Superconducting and magnetic anisotropy of LnFePO (Ln=La, Pr, and Nd) single crystals

R. E. Baumbach, J. J. Hamlin, P.-C. Ho, I. K. Lum, and M. B. Maple

Phys. Rev. B **85**, 104526 — Published 30 March 2012

DOI: 10.1103/PhysRevB.85.104526

Superconducting and magnetic anisotropy of *Ln*FePO (*Ln* = La, Pr, and Nd) single crystals

R. E. Baumbach[1], J. J. Hamlin[1], P.-C. Ho[2], I. K. Lum[1], and M. B. Maple[1]
[1]*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*
[2]*Department of Physics, California State University, Fresno, Fresno, California 93740, USA*

(Dated: February 9, 2012)

The superconducting and magnetic properties of PrFePO and NdFePO are reported. Measurements of the DC and AC magnetic susceptibility reveal that in comparison to the analogue compound without f-electrons, LaFePO, the superconducting transition temperatures T_c are only moderately affected by the lanthanide $4f$-electron magnetic moments. These results indicate that either the exchange interaction that leads to magnetic pair breaking is extremely weak or that the superconducting state is unconventional. Measurements of the upper critical field curves and the magnetic susceptibility also reveal that the magnetic field induced suppression of the superconducting state is not strongly correlated with spin polarization of the magnetic lanthanide ions.

I. INTRODUCTION

The iron-pnictide/chalcogenide (Fe-Pn/Ch) compounds have attracted intense interest recently, largely due to the observation of high temperature superconductivity (SC) throughout a broad range of chemical formulas, all of which include corrugated (Fe-Pn/Ch) layers.[1–3] The highest SC transition temperatures (T_c) are observed for the optimally doped *Ln*FeAsO compounds (*Ln* = lanthanide: e.g., $T_{c,max} \approx 55$ K for SmFeAsO$_{1-x}$F$_x$[Ref. 4]). However, the sharpest focus has been on the MFe$_2$As$_2$ (M = Ca, Sr, Ba) and Fe(S,Se,Te) analogues. Less attention has been given to the P-based examples *Ln*FePO, which have lower T_c's,[5–7] although variations of these compounds show enhanced SC properties (e.g., $T_c \approx 17$ K for Sr$_2$ScO$_3$FePO [Ref. 8] and $T_c \approx 14$ K (onset) for LaFePO under non-hydrostatic pressure.[6]

For all of these compounds, the microscopic mechanism for SC remains unclear, although a focused effort has been made to understand the order parameter symmetry and its relationship to the Fermi surface.[1,2,9,10] Many studies provide evidence for singlet spin-pairing of the superconducting electrons (e.g., ^{57}Fe Knight shift measurements on LaFeAsO$_{0.7}$ [Ref. 11]), corresponding to s- or d-wave orbital states. Additionally, Josephson tunneling experiments (e.g., for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [Ref. 12]) are consistent with the so-called $s\pm$ model. On the other hand, penetration depth[13,14] and thermal conductivity[15] measurements on LaFePO indicate the presence of nodes in the SCing energy gap, in contrast to what is expected from the $s\pm$ model. Therefore, it is unclear whether the gap function is the same for all Fe-Pn/Ch SCs.

One of the most intriguing issues is whether the SC of all high T_c Fe-Pn/Ch materials and their related low T_c analogues has the same origin. Support for a common mechanism of SC is provided by the observation that the Pn/Ch-Fe-Pn/Ch bond angle is correlated with T_c, which suggests that the crystalline anisotropy tunes the Fermi surface and, consequently, the SC state.[1,16–18] On the other hand, the introduction of magnetic *Ln* ions enhances T_c for the Fe-As 1111 compounds, but reduces T_c in the Fe-P analogues, indicating that the SC states for these classes of compounds may be influenced differently by magnetic interactions.[7]

We undertook a study of single crystals of *Ln*FePO (*Ln* = Pr and Nd) in order to address the affect of *Ln* magnetic moments on the SC in this system. Our results reveal that T_c is not strongly reduced by the *Ln* ions that carry magnetic moments. This result indicates that if the SC in the *Ln*FePO compounds is conventional (i.e., s-wave spin singlet BCS type), then the exchange interaction between the magnetic *Ln* ions and the electrons participating in the SC state is relatively weak. On the other hand, if the SC state is unconventional (e.g., d-wave spin singlet or p-wave spin triplet) then it is perhaps not surprising that the magnetic moments have such a small effect. We also find that the magnetic field induced suppression of the superconducting state is not strongly correlated with spin polarization of the magnetic lanthanide ions.

II. EXPERIMENTAL DETAILS

Single crystals of PrFePO and NdFePO were grown from elements and elemental oxides with purities $>$ 99.9% in a molten Sn:P flux as described previously.[6,7] Before measurements were performed, the crystals were heat treated at 700 °C for 24 hours under flowing O$_2$, since our previous work indicates that this process improves the SC volume fraction.[7] Measurements of the DC magnetic susceptibility $\chi_{\mathrm{DC}}(T)$ for $2\ \mathrm{K} \leq T \leq 300$ K at constant magnetic field ($H = 1$ T) and magnetization $M(H)$ for $0 \leq H \leq 7$ T at constant temperature ($T = 2$ K) were performed using a Quantum Design SQUID magnetometer. The specimens consisted of aligned mosaics of the platelet-like crystals, which were mounted on tape with the ab-plane either perpendicular ($\perp$) or parallel ($\|$) to H; 10 single crystals with a total mass near 0.105 mg and 5 single crystals with a total mass near 0.027 mg were used for PrFePO and NdFePO, respectively. The AC magnetic susceptibility $\chi_{\mathrm{AC}}(T)$ measurements were carried out using a mutual inductance

