Large decrease in the critical temperature of superconducting LaFeAsO$_{0.85}$ compounds doped with 3% atomic weight of nonmagnetic Zn impurities

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(Received 12 June 2010; revised manuscript received 19 July 2010; published 5 August 2010)

We observed a large decrease in $T_c$ by no more than 3 at. % of Zn doped into the $T_c$-optimized superconductor LaFeAsO$_{0.85}$ ($T_c=26$ K), confirmed by measurements of electrical resistivity, magnetic susceptibility, specific heat, Mössbauer spectroscopy, Hall coefficient, and an electron probe microanalysis. The rate $\sim$9 K%/ is remarkably higher than others achieved by nonmagnetic impurities. The $T_c$ suppression is likely due to pair breaking caused by scattering associated with the highly localized electronic state of Zn in the Fe$_2$As$_2$ layer. If this is true, the present result well accords with the theoretical prediction that suggests a sign reversal $s$-wave pairing model for the Fe-pnictide superconductors.

DOI: 10.1103/PhysRevB.82.054506

I. INTRODUCTION

Superconductivity (SC) found in the quaternary oxyarsenide LaFeAsO$_{1-x}$F$_x$ resumed great activities toward discovery of a new superconductor in scientific communities because of prospect for achieving high $T_c$.1 Within few years after the discovery, the $T_c$ went over 50 K by replacing La to other rare-earth element and materials varieties were rapidly developed: many Fe pnictides containing the Fe$_2$As$_2$ layer in each structure have been proved to become superconducting, e.g., AFe$_2$As$_2$ (A=alkaline earth),2 AFeAsF,3 and Sr$_2$Sc$_2$Fe$_2$P$_2$O$_6$.4 It is noteworthy that the Fe-based superconductors may have practical values because their upper-critical field is remarkably high.5

The SC of the Fe pnictide emerges after the spin-density wave (SDW) is suppressed by chemical or physical methods, being analogous with the SC of the Cu oxide.6 The Fe$_2$As$_2$ layer is believed to play a decisive role of establishing the SC as does the CuO$_2$ layer.7 These facts imply that the Fe pnictides and the Cu oxides may share common physics in part regarding the mechanism of the SC. To date tremendous activities were performed to reveal nature of the SC of the Fe pnictides; however, the nature seems not to be well uncovered yet. For example, the SC gap symmetry is still under debate. In early theoretical studies, there seems to be a consensus that the gap symmetry is of a sign-reversal $s$ wave (often notated as $s_\pm$ wave) as proposed independently by Mazin et al.,3 Kuroki et al.,9,10 and Tesanovic et al.11,12 Probable nesting between separated pockets of the Fermi surfaces may enhance spin fluctuations, helping to generate the SC. In the early studies, the SC gap has no nodes; full gap opening was predicted.13,14 The gap symmetry model was further supported by experiments including NMR studies,13,15,16 angle-resolved photoemission spectroscopy,17,18 microwave penetration depth measurements,19 μSR studies,20,21 and neutron-scattering studies22,23 on varieties of the Fe-based superconductors.

However, the pairing model seems not to meet results of impurity studies: many doped elements to the Fe-based superconductor rather work weakly for the SC. For example, Co, Ni, Ru, Rh, Pd, and Ir were found to even work to produce the SC by each doping, suggesting that the Fe-based superconductor is highly robust against an impurity.24–28 The observations seemed to sharply contrast to what is expected for the $s_\pm$-wave SC (Refs. 29 and 30) since the $s_\pm$-wave SC is supposed to be quite fragile against even a nonmagnetic impurity unlike the conventional $s$-wave SC (BCS SC is normally robust against nonmagnetic impurities as observed for MgB$_2$ for instance31).

Additional theoretical studies, however, suggested that the $s_\pm$-wave model can be possibly consistent with the robust SC if certain conditions such as a small impurity potential (<1 eV) and a large potential radius are effective in the SC.29,30 Nevertheless, the issue regarding inconsistency between the $s_\pm$-wave model and the results of the impurity studies seems to eventually complicate discussions about the mechanism of the SC of the Fe pnictide, and the issue is thus subjected for further studies. To our best knowledge, a fragile SC against a nonmagnetic impurity was not observed yet for any Fe-pnictide superconductor at the time of submission of this article.32,33 Before the high-pressure synthesis of LaFeAsO$_{0.85}$,34 it appeared that the doped Zn to LaFeAsO$_{1-x}$F$_x$ does not reduce $T_c$ (<10 at. % Zn).32 Meanwhile, the magnetic Mn-doped LaFeAsO$_{1-x}$F$_x$ shows a large $T_c$ decrease while the nonmagnetic Co-doped LaFeAsO$_{1-x}$F$_x$ slowly decreases $T_c$ over the doping.33,35

In this paper, we report a large $T_c$ decrease achieved by a minimal level of Zn (below 3 at. %) doped into the super-
condenser LaFeAsO$_{0.85}$.$^{34}$ We discuss role of Zn in the SC and compare the result with other results reported elsewhere.

