Electronic Structure of PrFeAsO$_{1-\delta}$ : An Investigation Using X-ray Absorption and Emission Spectroscopy

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Abstract. Soft X-ray absorption and emission spectroscopy was used to determine the electronic density of states of oxygen vacated PrFeAsO. The measured oxygen and iron spectra are in good agreement with mean field theory and local density approximations. Iron-arsenic hybridized spectral features reveal that Fe-As bonding is involved in the process of electron addition near the Fermi-level. X-ray emission and absorption spectra shows an increase in the Fe density of states at the Fermi-level as the doping decreases. This doping dependent electronic behavior indicates the possibility of a magnetic instability in the undoped compound.

1. Introduction

The recently discovered Fe-based rare-earth (RE)-pnictide high-temperature superconductors have attracted a great deal of attention.[1] These compounds form several classes including materials in which RE-substitution (RE = La, Ce, Pr, Nd, Sm, Gd) in REFeAsO$_{1-x}$F$_x$ or REFeAsO$_{1-\delta}$ has yielded superconducting transition temperatures ($T_c$) as high as 55 K in the case of RE = Sm.[2] Early reports suggested that the parent phase might be either a non-magnetic metal or an antiferromagnetic (AF) semi-metal[3] while experiments confirm the latter. It now accepted that the FeAs materials are not in a Mott insulating phase[4] but there is inconclusiveness concerning the degree of electronic correlations.[5] The basic magnetic nature of the parent phase is also debated, although neutron scattering shows convincingly an AF phase below temperatures typically of the order of 140 K. Therefore, it is important to study, experimentally, the electronic behavior in comparison with the cuprates and to reconcile the electronic properties with magnetic information.

The superconducting state is reached in REFeAsO materials by electron doping or hole doping the FeAs planes. Electron-doped FeAs superconductors have been fabricated in at least three ways. All of the doping steps e.g. fluorine-substitution for oxygen, oxygen deficiency, and...
the substitution of Th$^{4+}$ for $RE^{3+}$ occur in the charge reservoir $RE$-$O$ layer by substitution and induce electron carriers. The effect of electron-doping on the electronic structure has been studied theoretically and experimentally but, so far, the conclusions are indefinite. Local density approximation (LDA), dynamical mean field theory (DMFT), and spin-dependent LDA (LDSA) calculations have given differing results on the question of whether or not the FeAs family of superconductors are strongly correlated. Haule et al.[6] using DMFT, concluded that the materials are strongly correlated. In contrast, Kurmaev et al.[7] and Yang et al.[8] based on Fe 3d electronic structure measurements by x-ray absorption and emission spectroscopy, suggested the absence of strong electronic correlations. Angle-resolved[9] and integrated[10] photoemission spectroscopy results from the first reported iron-based superconductor, LaFeOP, as well as LaFeAsO$_{1-x}F_x$, support proposed itinerant magnetism ground state models of these materials. This claim is at variance with the strongly correlated electron picture that emphasizes an antiferromagnetic (AF) ground state Mott physics interpretation.

We report measurements of the electronic structure in the set of materials PrFeAsO$_{1-\delta}$ with $\delta = 0.15, 0.30$ and 0.35. Soft x-ray absorption and emission spectroscopy (XAS and XES) are used to extract element specific density of states (DOS) spectra that can be directly compared to theoretical calculations of the electronic structure of the PrFeAsO materials. XES of the Fermi-level crossing, Fe 3d states show a single, narrow dominant peak having an As hybridization shoulder in agreement with other experimental[7] and theoretical[11] results. The Fe conduction band onset shifts to higher energy as a function of electron doping (oxygen vacancy). From Fe XES data, we provide an estimate of the Fe 3d bandwidth $W$. An increase in the Fe electronic density of states at the Fermi-level is demonstrated for less doped samples. This electronic trend indicates an approach toward a magnetic instability in the parent phase of PrFeAsO$_{1-\delta}$.

2. Experimental Procedure
PrFeAsO$_{1-\delta}$ polycrystalline samples were synthesized at high pressure and high temperature using a cubic-anvil high-pressure apparatus.[12-14] The nominal oxygen deficiencies at the start of the synthesis were $\delta = 0.15, 0.30$, and 0.35 in PrFeAsO$_{1-\delta}$. Neutron scattering analysis[15] of NdFeAsO$_{1-\delta}$ indicated that the oxygen deficiencies were smaller than those of the starting materials. It is likely that a similar condition exists for PrFeAsO$_{1-\delta}$. This was likely due to the oxidation during the synthesis process of those materials and PrFeAsO$_{1-\delta}$. $RE$FeAsO are quaternary equiatomic compounds that have a rather simple structure of alternating FeAs and $RE$-$O$ layers with eight atoms in a tetragonal unit cell of space group P4/$nmm$ at 300 K.

