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Valence change of europium in $EuFe_2As_{1.4}P_{0.6}$ and compressed $EuFe_2As_2$ and its relation to superconductivity

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Superconductivity can be realized in Eu-containing pnictides by applying chemical (internal) and physical (external) pressure, the intrinsic physical mechanism of which attracts much attention in the studies of pnictide superconductors. Here we present the experimental evidence for the pressure-induced valence change of europium in $EuFe_2As_{1.4}P_{0.6}$ exposed to ambient pressure and $EuFe_2As_2$ to high pressure by x-ray absorption measurements on L_3-Eu edge. We found that the absorption spectrum of $EuFe_2As_{1.4}P_{0.6}$ showed a clear spectra weight transfer from divalent to trivalent state. Furthermore, a similar behavior of valence transition as in $EuFe_2As_{1.4}P_{0.6}$ was also observed in $EuFe_2As_2$ when pressure was applied. This reports the observation of valence change in pnictide superconductors and the analysis of its influence on superconductivity in $EuFe_2As_{1.4}P_{0.6}$ and compressed $EuFe_2As_2$.

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The discovery of Fe-based superconductor[1] opens a path for the understanding of high-temperature superconducting mechanism, which has been enigmatic for more than two decades. Experiments demonstrate that appropriate charge carrier doping or compressing the parent compounds of Fe-based pnictide superconductors can suppress the spin-density-wave (SDW)transition originated from the long-range antiferromagnetic order of the Fe moments at low temperature and expedite the appearance of superconducting state.[2–5] Comparing with superconductors of $R\text{FeAsO}_{1-x}\text{F}_x$ (R=La, Ce, Pr, Nd, Sm, etc.) oxyarsenides, $A'Fe_2As_2$ (A' =Ca, Sr, Ba, and Eu) is particularly interesting due to its oxygen-free and iron-rich features. Quite a large number of experiments were carried out to attempt to understand the nature of superconductivity in $A'Fe_2As_2$ (A'122) system. By hole or electron doping on A' and Fe sites, superconductivity has been achieved at 20–38 K in the A'122 system.[6–13]

Remarkably, recent studies indicate that the isovalent substitution arsenic with phosphorus in $A'Fe_2As_2$ system induces superconductivity at 13 K in $CaFe_2As_{1.7}P_{0.3}$, 27 K in $SrFe_2As_{1.3}P_{0.7}$, 30 K in $BaFe_2As_{1.4}P_{0.6}$, and 26 K in $EuFe_2As_{1.4}P_{0.6}$, respectively,[14–16] which is attributed to the chemical pressure introduced by the substitution of arsenic with phosphorus because the ionic radius of phosphorus is smaller than that of arsenic. Superconducting transitions have also been observed in undoped A'122 compounds when physical pressure was applied. The superconducting transition temperature emerges at 10–12 K at 0.5 GPa in $CaFe_2As_2$,[5,17] 27–29 K at 3–3.5 GPa in $SrFe_2As_2$,[18,19] 29 K at 4 GPa in $BaFe_2As_2$,[20–22] and 29–30 K at 2.6–2.8 GPa in $EuFe_2As_2$,[23,24] respectively. The experimental evidence obtained so far implies that either chemical or physical pressure can turn the undoped parent compounds to superconductors.

$EuFe_2As_2$ is a unique member in A'122 family due to its additional strong magnetic order of Eu^{2+} moments at ∼19 K in addition to magnetic order of the Fe moments.[25–27] Moreover, it is the only member with $4f$ electrons in A'122 family. It is known that the volume of Eu^{2+} with a $4f^7$ electron shell is larger than that of Eu^{3+} with a $4f^6$ electron shell, thus it is anticipatable that application of pressure may drive a valence transition of Eu ions in $EuFe_2As_2$ from divalent to trivalent. X-ray absorption spectroscopy (XAS) is one of the most important and useful techniques for the determination of valence transition, which has been widely applied in physics and chemistry. In this paper, we demonstrate ambient-pressure XAS studies on Eu ions for single crystal $EuFe_2As_2$, $EuFe_2As_{1.4}P_{0.6}$, and $EuFe_{1.715}Co_{0.285}As_2$. A clear valence transition from Eu^{2+} to Eu^{3+} was found only in $EuFe_2As_{1.4}P_{0.6}$ sample, revealing the special role of chemical pressure for the Eu's valence transition. We also investigated the high-pressure XAS on Eu ions for single crystal $EuFe_2As_2$ which has been reported its superconductivity at 2.6–2.8 GPa.[23,24] When applied external pressure on the *ab* plane of the $EuFe_2As_2$ sample, the valence change of Eu^{2+} ions was observed upon uploading beginning at 2.1 GPa. With further increasing pressure, the mean valence of the Eu ions increased and saturated at pressure above 9.8 GPa. For comparison, we also performed XAS measurements on electron-doped single crystal $EuFe_{1.715}Co_{0.285}As_2$ at ambient pressure, but did not observe any valence change of the divalent Eu ions in the sample. The increment of Eu's valence state, which is induced by chemical or physical pressure,

