A structural study of the hole-doped superconductors Pr$_{1-x}$Sr$_x$FeAsO

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New Journal of Physics 11 (2009) 083003 (12pp)
Received 29 April 2009
Published 4 August 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/8/083003

Abstract. The structural details of the Pr$_{1-x}$Sr$_x$FeAsO (1111) superconducting system are analyzed using data obtained from synchrotron x-ray diffraction and the structural parameters are carefully studied as the system moves from non-superconducting to hole-doped superconducting with an increase of the Sr concentration. Superconductivity emerges when the Sr doping amount reaches 0.221. The linear increase of the lattice constants proves that Sr is successfully introduced into the system, and the Sr concentration can be accurately determined by electron density analyses. The evolution of structural parameters with Sr concentration in Pr$_{1-x}$Sr$_x$FeAsO and comparison of them to other similar structural parameters of the related Fe-based superconductors suggest that the interlayer space between the conducting As–Fe–As layer and the insulating Pr–O–Pr layer is important for improving $T_c$ in hole-doped (1111) superconductors, which seems to be a different trend from that encountered in the electron-doped systems.
1. Introduction

Soon after the discovery of iron-based oxypnictide superconductors [1, 2], several structural families have been established to date, and now their structure is named, similarly to cuprates, as (1111), (122), (111) and (11) [3]–[8]. The highest superconducting transition temperature ($T_c$) achieved in an electron-doped system was 56.5 K in Ca$_{1-x}$Nd$_x$FeAsF [9] and 55 K in SmFeAsO$_{1-x}$F$_x$ [10], which are only surpassed by high-$T_c$ cuprates.

A lot of attention has so far been paid to electron-doped (1111) superconductors, and their structural details have been studied by x-ray and neutron diffraction experiments. The physical properties have also been clarified from the viewpoint of electronic transport as well as magnetic measurements, and the phase diagrams seem to be established. Recently, the symmetry of FeAs$_4$ tetrahedron is proposed to be one of the most essential parameters in controlling $T_c$ in the case of electron-doped (1111) systems from the systematic studies on REFeAsO$_{1-x}$ (RE = La and Nd) and CeFeAsO$_{1-x}$F$_x$ superconductors [11]–[13], i.e. the $T_c$ is maximum when the angle is close to 109°28’.

Although electron-doped (1111) superconductors have triggered a lot of attention toward achieving higher transition temperatures for superconductors by applying various rare-earth metals (RE = La–Nd, Sm, Gd, Tb, Dy and Ho), a small number of hole-doped superconductors adopting (1111) structure are reported to be possible in La$_{1-x}$Sr$_x$FeAsO [4, 14, 15], Pr$_{1-x}$Sr$_x$FeAsO [16], Nd$_{1-x}$Sr$_x$FeAsO [17], La$_{1-x}$Sr$_x$NiAsO [18] and Gd$_{0.9}$Sr$_{0.1}$ONiBi [19], and their structural details have not been established yet. The highest $T_c$ in these hole-doped systems is 25 K for La$_{1-x}$Sr$_x$FeAsO and the situation seems to be different from what has been experienced in the electron-doped (1111) systems. Especially, there are a lot of structural ambiguities, such as the actual Sr$^{2+}$ doping concentration and the influence of Sr$^{2+}$ on the structural parameters of these superconductors although these are very important to find the crucial factors for tuning superconductivity. Therefore, it is of great significance to prepare a high-quality hole-doped (1111) phase and to carry out careful structural studies on them, in order to understand the relationship between structure and $T_c$, and, furthermore, to examine the further possibility of elevating $T_c$. For this experimentally based reason, we have focused on high-quality sample preparation of the Pr$_{1-x}$Sr$_x$FeAsO series. This paper will present their structural parameters by using high-resolution synchrotron radiation and make a comparison of the relationships between structure and $T_c$ both for electron- and hole-doped systems.
2. Experimental

Pr$_{1-x}$Sr$_x$FeAsO samples with nominal Sr doping amount $x$ from 0.10 to 0.30 were successfully synthesized by using a two-step solid-state reaction method. Firstly, PrAs and SrAs precursors were obtained by making Pr chips (purity 99.95%) and Sr chips (purity 99.5%) react with As powder (purity 99.99%) in the ratio 1 : 1. The mixtures were ground and pressed into pellets. Then, they were sealed in evacuated quartz tubes, followed by heating at 700°C for 10 h. Secondly, the precursors were smashed and ground together with Fe powder (purity 99.99%) and Fe$_2$O$_3$ powder (purity 99.99%) in stoichiometry as per the formula Pr$_{1-x}$Sr$_x$FeAsO. These samples were pressed into pellets and sealed in evacuated quartz tubes and heated at about 940°C for 5 h, followed by annealing at 1150°C for 48 h. Then it was slowly cooled down to room temperature.

