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Arsenic K-edge XANES study of REFeAsO oxypnictides

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Abstract – Arsenic *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy has been used to investigate the local geometry around the pnictogen site in the REFeAsO (RE = La, Pr, Nd and Sm) oxypnictides, combined with full multiple-scattering calculations to understand different XANES features. The As *K*-edge XANES spectrum for the LaFeAsO is found to be significantly different from the other oxypnictides. The results suggest that interlayer order/disorder has a significant effect on the XANES features with the coupling between the FeAs and the REO spacers being important in the electronic and magnetic properties of the oxypnictides.

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Introduction. – Recently, enormous efforts have been made to understand superconductivity and magnetism in the Fe-based superconductors showing T_c as high as 55 K [1,2]. The REFeAsO (RE = rare earth) has layered structure with REO insulating layers and FeAs conducting blocks having similar structural topology of the cuprates in which the rock-salt blocks and the CuO₂ active layers are sandwiched. Another unifying link between the two families of materials is the appearance of superconductivity in the proximity of an antiferromagnetically ordered state [1,2]. Replacing certain amount of oxygen with fluorine atoms, the system becomes superconducting. Not only the fluorine substitution but also the oxygen deficiency or vacancies could induce superconductivity in the REFeAsO series [1,2]. In addition, the superconducting critical temperature is found to be correlated with the rare-earth (RE) ion size [1,2].

The superconductivity in the Fe-based pnictides is known to be linked with the topology of the FeAs₄ tetrahedrons, which is less distorted for the smaller rare-earth-containing REFeAsO [1]. The covalent nature of the Fe-As bondlengths has been known from the very beginning [3], and recently confirmed by the local structure studies using EXAFS measurements revealing the rigidity of this bond inspite of large chemical pressure exercised on the FeAs₄

block due to varying rare-earth size [4]. Since the superconductivity and itinerant striped magnetism occur in the FeAs blocks, most of the studies are focused to address characteristics of these blocks, overlooking the REO spacers. Recently, we have exploited RE *L*₃-edge X-ray absorption measurements which underline important role of the spacer layers in oxypnictides [5,6]. This is consistent with latest studies on the cuprates suggesting the importance of the spacer layers in which the atomic order/disorder appears to have a vital role in the superconductivity [7,8]. In addition, the misfit strain due to the spacer layer could easily modify the structural topology as well the atomic order, and hence the fundamental properties of the system [9–13]. In fact, while the maximum T_c of the doped system increases with reducing the RE ion size [14,15], the structural transition temperature (T_s) decreases for the undoped system [16,17], underlying importance of the local chemistry of the spacer layer. Indeed the EXAFS results show that, depending on the RE size, the As atom changes its vertical position with respect to the Fe-Fe plane indicating an increased interaction with the REO spacers [4–6]. In this case, the knowledge of local geometry around the As site, bridging the electronically active Fe-Fe plane and the REO spacers can be important to further understand the role of interlayer coupling.

X-ray absorption near-edge structure (XANES) is a fast ($\sim 10^{-15}$ s) and local (5–10 Å) experimental technique

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capable of describing short/medium-range order and electronic structure of materials [18]. The X-ray absorption coefficient $\mu(E)$ is given by the product of the matrix element and joint (empty) density of states for the electronic transitions from the initial to final states. The dipole matrix element from the initial state, the core level of well defined symmetry, selects the local and partial density of final states for the allowed electronic transitions. The XANES spectroscopy probes the final states in an energy range of about 50–60 eV (depending on the system) above the chemical potential. The XANES spectra can be solved in the real space describing the final state as an outgoing spherical wave that interferes with the waves back-scattered from the neighboring atoms [19]. Here, we have used As *K*-edge XANES spectroscopy to obtain information on the local geometry around the As atom in the REFeAsO (RE = La, Pr, Nd and Sm) oxypnictides. The real-space multiple-scattering calculations are employed to identify the nature of different absorption features as a function of RE size. The results suggest that the oxygen order/disorder in the spacers should have an important role to play in the properties of oxypnictides.

