Existence of Orbital Order and its Fluctuation in Superconducting $Ba(Fe_{1-x}Co_x)_2As_2$ Single Crystals Revealed by X-ray Absorption Spectroscopy

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(Received 6 August 2013; published 19 November 2013; corrected 18 December 2013)

We performed temperature dependent x-ray linear dichroism (XLD) experiments on an iron pnictide system, $Ba(Fe_{1-x}Co_x)_2As_2$ with $x = 0.00$, 0.05, 0.08, and 0.10 to experimentally verify the existence of orbital ordering (OO). Substantial XLD was observed in polarization dependent x-ray absorption spectra of Fe L edges. By exploiting the difference in the temperature dependent behaviors, OO, and structure contributions to XLD could be clearly separated. The observed OO signal indicates different occupation numbers for d_{yz} and d_{zx} orbitals and supports the existence of ferro-OO. The results are also consistent with the theoretical prediction. Moreover, we find substantial OO signal well above the structural and magnetic transition temperatures, which suggests the existence of strong OO fluctuations up to high temperatures.

DOI: 10.1103/PhysRevLett.111.217001 PACS numbers: 74.25.Jb, 74.70.Xa, 78.70.Dm

Various experimental results have shown that there are anomalous in-plane anisotropies in iron pnictides well below the transition temperatures [1,2]. A large anisotropy in nearest neighbor spin flip energies J_a and J_b along the crystal a and b axes was obtained from inelastic neutron scattering experiments on $CaFe_2As_2$ [1]. Quasiparticle interference patterns in scanning tunneling microscopy also suggest a large C_2 anisotropic behavior in the electronic structure of $CaFe_2As_2$ [2]. However, such large anisotropies were not observed in other early experiments such as angle resolved photoemission spectroscopy (ARPES) [3–5], x-ray absorption spectroscopy (XAS) [6], and optical measurements (IR) [7].

This inconsistency comes from the existence of twin domains [8]. However, it did not take long to devise a way to remove the twin domains [9] and an anisotropy was indeed obtained in transport [9,10], ARPES [11,12], and optical [13] measurements. The observed anisotropy is not only quite large but also anomalous. Resistivity measurements reveal that the antiferromagnetic (AFM) direction is more conductive than the ferromagnetic (FM) direction [10], which is opposite to the common expectation that AFM ordering suppresses the electrical conductivity. This anomalous anisotropy cannot be accounted for by the structural distortion of the orthorhombic phase either. The difference between in-plane lattice parameters of the orthorhombic phase is less than 1% [14], much smaller than the observed anisotropy.

It was subsequently proposed that orbital ordering (OO) may play a role [15–19]. The observed anisotropy between the AFM (often referred to as a or x) and FM (b or y) directions suggests that only d_{yz} and d_{zx} orbitals are important among the five Fe $3d$ orbitals since the others preserve an in-plane C_4 symmetry. In this respect, ferro-OO which occurs through unequal occupation of d_{yz} and d_{zx} orbital states was proposed [16,18,19]. The proposed OO may be responsible at least in part for the anisotropy in transport properties and also possibly drives the magnetic and structural transitions [15]. It is therefore important to experimentally verify the existence of such an OO.

It has been proposed that temperature dependent x-ray linear dichroism (XLD) experiment may reveal the signature of OO [19]. The difference between XAS data taken with linear polarizations along the AFM and FM directions (that is, XLD) is expected to have both structural and orbital components. To resolve the issue on the OO in pnictides, we performed XLD experiments on detwinned $Ba(Fe_{1-x}Co_x)_2As_2$ samples with various doping levels of $x = 0.00$, 0.05, 0.08, and 0.10. Clear XLD signals were obtained for all doping levels after the contribution from structural anisotropy was removed. Both the OO and structural signals were found to exist well above the structural and magnetic transition temperatures, indicating the existence of strong orbital fluctuations.