Table 1. The lattice parameters ($T_c$) of the PrFeAsO$_{1-\delta}$ samples.

| $\delta$ | $T_c$(K) | $a$(Å)     | $c$(Å)     |
|---------|----------|------------|------------|
| 0.15    | 3        | 3.9866     | 8.6046     |
| 0.30    | 43       | 3.9770     | 8.5869     |
| 0.35    | 48       | 3.9627     | 8.5721     |

Table 1 shows that the $a$-parameter systematically decreases upon increasing the nominal $\delta$, which means that the oxygen deficiencies of the samples systematically increased though, as stated above, there is some ambiguity in the absolute value of the oxygen deficiency parameter $\delta$. The $T_c$ of the PrFeAsO$_{1-\delta}$ samples were measured, using a SQUID magnetometer, under a magnetic field of 5 Oe after zero-field cooling from sufficiently far above $T_c$. 


X-ray absorption and emission spectroscopy was performed at the Advanced Light Source. XES intensity is proportional to the occupied partial density of states (DOS) of the valence band while XAS intensity is proportional to the unoccupied partial DOS associated with the conduction band. O 1s XAS and O Kα-edge XES were used to investigate the electronic structure of the oxygen-associated bands. O 1s XAS entails the 1s → 2p transition and O Kα XES records the intensity resulting from the O 2p → 1s transition. Transition metal (TM) edge x-ray spectroscopy is highly sensitive to the chemical environment of the TM atoms; therefore, we employed Fe 2p XAS and Fe L_{2,3}-edge XES. In an Fe L_{2,3}-edge XAS, Fe 2p electrons are excited into empty Fe 3d states. Fe L_{2,3} XES profiles were obtained by collecting x-ray emission resulting from the Fe 3d→2p transition. All samples were filed immediately before being placed in the ultra-high vacuum synchrotron end-station. All measurements were performed at room-temperature. The beamlines 7.0.1 and 8.0.1 undulators and monochromators produced intense x-ray beams with spot-sizes on the order of 100 microns and energy resolutions of 0.2 eV(0.2 eV) and 0.5 eV(0.6 eV) for oxygen(iron) x-ray absorption and emission, respectively. X-ray absorption spectra were measured in the total fluorescence yield (TFY) mode with a resolving power of E/∆E = 5000. All spectra were measured with the incident radiation impinging at 20° with respect to the sample surface. The x-ray emission spectrometer, mounted in the synchrotron orbit plane, used a grazing-incidence, two-dimensional multi-channel plate X-ray emission detector and a resolution of 0.35 eV.

3. Results and Discussion

Figure 1 shows the total fluorescence yield (TFY) mode of O 1s XAS from PrFeAsO_{1−δ} (δ = 0.15, 0.30, 0.35). The O XAS profiles, normalized by setting the maximum peak of each spectrum equal to unity, are plotted in a collapsed fashion showing the main absorption lines A, B, and C. The O 1s XAS data are consistent with numerous LDA band structure calculations.[16] A weak feature at 1 eV, together with more prominent O spectral band features at about 3 eV and 6 eV above E_F. The pre-peak labeled A is primarily due to the hybridization of Fe 3d, arsenic and oxygen states according to LDA[6,11,17-19] calculations. The main absorption edge B is due to the hybridization of Pr 5d states and oxygen. A band, C, of features at 537 eV forms due to strong hybridization bonds of oxygen with Pr states. Oxygen LDA band structure calculations show the presence of O 2p DOS in the range 1 to 2 eV above the Fermi-level where the bonding of Fe 3d [c.f. Fig. 2(a) of Ref. 17] and As 4p is the strongest. LDA predicts the spectral weight of the oxygen 2p DOS to be significantly less than that of the Fe or As DOS at low lying energies. The presence of very weak oxygen states near the Fermi-level is not surprising given that the O ions are separated from the FeAs layer. The small O DOS that exists at low energies may be explained in the following way: O 2p orbitals can hybridize with the Pr through Pr 5d states. Pr 5d states, in turn, hybridize with the empty As 5s and relatively long-range As 4p orbitals. Fe 3d electrons form covalent sp³ bonds with As 4p states in the superconducting layer. This complicated hybridization scheme, based on long-range oxygen intermixing, is consistent with band theory. In Ref [17] Sawatzky et al. stressed that the As 4p-Fe interaction is weaker than the planar hybridization found in the cuprates. Reported band structure calculations indicate that the O 2p hybridization in RE-FeAsO materials is even weaker than the Fe-As bonding, but nevertheless, it is clearly present in our experimental and theoretical results just above and below E_F. The long-range intermixing of the oxygen may play a role in the FeAs layer doping. While a doping mechanism based on weak oxygen intermixing might be plausible, one clearly must also include the electrostatic influence of the doped RE layers on the metallic FeAs layers.