Technical details. –

Arsenic K-edge X-ray absorption measurements. The X-ray absorption measurements were performed on powder samples of REFeAsO (RE = La, Pr, Nd, Sm) prepared using the solid-state reaction method [20]. Prior to the absorption measurements, the samples were characterized by X-ray diffraction for their structural properties [16]. As *K*-edge X-ray absorption near-edge structure measurements were performed at the XAFS beamline of the Elettra Synchrotron Radiation Facility, Trieste, where the synchrotron radiation emitted by a bending magnet source was monochromatized using a double-crystal Si(111) monochromator. The transmission mode (at 80 K) was used for the measurements using three ionization chambers mounted in series for the simultaneous measurements on the sample and a reference. Several absorption scans were collected to ensure the reproducibility of the spectra, in addition to the high signal to noise ratio.

Multiple-scattering calculations. To understand the electronic structure of the REFeAsO system, we have performed systematic simulations over the As *K*-edges, using the self-consistent real-space multiple-scattering FEFF8.2 code [21,22] within the muffin-tin approximation. The atomic potential is calculated self consistently using a cluster of up to 127 atoms within a radius of 8.0 Å. The multiple-scattering calculation converges for a cluster of 180 atoms within the radius of 8.8 Å. For the calculations, the energy and position dependent Hedin-Lundqvist optical potential [23] has been selected as the exchange-correlation potential. In order to account for the experimental resolution for the As *K*-edge, the real part of the Hedin-Lundqvist is shifted by 2 eV.

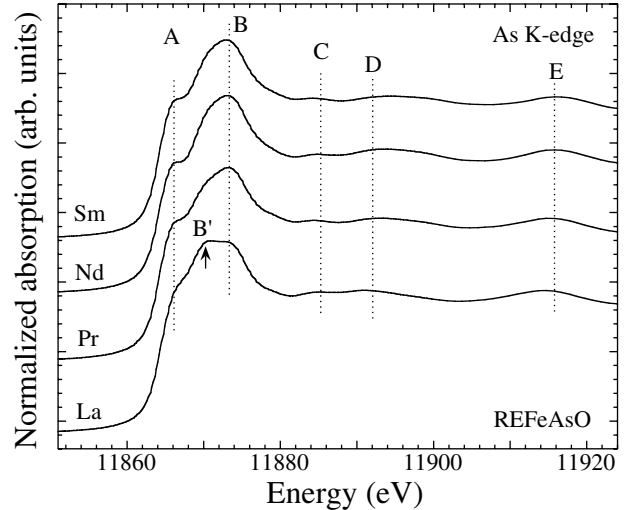


Fig. 1: Arsenic *K*-edge X-ray absorption near-edge structure (XANES) of REFeAsO (RE = La, Pr, Nd and Sm), measured at 80 K. The XANES spectra show five different features (A, B, C, D, E) in the range of 60 eV above the edge except a new feature B', distinctly evident only for the LaFeAsO.

Results and discussion. – Figure 1 shows As *K*-edge XANES spectra measured at 80 K on a series of REFeAsO (RE = La, Pr, Nd and Sm) samples. Apart from the one for the LaFeAsO, As *K*-edge of all the other REFeAsO (Pr, Nd and Sm) appear quite similar in spectral shape and peak positions. The shoulder structure A in all the REFeAsO is well aligned and the relative peak positions for feature B and C agree well, with a small change in that of feature D and E. Unlike the other REFeAsO, the LaFeAsO shows an additional distinct feature B', appearing between the shoulder feature A and the most intense feature B. Moreover, the intensity of the shoulder feature A in LaFeAsO shows an evident suppression.

To understand the origin of spectral features and their evolution with RE in the REFeAsO (RE = La, Pr, Nd and Sm), we have performed one electron multiple-scattering calculations at the As *K*-edge. Figure 2 shows the calculated As *K*-edge XANES for the REFeAsO, compared with the corresponding experimental spectra. The calculations could reproduce most of the spectral features in the experimental data of LaFeAsO, with a clear disagreement with the spectra for the other REFeAsO, relative to the B'. The feature B' (fig. 1) which appears in the theoretical spectra, is distinctly seen only in the LaFeAsO. Unlike the experimental spectra, the feature B' in the calculated XANES seems to have similar relative intensity (with respect to feature A) for the REFeAsO except in the LaFeAsO in which the relative intensity appears lower. For a further understanding, we have calculated the As *K*-edge XANES for the REFeAsO system with increasing number of atomic shells around the As atom, clarifying the effect of local geometry on the spectral features. The atomic potential was kept constant to the one calculated self-consistently within a cluster of 8 Å.