Synchrotron powder x-ray diffraction (XRD) experiments were performed on a large Debye–Scherrer camera installed at SPring-8 beam line BL02B2 by using an imaging plate as the detector. The wavelength of the x-ray was determined to be 0.60261 Å by using CeO$_2$ as the reference. Glass capillaries with an inner diameter of 0.3 mm were used to hold the powder samples in order to eliminate the preferred orientation. The Rietveld refinements were carried out using GSAS in the angle range of 2–70° with an increment of 0.01°.

3. Results

Pr$_{1-x}$Sr$_x$FeAsO ($x = 0.1–0.3$) polycrystalline samples with high purity were successfully synthesized using the two-step method mentioned above. We used the high-resolution synchrotron facility at SPring-8 to study the structural details of these samples. The Rietveld refinement results are listed in table 1, and a typical refinement pattern is shown in figure 1. All these samples adopt the tetragonal symmetry with the space group of $P4/nmm$ (129) at room temperature. Some samples have a small amount of Pr$_2$O$_3$ and FeAs as impurities, which hinder the decrease of $R_p$ and $R_wp$. The structure of Pr$_{1-x}$Sr$_x$FeAsO consists of interleaved two-dimensional FeAs and (Pr, Sr)O layers, as shown in the inset of figure 1. The FeAs layer is a conducting layer with Fe in fourfold coordination forming a FeAs$_4$ tetrahedron, whereas the (Pr, Sr)O layer is insulating and providing charge carriers to the conducting layer. Pr atoms are coordinated with four O atoms in the (Pr, Sr)O layer and are also weakly bonded with four As atoms in the neighboring FeAs layer. In the (Pr, Sr)O layer, Pr is positively trivalent (Pr$^{3+}$) and O is negatively divalent (O$^{2-}$); the counterpart FeAs layer is negatively monovalent with positively divalent Fe (Fe$^{2+}$) and negatively trivalent As (As$^{3-}$). The substitution of Pr$^{3+}$ with Sr$^{2+}$ causes the (Pr/Sr) site positive (3 − $\delta$) charges and, accordingly, the Fe site positive (2 + $\delta$) charge. The charge carriers are transferred through the Pr/Sr plane and the FeAs layer as indicated in figure 1. This suggests that the effect of Sr doping is to facilitate hole transfer to induce hole-doped superconductivity.

We first checked how much Sr was introduced into the structure. In all the samples with nominal compositions of Pr$_{1-x}$Sr$_x$FeAsO ($x = 0.1–0.3$), the Sr atom occupies the same atomic position (2c) as Pr with a certain amount of occupancy, which is precisely determined by the
Table 1. Rietveld refinements results of Pr$_{1-x}$Sr$_x$FeAsO by using synchrotron powder diffraction data at room temperature. Space group: $P4/nmm$. Atomic positions: Pr/Sr: 2c (1/4, 1/4, z); Fe: 2b (3/4, 1/4, 1/2); As: 2c (1/4, 1/4, z) and O: 2a (3/4, 1/4, 0). $U_{iso}$ is the isotropic displacement parameter constrained for the same chemical species. The occupation factors of Sr$^{2+}$ were refined and then fixed to appropriate values in the final refinement.