II. EXPERIMENTAL

Polycrystalline samples of Zn-doped LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ ($x=0,0.005,0.01,0.015,0.02,0.03,0.05$) were prepared by solid-state reaction under high pressure from powders of LaAs (lab-made), Fe$_2$O$_3$ (3N, Furuuchi Chem. Co.), ZnO (3N, Wako), and Fe (3N, 100 mesh, Rare Metallic Co.). LaAs was prepared in advance from La pieces (3N, Nilaco Co.) and As powder (5N, High Purity Chem.) with 1 at. % excess As by heating in an evacuated quartz tube at 500 °C for 20 h, followed by quenching to room temperature. The LaAs product was ground and reheated at 850 °C for 10 h. The lab-made LaAs powder was qualitatively studied by a method of powder x-ray diffraction (XRD) using Cu-Kα radiation in a diffractometer in RINT2200V/PC, Rigaku.

The starting mixture each was placed into a hexagonal boron nitrogen (h-BN) cell (preheated in advance at ~2000 °C for 1 h in nitrogen) and the cell was sealed in a gold capsule. The sample-contained capsule was heated each in a belt-type pressure apparatus, which is capable of maintaining 6 GPa during the heating, followed by quenching by heating in an evacuated quartz tube at 500 °C for 20 h, followed by quenching to room temperature. The LaAs product was ground and reheated at 850 °C for 10 h. The lab-made LaAs powder was qualitatively studied by a method of powder x-ray diffraction (XRD) using Cu-Kα radiation in a diffractometer in RINT2200V/PC, Rigaku.

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The samples of the oxygen vacancy-controlled LaFeAsO$_{1-\delta}$ ($\delta=0,0.12,0.15,0.22$) were prepared in the same way under high pressure, except the $\delta=0$ sample. The $\delta=0$ sample was synthesized in an evacuated quartz tube at 1100 °C for 30 h under ambient pressure because the pressurized conditions did not work better to improve the sample quality. The starting mixture each was placed into a hexagonal boron nitrogen (h-BN) cell (preheated in advance at ~2000 °C for 1 h in nitrogen) and the cell was sealed in a gold capsule. The sample-contained capsule was heated each in a belt-type pressure apparatus, which is capable of maintaining 6 GPa during the heating, followed by quenching to room temperature before releasing the pressure. To increase uniformity of the sample, the obtained pellet was carefully ground and reheated at the same condition.

All samples were qualitatively studied by the XRD method and selected samples (LaFeAsO$_{0.85}$ and LaFe$_{0.92}$Zn$_{0.05}$AsO$_{0.85}$) were further investigated by a synchrotron XRD (SRXD) method. The SRXD measurement was conducted at $\lambda=0.652973$ Å in a large Debye-Scherrer camera at the BL15XU beam line of SPring-8.$^{37}$ The sample capillary, Lindemann glass, was rotated during the measurement. The Rietveld analysis was carried out by using RIETAN-2000.$^{38}$ The samples of LaFeAsO$_{0.85}$ and LaFe$_{0.92}$Zn$_{0.05}$AsO$_{0.85}$ were further studied by a Mössbauer spectroscopy, which was carried out at room temperature by using a conventional constant acceleration drive and a 50 mCi $^{57}$Co/Rh source. The experimental spectra were analyzed by a least-squares fit procedure. The velocity calibration and isomer-shift (IS) zero are those of $\alpha$-Fe measured at room temperature.