The oxygen 1s absorption spectra of PrFeAsO_{1−δ} show a strong similarity to that of REFeAsO_{1−x}F_x.[20] The overall O 1s XAS spectra do not shift significantly with doping δ. We do not observe an onset shift that might reflect a change in the chemical potential; however, Kroll et al.[20] reported a trend in F-doped LaFeAsO such that onset of the O 1s XAS pre-peak
undergoes small shifts toward higher energies with increased electron doping. The O 1s XAS onset shift was interpreted as being due to the change in O Madelung potential and the change in the chemical potential due to electron doping. Higher energy absorption features B and C do not change energy as doping varies (inset Fig. 1.). This agrees with results from LaFeAsO$_{1-x}$F$_x$ where the higher energy peaks B and C were stationary with doping and the pre-peak A was observed to change position only by 100 meV as x was varied from $x = 0.0$ to 0.1.[20]

In Fig. 2 the XA and XE spectra are plotted to show the occupied and unoccupied oxygen partial density of states (PDOS). The O Kα XES contains four major peaks I-IV. I and II are due primarily to Pr, Fe and O hybridization. These features match those in the oxygen spectral weight (DOS) suggested by LSDA+U for PrFeAsO.[18] A dual peak structure occurs in the energy range 4.0 to 5.0 eV below $E_F$. Several FeAs LDA studies predict this structure, we attribute these peaks to be due to an oxygen band splitting induced by the Pr crystal field.[21] III and IV are thought to originate from the oxygen hybridization with Fe-$d$ and As-$4p$ states.[6] LDA calculations by Sawatzky et al. [17] support this spectral assignment [c.f. Fig. 2(a) of Ref. 17] by showing As DOS as the strongest spectral contribution located $~2 - 3$ eV below $E_F$. Arsenic $4p$ orbitals, possessing a longer range than O $2p$ orbitals, interact primarily with Fe states; therefore, As $4p$ orbitals, while bonding to Fe, simultaneously interact with the RE-layer, and thereby, may participate in the transfer of charge carriers to the superconducting layer by two observations i) LDA results show that the As DOS dominates the oxygen spectral weight near the Fermi-level and ii) DMFT, LDA and LSDA+U calculations suggest that the As contributions are distributed over a broad energy range. III and IV both appear to be due to Fe, As, and oxygen hybridization, but in this energy region, according to theoretical calculations, As dominates the near-$E_F$ O spectral weight. This fact may pose challenges in extracting doping dependent trends from O valence band spectra.

The Fe $L_{2,3}$ x-ray absorption spectrum for PrFeAsO$_{1-\delta}$ ($\delta = 0.15$) is shown in Fig. 3(a). The XA process yields a direct measurement of the unoccupied (hole) states of the Fe $3d$ band. X-rays tuned to the $L_{2,3}$-edge excited Fe $2p$ electrons ($2p^63d^5$) into empty Fe $3d$ states ($2p^53d^7$). Two major Fe $L_{2,3}$ spin-orbit split absorption features result at 707.6 eV (Fe $2p_{3/2} \rightarrow$ Fe $3d$) and 720 eV (Fe $2p_{1/2} \rightarrow$ Fe $3d$). The Fe XA spectral profile, Fig. 3(a), of PrFeAsO$_{0.85}$ closely matches that of pure Fe-metal.[8] The shoulder appearing at the high energy tail of the Fe $L_3$ peak is thought to be due to covalent $sp^3$ bonds between Fe $3d$ and As $4p$ states.[22] Fe XAS is a very sensitive tool for determining the chemical environment, electronic structure and valence of Fe ions in compounds.[23,24] The single-peak structure of the Fe $L_3$ line in addition to the S. O. splitting of 12.4 eV indicates that the Fe ion of PrFeAsO$_{1-\delta}$ is in a 2+ valence (high spin) state. [8,25] Fig. 3(b) displays non-resonant Fe $L$-edge XE spectra obtained with 740 eV incident photons. The $L$-edge XE profile of transition metals is composed of two major peaks due to the $3d \rightarrow 2p_{3/2}$ and $3d \rightarrow 2p_{1/2}$ de-excitation transitions. These XES peaks occur at 705 eV ($L_3$) and $~717$ eV ($L_2$) and are separated in energy by the S.O. splitting of the Fe $2p_{j=1/2,3/2}$ states.