| Atom   | $x = 0.157(1)$ | $x = 0.162(1)$ | $x = 0.221(1)$ |
|--------|----------------|----------------|----------------|
| $a$ (Å) | 3.9845(4)      | 3.9873(1)      | 3.9936(1)      |
| $c$ (Å) | 8.6224(9)      | 8.6190(2)      | 8.6539(1)      |
| $V$ (Å³) | 136.895(4)    | 137.031(5)     | 138.023(5)     |
| Pr/Sr  | $z$            | 0.1384(7)      | 0.1380(5)      | 0.1372(3)      |
|        | $U_{iso}$      | 0.0066(5)      | 0.0064(3)      | 0.0064(2)      |
| Fe     | $U_{iso}$      | 0.0079(4)      | 0.0087(8)      | 0.0102(1)      |
| As     | $z$            | 0.6546(7)      | 0.6546(9)      | 0.6543(5)      |
|        | $U_{iso}$      | 0.0060(1)      | 0.0057(6)      | 0.0055(4)      |
| O      | $U_{iso}$      | 0.0205(3)      | 0.0146(8)      | 0.0096(3)      |
| $R_p$ (%) | 3.13          | 3.84          | 3.46          |
| $R_{wp}$ (%) | 4.45        | 5.39         | 4.88         |

| Atom   | $x = 0.262(1)$ | $x = 0.263(7)$ | $x = 0.278(3)$ | $x = 0.314(1)$ |
|--------|----------------|----------------|----------------|----------------|
| $a$ (Å) | 3.9905(2)      | 3.9902(9)      | 3.9896(4)      | 3.9902(9)      |
| $c$ (Å) | 8.6486(7)      | 8.6369(8)      | 8.6473(8)      | 8.6439(9)      |
| $V$ (Å³) | 137.724(1)    | 137.521(7)     | 137.642(7)     | 137.633(8)     |
| Pr/Sr  | $z$            | 0.1380(3)      | 0.1381(1)      | 0.1381(4)      | 0.1378(9)      |
|        | $U_{iso}$      | 0.0064(8)      | 0.0064(6)      | 0.0067(1)      | 0.0064(8)      |
| Fe     | $U_{iso}$      | 0.0091(5)      | 0.0089(9)      | 0.0080(2)      | 0.0086(4)      |
| As     | $z$            | 0.6543(6)      | 0.6545(2)      | 0.6545(4)      | 0.6546(1)      |
|        | $U_{iso}$      | 0.0063(1)      | 0.0062(1)      | 0.0061(5)      | 0.0065(3)      |
| O      | $U_{iso}$      | 0.0183(6)      | 0.0173(1)      | 0.0206(2)      | 0.0230(7)      |
| $R_p$ (%) | 3.12          | 3.81          | 3.09          | 4.54          |
| $R_{wp}$ (%) | 4.59         | 5.59         | 4.76         | 6.31         |

electron density analysis at this site. The results show that the actual doping concentration varies from 0.157 to 0.314. These values deviate from the nominal compositions, but the increasing trend is basically the same. The actual doping concentration is used for the subsequent structural analyses. The atomic occupancies of Fe, As and O were confirmed to be nearly 100%.

Given the situation that the ionic radius of Sr$^{2+}$ (1.18 Å) is much larger than that of Pr$^{3+}$ (0.99 Å) [21], it is reasonable to see a remarkable increase of the lattice constants with an increase of Sr doping concentration. Actually, both $a$ and $c$ increase linearly with $x$ as shown in figure 2, where $x$ is the real doped Sr amount ranging from 0 to 0.314. The data for $x = 0$ were taken from the previous report [22]. The increase in $a$ is about 0.01 Å (increasing ratio = 0.25%), and the $c$-axis increases more obviously with 0.06 Å (increasing ratio = 0.7%) with this doping. Consequently, the unit cell volume evolves with Sr concentration in a linear relationship $V = 136.411 + 4.217x$, which proves the actual introduction of Sr into the structure.
Figure 1. Typical observed (red crosses) and calculated (green solid line) x-ray powder diffraction patterns of Pr$_{1-x}$Sr$_x$FeAsO. The three rows of vertical bars show the calculated positions of Bragg reflections for FeAs (blue), Pr$_2$O$_3$ (red) and Pr$_{1-x}$Sr$_x$FeAsO (black), respectively. The former two are impurities in small amounts. The purple solid line shown at the bottom of the figure indicates the differences between observations and calculations. The inset above the x-ray pattern is a schematic diagram defining the As–Fe–As block and the Pr–O–Pr block and illustrating the process of hole transfer.

