

Charge redistribution and a shortening of the Fe—As bond at the quantum critical point of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$

Jie Cheng,^{a,*} Peng Dong,^b Wei Xu,^c Shengli Liu,^d Wangsheng Chu,^{c,e} Xianhui Chen^f and Ziyu Wu^{c,e}

Received 27 January 2015

Accepted 29 April 2015

Edited by G. Grübel, HASYLAB at DESY, Germany

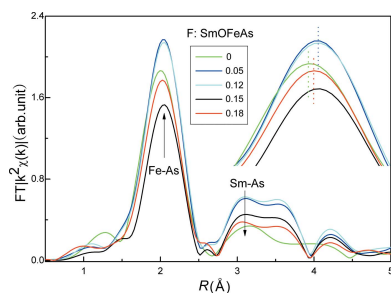
Keywords: quantum critical point; iron-based superconductor; XAS; electronic structure; local structure.

^aCollege of Science, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210023, People's Republic of China, ^bInformation Construction and Management Office, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210023, People's Republic of China, ^cBeijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, People's Republic of China, ^dNanjing University (Suzhou) High-Tech Institute, Suzhou, Jiangsu 215123, People's Republic of China, ^eNational Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China, and ^fHefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China. *Correspondence e-mail: chengj@njupt.edu.cn

Many researchers have pointed out that there is a quantum critical point (QCP) in the F-doped SmOFeAs system. In this paper, the electronic structure and local structure of the superconductive FeAs layer in $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ as a function of the F-doping concentration have been investigated using Fe and As K -edge X-ray absorption spectroscopy. Experiments performed on the X-ray absorption near-edge structure showed that in the vicinity of the QCP the intensity of the pre-edge feature at the Fe-edge decreases continuously, while there is a striking rise of the shoulder-peak at the As edge, suggesting the occurrence of charge redistribution near the QCP. Further analysis on the As K -edge extended X-ray absorption fine structure demonstrated that the charge redistribution originates mostly from a shortening of the Fe—As bond at the QCP. An evident relationship between the mysterious QCP and the fundamental Fe—As bond was established, providing new insights on the interplay between QCP, charge dynamics and the local structural Fe—As bond in Fe-based superconductors.

1. Introduction

The discovery of superconductivity in the new family of Fe-based compounds (Kamihara *et al.*, 2008) is currently attracting tremendous interest and attention (Chiao, 2008; Grant, 2008), not only because it is the only non-cuprate high- T_c superconductor (HTSC) which exhibits superconductivity beyond 55 K (Wang *et al.*, 2008), but also because of the striking differences in superconductivity between the new Fe-based and well established cuprate superconductors (Sadovskii, 2008). Nevertheless, there are many common properties shared by the Fe-based and cuprate superconductors (Sadovskii, 2008): (1) both systems have a two-dimensional (layered) structure, and the FeAs layer is considered as the superconductive layer, such as the characteristic CuO_2 layer in cuprates; (2) the parent phase for both classes of superconductors is antiferromagnetic; (3) the phase diagram of both systems represents the competition between antiferromagnetic ordering and superconductivity; and (4) the critical temperature T_c has a dome-shaped dependence on doping or pressure (Chen *et al.*, 2008; Medvedev *et al.*, 2009). Both the multi-band nature (Terashima *et al.*, 2009) and the strong isotope effect (Liu *et al.*, 2009) distinguish Fe-based



© 2015 International Union of Crystallography

superconductors as another class of HTSCs besides cuprates. Owing to the above considerations, numerous researches have been focused on the structural, electronic and magnetic behaviours revealing many important physical properties of Fe-based superconductors. However, a satisfactory understanding of the superconductivity is far from being achieved owing to the interplay among the atomic, charge and spin quantum states (Hosono, 2008; Sadovskii, 2008) as shown below.

In ordinary materials, the critical point is analogous to the phase transition, such as ice melting to water. However in the quantum world, the quantum critical point (QCP) is based on electronic carriers as well as quantum fluctuations (Broun, 2008). Researchers have found significant evidence of the QCP in Fe-based superconductors, and it was pointed out that the high- T_c superconductivity is driven by the QCP (Hashimoto *et al.*, 2012). Therefore, the study of the QCP might uncover some other mysteries existing in related superconductive materials and be a key to better understanding the high- T_c superconductivity of Fe-based systems (Broun, 2008; Fernandes & Schmalian, 2010).