A selected Zn-doped sample (LaFe$_{0.95}$Zn$_{0.05}$AsO$_{0.85}$) was studied in an electron probe microanalysis (EPMA) at an acceleration voltage of 15 kV (JXA-8500F, JEOL). A surface of the sample pellet was carefully polished using an alumina-coated sheet. The analysis confirmed that possible contamination from such as Au are below the EPMA background level. Expected peaks due to Zn were confirmed in a wavelength-dispersive spectrometry, indicating Zn is indeed incorporated in the sample. The same sample was further studied by an element mapping operation in EPMA regarding Zn over a square surface approximately 100 μm × 100 μm maximum in area. The doped Zn was observed to evenly spread out, suggesting that Zn-rich impurities are unlikely formed. Additional EPMA operations were carefully conducted regarding possible formation of the Zn-rich impurities; however, any trace of the possibility was undetected.

The magnetic susceptibility ($\chi$) of the samples was measured in the magnetic property measurement system, Quantum Design Inc. Loose powder was cooled to 2 K before applying a magnetic field (zero-field cooling; ZFC), followed by warming to 300 K in a magnetic field 10 Oe. The sample was then cooled down to 2 K in the field (field cooling; FC). The electrical resistivity ($\rho$) was measured in the physical properties measurement system (PPMS), Quantum Design Inc., by a four-probe method with a constant gauge current of 0.2 mA. Hall coefficient ($R_H$) was measured by rotating the sample by 180° in a field of 50 kOe in PPMS between 25 and 300 K. Specific heat ($C_p$) of the samples LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ ($x=0$ and 0.05) was measured in PPMS, between 2.2 and 300 K by a heat-pulse relaxation method.

III. RESULTS AND DISCUSSION

The powder XRD patterns at $\delta=0.15$ (LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$) are shown in Fig. 1(a). All peaks were well indexed by assuming the ZrCuSiAs-type structure with P4/nnm as was done for TbFeAsO$_{0.85}$.$^{39}$ Although the XRD analysis indicated that the samples are of high quality, the SXRD analysis [Figs. 1(b) and 1(c)] found a tiny amount of LaAs incorporated in the sample regardless of amount of Zn. The incorporated LaAs was actually confirmed by the EPMA. The impurity may result from the compositional issue of the starting LaAs powder prepared with the excess As.

Rietveld analysis of the SXRD patterns was carefully carried out and the results are shown in Figs. 1(b) and 1(c). A reliable structure solution was obtained.$^{40}$ The mean La-As distance is 3.3577(6) Å at $x=0$ and 3.3570(6) Å at $x=0.01$, and the Fe-As-Fe angle in the Fe$_2$As$_2$ layer is 113.09(9)° and 113.20(9)°, respectively. Although La-As distance and the angle were suggested to play a crucial role in controlling the effective bandwidth, thereby affecting the SC,$^{41}$ those were confirmed to change quite little over the Zn substitution.

The lattice parameters of the tetragonal unit cell, deduced from the XRD patterns, were plotted against the Zn concentration as shown in Figs. 2(a)–2(c). For a comparison, the lattice parameters of the oxygen vacancy-controlled samples LaFeAsO$_{1-\delta}$ were plotted along the Zn-doped data. Regarding LaFeAsO$_{1-\delta}$ the tetragonal lattice parameters $a$ and $c$ decrease with increasing $\delta$ as well as what was found for the compounds TbFeAsO$_{1-\delta}$.$^{36}$ This probably reflects combination of Coulomb attractive forces between the charged [LaO$_{1-x}$]$^{1+2\delta}$ and [FeAs]$_{1-2\delta}$ layers and amount of vacant sites for oxygen atoms. In sharp contrast to the observation, the Zn substitution resulted in an anisotropic change in the
lattice parameters: $c$ of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ increases (+0.02% at Zn$_{0.01}$) while $a$ decreases much efficiently (−0.08%) over the substitution. The distinctive feature is indicative of influence of the doped Zn over the unit cell. Besides, magnetic $T_c$ vs $c/a$ [Fig. 2(d)] indicates a tight relation between those (magnetic data are shown later). These facts clearly indicate that the Zn substitution is successful up to 5 at. % under the high-pressure condition. The EPMA analysis entirely supports the result. Usually, loss of ZnO becomes significant during heating above 1100 °C by volatility, thus experimental chances of Zn substitution to an oxide is often limited. Perhaps, the high-pressure condition might allow us to reduce the ZnO volatility during heating, resulting in the successful Zn substitution to LaFeAsO$_{0.85}$.

