAsO}_{1-y}\text{F}_y$  data taken from Ref.<sup>58</sup>

$Pn p$  electrons. The observation of a purely paramagnetic phase at 5.3 GPa with a Fe-As distance of  $\sim 2.38$  Å implies that the  $dp$  hybridization is not the only mechanism controlling the Fe magnetic moment. This is supported by measurements in  $\text{CeFeAsO}_{1-y}\text{F}_y$  where a reduction of the magnetic moment to zero with increasing F-substitution level while having a nearly constant Fe-As distance of  $\sim 2.405$  Å was observed.<sup>49,58</sup> That the Fe-As-Fe angle increases with increasing  $x$  but decreases with increasing  $p$  may also play a role. Additionally, the strong suppression to zero occurs between 4.5 and 5.2 GPa. In this pressure region a maximum in the magnetic phase transition temperature of the Ce 4f electrons was reported.<sup>28</sup> In  $\text{CeFeAs}_{0.78}\text{P}_{0.22}$  it was observed that the Ce 4f magnetic ordering temperature has a maximum at 1.95 GPa where the magnetic order changes from anti-ferromagnetic.<sup>29</sup> The resulting question is if the anti-ferromagnetic transition also occurs in  $\text{CeFeAsO}$  between 4.5 and 5.2 GP and if the Ce ferromagnetic order strongly suppresses the Fe magnetic order.

To derive an explanation of our obtained results we want to compare them with results from density-functional theory (DFT) in the La-1111 compounds and add the additional Ce 4f component later. Comparing  $\text{LaFeAsO}$  and  $\text{LaFePO}$  at ambient pressure shows that the Fermi surfaces (FS) are comparable with three hole pockets at  $\Gamma$  and two electron pockets at  $M$ .<sup>62,63</sup> The states at the Fermi level are mostly of Fe 3d character.<sup>64</sup> The difference is that one of the hole pockets is of 2D character in  $\text{LaFeAsO}$  and of 3D character  $\text{LaFePO}$ . This indicates better nesting in  $\text{LaFeAsO}$  and hence magnetic ordering than in  $\text{LaFePO}$ . It was shown that the FS topology is sensitive to the local Fe- $Pn$  arrangement, namely the Fe- $Pn$  distance and the corresponding tetrahedra angle.<sup>62,65</sup> This sensitivity is due to the hybridization of the Fe 3d and  $Pn p$  states.<sup>62</sup> Our experiments as well as

published results show that the  $FePn$  distance decreases with increasing pressure<sup>66</sup> and  $As \rightarrow P$  substitution<sup>27,67</sup> in 1111 compounds. An decreased  $FePn$  distance results in an enhanced  $FePn$  hybridization.<sup>62</sup>

DFT calculations in the paramagnetic state found that the density of states (DOS) at the Fermi level is smaller for LaFePO than for LaFeAsO.<sup>64</sup> DFT calculations on LaFeAsO under pressure in the magnetically order phase show that the FS topology is rather robust which implies that the nesting condition remains intact.<sup>68</sup> In this study it was also found that the DOS at the Fermi level decreases with increasing pressure in LaFeAsO.<sup>68</sup> This is consistent with the observation that the DOS at Fermi level is somewhat proportional to magnitude of the magnetic order parameter.<sup>69-71</sup> In summary DFT calculations in LaFeAsO indicate that  $As \rightarrow P$  substitution changes the dimensionality of one hole pocket from 2D to 3D and thus weakens the nesting properties while the FS remains robust under the application of pressure. This is consistent with observations in  $BaFe_2(As_{1-x}P_x)_2$  that the isovalent substitution changes the FS similar to charge doping.<sup>72</sup> This explains the differences in the magnetic properties on a qualitative level if it is taken into account that the application of  $\approx 8$  GPa in LaFeAsO has the same effect on the unit cell volume as the transition from LaFeAsO to LaFePO with the former showing magnetic order and the latter being paramagnetic.