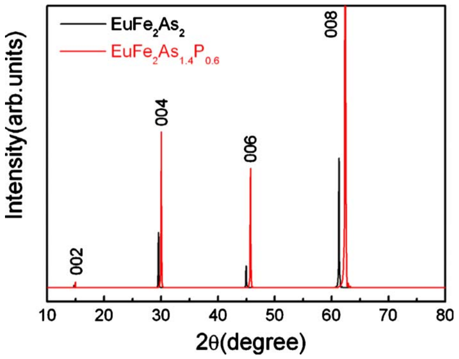

FIG. 1. (Color online) X-ray diffraction patterns of $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ single crystals measured at room temperature.

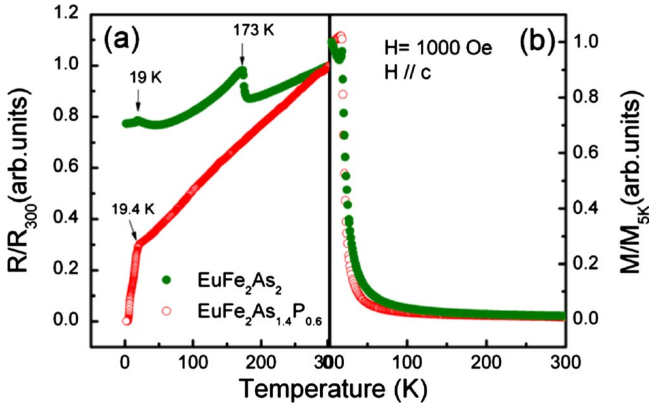

FIG. 2. (Color online) (a) In-plane resistance (R) under zero magnetic field and (b) dc magnetization of $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ samples as a function of temperature (T). The expanded plot of R-T curve is displayed in inset of (a).

indicated that Eu ionic layers may provide additional electrons to the FeAs layers and revealed that pressure-induced valence transition has a strong connection with the superconducting mechanism of $EuFe_2As_{1.4}P_{0.6}$ and compressed $EuFe_2As_2$.

Single crystals of $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ were prepared by solid reaction methods according to the stoichiometric composition. First, the polycrystalline $EuFe_2As_2$ and $EuFe_2As_{1.35}P_{0.65}$ were prepared in evacuated quartz tubes at 900 °C for 50 h and then the resulting materials were ground thoroughly, pressed into pellets, and loaded into Al_2O_3 crucibles. Then, the crucibles were sealed in evacuated quartz tubes, heated to 1190 °C, held at this temperature for 24 h, and finally cooled to 1100 °C over 100 h. Many platelike $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ crystals were obtained. Ambient-pressure and high-pressure XAS experiments were performed at Shanghai Synchrotron Radiation Facility (SSRF). High-pressure x-ray diffraction (XRD) measurements were carried out at Beijing Synchrotron Radiation Facility (BSRF). Pressure was created using a diamond-anvil cell. To maintain the sample in a hydrostatic pressure environment, Daphne 7373 was used as pressure medium in the high-pressure XAS and XRD measurements. Pressure was determined by ruby fluorescence.[28]