Here, we focus on the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ system (Liu *et al.*, 2008), which was the first Fe-based compound that exceeded the McMillan limit within the framework of the Bardeen–Cooper–Schrieffer theory (Bardeen *et al.*, 1957). As the F-doping concentration x approaches 0.14, the properties of the material change suddenly in three aspects: (1) a drastically different temperature dependence of the resistivity on both sides of the doping value $x \sim 0.14$ (Liu *et al.*, 2008); (2) a sharp change of the pressure coefficient $d(\ln T_c)/dP$ turning from positive to negative (Takabayashi *et al.*, 2008); (3) a crossover from orthorhombic ($x < 0.14$) to tetragonal ($x > 0.14$) symmetry for the superconducting phase, *i.e.* a complete suppression of the structural transition at $x \sim 0.14$ (Margadonna *et al.*, 2009). All these aspects strongly suggest the existence of a QCP around $x \sim 0.14$ in this system. In other words, the QCP plays an important role on the superconductivity of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ compounds and an investigation at the QCP in this system is highly desired.

Synchrotron-radiation-based X-ray absorption spectroscopy (XAS) is a well recognized local experimental technique capable of giving substantial information (*i.e.* local lattice and electronic structure) on a material (Cheng *et al.*, 2012, 2014; Chu *et al.*, 2013). Our previous report on the Sm L_3 -edge XAS of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ demonstrates a sudden turnaround of the white-line intensity at the QCP (Cheng *et al.*, 2011). As it is well known, in Fe-based superconductors the FeAs layer is considered as the superconductive layer. Thus in this contribution detailed investigations of the property of the FeAs layer at the QCP probed by Fe and As K -edge XAS may provide valuable microscopic information and could be crucial to a better understanding of Fe-based superconductors.

2. Experiments

Polycrystalline $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ compounds ($x = 0, 0.05, 0.12, 0.15, 0.18$) were synthesized by the conventional solid-state

reaction method using high purity SmAs, SmF_3 , Fe and Fe_2O_3 as starting materials (Liu *et al.*, 2008). We collected Fe K -edge X-ray absorption near-edge structure (XANES) spectra and As K -edge extended X-ray absorption fine structure (EXAFS) spectra of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ at room temperature in transmission mode at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF) and the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). Samples were ground into fine powders and then brushed onto tapes that were stacked together to give approximately one X-ray-absorption length (*i.e.* $\mu_x \sim 1$) at their corresponding absorption edges. The storage ring of BSRF was working at an electron energy of 2.5 GeV with a maximum stored current of about 250 mA, whereas the electron-beam energy of the SSRF ring is 3.5 GeV with a maximum current of 300 mA. Data were collected using a Si (111) double-crystal monochromator and normalized by the *IFEFFIT* program (Newville, 2001).

3. Results and discussion

Fig. 1 shows the normalized Fe K -edge XANES spectra for the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0, 0.05, 0.12, 0.15, 0.18$) system. In comparison with data of the parent compound SmOFeAs , Fe K -edge XANES of F-doped samples are identical in shape, indicating that F-doping in the SmOFeAs parent compound does not change significantly the structure of the FeAs layer. However, upon F-doping the intensity of the pre-edge feature A at the Fe K -edge decreases steadily [magnified view in Fig. 1(b)], pointing out an increase in the occupation of the Fe- d /As- p hybridized states just above the Fermi energy. A doping effect on the electronic structure of this system induced by F is also evident at the shoulder-peak (with Fe- d /As- p hybridized character) of the As K -edge XANES (displayed in Fig. 2). Interestingly, in the under-doped region ($x \leq 0.12$) the intensity of the shoulder-peak decreases with