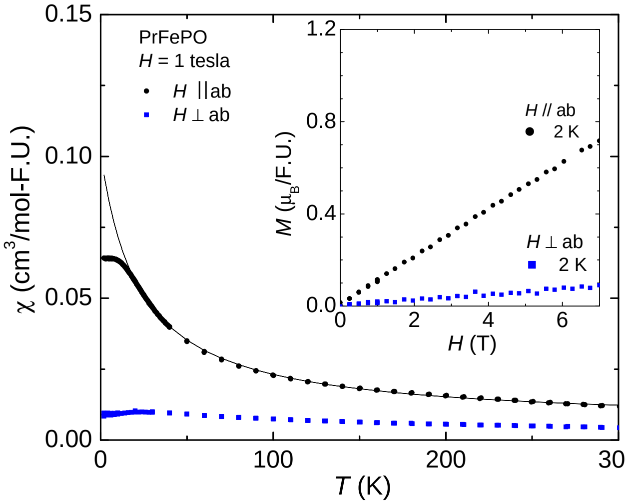

FIG. 1. DC magnetic susceptibility $\chi_{DC} = M/H$ vs. temperature T for the magnetic field H applied perpendicular and parallel to the ab plane for PrFePO. The solid lines are the CW fits to the data (see text). Inset: M vs. H for $H \parallel$ c and $H \perp$ c.

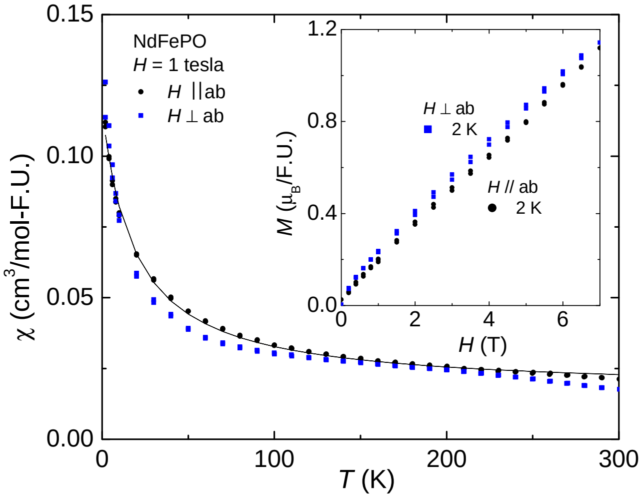

FIG. 2. DC magnetic susceptibility $\chi_{DC} = M/H$ vs. temperature T for the magnetic field H applied perpendicular and parallel to the ab plane for NdFePO. The solid lines are the CW fits to the data (see text). Inset: M vs. H for $H \parallel$ ab and $H \perp$ ab.

technique for 0.05 K $\leq T \leq$ 5.5 K in constant H over the range $0 \leq H \leq 2.5$ T at 17 Hz with a primary field of $\sim 0.05 - 0.15$. Collections of $\sim$ 30 single crystals of PrFePO and NdFePO were mounted on copper disks using GE varnish and aligned either perpendicular or parallel to H. We estimate an uncertainty of 5 degrees in the alignment for the $\chi_{\mathrm{AC}}(T)$ measurements, since space restrictions required stacking of the crystals.

III. RESULTS

The $\chi_{DC}(T)$ data (Fig. 1) for PrFePO reveal pronounced anisotropy, with the easy direction in the ab-plane. For $H \parallel$ ab, the data are described by a Curie-Weiss law for 20 K $\leq T \leq$ 300 K,

$$\chi(T) = \chi_0 + C/(T - \theta) \qquad (1)$$

where $\theta \approx$ -22 K and the effective magnetic moment $\mu_{eff} \approx 4.2\ \mu_B$ is somewhat larger than the Hund's rule value expected for Pr^{3+} ($4f^2$), for which $\mu_{eff} \approx 3.6\ \mu_B$. In order to describe the data using a CW expression, it is necessary to include a small constant, $\chi_0 \approx$ 0.006 cm^3/mol. For $T \leq$ 20 K, $\chi(T)$ deviates from the CW behavior and saturates towards a constant value of 0.064 cm^3/mol with decreasing T. This behavior was previously taken as evidence for a nonmagnetic ground state arising from crystalline electric field splitting of the Hund's rule multiplet.[7] In contrast, the $\chi_{DC}(T)$ data for NdFePO are nearly isotropic (Fig. 2). For $H \parallel$ ab, the data are described by a Curie-Weiss law for 2 K $\leq T \leq$ 300 K, where $\theta \approx$ -18 K and $\mu_{eff} \approx 3.9\ \mu_B$, close to the Hund's rule value expected for Nd^{3+} ($4f^3$), for which $\mu_{eff} \approx 3.6\ \mu_B$. Similar to PrFePO, it is necessary to include a small constant, $\chi_0 \approx$ 0.017 cm^3/mol in order to describe $\chi_{DC}(T)$ for NdFePO using a CW expression. Nearly identical CW fit parameters are found for $H \perp$ ab. Since the full moment CW behavior extends down to 2 K, it appears that crystalline electric field splitting does not play a significant role in the magnetic behavior of this system. We also note that for both $H \parallel$ and $\perp$ ab, there is evidence for a small amount of Fe$_2$P in the NdFePO specimens (although efforts were made to pick samples with minimal impurity), which introduces weak curvature in $\chi_{DC}(T)$ near 220 K.