Single crystals were synthesized by the self-flux method [20]. Both structure (T_S) and magnetic (T_N) transition temperatures of $x = 0.00$ sample were measured to be 135 K while $x = 0.05$ sample showed T_S and T_N at 67 and 56 K, respectively. The $x = 0.08$ and 0.10 samples do not show T_N and T_S, but exhibit superconductivity below 21 and 23 K, respectively. Detwinning was achieved by applying mechanical stress on samples and the amount of detwinning was close to 100% [11]. XAS experiments were performed at the beam line 2A of the Pohang Light Source (PLS) and at 17U of SPring-8. Samples were cleaved *in situ* under a pressure better than 1.0×10^{-7} Torr (1.33×10^{-7} mbar) and were transferred immediately into the measurement chamber at a pressure better than 7.5×10^{-11} Torr. All absorption spectra were recorded in the total electron yield mode and were normalized by the incident photon flux at a gold mesh. We further normalized the spectra with the area to account for a small difference in the total intensity which is mostly caused by nonidentical beam conditions. The direction of light polarization was controlled by rotating the sample in SPring-8 or by the undulator in PLS.

Figure 1 shows the Fe $L_{3,2}$ edge XAS spectra taken with polarizations along the FM (y) and AFM (x) directions for the $x = 0$ and 0.05 samples as well as their XLD signal (difference). The experimental geometry and definitions for the axes are shown in the inset of Fig. 1. Axes can be defined with respect to the direction of applied stress. We could obtain the XLD spectrum by a simple subtraction of the two normalized spectra. The resulting spectra show a clear XLD signal. With linear polarizations along the x and y axes, the only possibility for the dichroism comes from the difference in d_{yz} and d_{zx} orbital occupations because other d orbitals have the same parity with respect to both xz and yz planes. Therefore, the observed XLD implies that occupations of d_{yz} and d_{zx} orbital states are different.

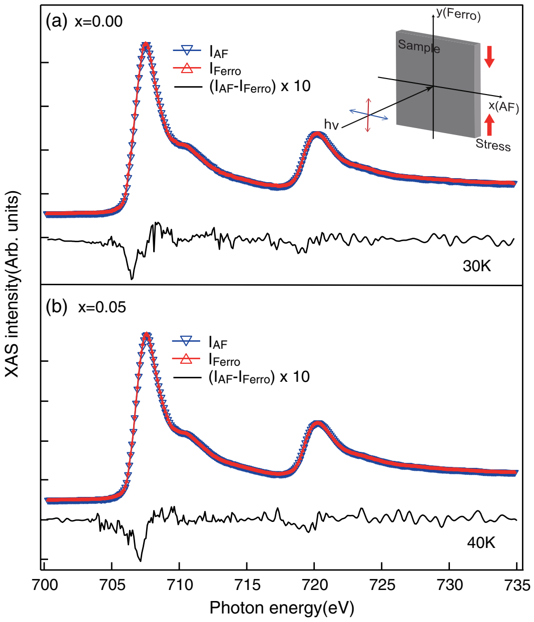

FIG. 1 (color online). (a) Fe $L_{3,2}$ edge XAS spectra from $BaFe_2As_2$ with two different polarizations $E \parallel x$ (blue, inverted triangle) and $E \parallel y$ (red, triangle) at 30 K. The lower curve is the XLD spectra multiplied by 10 for a different compound (black, solid line). The inset shows the experimental geometry and axes information.

However, one has to be careful in interpreting the XLD signal in Fig. 1 as being due to OO because it also contains contributions from the structural anisotropy [21]. The system has an orthorhombic structure with a broken C_4 symmetry below T_S, and thus we may expect additional XLD purely from structural symmetry lowering from C_4 to C_2 even without OO. Especially, the predicted structural contribution could have a behavior opposite to that from OO [see Fig. S1(a) [21]], which may make the overall XLD signal small [19]. We note that in our case of a $3d$ AF metal, magnetic contribution to XLD is negligible [21].

To separate structural and OO contributions, we performed a temperature dependent XLD experiment upon cooling and the results are plotted in Figs. 2(a) and 2(b). The total XLD (black solid lines) has a clear temperature dependence. Upon a closer inspection, the behavior is rather anomalous. Instead of a monotonic increasing with decreasing temperature, the XLD has a pronounced peak-dip behavior near T_S. In addition, the shape of the XLD spectra changes dramatically around T_S. Particularly, for the case of $x = 0.00$, the spectrum at 120 K not only shows a more pronounced dichroism but also has opposite sign near the edge compared to the 30 K spectrum. Such a pronounced XLD signal around T_S can be associated with the structure contribution because the OO contribution has not yet set in. As the temperature is lowered even further, the OO contribution comes in and cancels out the structure contribution, resulting in a smaller overall XLD signal [19].

