



# Pr magnetism and its interplay with the Fe spin-density wave in PrFeAsO<sub>1-x</sub>F<sub>x</sub> ( $x = 0, 0.15$ )

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We have studied the magnetism of the Pr<sup>3+</sup> ions in PrFeAsO<sub>1-x</sub>F<sub>x</sub> ( $x = 0, 0.15$ ) and its interaction with the Fe magnetic order (for  $x = 0$ ). Specific-heat data confirm the presence of a first excited crystal electric-field (CEF) level around 3.5 meV in the undoped compound PrFeAsO. This finding is in agreement with recent neutron-scattering experiments. The doped compound is found to have a much lower first CEF splitting of about 2.0 meV. The Pr ordering in PrFeAsO gives rise to large anomalies in the specific heat and the thermal-expansion coefficient. In addition, a field-induced transition is found at low temperatures that is most pronounced for the magnetostriction coefficient. This transition, which is absent in the doped compound, is attributed to a reversal of the Fe spin canting as the antiferromagnetic Pr order is destroyed by the external magnetic field.

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## I. INTRODUCTION

Layered FeAs materials have been studied extensively since the discovery of superconductivity in LaFeAsO<sub>1-x</sub>F<sub>x</sub> with transition temperatures  $T_c$  up to 28 K.<sup>1</sup> By exchanging the non-magnetic La with magnetic rare earths (REs) such as Pr or Sm the superconducting transition temperature could be increased above 50 K.<sup>2,3</sup> All parent compounds of the REFeAsO family ( $RE = \text{La, Ce, Pr, Nd, Sm, Gd}$ ) behave rather similarly:<sup>4-11</sup> They exhibit magnetic ground states with a structural distortion from a tetragonal to an orthorhombic lattice around 150 K and subsequent formation of a spin-density wave (SDW) of the Fe moments. Except for LaFeAsO additional antiferromagnetic (AFM) ordering of the RE moments is observed with transition temperatures of the order of 10 K.

PrFeAsO has the highest RE ordering temperature among the REFeAsO family with  $T_N^{\text{Pr}} \approx 12$  K.<sup>5,12</sup> The structural and SDW transitions take place around 153 and 127 K, respectively.<sup>5</sup> A delicate interaction between the Fe and Pr moments has been deduced from muon spin resonance ( $\mu\text{SR}$ )<sup>13</sup> and Mössbauer<sup>14</sup> experiments such that the ordering of each sublattice entails a reorientation of the other one. The magnetic properties of PrFeAsO are further complicated by crystal electric-field (CEF) effects: In tetragonal symmetry the free-ion ground-state multiplet of Pr<sup>3+</sup> is split into five singlets and two doublets, while the remaining degeneracy is lifted in any lower symmetry.<sup>15</sup> Inelastic neutron-scattering (INS) experiments revealed a first CEF excitation around 3.5 meV that is split above  $T_N^{\text{Pr}}$ .<sup>16</sup> However, the energetic position of the other levels remained unclear. Substitution of O by F changes the magnetism fundamentally: It leads to a simultaneous destruction of the Pr and Fe order.<sup>17</sup> Moreover, additional CEF excitations have been found around 10 meV for  $x = 0.13$ .<sup>16</sup>

In this paper we investigate the Pr magnetism in PrFeAsO and its interplay with the Fe SDW. We start with an estimation of the CEF level scheme of Pr<sup>3+</sup> in PrFeAsO<sub>1-x</sub>F<sub>x</sub> ( $x = 0, 0.15$ ). Fluorine doping is found to have a significant influence on the splitting, in agreement with the INS results. We find an additional low-lying level around 2 meV in

the F-doped compound, which was not seen before. The sensitive dependence of the splitting on the F substitution is discussed as a possible reason for the absence of Pr magnetic order in the doped compound. Subsequently we present thermal-expansion, magnetostriction, and magnetization data. PrFeAsO is found to undergo a field-induced transition below  $T_N^{\text{Pr}}$ , which is attributed to an Fe spin reorientation due to the destabilization of the AFM Pr order.

## II. EXPERIMENTAL DETAILS

Polycrystalline samples have been prepared by solid-state reaction as described in Ref. 18. The specific heat was studied in a physical property measurement system (PPMS from Quantum Design) by means of a relaxation technique. For the thermal-expansion and magnetostriction measurements a capacitance dilatometer was utilized, which allows a very accurate study of sample length changes  $dL/L$ .<sup>19</sup> The linear thermal-expansion coefficient  $\alpha$  was calculated as the first temperature derivative of  $dL/L$ , while the magnetostriction coefficient  $\beta$  is determined by the first derivative of  $dL/L$  with respect to the magnetic field  $B = \mu_0 H$ . Magnetization measurements were performed in a commercial vibrating sample magnetometer based on a superconducting quantum interference device (VSM SQUID from Quantum Design) at an oscillation frequency of 14 Hz.

## III. CEF SPLITTING OF Pr<sup>3+</sup>

First we will evaluate the crystal electric-field (CEF) level scheme of the Pr<sup>3+</sup> ions and the influence of fluorine doping by analyzing the specific heat of both compounds.