AC magnetic susceptibility measurements for PrFePO are shown in Fig. 3 for $H \parallel$ and $\perp$ ab. For H = 0 T, a large step appears in $\chi_{AC}(T)$ near $T_c \approx$ 4.4 K, which coincides with the signatures of SC that were previously observed in measurements of electrical resistivity, DC magnetic susceptibility, and specific heat. For each measurement, a linear background corresponding to the slope of the susceptibility above T_c has been subtracted from the data. A straight line extrapolation to $\chi_{AC}(T)$ = 0, as shown in Fig. 3, was used to define T_c. Curves of $H_{c2}(T)$ (Fig. 3 right panel) were thereby generated, revealing pronounced anisotropy between $H_{c2\parallel}(T)$ and $H_{c2\perp}(T)$. A similar data set is presented for NdFePO (Fig. 4) where T_c and curves of H_{c2} are defined in the same way as for PrFePO. For H = 0 T, this analysis again yields $T_c \approx$ 4.4 K, and pronounced anisotropy between $H_{c2\parallel}(T)$ and $H_{c2\perp}(T)$ is observed.

We calculated the Clogston-Chandrasekhar Pauli limiting field at zero T, given in units of tesla, by means of the expression $H_{p0} \equiv 1.84 T_c$, which for $T_c \approx$ 4.4 K gives $H_{p0} \sim$ 8.1 T. This value is well above the extrapolated zero T critical field lines for PrFePO and Nd-

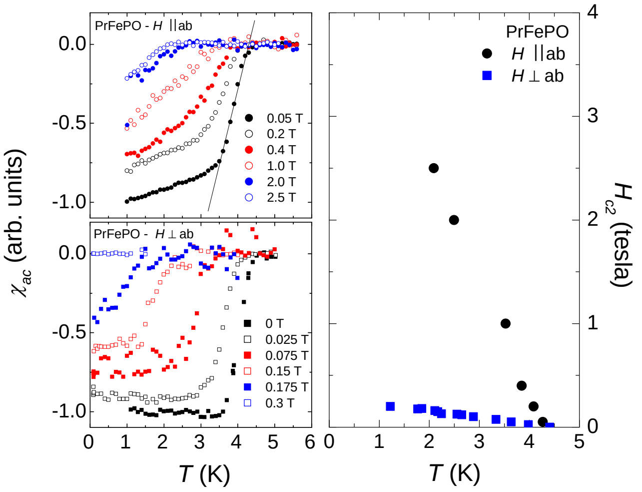

FIG. 3. Left panels: AC magnetic susceptibility χ_{AC} vs. temperature T for the magnetic field $H \parallel$ and $\perp$ to the ab-plane for PrFePO. Right panel: Upper critical field H_{c2} vs. T for $H \parallel$ and $\perp$ to the ab-plane.

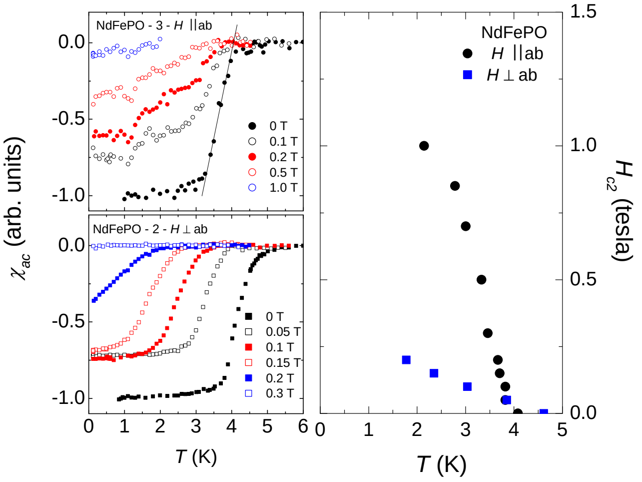

FIG. 4. Left panels: AC magnetic susceptibility χ_{AC} vs. temperature T for the magnetic field $H \parallel$ and $\perp$ to the ab-plane for NdFePO. Right panel: Upper critical field H_{c2} vs. T for $H \parallel$ and $\perp$ to the ab-plane.

FePO. Thus, the upper critical fields appear to be limited by orbital depairing. The zero T value of the orbital critical field can be approximated using the Werthamer-Hefland-Hohemberg (WHH) expression $H_{WHH}(0) = -0.693(dH_{c2}/dT)_{T_c}T_c$. Using the values $dH_{c2}^{\perp}/dT$ = -0.066 T/K and -0.065 T/K and $dH_{c2}^{\parallel}/dT$ = -1.135 T/K and -0.709 T/K, we find that $H_{WHH}^{\perp}(0) \approx 0.20$ T and 0.20 T while $H_{WHH}^{\parallel}(0) \approx 3.46$ T and 2.16 T for PrFePO and NdFePO, respectively.

We also calculated the Ginzburg - Landau coherence lengths parallel and perpendicular to the ab-plane, $\xi_{\parallel}$ and $\xi_{\perp}$, respectively, which can be estimated from the slopes of $H_{c2}^{\parallel}$ and $H_{c2}^{\perp}$ near T_c, *i. e.*,

$$(dH_{c2}^{\perp}/dT)_{T_c} = -\Phi_0/2\pi T_c\xi_{\parallel}^2 \qquad (2)$$

and

$$(dH_{c2}^{\parallel}/dT)_{T_c} = -\Phi_0/2\pi T_c\xi_{\perp}\xi_{\parallel}, \qquad (3)$$

where $\Phi_0 = hc/2e = 2.07 \times 10^{-7}$ G·cm^2 is the flux quantum. From the values for the initial slope of the critical field curves given above, we obtain $\xi_{\parallel}$ = 337 Å and $\xi_{\perp}$ = 19 Å and $\xi_{\parallel}$ = 339 Å and $\xi_{\perp}$ = 31 Å for PrFePO and NdFePO, respectively. These values are quite similar to what was earlier found for the analogue compound without f-electrons, LaFePO.[6] Results are summarized in Table I.