Replacing La by Ce and thus adding one  $4f$  electron the discussion follows the same arguments. Published calculations in the paramagnetic state used DFT + dynamical mean-field theory (DMFT) to account for the additional  $4f$  correlations.<sup>73</sup> Similar to the La-1111 compounds the DOS at the Fermi level is mostly of Fe  $3d$  character.<sup>73</sup> It was found that CeFePO has a smaller DOS at the Fermi level than CeFeAsO.<sup>73</sup> An applied pressure of  $\sim 5$  GPa on CeFeAsO yields the same DOS at the Fermi level as CeFePO.<sup>73</sup> In addition the hybridization of the Fe  $3d$  and Ce  $4f$  states in CeFeAsO is much smaller than in CeFePO.<sup>73</sup> This is consistent with angle-resolved photo emission spectroscopy measurements in the P-substitution series where a change in the FS and an increase in the  $3d-4f$  hybridization from  $x = 30$  to 100 % was observed.<sup>74,75</sup> The application of  $\sim 10$  GPa on CeFeAsO results in a hybridization similar to CeFePO.

The transferred magnetic hyperfine field due to the magnetic order of the Ce  $4f$  electrons is reduced from  $x = 0$  to 5 % and was not observed for 15 % and higher  $x$ . This implies that the ordered moment of the Ce  $4f$  electrons is strongly reduced as a function of  $x$ . This is consistent with reported results that the Ce  $4f$  ordering temperature is independent from  $x$  but the ordered moment is rapidly suppressed with increased  $x$ .<sup>27</sup>

The  $x$  dependence of the chemical shift is shown in the inset of Fig. 9 and in Tab. III. A reduction of the chemical shift  $\delta_c$  with increasing  $x$  was found. A reduction in  $\delta_c$  corresponds to an increase in the electron density at the Fe nucleus. It was reported that the  $Fe-Pn$  distance decreases with increasing  $x$ .<sup>27</sup> This may increase the hy-

bridization of the Fe  $3d$  and  $Pn p$  valence electrons.<sup>59,65</sup> The hybridization of the Fe  $3d$  with the Ce  $4f$  electrons as it was observed in CeFePO may also play a role.<sup>74,75</sup> As a consequence the shielding of the Fe  $4s$  electrons by the Fe  $3d$  is reduced resulting in an increased electron density at the nucleus.

## VI. SUMMARY AND CONCLUSION

In summary, we performed in-house and synchrotron Mössbauer spectroscopy experiments on  $CeFeAs_{1-x}P_xO$  powder and on CeFeAsO single crystals, the latter under hydrostatic pressure and provide an updated microscopical phase diagrams in combination with XRD measurements. A qualitatively similar suppression of the onset temperature of the Fe magnetic order as a function of  $x$  and  $p$  was found. In contrast, the low-temperature saturated magnetic hyperfine field is continuously suppressed to zero at  $x = 40$  % while it is reduced by 24 % between 0 and 4.5 GPa followed by an abrupt suppression to zero. Above  $x = 40$  % and  $p = 5.2$  GPa no Fe magnetic order was observed. It was found that the magnetic hyperfine field is proportional to the Fe-As distance above 2.38 Å for both hydrostatic pressure and P substitution. The observation of a paramagnetic phase for a Fe-As distance of 2.38 Å which is above the threshold value of 2.36 Å implies that the magnetic moment is not only controlled by the  $dp$  hybridization. Our study suggests that the size of the Fe magnetic moment is the result of a delicate interplay of the Fe  $3d$ ,  $Pn p$ , and Ce  $4f$  electrons and goes beyond the Fe  $3d - Pn p$  hybridization. We conclude that hydrostatic pressure change both the crystallographic and electronic properties of the system differently than P substitution.

## ACKNOWLEDGMENTS

Part of this work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – MA 7362/1-1, JE 748/1, WU595/3-3, BU887/15-1, and the research training group GRK-1621. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Parts of this work were performed at GeoSoilEnviroCARS (Sector 13), Partnership for Extreme Crystallography program (PX<sup>2</sup>), Advanced Photon Source (APS), and Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1634415) and Department of Energy-Geosciences (DE-FG02-94ER14466). The COMPRES-GSECARS gas loading system and the PX<sup>2</sup> program are supported by COMPRES under NSF Cooperative Agreement EAR-1661511. We thank S. Tkachev for help with

the Ne loading of the DAC.

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