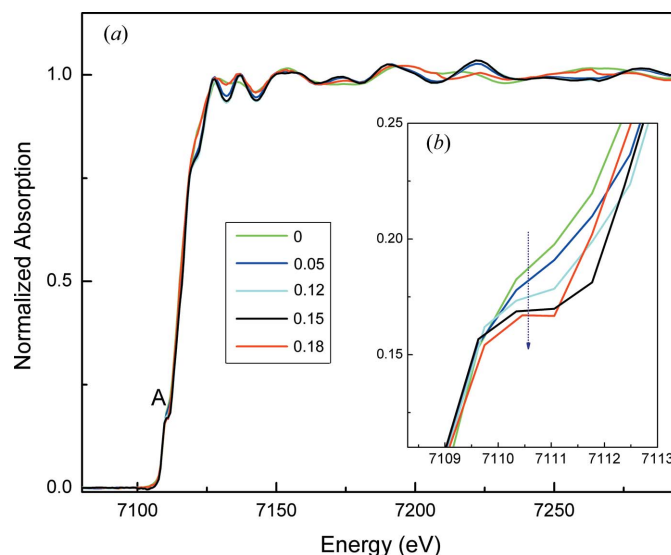
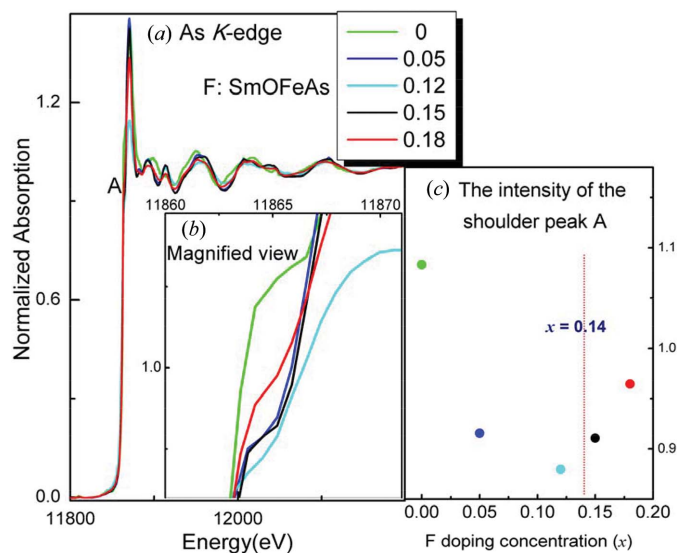


Figure 1 Normalized Fe K -edge XANES spectra for the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0, 0.05, 0.12, 0.15, 0.18$) samples. Inset (b) is the corresponding magnified view of pre-edge peak A.

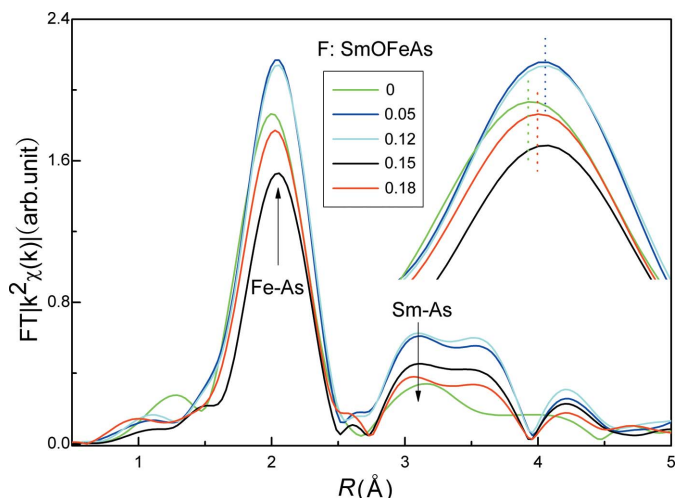

Figure 2

(a) Normalized As *K*-edge XANES spectra for the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0, 0.05, 0.12, 0.15, 0.18$) samples. (b) Magnified view of the shoulder peak A. (c) Intensity of the shoulder peak A as a function of F-doping concentration x ; the dotted line indicates the F concentration of the QCP ($x = 0.14$) in $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$.

F-doping; however, at $x = 0.15$, the intensity rises sharply and then it further increases at $x = 0.18$. This anomalous turn-around of the shoulder-peak intensity at the As edge reminds us about the QCP ($x \sim 0.14$) of the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ system proposed by other previous measurements (Liu *et al.*, 2008; Margadonna *et al.*, 2009; Takabayashi *et al.*, 2008), implying potential changes of the electronic structure at the QCP.