Figure 1(a) shows the specific heat  $c_p$  of PrFeAsO<sub>1-x</sub>F<sub>x</sub> ( $x = 0, 0.15$ ) as  $c_p/T$  for  $T \leq 60$  K. Data for  $x = 0$  at higher  $T$  are similar to those published in Ref. 20 with anomalies due to the structural transition at  $T_s = 145$  K and the SDW formation at  $T_N^{\text{Fe}} = 129$  K.<sup>21</sup> These anomalies are absent for  $x = 0.15$ . Here, we focus on the regime below 60 K. The undoped sample exhibits a sharp anomaly with a maximum at 11.3 K, which

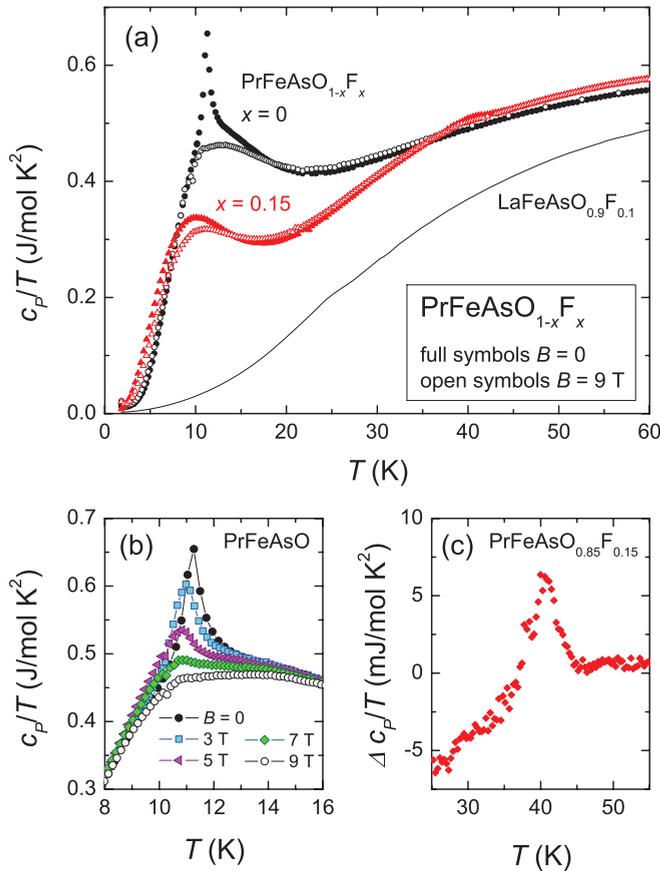


FIG. 1. (Color online) (a) Specific heat  $c_p$  divided by temperature  $T$  for  $\text{PrFeAsO}_{1-x}\text{F}_x$  ( $x = 0, 0.15$ ) in zero magnetic field and 9 T. For  $x = 0$  a clear anomaly with a maximum at 11.3 K is observed in zero field originating from the magnetic ordering of the  $\text{Pr}^{3+}$  ions at  $T_N^{\text{Pr}}$ . The specific heat of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$  used as a phonon background is also shown for comparison. (b) Behavior of the anomaly at  $T_N^{\text{Pr}}$  of  $\text{PrFeAsO}$  in magnetic field. (c) The superconducting transition of the sample with  $x = 0.15$  gives rise to a small anomaly seen in  $\Delta c_p/T = c_p(0)/T - c_p(9\text{T})/T$ .

is on top of a broad hump. This behavior is attributed to the magnetic ordering of the  $\text{Pr}^{3+}$  moments in the presence of CEF splitting. The evolution of the anomaly in an applied magnetic field is shown in Fig. 1(b). Small fields of 3 and 5 T lead to a weak shift to lower  $T$  and a reduction in height. At 7 T, the anomaly is hardly seen anymore. Application of a field of 9 T suppresses the anomaly completely and leaves only the hump and a tiny kink. This behavior is in line with a suppression of the antiferromagnetic Pr order by the external magnetic field. On the other hand, the hump due to the CEF splitting is scarcely changed by the field, because the corresponding energy scale is much larger than the Zeeman splitting. For the sample with 15% fluorine doping, no Pr ordering is observed down to 1.5 K, and the hump is shifted to lower  $T$ . In addition, a small anomaly is found at the superconducting transition, which is largely suppressed at 9 T. The difference between the zero-field and 9-T data reveals a small  $\lambda$ -shaped anomaly at  $T_c = 42$  K [cf. Fig. 1(c)].