Temperature dependences of electric resistivity under zero field and magnetic susceptibility measured with the zero-field-cooling mode below 20 Oe are shown in figure 3. The samples with doping amount lower than 0.221 do not show superconductivity, even though their lattice constants obviously increase. However, the electric resistivity and the magnetic susceptibility measurements give a clear superconductivity transition for the samples with the doping amount of 0.221–0.314. The onset temperature of superconductivity ($T_{\text{onset}}$) is determined by the first derivative of the electric resistivity as depicted in the inset of figure 3(a). $T_{\text{onset}}$ varies from 13.5 to 15.1 K, with a maximum of 15.1 K at $x = 0.221$. In addition, the sample with $x = 0.221$ also gives the largest superconducting volume fraction as shown in figure 3(b), indicating that the optimal doping concentration is around 0.221.

In order to study the structure change influenced by doping, we carried out Rietveld refinements in detail based on the synchrotron x-ray powder diffraction patterns. The refinement results are listed in table 1. Figure 4 summarizes the influence of Sr doping on the crystal structure of Pr$_{1-x}$Sr$_x$FeAsO. In the (Pr, Sr)O layer, one could see that the Pr–O bond distance slightly increases to an extent of 0.0025 Å in total, whereas the two O–Pr–O bond angles increase more obviously with $x$. The largest increases of the two bond angles are by 0.4$^\circ$ and 0.2$^\circ$ at the $x = 0.221$ stoichiometry when $x = 0.157$ is taken as the reference. We define the Pr–O–Pr and the As–Fe–As block distances as the vertical distance between the Pr atoms residing at the top and bottom of the (Pr, Sr)O layer and the vertical distance between the As atoms in the FeAs layer, respectively (as shown in figure 1). The increase in the Pr–O bond distance is not sufficient to compensate for the large increase in the two O–Pr–O bond angles, which unambiguously can explain the Pr–O–Pr block shrinkage. Especially, a remarkable reduction of the block distance, namely by 0.013 Å, is observed at $x = 0.221$, taking $x = 0.157$ as the reference.
Figure 2. Lattice constants versus Sr doping amount in Pr$_{1-x}$Sr$_x$FeAsO. The dashed lines are the linear simulation for various parameters. The data of non-doped PrFeAsO are cited from another report [22].

Figure 3. Temperature dependences of electric resistivity (a) under zero field and magnetic susceptibility (b) measured with the zero-field-cooling mode below 20 Oe in Pr$_{1-x}$Sr$_x$FeAsO. The determination of the onset temperature of superconductivity ($T_{\text{onset}}$) is depicted in the inset of (a).
Figure 4. Structural evolution of $\text{Pr}_{1-x}\text{Sr}_x\text{FeAsO}$ as a function of Sr doping amount from the analysis of the synchrotron XRD data. The atomic positions of $\text{Pr}_{1-x}\text{Sr}_x\text{FeAsO}$ are shown in table 1 and the effect of Sr doping is to shrink the Pr–O–Pr block and to expand the As–Fe–As block, but with a total expansion of the interlayer space. (a) O–Pr–O bond angles as a function of Sr doping. (b) Pr–O bond distance and Pr–O–Pr block distance as a function of Sr doping. (c) Fe–As–Fe bond angles as a function of Sr doping. (d) Fe–As bond distance and As–Fe–As block distance as a function of Sr doping. The dashed lines are the linear simulations for various parameters.

In the As–Fe–As block, one could see small changes in the Fe–As bond distance and the two Fe–As–Fe bond angles. The Fe–As bond distance increases monotonically up to 0.005 Å with $x$. Meanwhile, the decrease of the two Fe–As–Fe bond angles is about 0.08° and 0.04°. Accordingly, the changes in the bond distance and angles synergistically expand the As–Fe–As block distance from 2.667 to 2.673 Å. It should be noted that this expansion is less than half of the change observed in the Pr–O–Pr block, which results in a remarkable increase of the interlayer distance.