With this temperature dependence, we were able to distinguish OO and the structure contributions from the total XLD [21]. In Figs. 2(c) and 2(d), extracted OO (structure) contributions are represented by red dashed lines (blue solid lines). Shapes for different doping levels are similar and consistent with the theoretical prediction [19]. OO contributions at other temperatures are overlaid in Figs. 2(a) and 2(b) (red dashed lines). Note that all the OO spectra have a consistent shape and only the magnitude decreases as the temperature increases. The monotonic temperature behavior for the OO contributions is clearly shown in Figs. 2(e) and 2(f). Eventually, the OO contribution disappears at around 170 K for $x = 0.00$ and 140 K for $x = 0.05$. However, the 170 K spectrum of $x = 0$ still shows a small dichroism signal. We attribute this to signal due to out-of-plane polarization as observed earlier [6].

To analyze the OO contributions in detail, we plot the OO signals for four different samples $x = 0.00$, 0.05, 0.08, and 0.10 in Fig. 3. All spectra show a dip feature and relatively small peak. As we aligned the light polarization along the x (AFM) and y (FM) directions, spectrum taken

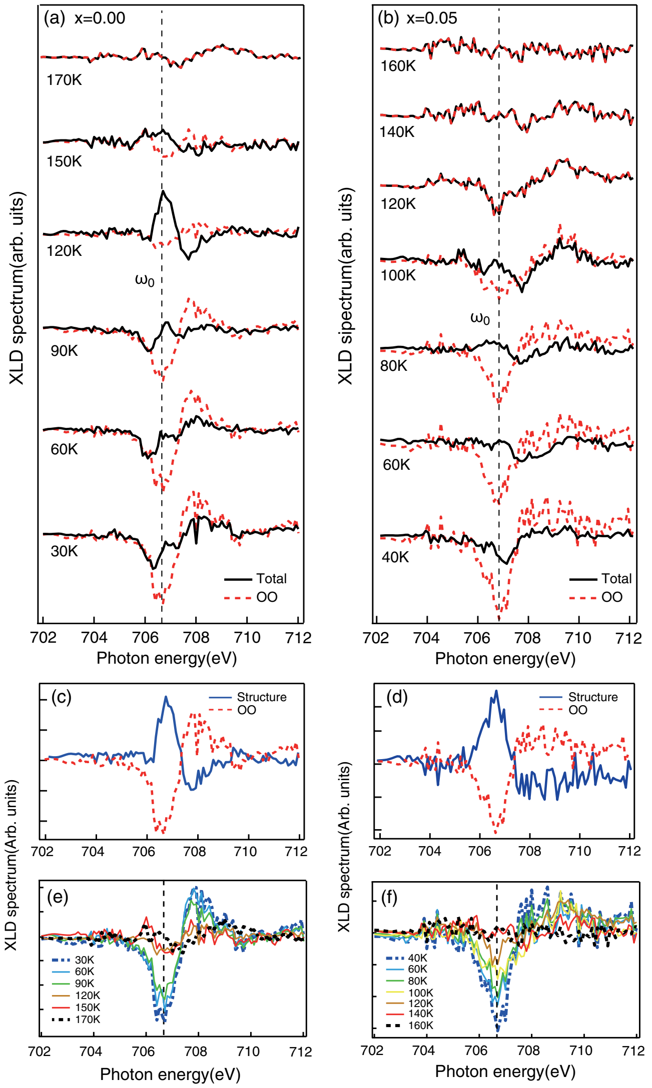

FIG. 2 (color online). Total XLD (solid black lines) and OO contribution (dashed red) at various temperatures for (a) $x = 0.00$ and (b) $x = 0.05$ compounds, respectively. Extracted structure (blue line) and OO (red line) contributions to XLD for (c) $x = 0.00$ and (d) $x = 0.05$ compounds. Overlaid OO contributions at various temperatures for (e) $x = 0.00$ and (f) $x = 0.05$ compounds.

with the x (y) polarization detects d_{zx} (d_{yz}) orbital. Therefore, a dip in the data means d_{yz} has higher density of states than d_{zx}. This fact directly connects to unequal occupation numbers for d_{yz} and d_{zx} (i.e., d_{yz} state is less occupied than d_{zx} as theoretically predicted [16,18,19] and experimentally observed [3,11,22]). On the other hand, a peak feature on the higher energy side implies the opposite situation. However, we note that the area of the dip feature is larger than that of the peak feature for both compounds. Thus, it does not alter our conclusion that d_{yz} is less occupied.