There is a significant magnetic contribution  $c_{\text{mag}}$  to the specific heat of  $\text{PrFeAsO}_{1-x}\text{F}_x$  stemming from the  $\text{Pr}^{3+}$  ions. An exact determination of  $c_{\text{mag}}$  is impossible due to the

presence of the various phase transitions. In order to get a rough estimate of the magnetic contributions  $c_{\text{mag}}^{\text{est}}$ , we used  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$  as a nonmagnetic reference. This is reasonable, as a substitution of the rare-earth ion is not expected to change the phonon spectrum significantly and the anomaly due to the superconducting transition of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$  at 26 K is very small. Therefore, its contribution to  $c_p$  is negligible compared to the Pr contribution. However, one has to keep in mind that there might be a different electronic contribution to  $c_p$  (see discussion below).  $c_{\text{mag}}^{\text{est}}$  is obtained by subtracting the specific heat of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ , which is shown for comparison in Fig. 1(a), from the one of  $\text{PrFeAsO}_{1-x}\text{F}_x$ . The result is plotted in Fig. 2 as  $c_{\text{mag}}^{\text{est}}/T$ . Both  $\text{PrFeAsO}_{1-x}\text{F}_x$  samples exhibit Schottky-like anomalies, whereas the maximum occurs at lower  $T$  for the sample with fluorine doping. This demonstrates already that the doping changes the CEF level scheme and results in a lowering of the first excited level.

For  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  no magnetic ordering is observed down to 1.5 K. This is in line with susceptibility measurements (not shown) and neutron-scattering experiments,<sup>5,12</sup> which revealed no indication for any type of magnetic order down to 0.4 K (in case of Ref. 5 on a sample from the same batch as used in our investigation). Therefore,  $c_{\text{mag}}$  is only due to the thermal occupation of higher CEF states. We may use  $c_{\text{mag}}^{\text{est}}$  to estimate the CEF splitting. The data range between 20 and 45 K, which contains the superconducting anomalies, was omitted for the fitting. The best description of the data is

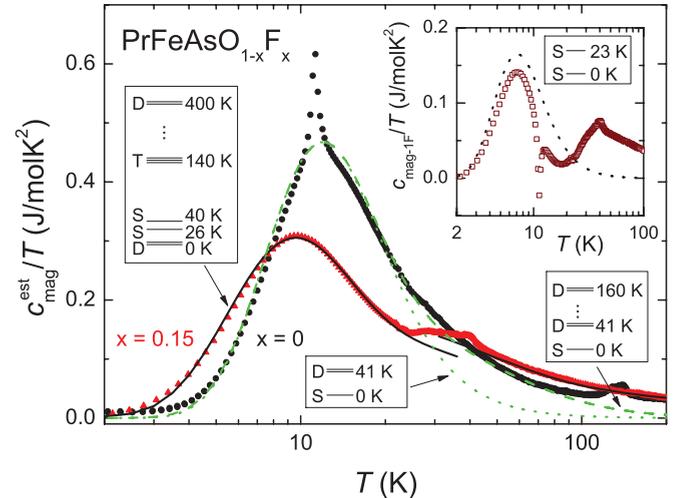


FIG. 2. (Color online) Estimate of the magnetic contribution to the specific heat of  $\text{PrFeAsO}_{1-x}\text{F}_x$  ( $x = 0, 0.15$ ) calculated by subtracting the data of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ . The solid lines are the results of a fit to a Schottky contribution from CEF splitting for  $x = 0.15$ . Above  $T_c$  an additional charge carrier contribution  $\Delta\gamma = 25.2$  mJ/mol K<sup>2</sup> is taken into account, which leads to a shift of the line. The dotted line is the calculated Schottky contribution for a ground-state singlet and an excited doublet at 41 K. The agreement with the data for  $x = 0$  is much improved by adding a second doublet at 160 K (dashed line). Inset: estimated contribution to  $c_{\text{mag}}$  of  $x = 0.15$  from sites with one or more fluorine neighbors in a model with different CEF schemes for differing environments<sup>16</sup> as explained in the text. The dotted line is the calculated contribution expected for two singlet states at 0 and 23 K for 37% of the Pr sites.

obtained for a ground-state doublet (D) with excited singlets (S) at 26 and 40 K. Two more levels are found at 140 K [quasitriplet (T)] and at 400 K (quasidoublet). These two levels may in fact consist of three or two close-lying singlets, which, however, cannot be resolved from our data. In our fit we also accounted for a difference between the electronic contributions of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$  and  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ . Below the superconducting transitions it was taken as zero assuming that all charge carriers are condensed to Cooper pairs. Above  $T_c$  we obtain a value of  $\Delta\gamma = 25 \text{ mJ}/(\text{mol K}^2)$  in addition to the Sommerfeld coefficient of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$  of  $6.5 \text{ mJ}/(\text{mol K}^2)$ .<sup>21</sup> Thus, we may estimate  $\gamma = 31.5 \text{ mJ}/(\text{mol K}^2)$  for  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ , which is comparable to the value of  $34 \text{ mJ}/(\text{mol K}^2)$  determined for  $\text{PrFeAsO}$ .<sup>20</sup>