The XA spectrum in Fig. 3(a) was reduced from raw data, in Fig. 4(a), taken from the samples PrFeAsO$_{1-\delta}$ ($\delta = 0.15$, 0.30 and 0.35). Each raw PrFeAsO$_{1-\delta}$ spectrum consists of the Fe $L_3$ mainline and an extraneous shoulder on the high-energy tail. The additional spectral feature originates from the crystal field splitting of a small, unreacted portion of one of the starting materials[14] Fe$_2$O$_3$. Of the two major Fe$_2$O$_3$ XAS peaks $A^*$ and $B^*$, only $B^*$ appears prominently in the PrFeAsO$_{1-\delta}$ data. The relative intensity of $A^*$ and $B^*$ is well-known for Fe$_2$O$_3$ but it is not manifested in the $L_3$ band of the raw PrFeAsO$_{1-\delta}$ spectra indicating that Fe$_2$O$_3$ has a non-dominant concentration.

In order to further explore this point, the experimental spectra of Fig. 4(a) were fitted to determine the Fe$_2$O$_3$ spectral contribution to the PrFeAsO$_{1-\delta}$ XA profile. A superposition of Gaussian functions, 1 - 4, was used in a non-linear least squares fit (gray line in Figure 4(b))
to estimate the contribution of four major characteristics (see vertical hash marks) of the raw PrFeAsO$_{1-\delta}$ spectra. A fit of pure Fe$_2$O$_3$ determined the relative magnitudes and widths of the spectral components of the unreacted material. The Fe$_2$O$_3$ peaks (see Figure 4(c)) were scaled to the extraneous component, 2, of the raw PrFeAsO$_{1-\delta}$ Fe XAS data. This step ensured that the appropriate magnitude of the Fe$_2$O$_3$ spectral contribution was attributed to the raw XAS PrFeAsO$_{1-\delta}$ profiles. The fitted line program assumed [26] the profile of raw PrFeAsO$_{1-\delta}$ to be a linear superposition of Fe$_2$O$_3$ and the actual PrFeAsO$_{1-\delta}$ spectral intensity. Accordingly, Fe$_2$O$_3$ was isolated from the raw data to obtain the resulting PrFeAsO$_{0.70}$ spectral line shape in Fig. 4(d). Similar spectra obtained for PrFeAsO$_{1-\delta}$ ($\delta = 0.15$ and 0.35) were found to be in excellent agreement with XAS reported [7,8,20,22,27] for other iron-arsenide materials. For consistency, this analysis approach was applied to the oxygen XA spectra. We investigated the presence of Fe$_2$O$_3$ in the raw PrFeAsO$_{1-\delta}$ oxygen XAS data. Fe$_2$O$_3$ has two crystal-field split pre-peaks (at 530 eV) below the O 1s edge. [28,29] An Fe$_2$O$_3$ signature is absent from the O 1s XAS pre-peak region of the raw PrFeAsO$_{1-\delta}$ spectra (Figure 1). The close similarity of the raw PrFeAsO$_{1-\delta}$ O 1s pre-peaks in all of the samples rules out the presence of random oxygenation and provides direct evidence that any extraneous oxidation due to Fe$_2$O$_3$ is negligibly small [30] in the oxygen spectra. The intensity minimum [29] in the O 1s XA profile of Fe$_2$O$_3$ at 532 eV results in an insignificant contribution to the XAS of PrFeAsO$_{1-\delta}$ at this energy. Thus, the small amount of unreacted Fe$_2$O$_3$ has a negligible effect on the oxygen XA spectra.