For detailed investigation of the temperature dependence, we plot the magnitudes (their definition is given in the Supplemental Material [21]) of the structure and OO contributions as a function of temperature along with the total XLD for $x = 0.00$, 0.05 in Figs. 4(a) and 4(b). On the other hand, for $x = 0.08$, 0.10, only the total XLD are given in Figs. 4(c) and 4(d) for reasons explained in the Supplemental Material [21]. Unlike the total XLD, partial contributions show monotonic behaviors for both $x = 0.00$ and 0.05 compositions. A noticeable aspect is that both structural and OO contributions appear well above the transition temperature T_S. As the system has a C_4 symmetry above T_S, such anisotropic signal could not appear without an additional order. However, this anisotropic behavior above T_S in detwinned samples is consistently observed in resistivity [10] and ARPES [12] measurements.

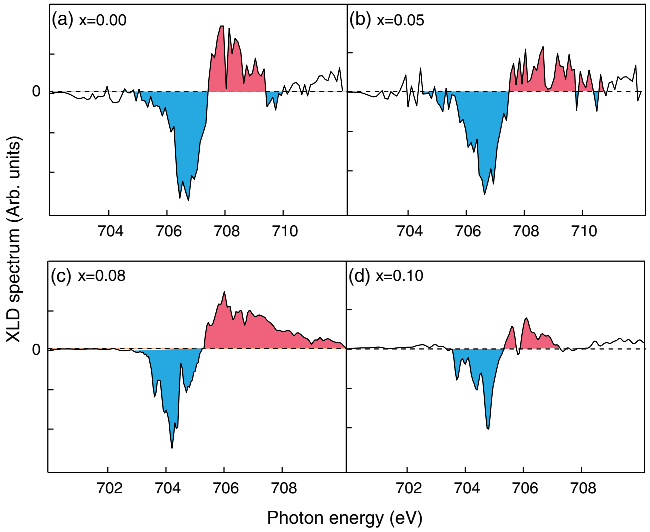

FIG. 3 (color online). (a)–(d), OO contribution to the XLD signal for $x = 0.00$, 0.05, 0.08, and 0.10 compounds.

It was recently found that applied stress for detwinning affects both structure and magnetic transitions in $BaFe_2As_2$ [23,24]. Both T_S and T_N are found to move to higher temperatures and the transition widths become broader. For the magnetic transition, it was claimed that applied stress stabilizes and aligns the spin fluctuation so that it breaks the C_4 symmetry above T_N. These imply that intrinsic spin fluctuation exists above T_N in pristine samples.

Employing the same argument, the OO and structure signals in our data at high temperature can be accounted for by an intrinsic OO fluctuation. Temperature evolution of the structure signal in our study can be attributed as T_S is pushed up to much higher temperatures T_{S^*} [indicated by blue arrows in Figs. 4(a)–4(d)]. OO signal also starts to appear at a similar or higher temperature, T_{OO^*} [indicated by red arrows in Figs. 4(a)–4(d)]. These features could be interpreted as a result of stabilization and alignment of OO fluctuation upon application of stress. It may also explain the monotonic behavior of OO contribution without the signature of the transition as the aligned fluctuation converts the short-range to long-range transition to smooth crossover. Therefore, we argue that OO fluctuation exists