The result of the fitting is shown as lines in Fig. 2 together with a schematic drawing of the corresponding level scheme. Our fit describes the data very well. However, the proposed ground-state doublet raises the question why no magnetic ordering is observed in  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ . We would like to mention that a description of the data using a ground-state singlet was not possible. This might indicate that  $c_{\text{mag}}^{\text{est}}$  is not sufficiently precise to allow estimating the CEF contribution. However, the presence of two singlets at 26 and 40 K above a ground-state doublet suggested by our fit is determined mainly by the data below 20 K. In this temperature range, the estimate for  $c_{\text{mag}}$  is rather good, because the phonon contribution is comparably small. A possible answer is given by a recent neutron-diffraction experiment. Goremychkin *et al.* studied CEF excitations in  $\text{PrFeAsO}_{1-x}\text{F}_x$  ( $x = 0, 0.13$ ).<sup>16</sup> The undoped compound was found to have an excitation around 3.5 meV that is split above  $T_N^{\text{Pr}}$ . Substitution of fluorine removed the splitting and led to a reduction of that peak. In addition, two more peaks were observed at 9.7 and 11.8 meV. The authors explained their observation by the presence of two different well-defined charge environments resulting from a random distribution of fluorine on the oxygen sites. This leads to five different nearest-neighbor configurations for the  $\text{Pr}^{3+}$  ions, the most common of which are those with zero (58%) and one (35%) F neighbor. The excitation at 3.5 meV with reduced height was attributed to the  $\text{Pr}^{3+}$  ions with unchanged nearest-neighbor configuration, while the two additional peaks were attributed to  $\text{Pr}^{3+}$  ions with one fluorine as nearest neighbor.

This idea can be also applied to our specific-heat data: We assume that  $c_{\text{mag}}^{\text{est}}$  of  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  contains a CEF contribution from the 52%  $\text{Pr}^{3+}$  ions (for  $x = 0.15$ ) without fluorine neighbor. It can be estimated from  $c_{\text{mag}}^{\text{est}}$  of  $\text{PrFeAsO}$ , because the entropy change related to the magnetic ordering in the undoped compound is rather small. After subtracting this contribution we end with a magnetic specific heat  $c_{\text{mag-1F}}$  dominated by the CEF contribution from the 37% ions with one F neighbor. The resulting curve is shown in the inset of Fig. 2. The low-temperature part is dominated by a Schottky-like anomaly, which is surprisingly well described by two singlets at 0 and 23 K at 37% of the Pr sites. Due to the various approximations used so far, we refrain from a further analysis of  $c_{\text{mag-1F}}$ . However, the broad maximum observed at higher temperatures may be ascribed to the CEF levels around 10 meV found in the neutron-scattering experiments. The splitting of 23 K determined from  $c_{\text{mag-1F}}$  is close to the lowest splitting of 26 K determined by our fit of  $c_{\text{mag}}^{\text{est}}$ . Therefore,

our data clearly prove the presence of a first excited level at about 2 meV for  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ . No respective excitation was observed in the neutron-scattering experiment. We suggest that it probably corresponds to a forbidden transition.

We now turn to the undoped compound. A CEF excitation around 3.5 meV has been found in the neutron-scattering experiment mentioned above.<sup>16</sup> We use this value to model our magnetic specific heat. A quite good description of the low-temperature part is indeed obtained assuming a singlet ground state with a doublet at 41 K corresponding to 3.5 meV (cf. dotted green line in Fig. 2). The agreement at high  $T$  is significantly improved by assuming a second doublet at 160 K, which is at the limit of the measurement range in Ref. 16. The other states are supposed to lie at even higher energy.

Summarizing the analysis presented so far we conclude the following: Our specific-heat data for  $\text{PrFeAsO}$  are consistent with a singlet ground state and excited doublets around 41 and 160 K, whereas the remaining levels lie at higher energy.  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  has a first excited state at significantly lower energy corresponding to about 23–26 K. This low-lying singlet is responsible for the shift of the hump in  $c_p$  to lower  $T$  [cf. Fig 1(a)]. Our data are also in line with neutron-scattering results, which suggest different Pr sites for  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ , depending on their environment. In this model, 52% of the Pr ions have no fluorine neighbor and CEF levels similar to  $\text{PrFeAsO}$  with a first excited state being a doublet at 41 K. The 37% Pr ions with one fluorine neighbor have a different splitting, whereas the first excited state is a singlet at 23 K.

#### IV. INTERPLAY OF Fe AND Pr MAGNETISM

We now turn to the interplay of Fe and Pr magnetism in  $\text{PrFeAsO}$ . For this purpose we present thermal-expansion, magnetostriction, and magnetization data.

The linear thermal-expansion coefficient  $\alpha$  of  $\text{PrFeAsO}_{1-x}\text{F}_x$  ( $x = 0, 0.15$ ) measured in zero magnetic field and 9 T is shown in Fig. 3. The structural and SDW transitions of the undoped compound give rise to a large, broad anomaly around 150 K.<sup>22</sup> Both transitions cannot be distinguished in our data, probably due to the small height of one of the anomalies. The ordering of the  $\text{Pr}^{3+}$  moments in  $\text{PrFeAsO}$  shows up as another, positive anomaly with a maximum at 11.4 K, close to the maximum in  $c_p/T$ . This anomaly is rather sharp and symmetric, which suggests that the transition might in fact be of first-order type. The shape of our specific-heat anomaly is also in line with a broadened first-order transition, yet we cannot exclude that it is a second-order one.