Looking at the structure of the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ -based system, the superconductive FeAs layer is separated by the SmO charge reservoir layers. F-doping induces extra electrons to SmO layers, and then the electrons could transfer from the SmO to FeAs layers through the connected Sm–As bonds. Here, in the F under-doped regime, both the intensity of the pre-edge feature at the Fe edge and the shoulder-peak at the As edge decreases, demonstrating the gradually increasing electron occupation of FeAs layers. In the vicinity of the QCP the intensity of the pre-edge feature at the Fe edge decreases continuously, while there is a striking rise of the shoulder-peak at the As edge. This significant phenomenon could be interpreted in the scenario of charge redistribution (*i.e.* charge transfer from As to Fe atoms), a result compatible with our conjecture about the changes of the electronic structure at the QCP. Meanwhile, the charge redistribution behaviour is also observed in the (F, Zn)-co-doped LaFeAsO system (Cheng *et al.*, 2012) and the low-temperature behaviour of $\text{SmO}_{0.931}\text{F}_{0.069}\text{FeAs}$ (Zhang *et al.*, 2010), pointing out an intimate relationship between charge redistribution and the superconductivity in Fe-based superconductors.

Material properties are closely connected to the local lattice structure, so we could speculate in the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ system whether the charge redistribution at the QCP originates from the fundamental changes of local structure in FeAs layers. To this purpose, Fourier transforms (FT) of the As


Figure 3

Fourier transforms of the EXAFS spectra on the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ system at the As *K*-edge. The first peak from the Fe–As contribution at about 2 Å is magnified in the inset.

K-edge EXAFS spectra for the $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ system are plotted in Fig. 3. From the As *K*-edge data, it can be seen that the overall features of F-doped samples are similar to those of the pure SmOFeAs compound while their intensity and position vary slightly, suggesting the structure of FeAs layers does not change significantly upon F-doping, in agreement with the XANES data. For the FT data, the first peak results from a simple backscattering of the photoelectrons from the first coordination shell of four Fe atoms, and the second peak at about 3.1 Å is due to the contribution of four Sm atoms. In F-doped samples the second peak shifts to the low- R region suggesting a shorter Sm–As bond, which could reduce the distance between FeAs and SmO layers, and promote the interlayer electron transfer. The effect can be beneficial to the superconductivity. Furthermore, it is worth paying special attention to the change of the first peak characterized by the superconductive layer (*i.e.* the Fe–As bond).

From Fig. 3, it can be found that the position of the Fe–As feature was closely related to the F-doping concentration. In the under-doped region ($x \leq 0.12$), the Fe–As peak moves to the high- R direction, and then it returns to the low- R position after the QCP; thus the distance of the Fe–As bond increases in the under-doped region but shortens in the vicinity of the QCP. In order to give quantitative information, we fit the Fe–As peak and the fitting results are given in Table 1. The variation of the Fe–As bond length is shown in Fig. 4. Interestingly, the trend of the Fe–As bond length is consistent as retrieved from the Fe and As edge XANES, which means the charge redistribution (*i.e.* charge transfer from As to Fe atoms) at the QCP is mostly associated with the shortening of the Fe–As bond.

In Fe-based superconductors, the Fe–As bond is widely recognized as an important parameter determining the superconducting transition temperature T_c and their superconductive properties. For example, in the BaFe_2As_2 system the Fe–As bond length is found to be slightly reduced by both Co and K substitutions (Granado *et al.*, 2011); B. Joseph

Table 1
Fitting results of Fe—As distance as a function of F-doping level.