Additionally, selected Zn-doped samples were further characterized by measurements of Hall coefficient, conducted from 300 to 25 K. The data are shown in Fig. 3 for the samples with and without 2 at. % doped Zn. The features are essentially identical, indicating that the electron count changes little over the Zn substitution. The carrier concentration at 300 K for LaFeAsO$_{0.85}$ is $3.9 \times 10^{21}$ cm$^{-3}$, corresponds to 1.1 electrons per the primitive cell, being comparable with the values reported for the F-doped LaFeAsO.34

Let us see the superconducting properties of the Zn-doped samples of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$. Figures 4(a)–4(g) show Zn concentration dependence of $\chi$ vs $T$. In Fig. 4(a), the Zn-free sample with optimally carrier doped ($\delta=0.15$) clearly undergoes a superconducting transition at $\sim 26$ K as was reported elsewhere.34 Employing the calculated density of 7.85 g/cm$^3$, the magnetic shielding fraction is estimated to be 1.13 (1.00 is expected for the perfect shielding), indicating homogeneous SC of the sample. In contrast, the Meissner fraction (5 K, FC curve) is fairly small, less than 0.1. The contrastive features between the magnetic shielding and the Meissner fractions were commonly observed for the oxygen-deficient 1111 systems39 probably because of possible effi-

FIG. 1. Powder XRD patterns of (a) LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ ($x=0–0.05$) and Rietveld analysis of the SXRD patterns of (b) LaFeAsO$_{0.85}$ and (c) LaFe$_{0.99}$Zn$_{0.01}$AsO$_{0.85}$. Dots and lines represent the observed and the calculated intensities, respectively. Each difference curve is shown at the bottom. Small vertical bars indicate calculated Bragg reflection positions. Inset each shows the Mössbauer spectrum at room temperature.

FIG. 2. (a)–(c) Unit-cell evolution of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ (bottom axes) and LaFeAsO$_{1-y}$ (top axes, taken from Ref. 34). (d) $T_c$ vs $c/a$. The dashed lines are guide to the eyes.

FIG. 3. $T$ dependence of the Hall number ($n=|e/R_H|$) of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ ($x=0$ and 0.02). The sign of $R_H$ is negative over the $T$ range studied.

FIG. 4. (a)–(g) Superconducting properties of the Zn-doped samples of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$. The dashed lines are guide to the eyes.
In the ZFC and FC conditions. Open and closed symbols represent data of independent set of samples. (b) $T_c$ vs $x$. The feature highly contrasts with what was observed for the Co-doped LeFeAsO$_{1-x}$F$_x$ (Ref. 33 and 35) and is nearly comparable with the magnetic Mn-doped LeFeAsO$_{1-x}$F$_x$.33 Besides, the nonmagnetic Zn result is highly contrastive with what were observed by $d$ elements doping studies such as Ni, Ru, Rh, Pd, and Ir, which weakly suppresses $T_c$ or even produces the SC.24–28 Moreover, the large $T_c$ decrease by Zn is not at all comparable with the recent result for the Zn-doped LeFeAsO$_{1-x}$F$_x$;32 thus we tested a possible run-to-run error in our synthesis. We actually repeated the synthesis of all the Zn-doped LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ samples (except $x=0.05$) four times in total. An independent set of the magnetic data are for instance shown in Figs. 4(a)–4(g) simultaneously, confirming reproducibility of the essential part of the result.

Figures 5(a) and 5(b) show the temperature dependence of $\rho$ of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ and LaFeAsO$_{1-x}\beta$ respectively. Regarding the stoichiometric LaFeAsO, $\rho$ at 300 K is $\sim$6 m$\Omega$cm, being comparable with the normalized mean-

FIG. 4. (a)–(g) $T$ and $x$ dependence of $\chi$ of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ measured at 10 Oe in the ZFC and FC conditions. Open and closed symbols represent data of independent set of samples. (b) $T_c$ vs $x$.showing the temperature dependence of $\rho$ of LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ and LaFeAsO$_{1-x}\beta$ respectively. Regarding the stoichiometric LaFeAsO, $\rho$ at 300 K is $\sim$6 m$\Omega$cm, being comparable with the normalized mean-

FIG. 5. $T$ dependence of $\rho$ of (a) LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ and (b) LaFeAsO$_{1-x}\beta$. Inset shows an expansion. The dotted line corresponds to the scale indicated by the solid arrow.
efficient and $\gamma$ is the Sommerfeld coefficient, we obtained $\beta$ of $2.79(1) \times 10^{-4}$ J mol$^{-1}$ K$^{-2}$ and $\gamma$ of $2.0(1)$ mJ mol$^{-1}$ K$^{-2}$ for LaFeAsO$_{0.85}$ by a fit to the linear part (inset to Fig. 6). We obtained $T_D$ (the Debye temperature) of 299(1) K from $\beta = 12\pi^2 R/5T_D^3$. The $\gamma$ and $T_D$ are indeed comparable with those of the Co- and F-doped LaFeAsO superconductors.\textsuperscript{35,47}