Although the pronounced background hinders the precise determination of the anomalous changes, the hydrostatic pressure dependence can be extracted quantitatively from the anomalies in  $\alpha$  and  $c_p$  by means of either the Clausius-Clapeyron or the Ehrenfest relation depending on the nature of the phase transition. Supposing a weak first-order character of the anomaly, analyzing the data in Figs. 1(b) and 3 yields a volume change of  $\Delta V = \int 3 \cdot \Delta\alpha(T)dT \approx 3.9 \cdot 10^{-6}/\text{K}$  and an entropy change of  $\Delta S \approx 0.13 \text{ J}/(\text{mol K})$  at the transition. Applying these estimates we obtain the hydrostatic pressure

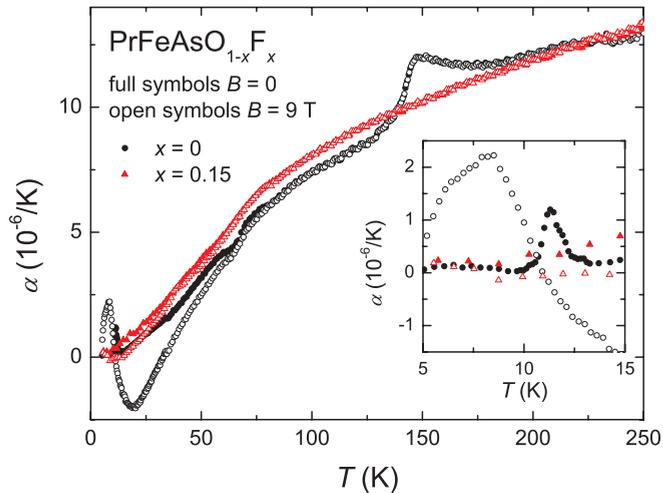


FIG. 3. (Color online) Temperature dependence of the linear thermal-expansion coefficient  $\alpha(T)$  of  $\text{PrFeAsO}_{1-x}\text{F}_x$  ( $x = 0, 0.15$ ) in magnetic fields of 0 and 9 T. Clear anomalies are seen in the zero-field thermal-expansion curve for  $x = 0$  at the structural and SDW transitions and at the magnetic ordering temperature of the  $\text{Pr}^{3+}$  ions. These are absent for the doped compound. Application of a magnetic field leads to a strong change of  $\alpha(T)$  for  $\text{PrFeAsO}$  below 70 K. By contrast, there is almost no effect on  $\alpha(T)$  for the doped compound. Inset: low- $T$  part on a larger scale.

dependence:

$$\frac{\partial T_N^{\text{Pr}}}{\partial p} = V_{\text{mol}} \cdot \frac{\Delta V}{\Delta S} \approx 1.2 \text{ K/GPa}. \quad (1)$$

A similar value is obtained assuming that the transition is of second order. In this case the pressure dependence is determined from the jump heights  $\Delta\alpha \approx 1.0 \cdot 10^{-6}/\text{K}$  and  $\Delta c_p \approx 1.4 \text{ J}/(\text{mol K})$ , which yields

$$\frac{\partial T_N^{\text{Pr}}}{\partial p} = T V_{\text{mol}} \cdot \frac{3\Delta\alpha}{\Delta c_p} \approx 1.0 \text{ K/GPa}. \quad (2)$$

So far, no pressure experiments have been performed on  $\text{PrFeAsO}$ . However, the estimated pressure dependence of  $T_N^{\text{Pr}}$  is comparable to the one of the Ce ordering temperature in  $\text{CeFeAsO}$  of 0.9 GPa/K.<sup>23</sup>

A field of 9 T leads to a strong decrease of the thermal-expansion coefficient of  $\text{PrFeAsO}$  below approximately 50 K. The sharp anomaly at 11 K is suppressed. Instead a broad maximum is observed around 8 K as seen in the inset of Fig. 3, which shows the low- $T$  part of  $\alpha(T)$  on a larger scale. Since no anomaly is found in the corresponding specific-heat curve, this feature is not related to a phase transition, but rather to thermal population of higher  $\text{Pr}^{3+}$  states. Contrary to the undoped compound, the thermal expansion coefficient of  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  exhibits a smooth temperature dependence. No anomaly is found at the superconducting transition, similar to the findings in  $\text{LaFeAsO}_{1-x}\text{F}_x$ .<sup>19</sup> Most probably, it is too small to be seen in our data. Application of a magnetic field of 9 T leads to a lowering of  $\alpha$ , which, however, is much weaker than for the undoped system.