Figure 1 shows x-ray diffraction patterns of $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ samples measured using single-crystal x-ray diffraction instrument (SMART, APEXII) at room temperature. The results demonstrate that the samples investigated are single crystalline. Calculations on c axis gave $c=1.207(7)$ nm and 1.188(7) nm for $EuFe_2As_2$, and $EuFe_2As_{1.4}P_{0.6}$, respectively, which were close to the c value reported.[14] It is reasonable that the c value of $EuFe_2As_{1.4}P_{0.6}$ is smaller than that of $EuFe_2As_2$ due to the smaller radii of phosphorus than that of arsenic, which results in As(P)-Fe layer thinner. In Fig. 2, we present the temperature dependence of the in-plane electrical resistance and magnetization data of the two samples. For the undoped sample, the resistance exhibits an anomaly at ~173 K, which is considered to be related to a structural phase transition and SDW formation.[25,27] The kink at 19 K in undoped $EuFe_2As_2$ is related to the magnetic ordering of localized Eu^{2+} moment. With phosphorus doping, the anomaly around 173 K which is associated with SDW transition in the undoped sample was completely suppressed and the resistance plunged at 19.4 K, meanwhile the zero resistance was observed [Fig. 2(a)], indicating a superconducting transition. Close inspection of resistance data below 19.4 K, as displayed in inset of Fig. 2(a), a kink was found around 7 K. We attributed this feature to an evidence of reentrant superconducting state because the complete formation of superconducting state was interrupted by the ordering of Eu^{2+} sublattice below superconducting transition temperature. This phenomenon has been also observed in polycrystalline $EuFe_2As_{1.4}P_{0.6}$ sample[14] and parent $EuFe_2As_2$ sample when physical pressure was applied above 2.3 GPa.[24] In Fig. 2(b), we illustrate temperature dependence of dc magnetization for the undoped and P-doped samples under 1000 Oe. The magnetization in these two samples increases significantly with decreasing temperature and saturates at around 20 K, as reported previously.[14] Due to the strong ferromagnetic ordering of Eu ion at ~20 K which was close to the temperature (19.4 K) of the resistive drop in the P-doped sample, no superconducting diamagnetism was observed directly from the dc magnetization measurements. To further identify the coexistence of ferromagnetic ordering and superconducting state in single crystal $EuFe_2As_{1.4}P_{0.6}$, we performed ac susceptibility measurements on undoped, P-doped, and $EuFe_{1.715}Co_{0.285}As_2$ [$T_c=24$ K (Ref. 13)] samples. In Figs. 3(a) and 3(b), we show the temperature dependence of real parts and imaginary parts of ac susceptibility measured at 100 Hz and 3 Oe for the three samples. The real parts of the ac-susceptibility data for the undoped and P-doped sample were very consistent with dc results [Fig. 3(a)]. However, the imaginary parts of the ac susceptibility for those samples were found to be quite different [Fig. 3(b)]. We note that the imaginary part of the susceptibility is featureless for the undoped sample but goes up for the P-doped and Co-doped samples. The increases of imaginary part below 20 K for the P-doped and Co-doped samples, together with the simultaneous occurrence of zero resistivity, indicate the existence of superconductivity. As for that no superconducting diamagnetism was detected from the P-doped sample, it is due to the strong existing ferromagnetism which greatly enhanced the overall susceptibility.

To identify the valence changes induced by chemical and physical pressure, XAS experiments on L_3-Eu absorption

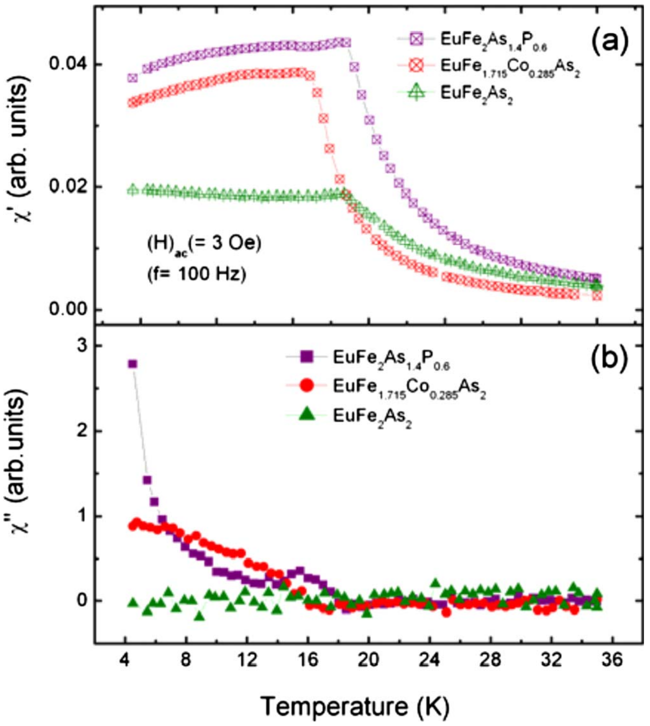

FIG. 3. (Color online) Temperature dependence of (a) real part and (b) imaginary part of ac susceptibility measured at 100 Hz and 3 Oe for $EuFe_2As_2$, $EuFe_2As_{1.4}P_{0.6}$, and $EuFe_{1.715}Co_{0.285}As_2$ single crystals.

edge were carried out. Figure 4(a) shows the energy dependence of normalized XAS data collected at room temperature and at ambient pressure for $EuFe_2As_2$, $EuFe_2As_{1.4}P_{0.6}$, and $EuFe_{1.715}Co_{0.285}As_2$ samples. The main peak and the satellite peak in the figure are associated to Eu^{2+} and Eu^{3+}, respectively. Only in the P-doped sample, the intensity decrease in the main peak and the intensity increase in the satellite peak were observed. The obvious spectra weight transfer implies that the valence state of Eu ions in $EuFe_2As_{1.4}P_{0.6}$ is transferred from a divalent magnetic ($4f^7$, $J=7/2$) state into a trivalent nonmagnetic ($4f^6$, $J=0$) state. We estimated the mean valence of Eu ions in the $EuFe_2As_{1.4}P_{0.6}$ sample to be about 2.32 using the widely used method:[29,30] $\upsilon=2+[I^{\text{satellite}}/(I^{\text{main}}+I^{\text{satellite}})]$, where I^{main} and $I^{\text{satellite}}$ are amplitudes of peaks corresponding to Eu^{2+} and Eu^{3+} on XAS spectrum. Based on the XAS data obtained, it was found that the chemical pressure-induced valence transition from Eu^{2+} to $Eu^{+2.32}$ provided additional 16% charges into the FeAs layer of single crystal $EuFe_2As_{1.4}P_{0.6}$, comparable with the percent of charges (~14.3%) provided by Co^{3+} in the optimally doped $EuFe_{1.715}Co_{0.285}As_2$.