TABLE I. Data summarizing the magnetic and SC properties of LnFePO (Ln = La, Pr, and Nd). Data for LaFePO are from Ref. 6. Data for PrFePO and NdFePO are from this work. The listed quantities are the following: SC transition temperature T_c, initial slope of the upper critical field curve for H perpendicular and parallel to the ab plane, $(dH_{c2}^{\perp}/dT)_{T_c}$ and $(dH_{c2}^{\parallel}/dT)_{T_c}$, coherence lengths $\xi_{\perp}$ and $\xi_{\parallel}$ calculated using eqns. 2 and 3, magnetic susceptibilities at 2 K, $\chi_{\perp,2K}$ and $\chi_{\parallel,2K}$, anisotropies of the initial slopes of the critical field curves $\gamma_{Hc2} = (dH_{c2}^{\perp}/dT)_{T_c}/(dH_{c2}^{\parallel}/dT)_{T_c} = \xi_{\perp}/\xi_{\parallel}$, and anisotropies of the magnetic susceptibilities at 2 K $\gamma_{\chi,2K} = \chi_{\perp,2K}/\chi_{\parallel,2K}$. *Note that for LaFePO, the reported value for χ_{2K} is for a randomly oriented collection of crystals.[6]

	LaFePO	PrFePO	NdFePO
T_c (K)	6.6	4.4	4.4
$(dH_{c2}^{\perp}/dT)_{T_c}$ (T/K)	-0.017	-0.066	-0.065
$(dH_{c2}^{\parallel}/dT)_{T_c}$ (T/K)	-0.86	-1.14	-0.71
$\xi_{\perp}$ (Å)	34	19	31
$\xi_{\parallel}$ (Å)	170	337	339
$\chi_{\perp,2K}$ (cm^3/mol)	0.002*	0.009	0.126
$\chi_{\parallel,2K}$ (cm^3/mol)	—	0.064	0.112
γ_{Hc2}	0.200	0.056	0.091
$\gamma_{\chi,2K}$	—	0.14	1.1

IV. DISCUSSION

The T_c's of 4.4 K for the two compounds PrFePO and NdFePO, considered herein, and 3.1 K for the compound SmFePO, reported in Ref. 19, are appreciably reduced with respect to the T_c of 6.6 K for LaFePO. This reduction of T_c for Ln = Pr, Nd and Sm relative to La in the LnFePO series is in marked contrast to the increase of T_c for Ln = Pr, Nd, Sm relative to La in the LnFeAsO series, after the later compounds have been appropriately doped with charge carriers through F substitution or reduction of oxygen to suppress the spin density wave and induce superconductivity [Ref. 7 and references cited therein]. One possible explanation for the depression of T_c for Ln = Pr, Nd and Sm in the LnFePO compounds, assuming conventional BCS singlet-spin s-wave superconductivity, is superconducting electron pair breaking due to the exchange interaction between the spins of the conduction electrons and the magnetic moments of the Pr, Nd and Sm ions.[20] However, the strength of the exchange interaction and the resultant depression of T_c would have to be small enough to allow the Pr, Nd and Sm compounds to remain superconducting, in spite of the complete occupation of Ln sublattice by Ln ions that carry magnetic moments. Such a situation occurs, for example, in the ternary lanthanide compounds $Ln\mathrm{Mo}_6X_8$ (X = S, Se) and $Ln\mathrm{Rh}_4\mathrm{B}_4$, and the quaternary Ln compounds $Ln\mathrm{Ni}_2\mathrm{B}_2\mathrm{C}$, which have been studied extensively with respect to the interrelation of superconductivity and magnetic order.[21,22] In these compounds, the strength of the exchange interaction is small enough to allow the compounds to remain superconducting, but large enough to produce magnetic ordering of the Ln ions via the RKKY interaction with magnetic ordering temperatures T_M that are comparable to T_c. The comparable values of T_c and T_M allow the interplay between superconducting and magnetic order to be investigated in these materials. In contrast, in many superconductors, the exchange interaction is so strong that the superconductivity is suppressed to 0 K at Ln concentrations x_{cr} of a few atomic percent or less (e.g., $\mathrm{La}_{1-x}\mathrm{Gd}_x$ where $x_{cr} \approx 1\%$ [Ref. 23]; $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{Al}_2$ where $x_{cr} \approx 0.6\%$ [Ref. 24]). When T_c is reduced by pair breaking, the initial depression of T_c with concentration x of Ln ions with partially-filled f-electron shells is linear with a rate, -dT_c/dx, that scales with $\jmath^2(g_J\text{-}1)^2J(J+1)$, where $\jmath$ is the exchange interaction parameter that describes the strength and sign of the exchange interaction, $(g_J\text{-}1)^2J(J+1)$ is the deGennes factor,[25] and g_J and J are, respectively, the Landé g-factor and total angular momentum of the Hund's rule ground state of the Ln ion. Since the magnitude of J is roughly constant as one moves across the Ln series, except for Ce, the depression of T_c goes through a pronounced peak in the middle of the Ln series at Ln = Gd. However, for the case of Ce, hybridization between the Ce^{3+} localized 4f and conduction electron states generates a large negative contribution to the exchange interaction and, in turn, the Kondo effect, both of which conspire to produce an anomalously large depression of T_c.[20,26] In fact, this may be the reason that the compound CeFePO does not display superconductivity down to 400 mK, the lowest temperature to which it has been measured.[27] Since values of T_c are only known for the light Ln elements La through Sm, it is not possible to make a definitive test of the deGennes scaling of the depression of T_c to obtain information regarding the question of whether the LnFePO compounds exhibit BCS superconductivity or some type of unconventional superconductivity. Studies of two heavy fermion compounds containing Ln ions with partially-filled 4f electron shells that show unconventional superconductivity, UPt_3 [Ref. 28] and CeCoIn_5 [Ref. 29], have revealed that the rate of depression of T_c scales with the mean free path λ and superconductivity is quenched when λ is comparable to the coherence length.