4. Discussions

Some relatively large Sr$^{2+}$ (1.18 Å) substitute for the smaller Pr$^{3+}$ (0.99 Å) at the same atomic site, thereby causing the expansion of the unit cell, which was confirmed by x-ray analyses as shown in table 1 and figure 2. The unit cell shows a linear expansion and obeys Vergaard’s law,
Figure 5. Evolution of Pr–As distance as a function of Sr doping in Pr$_{1-x}$Sr$_x$FeAsO. The dashed lines are the linear simulations for various parameters.

giving further experimental evidence that a replacement of Pr by Sr takes place. Moreover, the introduction of Sr modifies the crystal structure in a delicate way as summarized in figure 4. The Pr–O and Fe–As bond distances increase slightly with $x$; nevertheless, the values are still comparable with other related compounds. The two Fe–As–Fe bond angles decrease with $x$, slowly moving toward the ideal values of the perfect FeAs$_4$ tetrahedron. The evolution of $T_c$ as a function of M–Pn–M bond angle is illustrated in figure 7(c) together with those reported for the electron-doped systems [13]. As was admitted in the case of electron-doped pnictide systems, the regular angle of the $MnP_n$ tetrahedron is crucial for enhancement of $T_c$. The rich crystallographic information so far available for electron-doped systems shows a clear tendency that the highest $T_c$ is achieved at the nearly perfect $MnP_n$ tetrahedral point. In contrast, only three sets of detailed structural parameters are available for hole-doped systems, i.e. Nd$_{1-x}$Sr$_x$FeAsO [17], Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [6] and Pr$_{1-x}$Sr$_x$FeAsO (in the present work). Although one can see a similar tendency for hole-doped systems as well, i.e. the regular angle of the FeAs$_4$ tetrahedron helps enhance $T_c$, nevertheless the $T_c$ values are always much smaller than those in electron-doped systems. This phenomenon implies that the Fe–As–Fe bond angle should not be regarded as the only parameter important for tuning superconductivity in hole-doped systems.

In contrast to the slight changes in the Pr–O and Fe–As bond distances as well as the Fe–As–Fe bond angles, the Sr doping greatly changes the two O–Pr–O bond angles and results in the shrinkage of the Pr–O–Pr block. As a consequence, the Pr–As bond distance is largely increased as shown in figure 5. The Pr–As distance increases greatly with $x$ and reaches a maximum of 0.034 Å compared with the parent PrFeAsO [22]. The Pr–As bond distance can give a measure of the interlayer space between the Pr–O–Pr insulating block and the As–Fe–As conducting block.

Figure 6 shows the influence of the Pr–As distance on $T_{\text{onset}}$, which was deduced from $d\rho/dT$ as given in figure 3(a). In the superconductivity region, $T_{\text{onset}}$ increases linearly with the Pr–As distance, indicating that the larger interlayer space favors the improvement of $T_c$. Actually, this is observed in the other two hole-doped systems as well. Figure 7(a) shows $T_c$ as a function of $M$–As bond distance in the three hole-doped pnictide superconductors, where $M$ is Ba/K for Ba$_{1-x}$K$_x$Fe$_2$As$_2$, Nd/Sr for Nd$_{1-x}$Sr$_x$FeAsO and Pr/Sr for the present system. The $M$–As bond distances in these compounds are calculated from the reported structural
Figure 6. Impact of Pr–As bond distance on $T_{\text{onset}}$. $T_{\text{onset}}$ is deduced from $d\rho/dT$ as given in figure 3(a). In the superconductivity region, $T_{\text{onset}}$ increases linearly with the Pr–As distance, indicating the larger interlayer space favors an improved superconducting transition temperature.

information. Clearly, superconductivity emerges when the interlayer space is expanded to a large extent in all these hole-doped superconductors. The situation can be compared with the different extent that the interlayer space is decreased in several electron-doped (1111) systems. For instance, the Ce–As distance in CeFeAsO$_{1-x}$F$_{x}$ decreases linearly from 3.33 to 3.28 Å with $x = 0–0.16$ [12], which is believed to help bring the Ce(O,F) charge transfer layer closer to the superconducting FeAs one, thereby facilitating electron carrier transfer. Figure 7(b) shows the evolution of $T_{c}$ as a function of the RE–As bond distance in the REFeAsO$_{1-x}$F$_{x}$ (RE = Ce) and REFeAsO$_{1-x}$ (RE = La and Nd) systems [11]–[13]. The observed feature is opposite to the case discussed earlier in the hole-doped systems.