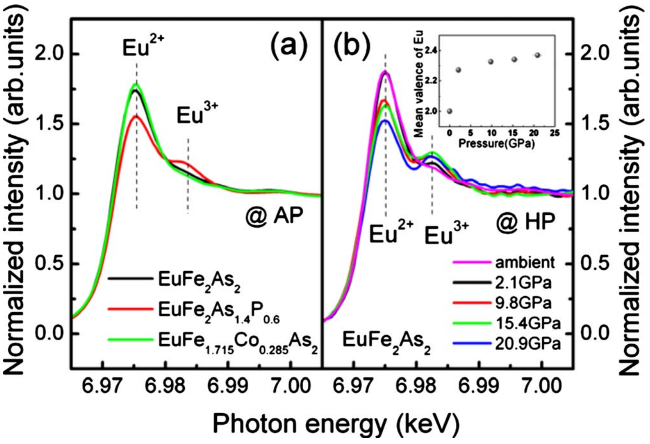

FIG. 4. (Color online) X-ray absorption spectra data obtained (a) at ambient pressure for the three samples (b) at high pressure for $EuFe_2As_2$ sample (the inset shows an expanded plot of pressure dependence of Eu's mean valence in $EuFe_2As_2$ single crystal).

High-pressure XAS experiments on undoped $EuFe_2As_2$ sample were also performed to get a deeper insight into the connection between the valence change of Eu ions and pressure-induced superconductivity in the sample. The pressure dependence of L_3-Eu absorption spectra was plotted in Fig. 4(b). A noticeable increase in intensity of the satellite peak which is associated with Eu^{3+} configuration reflects individual response to high pressure of Eu ions exposed to different local environments. The valence transition of Eu ions begins at 2.1 GPa where Eu's mean valence is about 2.27. With increasing pressure, the mean valence of Eu ions is enhanced up to 2.33 and saturated at pressure above 9.8 GPa, as displayed in the inset of the Fig. 4(b). The observed results indicate that physical pressure can also drive Eu's valence transform from divalent to trivalent state.

To investigate the pressure value generated by phosphorous substitution in $EuFe_2As_{1.4}P_{0.6}$, and pressure-induced lattice changes in $EuFe_2As_2$ and their relation to the valence change of Eu ions as well as the superconductivity, high-pressure x-ray diffraction measurements on the two polycrystalline samples ground from the same batch of the single crystal were carried out at Beijing Synchrotron Radiation Facility. We found that the undoped $EuFe_2As_2$ reduced the same volume (3.2%) at 2.8 GPa, as the $EuFe_2As_{1.4}P_{0.6}$ possessed at ambient pressure. It has been reported that superconductivity in the $EuFe_2As_2$ sample can be achieved at 2.8 GPa.[23] From our XAS data, we found that the mean valence of the undoped sample subjected to this pressure point is about 2.30, very close to the valence value (2.32) of the P-doped sample.

Our finding shows that there are two factors influencing the superconductivity of Eu122 compounds: one is the pressure-induced lattice shrinkage which may affect electronic band structure,[31–33] the other is the pressure-induced valence transitions observed in this study. Our results provide a direct link among changes of lattice structure, valence state, and T_c in Eu-containing 122 systems, and based on it, further theoretical efforts on the superconducting mechanism in Eu122 system are deserved.

In conclusion, the valence transition of Eu ions from Eu^{2+} to Eu^{3+} was observed in the $EuFe_2As_{1.4}P_{0.6}$ and compressed $EuFe_2As_2$. Our data indicated that either chemical pressure or physical pressure can change the Eu's valence. In both compounds, as an alternative way of chemical doping, pressure-induced valence change makes ionic Eu layers provide additional charges to the FeAs layers, which have a positive contribution to the superconducting properties. This is an observation that increased valence steers the superconductivity in pnictides. Such phenomenon has not been observed in other pnictide superconductors, which makes Eu122 system with unique nature. Furthermore, the evidence of chemical and physical pressure-induced valence change may introduce a new clue for experimental studies on the synthesis of superconductors and unfold a way to investigate the physical mechanism of superconductivity in pnictide superconductors.

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