SmO _{1-x} F _x FeAs	σ^2 (10^{-3} Å ²)	$R_{\text{Fe-As}}$ (Å)
$x = 0$	4.309 ± 0.002	2.39419 ± 0.00005
$x = 0.05$	3.404 ± 0.005	2.39732 ± 0.00003
$x = 0.12$	3.448 ± 0.004	2.39781 ± 0.00001
$x = 0.15$	6.021 ± 0.004	2.39737 ± 0.00008
$x = 0.18$	4.763 ± 0.003	2.39558 ± 0.00005

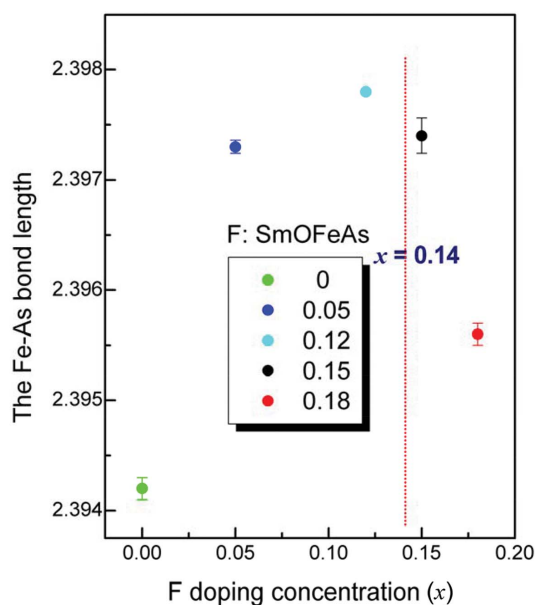


Figure 4
Fe—As bond length as a function of F-doping concentration x . Error bars correlating with the uncertainty value are given. The dotted line indicates the F concentration of the QCP ($x = 0.14$) in SmO_{1-x}F_xFeAs.

demonstrated that a harder Fe—As bond is favourable for a higher T_c in oxypnictide systems (Joseph *et al.*, 2011); furthermore, the Fe—As distance is more directly related with the local Fe moments, and then modulates the phase diagram in Fe-based superconductors (Johannes *et al.*, 2010). From the above conclusions, it can be easily found that the investigation of the Fe—As bond is becoming increasingly important to reveal the superconductive mechanism of Fe-based superconductors. Fortunately, in this contribution, by using Fe and As K -edge XAS we can propose a direct relationship of the mysterious QCP and the most fundamental parameter of the Fe—As bond in the F-doped SmOFeAs system, offering new insights on the interplay between the QCP, charge dynamics and the local structural Fe—As bond in Fe-based superconductors.

4. Conclusion

We analyzed the electronic and the local structures of the superconductive FeAs layer in SmO_{1-x}F_xFeAs compounds probed by Fe and As K -edge XANES and EXAFS spectroscopy. The data indicated that in the under-doped region the extra electrons induced by F-doping could gradually increase

the electron occupation of FeAs layers. In the vicinity of the QCP there is a striking rise of the shoulder-peak at the As edge while the intensity of the pre-edge feature at the Fe edge decreases continuously, demonstrating the electron transfer from the As to Fe atoms in FeAs layers. Further investigation in terms of local structure showed that the charge redistribution near the QCP is intimately related to a shortening of the Fe—As bond. So, in this contribution, we established the delicate interplay between the QCP and the character of the Fe—As bond, hoping this new point of view could be beneficial to our understanding of the QCP in Fe-based superconductors.

Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (NSFC 11405089), the Natural Science Foundation of Jiangsu Province of China (Nos. BK20130855 and BK20130376), and the Scientific Research Foundation of Nanjing University of Posts and Telecommunications (No. NY213053).