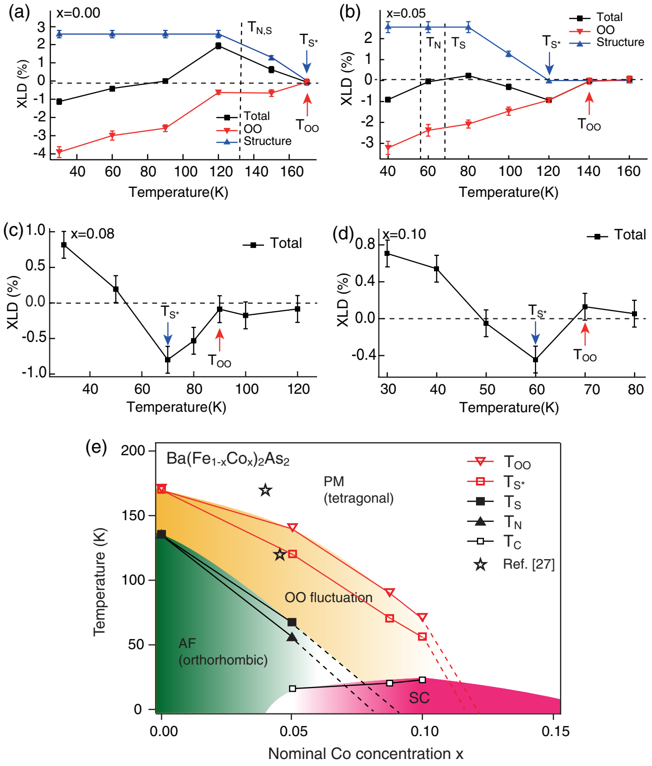

FIG. 4 (color online). (a) and (b) Temperature dependent XLD magnitude for total (black, square), OO (red, inverted triangle), and structure (blue, triangle) contributions for $x = 0.00$ and $x = 0.05$ compounds. (c) and (d) Temperature dependence of total XDL magnitudes for $x = 0.08$ and $x = 0.10$ compounds. (e) Phase diagram of OO fluctuation. T_{S^*} (T_{OO}) are indicated with blue downward (red upward) arrows in pannels (a) and (b). Open star indicates OO fluctuation temperature determined by Ref. [27]

within certain temperature range above T_S and T_N even before application of the stress. The coexistence and a similar behavior of OO and spin fluctuations may also suggest a close relation between the two [25,26]. A possibility is that stabilization of OO drives spin ordering or vice versa.

Temperature and doping dependence of OO fluctuation range is summarized in the phase diagram in Fig. 4(e). The OO fluctuation region covers the superconducting dome and is enhanced as doping increases. The overall shape of the phase diagram is consistent with that obtained with recent point contact spectroscopy result (indicated with open stars) [27]. Furthermore, even when the dopant is different, our finding is also consistent with the phase diagram of electronic nematic phase in $BaFe_2(As_{1-x}P_x)_2$ [28], which may has OO fluctuation as an origin.

The presence of OO fluctuation as well as its enhancement upon doping could mean an important role of OO fluctuation for the superconductivity in iron pnictides. Indeed, it was recently proposed that OO fluctuation could act as a glue for the pairing in iron pnicitides. An important aspect of OO fluctuation mediated superconductivity is that the superconducting gap has s_{++} symmetry [29,30]. The gap symmetry, whether it is s_{++} or s_{+-}, is a crucial information in understanding the superconductivity. Our finding supports the discussion in a recent report [29] and could explain why some systems seem to have s_{++} gap symmetry while others s_{+-}, depending on which of OO or spin fluctuation prevails. A comparative XLD studies of materials with s_{++} or s_{+-} gap symmetries could further resolve the issue.

The authors would like to thank Ch. Kim and K. D. Lee for experimental supports. This work was supported through NRF Grants funded by the MEST (No. 20100018092) and GRL (No. 2011-00329) through the NRF funded by the Ministry of Science, ICT, and Future Planning. The work at SNU was supported by The Basic Science Research Program (No. 2012-008233) funded by Korean Federation of Science and Technology Societies. The work at Spring-8 was supported by Grants-in-Aid for Scientific Research (A) Grant No. 21244049 from JSPS and was performed with the approval of RIKEN (Proposal No. 20110028). Experiments at PLS were supported by MSIP through NRF Grants No. 2010-0018092 and No. 2009-0088969 and KICOS Grant No. K20062000008. T. P. D. and C.-C. C. acknowledge support from the U.S. DOE Contract No. DE-AC02-76SF00515. C.-C. C. is also supported by the Aneesur Rahman Postdoctoral Fellowship at Argonne National Laboratory, operated under the U.S. DOE Contract No. DE-AC02-06CH11357.

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