An applied magnetic field and polarization of the Ln magnetic moments by a magnetic field also break superconducting electron pairs in a BCS superconductor. This generally leads to a suppression of the upper critical field $H_{c2}(T)$, where the suppression is larger in the easy direction of magnetization of the Ln ions.[30,31] Since the anisotropy of the $H_{c2}(T)$ does not correlate with the easy axis of magnetization of the Pr and Nd ions in the LaFePO compounds studied in this work, the coupling of the Ln magnetization to the conduction electron spins is weak, consistent with a small exchange interaction for a BCS superconductor, or some type of unconventional superconductivity that is relatively insensitive to magnetic interactions (e.g., spin-triplet p-wave superconductivity).

We further remark that our values for T_c for Ln = Pr and Nd may not be optimized, as is implied by several factors. First, bulk SC only appears in these samples following the heat treatment described earlier. However, the affect of this procedure is not well understood; i.e., it is unclear whether it influences the oxygen content, internal strain, or some other quantity. Further evidence that ideal specimens might exhibit higher T_c's is provided by the broad SC transitions, which suggest that a range of T_c's may be found within a given sample. Moreover, recent point contact spectroscopy measurements indicate that the onset of SC occurs at higher temperatures than would be inferred from bulk measurements.[32]

We also find that, while the magnetic anisotropies for Ln = Pr and Nd are dramatically different, the anisotropies of $H_{c2}(T)$ for Ln = La, Pr, and Nd are quite similar. As summarized in table I, $\chi_{\perp,2K}$ and $\chi_{\parallel,2K}$ differ by factors of 14 and 1.75 between PrFePO and NdFePO, respectively. In contrast, there is little variation between the initial slopes of the critical field curves for PrFePO and NdFePO; for $H \perp$ c, they are nearly identical and for $H \parallel$ c they differ by a factor of 1.6. Therefore, for $H \perp$ c, it is clear that even though there is a dramatic difference in $\chi_{\perp,2K}$, the polarization of the Ln spins in this direction does not influence the superconducting state. However, for $H \parallel$ c, the difference in $\chi_{\parallel,2K}$ may be correlated with the initial slopes of the critical field curves: i.e., spin polarization in this direction may suppress the upper critical field curve more strongly for NdFePO than for PrFePO. However, we point out that this relationship may be coincidental, particularly if we consider the fact that the initial slope of the upper critical field curve for $H \parallel$ c for LaFePO is comparable to that of both PrFePO and NdFePO.

Motivated by the weak relationship between the magnetic and SC states in these materials, we searched for other possible correlations between easily obtained

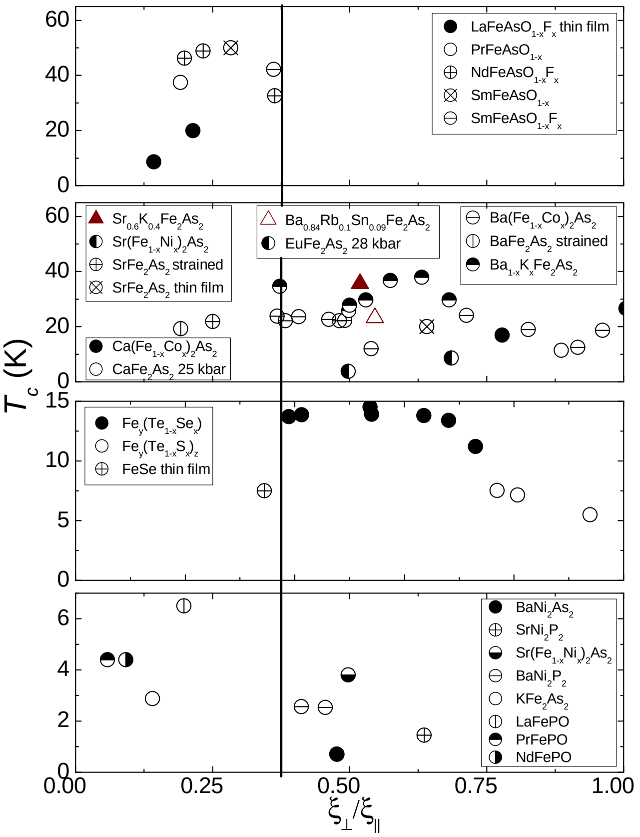

FIG. 5. SC transition temperature T_c vs. the anisotropy of the initial slope of the upper critical field curves $(dH_{c2}^{\perp}/dT)_{T_c}/(dH_{c2}^{||}/dT)_{T_c} = \xi_\perp/\xi_{||}$ (according to eqns. 2 and 3). Data for PrFePO and NdFePO are from this work. Data for LnFeAsO (Ln = La, Pr, Nd, and Sm) compounds are from Refs. 33–39. Data for $M(\mathrm{Fe}_{1-x}T_x)_2\mathrm{As}_2$ (M = Ca, Sr, Ba and T = Co, Ni), $M_{1-x}A_x\mathrm{Fe}_2\mathrm{As}_2$ (A = K, Rb), and EuFe$_2$As$_2$ are from Refs. 40–60. Data for Fe$_y$(Te$_{1-x}$Se$_x$), Fe$_y$(Te$_{1-x}$S$_x$)$_z$ and FeSe are from Refs. 61–69. Data for stoichiometric low T_c materials are from Refs. 6, 70–75.