In view of the large change of  $\alpha$  of  $\text{PrFeAsO}$  induced by a magnetic field we expect a sizable magnetostrictive effect in the material. In Fig. 4 we present the magnetostriction

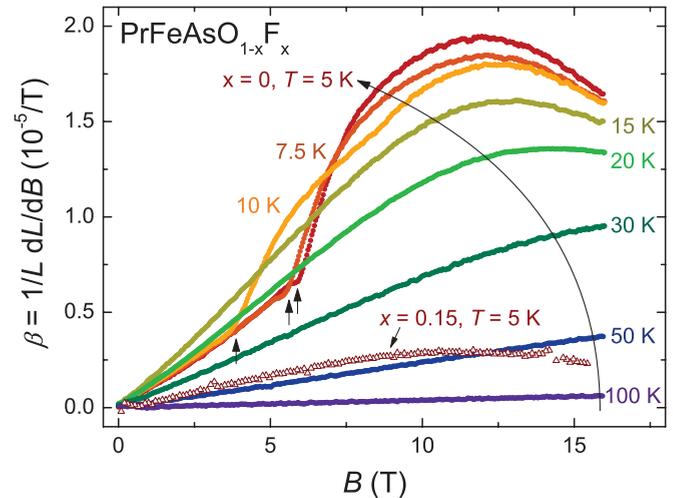


FIG. 4. (Color online) Magnetostriction coefficient  $\beta$  vs magnetic field  $B$  of  $\text{PrFeAsO}$  at different temperatures up to 100 K (full symbols). For  $T = 5, 7.5,$  and  $10$  K kinks marked by arrows are observed at 5.8, 5.4, and 3.7 T, respectively. At higher  $T$  the transition disappears. For comparison, data for  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  measured at 5 K are shown (open symbols). At higher temperature,  $\beta$  is even smaller for this compound.

coefficient  $\beta = 1/L dL/dB$  of  $\text{PrFeAsO}$  at different temperatures up to 100 K and in magnetic fields up to 16 T. At high temperatures, an almost linear dependence  $\beta(B)$  is found. With decreasing  $T$ , the magnetostriction coefficient increases, and a maximum in  $\beta(B)$  develops at higher fields. Below the Pr ordering temperature, the behavior of  $\beta(B)$  changes qualitatively. In low fields,  $\beta(B)$  increases linearly with a temperature-independent slope. Interestingly, this slope is smaller, than the one observed at 15 K, i.e., above the phase transition. At higher fields, kinks are observed in  $\beta(B)$  at 5.8, 5.4, and 3.7 T for 5, 7.5, and 10 K, respectively. For fields larger than approximately 10 T, the low- $T$  magnetostriction resembles the field dependence observed above 15 K. For comparison, a curve measured at 5 K on  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  is also shown in Fig. 4. As expected from the small change of the thermal expansion coefficient in magnetic field, the magnetostriction is much weaker than for the undoped compound.

The magnetostrictive effect observed in  $\text{PrFeAsO}$  below about 50 K, i.e., well above  $T_N^{\text{Pr}}$ , is rather large. This is surprising since the magnetostrictive effect for  $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$  is significantly weaker. Apart from the Pr magnetic ordering there are two important differences between the undoped and the doped compound:

(1) In addition to the Pr order, the Fe spins form a SDW below 129 K in  $\text{PrFeAsO}$ . It may not be directly responsible for the large magnetostriction. For comparison: measurements on  $\text{LaFeAsO}$  allow estimating an upper limit of  $\beta < 5 \times 10^{-8}/\text{T}$  for this compound, despite the presence of Fe SDW order.<sup>24</sup> However, the Fe SDW induces a polarization of the  $\text{Pr}^{3+}$  moments already well above  $T_N^{\text{Pr}}$ .<sup>13</sup> The applied magnetic field thus acts on a compound with net magnetic moments from both the Fe SDW and the Pr sublattice, which may be the reason for the large magnetostrictive effect.

(2) As evident from neutron-scattering data<sup>16</sup> and our specific-heat analysis, fluorine substitution changes the CEF

level scheme of part of the ions. This may explain the observed suppression of  $\beta(B)$  at least to some extent. Only 52% Pr ions without fluorine neighbor have an unchanged CEF scheme. Therefore, one expects about half the magnetostrictive effect of PrFeAsO for the fluorine-doped compound from these sites. Moreover, we do not know the magnetostriction contribution of the remaining 48% Pr ions with at least one fluorine neighbor. In addition, the strain induced by the differing favored expansion coefficients of neighboring cells will lead to a more difficult behavior than a simple sum of the effects. Measurements on samples with different fluorine content might clarify the relevance of the specific CEF level scheme and the presence of the Fe SDW for the large magnetostriction of PrFeAsO. We would like to mention at this point that the absence of a kink in the low-temperature magnetostriction of PrFeAsO<sub>0.85</sub>F<sub>0.15</sub> is not contradictory to this picture of Pr ions with different environments. As discussed in more detail below, the kinks are caused by the field-induced suppression of the Pr order accompanied by a decoupling of the Fe spins. Since no magnetic ordering takes place in the doped compound, no kink is expected.