It is most noteworthy that the Zn-doped sample shows additional anomaly at the low-temperature limit; a broad upturn appears on cooling and $C_p/T$ approaches to $\sim 12$ mJ mol$^{-1}$ K$^{-2}$ at the limit. Although we expected a Schottky anomaly in the data because of possible Zn-induced magnetic moments in the Fe$_2$As$_2$ layer, the broad upturn was eventually observed instead. Although a similar upturn was observed for the Zn-doped YBCO, which was discussed using Kondo-screened moments,\textsuperscript{48} our observation for the low-temperature $C_p$ of LaFe$_{0.95}$Zn$_{0.05}$AsO$_{0.85}$ is not well explained.

We attempted to measure the oxygen content of the samples LaFe$_{1-x}$Zn$_x$AsO$_{1-y}$ (x $\leq$ 0.02) by a thermogravimetric method. About 10 mg of each sample was fully oxidized at 1500 °C in air for 24 h, followed by cooling slowly to room temperature. The final product was identified to be LaFeO$_3$ in the XRD study, indicating that the following reaction was proceeded: LaFeAsO$_{1-d}$+[4.5−(1−$\delta$)]/2O$_2$ $\rightarrow$ LaFeO$_3$+0.5As$_2$O$_3$. The net oxygen content was calculated by monitoring the weight loss. Assumed that Zn is fully evaporated in the heating, the net oxygen content is within the range 0.83–0.85 per the formula unit, being in good agreement with the nominal. Although uncertainty of the exact Zn amount results in a possible error, it should be smaller than 0.014 per the formula unit. It thus appears that the oxygen content variation unlikely accounts for the large $T_c$ decrease.\textsuperscript{34,36}

Additionally, we studied the Mössbauer effect of the $x=0$ ($T_c=26$ K) and 0.01 ($T_c=10$ K) samples. As shown in Figs. 1(b) and 1(c), both the spectra are nearly identical, suggesting the Fe valence is unaltered between the two samples. In more details, the hyperfine parameters and the IS values are the same and the quadrupole splitting is negligibly small. The line width is 0.265(5) mm/s. IS(relative to Fe) =0.451(2) mm/s, QSP=0.090(3) mm/s for the $x=0$ sample, and 0.277(5), 0.455(2), and 0.096(3), respectively, for the $x=0.01$ sample. The oxygen content variation is again confirmed little.

Let us focus on the role of the doped Zn. The divalent Zn has the 3d$^10$ configuration; the d orbital is fully occupied in contrast to Co$^{2+}$ (3d$^7$) and Ni$^{2+}$ (3d$^8$), resulting in a highly localized nature. Indeed, the Zn 3d states are located at $\sim$8 to $\sim$6.5 eV far below the Fermi level in LaZnAsO.\textsuperscript{49} It is therefore reasonable that doped Zn in the Fe site holds a strong localization nature and thus does not add itinerant electrons into the Fe$_2$As$_2$ layer. It should be noted that the small $T_c$ suppression of the Co-doped LaFeAsO$_{1-x}$F$_x$ may be due to weaker localization of Co.\textsuperscript{33} Since the $T_c$ suppression is achieved by no more than 3 at. % of Zn, it is most likely that the doped Zn works as a scattering center as predicted in a recent theoretical work: the scattering may effect pair breaking of the $s_\pm$-wave SC.\textsuperscript{50} Our observation probably accords with the prediction. Independent theoretical studies on a 5d-orbital model also predicted that the Anderson’s theorem is violated for the $s_\pm$-wave state due to strong interband impurity scatterings, suggesting a significant nonmagnetic impurity effect on the SC.\textsuperscript{29,30} This may explain our results for the large $T_c$ decrease achieved by the few atomic percent Zn.