physical quantities for the T-Pn/Ch superconductors. In particular, we attempted to relate T_c and the anisotropy of the initial slope of the critical field curves $(dH_{c2}^{\perp}/dT)_{T_c}/(dH_{c2}^{||}/dT)_{T_c} = \xi_\perp/\xi_{||}$ (according to eqns. 2 and 3) (Fig. 5). We have reproduced the published data as accurately as possible, but the reader is referred to the literature cited in the figure caption for the definitive data sets. From this treatment, we first see that there is a broad range of anisotropies, but $(dH_{c2}^{\perp}/dT)_{T_c} \leq (dH_{c2}^{||}/dT)_{T_c}$. This result likely reflects the underlying crystalline anisotropy. A noteworthy exception to this trend is seen for SrNi$_2$As$_2$, for which $(dH_{c2}^{\perp}/dT)_{T_c}/(dH_{c2}^{||}/dT)_{T_c} \approx 1.4$.[71] Upon further inspection, it is also apparent that the 1111 compounds tend to have larger anisotropies than the 122 and 11 compounds, as indicated by the vertical line in Fig. 5. It also appears that for the high T_c compounds (Fig. 5, top three panels), the maximum values for T_c may be clustered around limited ranges of $\xi_\perp/\xi_{||}$, which differ for 1111s, 122s, and 11s. However, we emphasize that this observation is not definitive since the peaked regions are not sharp, include data points which do not fall on the peaks, and are composed of data from several different studies. For the low T_c compounds (Fig. 5, bottom panel), T_c appears to decrease with decreasing anisotropy.

V. CONCLUSION

The SC and magnetic properties of PrFePO and NdFePO reveal that the superconductivity of these compounds is only weakly affected by the lanthanide magnetic moments. These results indicate that either the exchange interaction that leads to magnetic pair breaking is weak or that the SC state is unconventional. We also find that the magnetic field induced suppression of the superconducting state is not strongly correlated with spin polarization of the magnetic lanthanide ions.

VI. ACKNOWLEDGEMENTS

Measurements were supported by the National Science Foundation under grant No. DMR0802478. The crystal growth work was supported by the US Department of Energy under research grant No. DE FG02-04ER46105.

VII. REFERENCES

---

[1] D. C. Johnston, *Advances in Physics* **59**, 803 (2010).
[2] J. P. Paglione and R. L. Greene, *Nature Physics* **6**, 645 (2010).
[3] G. R. Stewart, *Reviews of Modern Physics* **83**, 1589 (2011).
[4] R. Zhi-An, L. Wei, Y. Jie, Y. Wei, S. Xiao-Li, Zheng-Cai, C. Guang-Can, D. Xiao-Li, S. Li-Ling, Z. Fang, and Z. Zhong-Xian , *Chinese Physics Letters* **25**, 2215 (2008).
[5] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *Journal of the American Chemical Society* **128**, 10012 (2006).
[6] J. J. Hamlin, R. E. Baumbach, D. A. Zocco, T. A. Sayles, and M. B. Maple, *Journal of Physics: Condensed Matter* **20**, 365220 (2008).
[7] R. E. Baumbach, J. J. Hamlin, L. Shu, D. A. Zocco, N. M. Crisosto, and M. B. Maple, *New Journal of Physics* **11**,

025018 (2009).

[8] H. Ogino, Y. Matsumura, Y. Katsura, K. Ushiyama, S. Horii, K. Kishio, and J. Shimoyama, *Superconductor Science and Technology* **22**, 075008 (2009).

[9] I. I. Mazin and J. Schmalian, *Physica C* **469**, 614 (2009).

[10] I. I. Mazin, *Nature* **464**, 183 (2010).

[11] N. Terasaki, H. Mukuda, M. Yashima, Y. Kitaoka, K. Miyazawa, P. M. Shirage, H. Kito, H. Eisaki, and A. Iyo, *Journal of the Physical Society of Japan* **78**, 013701 (2009).

[12] X. Zhang, Y. S. Oh, Y. Liu, L. Yan, K. H. Kim, R. L. Greene, and I. Takeuchi, *Physical Review Letters* **102**, 147002 (2009).

[13] J. D. Fletcher, A. Serafin, L. Malone, J. G. Analytis, J.-H. Chu, A. S. Erickson, I. R. Fisher, and A. Carrington, *Physical Review Letters* **102**, 147001 (2009).

[14] C. W. Hicks, T. M. Lippman, M. E. Huber, J. G. Analytis, J.-H. Chu, A. S. Erickson, I. R. Fisher, and K. A. Moler, *Physical Review Letters* **103**, 127003 (2009).

[15] M. Yamashita, N. Nakata, Y. Senshu, S. Tonegawa, K. Ikada, K. Hashimoto, H. Sugawara, T. Shibauchi, and Y. Matsuda, *Physical Review B* **80**, 220509(R) (2009).

[16] C.-H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, *Journal of the Physical Society of Japan* **77**, 083704 (2008).

[17] C.-H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, R. Kumai, K. Miyazawa, K. Kihou, H. Matsuhara, M. Braden, and K. Yamada, *Journal of the Physical Society of Japan* **77 Suppl. C**, 44 (2008).