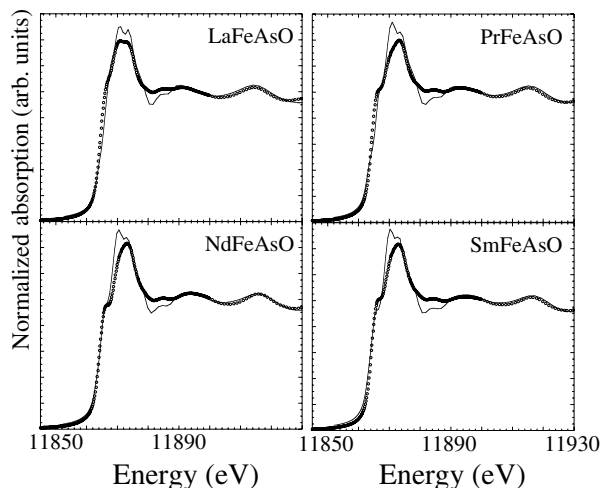


Fig. 2: Theoretical calculation of the As K -edge spectra of REFeAsO (RE=La, Pr, Nd, Sm) using the FEFF8.2 code (solid curves) compared with the experimental data (symbols).

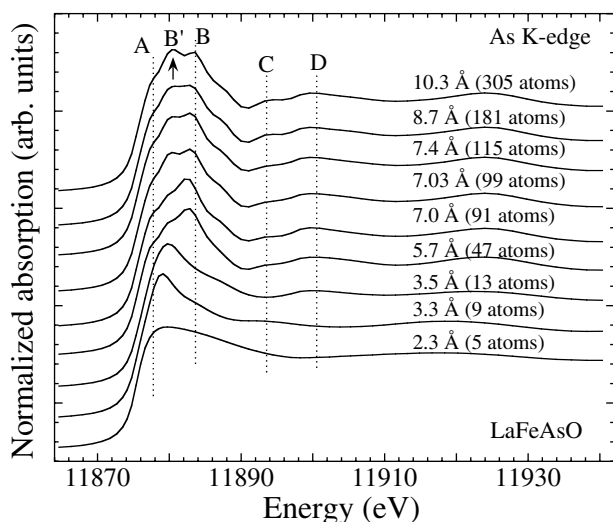


Fig. 3: The multiple-scattering calculations of As K -edge XANES of the LaFeAsO with increasing cluster size.

Figure 3 shows the multiple-scattering calculations for the representative LaFeAsO system with an increasing number of atomic shells around the absorbing Arsenic atom. The feature A emerges in the calculations for the first shell (4 Fe at 2.3 Å) while the features B and C appear only with an increased cluster size up to 5.7 Å (including 47 atoms). Interestingly, distant atoms from the absorber (greater than 7 Å) has significant contribution to the feature B'. With increasing cluster size from 7 Å (91 atoms) to 7.03 Å (99 atoms) (by adding eight oxygen atoms in the La-O layer (5.5 Å) above the As-Fe layer), the intensity of feature B' increases significantly. This points out that feature B' should be directly correlated with the local geometry of the REO spacers. Therefore, an evident absence of this feature B' in the experimental spectra of REFeAsO (RE=Nd, Pr and Sm) could be due to local disordering of the oxygen with respect to the As site. This