In order to understand the expansion of the interlayer space in the hole-doped systems, the valence state at the Pr site can be considered. We employed the bond valence sum (BVS) theory to evaluate the valence state of Pr [23], where each bond with a distance $r$ contributes to the valence $v = \exp[(d - r)/0.37]$ with $d$ being an empirical parameter. Considering the coordination of the Pr site, Pr is bonded with four O atoms in the Pr–O–Pr block and with the other four As atoms in the As–Fe–As block. In the non-superconducting compound with $x = 0.157$, the four Pr–O bonds are estimated to contribute 2.392 to the Pr-BVS after correction for the Sr doping. The four Pr–As bonds, which are significantly longer, contribute 0.827 to the Pr-BVS. The total Pr-BVS, 3.219, is in good agreement with the expected Pr valence. In the superconducting compound with $x = 0.221$, the increase in the Pr–O and Pr–As bond distances reduces the Pr-BVS to 2.382 and 0.793, respectively, which gives a total Pr-BVS value of 3.175. These values clearly show that the increase of Pr–As bond distance plays an important role in the reduction of Pr-BVS, and they further confirm that the replacement of Sr decreases the charge at the Pr site. Considering the layer structure of Pr$_{1-x}$Sr$_{x}$FeAsO, Pr/Sr resides at the top and bottom of the Pr–O–Pr block, whereas As resides at the top and bottom of the As–Fe–As block. Therefore Coulombic interactions between the neighboring Pr–O–Pr and As–Fe–As blocks are weakened significantly by Sr doping so that the interlayer space can be expanded.

The expansion of the interlayer space in the hole-doped pnictide systems is reminiscent of the layer-structured metal nitrides, $\beta$-MNCI ($M = Zr$ and Hf) [24]. Upon expansion of the interlayer space by the intercalation of Li and tetrahydrofuran in this system, higher transition temperatures are observed. Due to the limitations of the structural information for the hole-doped systems at present, we cannot strictly describe how the interlayer expansion favors the
Figure 7. (a) $T_c$ as a function of $M$–As bond distance in various hole-doped superconductors, where $M$ is Ba/K for $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, Nd/Sr for $\text{Nd}_{1-x}\text{Sr}_x\text{FeAsO}$ and Pr/Sr for the present system, respectively. (b) $T_c$ as a function of $M$–As bond distance in various electron-doped systems, where $M$ is Nd for $\text{NdFeAsO}_{1-y}$, La for $\text{LaFeAsO}_{1-y}$ and Ce for $\text{CeFeAsO}_{1-x}\text{F}_x$, respectively. Clearly, superconductivity emerges when the interlayer space is expanded to a large extent in the hole-doped systems. In contrast, the interlayer space is shrunk in the electron-doped systems. (c) $T_c$ as a function of the bond angle 1 in various pnictide superconductors. The bond angle 1 was defined as the larger angle between transition metal and pnictide as shown in figure 4(c). Some of these data were taken from [13]. The angle dependence of $T_c$ is largely weakened in the hole-doped systems, as compared with the electron-doped systems.
increase of $T_c$ in the hole-doped (1111) systems, but the present result will provide the important suggestion that the larger interlayer space between the conducting layer and the carrier-providing insulating layer is one of the key parameters for improving $T_c$ in the hole-doped systems.

5. Conclusion

We successfully synthesized the hole-doped (1111) superconductors Pr$_{1-x}$Sr$_x$FeAsO. Superconductivity emerges when $x$ is larger than 0.221 with a large superconducting fraction. Careful comparison between the structural parameters and $T_c$ among the various Fe-based superconductors reveals that the interlayer space expands systematically in Pr$_{1-x}$Sr$_x$FeAsO with increasing $T_c$. $T_c$ reaches its peak when the interlayer space is the largest. This suggests that interlayer space is one of the crucial parameters for achieving higher $T_c$ in hole-doped (1111) systems. This is a different trend from that encountered for electron-doped (1111) systems.

Acknowledgments

This work was supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (numbers 18204030, 19014001, 18651075 and 18204032). The work was also supported by a Grant-in-Aid for Scientific Research on Priority Areas ‘New Materials Science Using Regulated Nano Spaces-Strategy in Ubiquitous Elements’ from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The synchrotron radiation experiments were performed with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) as a Nanotechnology Support Project. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) (grant no. P07025). The work was partially supported by the Tohoku University GCOE program.

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