Now we turn to the transition observed in the magnetostriction coefficient of PrFeAsO. It is expected to give also rise to an anomaly in the magnetization  $M(B)$  of the material. We performed measurements of  $M(B)$  in fields up to 7 T and for temperatures between 1.8 and 50 K. The magnetization is found to increase almost linearly with field. A small change in slope is found for  $T < 12.5$  K, that is more obvious from the derivative  $dM/dB$ . As an example, the inset of Fig. 5 shows  $M(B)$  measured in 10 K. Deviations from a linear behavior are observed above 4 T as indicated by the dashed line. This corresponds to a step at this field in the derivative  $dM/dB$  shown in the main plot of Fig. 5 for different temperatures. With increasing

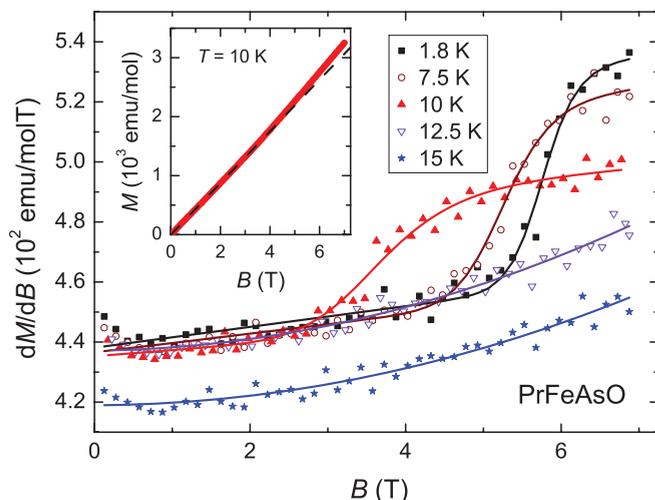


FIG. 5. (Color online) Inset: example for the field dependence of the magnetization  $M(B)$  of PrFeAsO at 10 K.  $M(B)$  exhibits an almost linear behavior with small deviations above approximately 4 T, as illustrated by the dashed line. They are better seen as a step in  $dM/dB$  shown in the main plot for different temperatures. The solid lines for 1.8, 7.5, and 10 K are fits to an empiric formula as explained in the text. The lines for 12.5 and 15 K are guides to the eye. For clarity, not all investigated temperatures are shown.

temperature, the transition field  $B_0$  shifts to lower  $B$ . At 12.5 K the transition has disappeared. In order to determine the position of the transition we fitted  $dM/dB$  with an empiric formula  $dM/dB = A_0 + A_1 B - h/[1 + (B/B_0)^z]$ . For  $z \geq 2$  this equation describes a broadened steplike function with step height  $h$ . The broadening is determined by the parameter  $z$ . At  $B_0$  half of the step height is reached. The parameters  $A_0$  and  $A_1$  account for a linear background. As a measure for the uncertainty in  $B_0$  we take the full width at half maximum (FWHM) of the derivative of the fit. The fits are also shown in the main plot of Fig. 5.

Taking the transition fields determined from the magnetostriction coefficient and the  $B_0$  values determined from the magnetization curves, we can draw a magnetic phase diagram for PrFeAsO, which is shown in Fig. 6. The error bars given for  $B_0$  are determined from the FWHM in the derivatives of the fits as explained above. Unfortunately, our specific heat and thermal-expansion data do not allow extracting clear transition temperatures. In particular, no unambiguous conclusion on the character of the transition even in zero and small magnetic fields is possible since it can be either continuous or weakly first order. However, the transition is clearly suppressed in external magnetic field and the peak maxima provide a lower limit for the transition temperatures. The actual transitions may occur between the maxima in  $c_p/T(T)$  and  $\alpha(T)$  and the kinks in the data at the end of the anomalies. These ranges are marked by dotted lines in Fig. 6. In addition we also plot the peak maxima of the anomalies.

Figure 6 evidences what has been noted before: The kinks in  $M(B)$  and  $\beta(B)$  are observed only below  $T_N^{\text{Pr}}$ . In fact, the

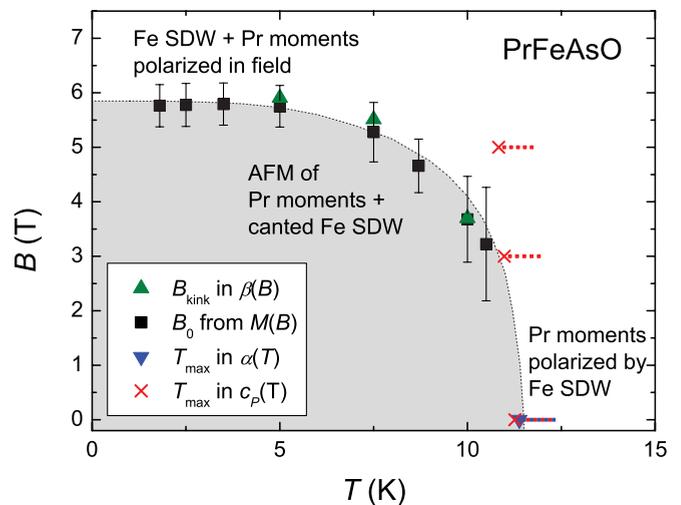


FIG. 6. (Color online) The magnetic phase diagram of PrFeAsO, which was obtained from the magnetostriction (green triangles) and the magnetization (black squares) data. The error bars for the magnetization results have been determined from the width of the transition in  $dM/dB$  as explained in the text. The red crosses indicate the positions of the maxima in  $c_p/T$ , while the blue triangle corresponds to the maximum in the thermal expansion coefficient. The adjacent dotted lines mark the potential range for the phase transitions. The zero-field ranges for  $c_p/T$  and  $\alpha$  are almost identical and therefore hard to distinguish in the plot. The dashed line is a guide to the eye, whereas the shaded area marks the region of Pr AFM order at low  $T$  and  $B$ .