[18] K. Horigane, H. Hiraka, and K. Ohoyama, *Journal of the Physical Society of Japan* **78**, 074718 (2009).

[19] Y. Kamihara, H. Hiramatsu, M. Hirano, Y. Kobayashi, S. Kitao, S. Higashitaniguchi, Y. Yoda, M. Seto, and H. Hosono, *Physical Review B* **78**, 184512 (2008).

[20] M. B. Maple, in *MAGNETISM: A Treatise on Modern Theory and Materials*, H. Suhl. Ed., Vol. V, pp. 289-325 Academic Press, New York (1973).

[21] *Superconductivity in Ternary Compounds II, Topics in Current Physics* , M. B. Maple and Ø. Fischer, Eds., Springer, Berlin, Heidelberg, New York, (1982).

[22] P. C. Canfield, P. L. Gammel, and D. J. Bishop, *Physics Today* **51**, 40 (1998).

[23] B. T. Matthias, H. Suhl and E. Corenzwit, *Physical Review Letters* **1**, 92 (1958).

[24] M. B. Maple, *Physics Letters A* **26**, 513 (1968).

[25] P. G. DeGennes, *J. Phys. Radium* **23**, 510 (1962).

[26] M. B. Maple, *Applied Physics* **1**, 179 (1976).

[27] E. M. Bruning, C. Krellner, M. Baenitz, A. Jesche, F. Steglich, and C. Geibel, *Physical Review Letters* **101**, 117206 (2008).

[28] Y. Dalichaouch, M. C. de Andrade, D. A. Gajewski, R. Chau, P. Visani, and M. B. Maple, *Physical Review Letters* **75**, 3938 (1995).

[29] J. Paglione, T. A. Sayles, P.-C. Ho, J. R. Jeffries and M. B. Maple, *Nature Physics* **3**, 703 (2007).

[30] H. Zhou, S. E. Lambert, M. B. Maple, and B. D. Dunlap, *Philosophical Magazine* **89**, 1861 (2009).

[31] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Physical Review* **148**, 362 (1966).

[32] R. Escudero, Private communication (2011).

[33] E. Backen, S. Haindl, T. Niemeier, R. Hühne, T. Freudenberg, J. Werner, G. Behr, L. Schultz, and B. Holzapfel, *Superconductor Science and Technology* **21**, 122001 (2008).

[34] M. Kidszun, S. Haindl, E. Reich, J. Hänisch, K. Iida, L. Schultz, and B. Holzapfel, *Superconductor Science and Technology* **23**, 022002 (2010).

[35] R. Okazaki, M. Konczykowski, C. J. van der Beek, T. Kato, K. Hashimoto, M. Shimozawa, H. Shishido, M. Yamashita, M. Ishikado, H. Kito, A. Iyo, H. Eisaki, S. Shamoto, T. Shibauchi, and Y. Matsuda, *Physical Review B* **79**, 064520 (2009).

[36] J. Jaroszynski, F. Hunte, L. Balicas, Y.-J. Jo, I. Raicević, A. Gurevich, D. C. Larbalestier, F. F. Balakirev, L. Fang, P. Cheng, Y. Jia, and H. H. Wen, *Physical Review B* **78**, 174523 (2008).

[37] Z. Pribulova, T. Klein, J. Kacmarcik, C. Marcenat, M. Konczykowski, S. L. Budko, M. Tillman, and P. C. Canfield, *Physical Review B* **79**, 020508(R) (2009).

[38] Y. Jia, P. Cheng, L. Fang, H. Luo, H. Yang, C. Ren, L. Shan, C. Gu, and H. Wen, *Applied Physics Letters* **93**, 032503 (2008).

[39] H.-S. Lee, M. Bartkowiak, J.-H. Park, J. Y. Lee, J.-Y. Kim, N.-H. Sung, B. K. Cho, C.-U. Jung, J. S. Kim, and H.-J. Lee, *Physical Review B* **80**, 144512 (2009).

[40] G. F. Chen, Z. Li, J. Dong, G. Li, W. Z. Hu, X. D. Zhang, X. H. Song, P. Zheng, N. L. Wang, and J. L. Luo, *Physical Review B* **78**, 224512 (2008).

[41] M. S. Torikachvili, S. L. Bud'ko, N. Ni, P. C. Canfield, and S. T. Hannahs, *Physical Review B* **80**, 014521 (2009).

[42] A. Yamamoto, J. Jaroszynski, C. Tarantini, L. Balicas, J. Jiang, A. Gurevich, D. C. Larbalestier, R. Jin, A. S. Sefat, M. A. McGuire, B. C. Sales, D. K. Christen, and D. Mandrus, *Applied Physics Letters* **94**, 062511 (2009).

[43] M. Kano, Y. Kohama, D. Graf, F. Balakirev, A. S. Sefat, M. A. Mcguire, B. C. Sales, D. Mandrus, and S. W. Tozer, *Journal of the Physical Society of Japan* **78**, 084719 (2009).

[44] N. Kumar, R. Nagalakshmi, R. Kulkarni, P. L. Paulose, A. K. Nigam, S. K. Dhar, and A. Thamizhavel, *Physical Review B* **79**, 012504 (2009).

[45] S. R. Saha, N. P. Butch, K. Kirshenbaum, J. P. Paglione, and P. Y. Zavalij, *Physical Review Letters* **103**, 037005 (2009).

[46] S. A. Baily, Y. Kohama, H. Hiramatsu, B. Maiorov, F. F. Balakirev, M. Hirano, and H. Hosono, *Physical Review Letters* **102**, 117004 (2009).