PrFeAsO$_{1-\delta}$ possesses an XE edge intensity ratio $I(L_2)/I(L_3)$ (c.f. Ref. [31]) value that is identical to that of other FeAs materials such as CaFe$_2$As$_2$ [27] and LiFeAs [27]. Kurmaev et al. [27] in the case of other iron arsenides, noted the proximity of their $I(L_2)/I(L_3)$ values to that of Fe-metal. In Fig. 5 we present a non-resonant VB Fe L$_3$ XE spectral profile that possesses a single dominant peak and a low-energy shoulder in agreement with other studies. [7] The main peak is due primarily to Fe 3$d$ bands [7,32-33] and we interpret the shoulder near 704 eV to originate from the hybridization of Fe 3$d$ and As 4$p$ states. [6] This assignment is supported by LDSDA+$U$ calculations which show that the spectral weight $\sim$ 3.0 eV below $E_F$ derives from both Fe and arsenic states. [16] The Fe XES can be used to ascertain information about the bandwidth of the Fe 3$d$ states. A measurement of the XES full-width at half maximum (FWHM) yields a width of 3.1 eV; however, this value is core-hole lifetime and multiplet broadened and cannot be taken as a direct measurement of the Fe 3$d$ bandwidth. The width $2$ eV of the dominant portion of the Fe L$_3$ XE peak can serve as an upper limit of the Fe 3$d$ bandwidth $W$. In other words, the Fe 3$d$ width should be no greater than 2 eV. A range of reported values for the Coulomb parameter $U$, from $0.8$ eV [34] for a basis consisting of only Fe 3$d$ orbitals to $2$ eV [17-18,35] for an As $p$ - Fe 3$d$ mixing model, [35-36] is consistent with our O and iron spectra. Recently, Wang et al. [8] argued that $U \sim 2$ eV based on theoretical calculations that matched x-ray spectroscopy in the limiting condition. These values imply that the magnitude of $U$ is similar to or less than that of the estimated Fe 3$d$ bandwidth. Importantly, the relative magnitude of $U$ and $W$ can implicate the extent of electron correlations in PrFeAsO$_{1-\delta}$. In the present case, $U/W \sim 1$ suggests that PrFeAsO$_{1-\delta}$ system is in an intermediate state between the metallic and insulating phases. [6,17]

In Fig. 6(a) we present a magnified view of the low-energy tail of the Fe L$_3$ XAS peaks of PrFeAsO$_{1-\delta}$ ($\delta = 0.15$, 0.30 and 0.35). The peak onset (see the arrow), defined as 10 percent of the absorption maximum, shifts as a function of doping. The onset’s upward shift of $\sim 900$ meV to higher energies is due to the addition of electrons to Fe metallic sites. Equivalently, the onset shifts represent a reduction in the XAS intensity (hole DOS) near the Fermi-level. Figure 6(b) shows normalized XA spectra and Fe L-edge XES. All the doped PrFeAsO$_{1-\delta}$ samples are arranged in composite intensity profiles. If PrFeAsO$_{1-\delta}$ is taken to be metallic, the Fermi-level $E_F$ can be approximated as the intersection of the Fe XE and XA spectral profiles.
and Fe L-edge XE spectral intersection points are reduced relative to the valence and conduction band maxima. In addition, these points shift by ~200 meV (Fig. 6(b)) on account of the doping δ. A closer examination of this shift is afforded by the left inset of Fig. 6(b) where the arrows indicate the positions of the points of intersection of the XA and XE spectra. The Fe L3 XAS main-line shifts by ~0.15 eV upward with doping from δ = 0.15 to 0.35; therefore, the Fe conduction band (CB) maximum and low-energy electronic structure i.e., the onset, undergoes an observable change as a result of doping. Evolution of the Fe L3 peak onset as δ goes from 0.15 to 0.35 indicates the addition of doped electrons to the low-energy Fe states. The removal of low energy (near-E_F) unoccupied spectral weight is equivalent to electron addition per Fe atom.

The changes in the Fe DOS near the Fermi-level are accompanied by a systematic increase in the hole DOS at the Fe-As hybridization peak (shoulder). Spectral changes in the high energy shoulder of the Fe L3-edge XA peak suggest that, concomitant with the addition of electrons to states near E_F, doping induces the removal of electrons from covalent bonding states associated with Fe and As atoms. This suggests the DOS at the Fermi-level D(E_F), (right inset of Fig. 6(b)) increases as the doping decreases, giving a signal of a possible approach toward a parent phase antiferromagnetic instability.[37-38] The trend also suggests that the parent compound is in the itinerant magnetism regime. The mechanism of the magnetic instability in FeAs parent materials is not yet known. While the spin-density wave (SDW) in LaFeAsO was argued to originate from the Fermi-surface nesting[39] of electron and hole pockets, an alternative proposal argued that the super exchange interaction of Fe ions mediated through the off-plane As atoms was important.[32,40-41] The doping behavior, presented here, of the Fe L3 XAS shoulder is consistent with the notion that the Fe-As bonding might play an important role in the occurrence of the magnetic instability of the parent phase. Therefore, XES offers a method to access the link between the electronic structure at the Fermi-level and the magnetic behavior in FeAs superconductors.