Although our results well match with the theoretical predictions, those firmly contradict the results of the Zn-doped studies on LaFeAsO$_{1-x}$F$_{0.1}$,\textsuperscript{29,30} which concluded that the doped Zn does not suppress the SC. It was stated in Ref. 32 that the SC remains almost unperturbed or even enhanced by the Zn substitution (<10 at. %), being strictly contrasting with the present results. However, the same research group reported additional results,\textsuperscript{51} showing clearly a large $T_c$ decrease in the overdoped region as well as what we observed for the LaFe$_{1-x}$Zn$_x$AsO$_{1-y}$. It appeared that degree of the $T_c$ suppression may depend on F concentration as discussed in Ref. 52. This may be relevant to what was found in recent NMR studies on P-doped BaFe$_2$As$_2$ (Ref. 52) and theoretical studies on local structures of the Fe$_2$As$_2$ layer,\textsuperscript{10} those suggested the gap symmetry can possibly change depending on minute factors. Eventually, the fragile SC of the doped LaFeAsO was confirmed by two independent experiments using the nonmagnetic Zn, although our observation was carried out for the optimally carrier doped LaFeAsO$_{0.85}$ and the other observation was done for the overdoped LaFeAsO$_{1-x}$F$_x$. In order to further investigate the carrier-concentration dependence of the Zn effect, we design further studies of the underdoped and the overdoped LaFeAsO$_{1-x}$F$_x$.

In contrast to the 1111 compound, the 122 compound Ba$_{10}$K$_{0.5}$Fe$_2$As$_2$ was recently found to be insensitive to the doped Zn,\textsuperscript{53} the issue, how the distinction of the sensitivity to the doped Zn between the 1111 system and the 122 system comes from, is left for future studies.

In summary, a large $T_c$ decrease from the optimum $T_c$ of 26 K was observed by a minimal amount of Zn (<3 at. %) doped into LaFeAsO$_{0.85}$. The $T_c$ suppression rate of Zn was found to be $\sim$9 K/%, being remarkably higher than the rate ($\sim$2.5 K/%) of the nonmagnetic impurity study on LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_x$ (Ref. 33) and almost comparable with the rate of the magnetic impurity study on LaFe$_{1-x}$Mn$_x$AsO$_{1-y}$F$_x$.\textsuperscript{33} The present data indicated that the...
doped Zn likely plays a dominant role of effecting pair breaking due to scatterings associated with the highly localized state of Zn in the Fe$_2$As$_2$ layer. If this is true, the $T_c$ suppression is consistent with the prediction from the $s_\pm$-wave model. For further clarification of the role of Zn, NMR measurements are in progress. Although the present results indicate that the conventional $s_\pm$-wave model and the nodal $d$-wave model remain equally possible. Although many theoretical studies suggested that the $s_\pm$-wave model is much likely for the Fe pnictides, the present nonmagnetic impurity study is, however, unable to judge which is most likely.

**ACKNOWLEDGMENTS**

We thank D. J. Singh for valuable discussion and K. Kosuda for the EPMA study. This research was supported in part by the World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics from MEXT, Japan; the Grants-in-Aid for Scientific Research (20360012, 22246083) from JSPS, Japan; and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) from JSPS.

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38 F. Izumi and T. Ikeda, Mater. Sci. Forum 321-324, 198 (2000); isotropic atomic displacement parameters and isotropic Debye-Waller factor were assigned to all the atoms.


40 Space group: P4/mnm. g = 0.85 for O, 1 for La, Fe, As. a = 4.03247(13) Å, c = 8.7135(3) Å, \( V = 141.689(8) \, \text{Å}^3 \); \( R_{wp} = 3.73\% \), \( R_p = 2.45\% \), and \( R_F = 2.98\% \), for LaFeAsO\(_{0.85}\); and \( a = 4.024916(13) \, \text{Å}, \ c = 8.7150(3) \, \text{Å}, \ V = 141.480(8) \, \text{Å}^3 \); \( R_{wp} = 5.35\% \), \( R_p = 3.40\% \), and \( R_F = 2.31\% \) for LaFe\(_{0.99}\)Zn\(_{0.01}\)AsO\(_{0.85}\). \( \gamma(\text{La}) = 0.14364(10), 0.14386(9); \ \gamma(\text{As}) = 0.65289(17), 0.65242(16); \ B(\text{La}) = 0.60(2), 0.51(2) \, \text{Å}^2; \ B(\text{Fe}) = 0.70(5), 0.57(4) \, \text{Å}^2; \ B(\text{As}) = 0.79(3), 0.74(3) \, \text{Å}^2; \ B(\text{O}) = 0.5, 0.5 \, \text{Å}^2 \) for LaFeAsO\(_{0.85}\) and LaFe\(_{0.99}\)Zn\(_{0.01}\)AsO\(_{0.85}\) respectively.