maxima of the anomalies in  $c_p/T(T)$  and  $\alpha(T)$  in zero field fit well to the phase line. However, the specific-heat anomaly at 5 T and most probably also the one at 3 T is observed at higher  $T$ . More precisely, the line marking the possible range for the Pr magnetic ordering transition at 5 T clearly does not cut the phase border. This suggests that the transition observed in  $M(B)$  and  $\beta(B)$  has a different origin and is not caused directly by the field-induced suppression of the Pr order. In fact, the observation of a kink in both properties is a rather unusual behavior for such an effect. Typically an abrupt reorientation of magnetic moments shows up as steplike anomalies in  $\beta(B)$  and  $M(B)$ .

One may speculate that the presence of two magnetic subsystems with competing magnetic structures is responsible for the observed behavior. A model for the magnetic structure of PrFeAsO has been proposed from  $\mu$ SR experiments:<sup>13</sup> Below 127 K, the Fe moments order in an antiferromagnetic stripe structure parallel  $a$ .<sup>5</sup> The resulting internal field induces a magnetic moment on the Pr<sup>3+</sup> site along  $c$ . The Pr order below  $T_N^{\text{Pr}}$  leads to a reorientation of both subsystems. The Pr<sup>3+</sup> moments are now oriented along  $a$ , which, in turn, leads to a canting of the iron moments with a significant component along  $c$ . A Fe spin reorientation upon Pr ordering was also deduced from Mössbauer spectroscopy.<sup>14</sup> Thus, it appears that the preferred magnetic structures of the Pr and Fe subsystems compete with each other.

We suggest the following picture for PrFeAsO: In zero field the Pr moments order below  $T_N^{\text{Pr}}$ , which is accompanied by a canting of the Fe spins. Application of a magnetic field destabilizes the antiferromagnetic Pr order as confirmed by the observed small shift of the specific-heat anomaly to lower  $T$ . This weakening of the Pr order allows the Fe sublattice to keep its preferred orientation down to lower  $T$ . Above a field of about 6 T the Pr ordering is suppressed completely and only a polarization by the Fe SDW and the external field remains. With regard to our field-dependent measurements, the weakening of the Pr order leads to a decoupling of the Fe SDW above a certain field, at which the Fe spins resume their preferred orientation. The kink observed in our magnetostriction data then does not correspond to a sudden flip of Pr moments upon increasing field, but rather to a slow rotation, which changes speed, as the Fe SDW is released. This picture of a field-induced rotation of the Pr moments accompanied by a decoupling of the Fe SDW is also supported by recent measurements of the resistivity  $\rho$ .<sup>20</sup> A weak maximum was observed in  $\rho(T)$  around 6 K in fields up to 6 T. Since the the FeAs layers are responsible for the

charge transport it was attributed to a reorientation of the Fe moments induced by the Pr order below  $T_N^{\text{Pr}}$ . The authors corroborated their interpretation by the observation of a broad hump around 6 K in the derivative of the specific heat divided by temperature. This latter feature may be also ascribed to the Schottky anomaly from the excited doublet at 41 K, which has a maximum in  $d(c_{\text{mag}}/T)/dT$  at 6.7 K. On the other hand, the interpretation of the resistivity maximum as a signal of Fe moment reorientation caused by the Pr order is in line with our discussion: The maximum in  $\rho(T)$  is observed only in fields below 6 T. At higher fields the Pr order is very weak or even destroyed as confirmed by the tiny anomaly in  $c_p$  observed at 7 T [see Fig. 1(b)]. As a result the Fe moments keep their preferred orientation and the maximum in  $\rho(T)$  disappears. Moreover, a kink was found in  $\rho(B)$  at low temperatures by several groups.<sup>20,25,26</sup> The positions of these kinks fit rather well to our phase line, whereas small deviations may be due to the slightly different  $T_N^{\text{Pr}}$  values. Therefore, we suggest that these kinks are also a signature of the field-induced rotation of the Pr ions accompanied by Fe spin reorientation.

## V. SUMMARY

In summary we have studied the Pr magnetism in PrFeAsO<sub>1-x</sub>F<sub>x</sub> ( $x = 0, 0.15$ ). The CEF level scheme of the Pr<sup>3+</sup> ions is strongly influenced by fluorine doping. The first excited CEF level in PrFeAsO is found around 40 K, whereas a significantly lower splitting corresponding to about 23–26 K is determined for PrFeAsO<sub>0.85</sub>F<sub>0.15</sub>. This lowering as well as a different CEF splitting for Pr sites with different environments may be the reason for the absence of Pr order in the fluorine-doped compound.

At low temperatures, a field-induced transition is found for PrFeAsO, that is not directly related to the suppression of the AFM Pr order. Instead it comes from the interplay between the Fe and Pr moments, which appears to be very sensitive to application of magnetic fields. The transition is attributed to a reversal of the Fe moment canting induced by the Pr ordering as the Pr order is suppressed in magnetic field.

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