4. Conclusion
Oxygen and iron soft X-ray emission and absorption data has been used to probe the structure of the low-lying electronic states of PrFeAsO_1−δ as a function of doping. The results indicate that the oxygen density of states of PrFeAsO_1−δ is well hybridized and is consistent with a band structure models for this material. The O 2p states are shown to be involved in long-range mixing, into the FeAs hybridized states, which might facilitate electron transfer between the layers. This long-range, non-planar mechanism is consistent with band structural calculations as well as the report of three-dimensional superconductivity and the magnetism in some FeAs materials. The oxygen XAS and XES are well-described by LDA + small-U, LSDA and, DMFT calculations; however, only LDA + small-U matches the observed low energy O DOS just above and below E_F. The PrFeAsO_1−δ occupied and unoccupied O bands show behavior that is similar to that observed in the fluorine-doped material REFeAsO_1−xF_x. However, the energy shifts in the onset of the Fe unoccupied band, as given by the Fe XAS, is consistent with electron doping. The Fermi-level density of states D(E_F) increases as the parent phase is approached. This behavior reveals the tendency toward itinerant magnetism with decreasing doping. We believe that the experimental spectra given here are robust and should guide future theoretical models and understanding.

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Fig. 1. (a) Oxygen 1s x-ray absorption spectra of PrFeAsO$_{1-\delta}$ ($\delta = 0.15, 0.30$ and $0.35$) taken in total fluorescence yield (TFY) mode. Feature A is the oxygen pre-peak due to O-Fe 3d and As 4p hybridization; B is an O-Pr 5d hybridization peak. Features A, B and C (see inset) do not shift with respect to oxygen vacancy concentration.

Fig. 2. Normalized O 1s XA and O K$\alpha$ XE spectra of PrFeAsO$_{1-\delta}$ ($\delta = 0.15, 0.30$ and $0.35$). The XES(XAS) reflect the occupied(unoccupied) oxygen partial density of states. The major spectral features I-IV, A, B and C are discussed in the text.

Fig. 3. Fe L-edge X-ray absorption and emission spectra of PrFeAsO$_{0.85}$ $T_c = 3$ K. (a) the total electron yield (TEY) mode Fe 2p XA intensity plotted as a function of photon energy. (b) The non-resonant Fe L-edge XE intensity profile collected at an incident energy of 740 eV.

Fig. 4. The Fe TFY $L_3$ XAS band of (a) raw PrFeAsO$_{1-\delta}$ ($\delta = 0.15, 0.30$ and $0.35$). Both raw PrFeAsO$_{0.70}$ (b) and Fe$_2$O$_3$ (c) Fe $L_3$ XA spectra are shown with fitted curves (gray lines) based on Gaussian functions (see text). (d) PrFeAsO$_{0.70}$ Fe $L_3$ XA spectrum.

Fig. 5. A Comparison of Fe 2p XAS and Fe $L_{2,3}$ XES data of FeO, PrFeAsO$_{0.85}$ and Fe-metal. The ratio $I(L_2)/I(L_3)$ of the integrated XES main peak intensities of samples FeO, Fe-metal and PrFeAsO$_{0.85}$.

Fig. 6. Enhanced views of the normalized Fe 2p XA and Fe $L_{2,3}$ XE spectra of PrFeAsO$_{1-\delta}$ ($\delta = 0.15, 0.30$ and $0.35$). (a) The onset of the leading edge of the Fe $L_3$ XA edge undergoes a shift as a function of oxygen vacancy doping. (b) The XE and XA spectra are juxtaposed in order to depict the Fe band occupied and unoccupied electronic bandwidth versus doping. XE spectra, collected at an incident photon energy of 740 eV, do not change with doping. Fe 2p XA spectra show that the conduction band maximum does not shift with electron doping. A shift in the chemical potential is revealed (inset) as a change in the normalized intensity of the XE and XA spectral intersection.
Figure 1, Freelon et al.

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