[47] N. P. Butch, S. R. Saha, X. H. Zhang, K. Kirshenbaum, R. L. Greene, and J. Paglione, *Physical Review B* **81**, 024518 (2010).

[48] N. Ni, S. L. Bud'ko, A. Kreyssig, S. Nandi, G. E. Rustan, A. I. Goldman, S. Gupta, J. D. Corbett, A. Kracher, and P. C. Canfield, *Physical Review B* **78**, 014507 (2008).

[49] N. Ni, M. E. Tillman, J.-Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud'ko, and P. C. Canfield, *Physical Review B* **78**, 214515 (2008).

[50] M. M. Altarawneh, K. Collar, C. H. Mielke, N. Ni, S. L. Budko, and P. C. Canfield, *Physical Review B* **78**, 220505(R) (2008).

[51] Z. S. Wang, H. Q. Luo, C. Ren, and H. H. Wen, *Physical Review B* **78**, 140501(R) (2008).

[52] D. L. Sun, Y. Liu, and C. T. Lin, *Physical Review B* **80**, 144515 (2009).

[53] H. J. Kim, Y. Liu, Y. S. Oh, S. Khim, I. Kim, G. R. Stewart, and K. H. Kim, *Physical Review B* **79**, 014514 (2009).

[54] H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Bailey, G. F. Chen, J. L. Luo, and N. L. Wang, *Nature* **457**, 565 (2009).

[55] U. Welp, R. Xie, A. E. Koshelev, W. K. Kwok, H. Q. Luo, Z. S. Wang, G. Mu, and H. H. Wen, *Physical Review B* **79**, 094505 (2009).

[56] M. A. Tanatar, N. Ni, C. Martin, R. T. Gordon, H. Kim, V. G. Kogan, G. D. Samolyuk, S. L. Bud'ko, P. C. Canfield, and R. Prozorov, *Physical Review B* **79**, 094507 (2009).

[57] Y. Nakajima, T. Taen, and T. Tamegai, *Journal of the Physical Society of Japan* **78**, 023702 (2009).

[58] J. S. Kim, T. D. Blasius, E. G. Kim, and G. R. Stewart, *Journal of Physics: Condensed Matter* **21**, 342201 (2009).

[59] T. Terashima, M. Kimata, H. Satsukawa, A. Hirada, K. Hazama, S. Uji, H. S. Suzuki, T. Matsumoto, and K. Murata, *Journal of the Physical Society of Japan* **21**, 342201 (2009).

[60] Z. Bukowski, S. Weyeneth, R. Puzniak, P. Moll, S. Katrych, N. D. Zhigadlo, J. Karpinski, H. Keller, and B. Batlogg, *Physical Review B* **79**, 104521 (2009).

[61] D. Braithwaite, G. Lapertot, W. Knafo, and I. Sheikin, *Journal of the Physical Society of Japan* **79**, 053703 (2010).

[62] M. Fang, J. Yang, F. F. Balakirev, Y. Kohama, J. Singleton, B. Qian, Z. Q. Mao, H. Wang, and H. Q. Yuan, *Physical Review B* **81**, 020509 (2010).

[63] S. Khim, J. W. Kim, E. S. Choi, Y. Bang, M. Nohara, H. Takagi, and K. H. Kim, *Physical Review B* **81**, 184511 (2010).

[64] T. Kida, M. Kotani, Y. Mizuguchi, Y. Takano, and M. Hagiwara, *Journal of the Physical Society of Japan* **79**, 074706 (2010).

[65] M. Bendele, S. Weyeneth, R. Puzniak, A. Maisuradze, E. Pomjakushina, K. Conder, V. Pomjakushin, H. Luetkens, S. Katrych, A. Wisniewski, R. Khasanov, and H. Keller, *Physical Review B* **81**, 224520 (2010).

[66] H. Lei, R. Hu, E. S. Choi, J. B. Warren, and C. Petrovic, *Physical Review B* **81**, 094518 (2010).

[67] R. Hu, E. S. Bozin, J. B. Warren, and C. Petrovic, *Physical Review B* **80**, 214514 (2009).

[68] H. Lei, R. Hu, E. S. Choi, J. B. Warren, and C. Petrovic, *Physical Review B* **81**, 184522 (2010).

[69] M. Jourdan and S. Haaf, *Journal of Applied Physics* **108**, 023913 (2010).

[70] F. Ronning, N. Kurita, E. D. Bauer, B. L. Scott, T. Park, T. Klimczuk, R. Movshovich, and J. D. Thompson, *Journal of Physics:Condensed Matter* **20**, 342203 (2008).

[71] E. D. Bauer, F. Ronning, B. L. Scott, and J. D. Thompson, *Physical Review B* **78**, 172504 (2008).

[72] F. Ronning, E. D. Bauer, T. Park, S.-H. Baek, H. Sakai, and J. D. Thompson, *Physical Review B* **79**, 134507 (2009).

[73] P. Shirage, K. Miyazawa, M. Ishikado, K. Kihou, C. Lee, N. Takeshita, H. Matsuhata, R. Kumai, Y. Tomioka, T. Ito, H. Kito, H. Eisaki, S. Shamoto, and A. Iyo, *Physica C* **469**, 355 (2009).

[74] Y. Tomioka, S. Ishida, M. Nakajima, T. Ito, H. Kito, A. Iyo, H. Eisaki, and S. Uchida, *Physical Review B* **79**, 132506 (2009).

[75] T. Terashima, M. Kimata, H. Satsukawa, A. Harada, K. Hazama, S. Uji, H. Harima, G.-F. Chen, J.-L. Luo, and N.-L.Wang, *Journal of the Physical Society of Japan* **78**, 063702 (2009).