References

- Bardeen, J., Cooper, L. N. & Schrieffer, J. R. (1957). *Phys. Rev.* **108**, 1175–1204.
- Broun, D. M. (2008). *Nat. Phys.* **4**, 170–172.
- Chen, G. F., Li, Z., Wu, D., Li, G., Hu, W. Z., Dong, J., Zheng, P., Luo, J. L. & Wang, N. L. (2008). *Phys. Rev. Lett.* **100**, 247002.
- Cheng, J., Chu, S., Chu, W., Xu, W., Zhou, J., Zhang, L., Zhao, H., Liu, R., Chen, X., Marcelli, A. & Wu, Z. (2011). *J. Synchrotron Rad.* **18**, 723–727.
- Cheng, J., Xu, W., Liu, L. J., Dong, P. & Liu, S. L. (2014). *J. Supercond. Nov. Magn.* **27**, 2719–2723.
- Cheng, J., Zhou, J., Hu, R., Xu, W., Li, Y. K., Zhang, L. J., Marcelli, A., Chu, W. S., Xu, Z. A. & Wu, Z. Y. (2012). *New J. Phys.* **14**, 033005.
- Chiao, M. (2008). *Nat. Phys.* **4**, 446.
- Chu, W. S., Cheng, J., Chu, S. Q., Hu, T. D., Marcelli, A., Chen, X. H. & Wu, Z. Y. (2013). *Sci. Rep.* **3**, 1750.
- Fernandes, R. M. & Schmalian, J. (2010). *Phys. Rev. B*, **82**, 014521.
- Granado, E., Mendonça-Ferreira, L., Garcia, F., Azevedo, G. de M., Fabbri, G., Bittar, E. M., Adriano, C., Garitezi, T. M., Rosa, P. F. S., Bufaical, L. F., Avila, M. A., Terashita, H. & Pagliuso, P. G. (2011). *Phys. Rev. B*, **83**, 184508.
- Grant, P. M. (2008). *Nature (London)*, **453**, 1000–1001.
- Hashimoto, K. *et al.* (2012). *Science*, **336**, 1554–1557.
- Hosono, H. (2008). *J. Phys. Soc. Jpn.* **77**(Suppl. C), 1–8.
- Johannes, M. D., Mazin, I. I. & Parker, D. S. (2010). *Phys. Rev. B*, **82**, 024527.
- Joseph, B., Iadecola, A., Malavasi, L. & Saini, N. L. (2011). *J. Phys. Condens. Matter*, **23**, 265701.
- Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. (2008). *J. Am. Chem. Soc.* **130**, 3296–3297.
- Liu, R. H., Wu, G., Wu, T., Fang, D. F., Chen, H., Li, S. Y., Liu, K., Xie, Y. L., Wang, X. F., Yang, R. L., Ding, L., He, C., Feng, D. L. & Chen, X. H. (2008). *Phys. Rev. Lett.* **101**, 087001.
- Liu, R. H., Wu, T., Wu, G., Chen, H., Wang, X. F., Xie, Y. L., Ying, J. J., Yan, Y. J., Li, Q. J., Shi, B. C., Chu, W. S., Wu, Z. Y. & Chen, X. H. (2009). *Nature (London)*, **459**, 64–67.
- Margadonna, S., Takabayashi, Y., McDonald, M. T., Brunelli, M., Wu, G., Liu, R. H., Chen, X. H. & Prassides, K. (2009). *Phys. Rev. B*, **79**, 014503.
- Medvedev, S., McQueen, T. M., Troyan, I. A., Palasyuk, T., Eremets, M. I., Cava, R. J., Naghavi, S., Casper, F., Ksenofontov, V., Wortmann, G. & Felser, C. (2009). *Nat. Mater.* **8**, 630–633.

- Newville, M. (2001). *J. Synchrotron Rad.* **8**, 322–324.
- Sadovskii, M. V. (2008). *Phys. Usp.* **51**, 1201–1227.
- Takabayashi, Y., McDonald, M. T., Papanikolaou, D., Margadonna, S., Wu, G., Liu, R. H., Chen, X. H. & Prassides, K. (2008). *J. Am. Chem. Soc.* **130**, 9242–9243.
- Terashima, K., Sekiba, Y., Bowen, J. H., Nakayama, K., Kawahara, T., Sato, P., Richard, T., Xu, Y.-M., Li, L. J., Cao, G. H., Xu, Z.-A., Ding, H. & Takahashi, T. (2009). *Proc. Natl Acad. Sci. USA*, **106**, 7330–7333.
- Wang, C., Li, L., Chi, S., Zhu, Z., Ren, Z., Li, Y., Wang, Y., Lin, X., Luo, Y., Jiang, S., Xu, X., Cao, G. & Xu, Z. (2008). *Europhys. Lett.* **83**, 67006.
- Zhang, C. J., Oyanagi, H., Sun, Z. H., Kamihara, Y. & Hosono, H. (2010). *Phys. Rev. B*, **81**, 094516.