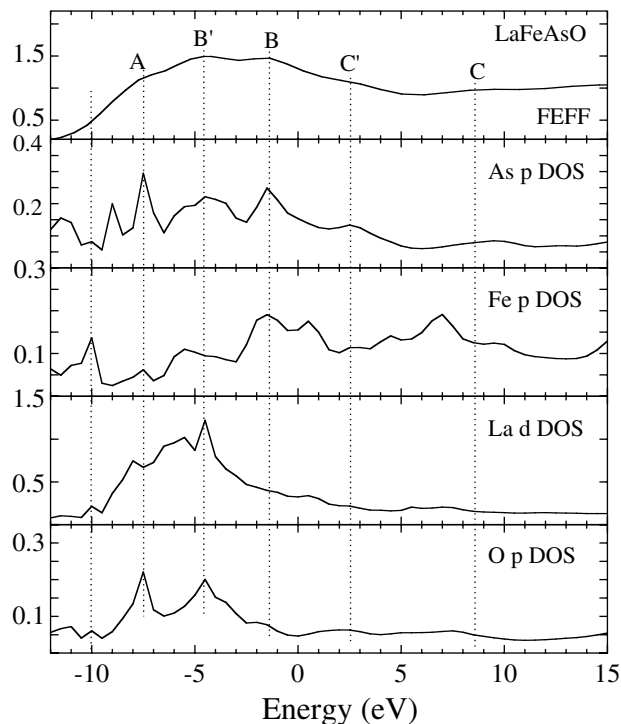


Fig. 4: The theoretical spectrum of LaFeAsO at the As K -edge and site-projected density of states. The Fermi energy (E_F) is indicated by the vertical dotted line at about -10 eV.

observation is consistent with the conclusion of our recent study on the rare-earth L_3 -edge XANES of the REFeAsO system suggesting order/disorder in the spacer layer being important for the superconductivity of the REFeAsO system [5,6]. We will come back to discuss this later.

Let us now look at the electronic structure. For this purpose we have calculated site projected density of states (DOS) for the REFeAsO. Incidentally the gross features in the projected DOS are similar for all REFeAsO. Figure 4 shows the projected DOS along with the calculated As K edge-XANES for the representative LaFeAsO system. The ground state electronic configuration of Arsenic atom is $[\text{Ar}]3d^{10}4s^2 4p^3$ and the As K -edge spectra probes the transition of core $1s$ electrons to the empty p states. Indeed, the shape of As $4p$ DOS correspond well to the XANES features (fig. 4), suggesting that the As K -edge XANES is well described by transition from the $1s$ to $4p$ states. With a brief look, it can be concluded that the absorption jump feature A has predominant As $4p$ character with admixed La d and O p states. The feature B is due to As $4p$ admixed with Fe p states. Also, the distant features C' and C appear to have predominantly As $4p$ character. On the other hand, the feature B' is more likely to be due to the $4p$ states of Arsenic atoms highly admixed with the Lanthanum d states. Furthermore, this feature should also have some admixing of O p and Fe p states. From the DOS calculations it can be further concluded that the B' has a direct correlation with the local geometry of the LaO spacer layers with

important implication on the electronic states derived by the constituents (*i.e.* La and O).

Recently, we have investigated the rare-earth L_3 -edge XANES of the REFeAsO system, suggesting that the oxygen order/disorder should have significant role in the properties of the oxypnictides. It was found that interlayer disorder is relatively lower in the case of LaFeAsO in comparison to the SmFeAsO in which it appears significant due to higher interlayer coupling (higher vertical position of the As atoms). We should also underline that the misfit strain between the REO and the FeAs slabs could easily control the interlayer order/disorder. In the SmFeAsO, FeAs slabs are less strained while the vertical position of As atoms is higher [4], with a high interlayer coupling and hence more interlayer disorder. On the other hand, the vertical position of As atoms is lower in the case of LaFeAsO, leading a higher interlayer order. Incidentally higher interlayer disorder appears to induce higher order within the REO block layers, shown by shape resonance peaks in the rare-earth L_3 -edge spectra of REFeAsO [5].

Summary. – In summary, we have investigated the arsenic K -edge XANES of the REFeAsO oxypnictides. The experimental spectra of the REFeAsO (RE = Pr, Nd and Sm) are found to be different from the spectrum for the LaFeAsO in which a distinct feature appears. Multiple-scattering calculations are performed to understand the near-edge features, combined with the projected density of states (DOS) calculations. The results are consistent with a reduced interlayer disorder in the LaFeAsO in comparison to the other oxypnictides. The disordering seems significant in the SmFeAsO system due to a higher interlayer coupling (higher vertical position of the As atoms) and a smaller misfit strain [16]. Once doped by substitution in the REO layer, the SmFeAsO with higher interlayer disorder shows higher T_c . The present results suggest an intimate relation or an interplay between the superconductivity and the order/disorder in the spacer layers, recalling the out-of-plane disorder-controlled superconductivity already addressed in the cuprate superconductors [7,8].

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