Magnetic scattering and electron pair breaking by rare-earth-ion substitution in BaFe$_2$As$_2$ epitaxial films

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Abstract. The effect of electron doping by trivalent charge state rare-earth-ion (RE = La, Ce, Pr and Nd) substitutions on the superconductivity in BaFe$_2$As$_2$ was examined using epitaxial films. Each of the RE substitutions suppressed the resistivity anomaly associated with magnetic/structural phase transitions, leading to resistivity drops and superconductivity transitions. Bulk superconductivity was observed at the maximum onset critical temperature ($T_{\text{onset}}$) of 22.4 K for La doping and 13.4 K for Ce doping, while only broad resistivity drops were observed at 6.2 K for Pr doping and 5.8 K for Nd doping although zero resistivity and the distinct Meissner effect were not observed at least down to 2 K. The decrease in $T_{\text{onset}}$ with increasing the number of RE 4f electrons cannot be explained in terms of the crystalline quality or crystallographic structure parameters of BaFe$_2$As$_2$ films. It was clarified, based on resistivity–temperature analyses, that magnetic scattering became increasingly significant in the above

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order of RE dopants. The negative magnetoresistance was enhanced by Ce and Pr doping, implying that the decrease in $T_c$ originates from magnetic pair breaking by interaction of the localized 4f orbitals in the RE dopants with the itinerant Fe 3d orbitals.

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1. Introduction

In the few months since the report on high critical temperature ($T_c$) superconductivity at 26 K in the 1111-type iron pnictide LaFeAs(O$_{1-x}$F$_x$) [1], 122-type AEF$_2$As$_2$ (where AE = alkaline earth) [2] has also joined the family of iron-based high-$T_c$ superconductors as a parent material. To induce its high-$T_c$ superconductivity, both types of doping carrier, i.e. holes and electrons, are typically used by selection of appropriate aliovalent dopants. To date, most such carrier doping processes have been performed by substituting the AE sites with alkali metals with different ion charges, such as K (e.g. in hole-doped $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$) [2], and by substituting the Fe sites with transition metals with excess 3d electron numbers, such as Co (e.g. in electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$) [3]. The doping sites are categorized into two modes for 122-type AEF$_2$As$_2$, i.e. ‘indirect doping’ for doping at sites other than the Fe sites, and ‘direct doping’ for doping at the Fe sites, because the AE and the FeAs layers are spatially separated and the Fermi level is composed mainly of Fe 3d orbitals [4].

The maximum $T_c$ value for each parent material of the iron-based superconductors was obtained by indirect doping [2, 5–7] because direct doping has a major influence on carrier transport in the conducting Fe layer. It was therefore expected that a new indirect electron doping mode for AEF$_2$As$_2$, e.g. at the AE sites, would lead to high-$T_c$ superconductors, similar to the effects of other indirect doping methods, such as K doping at AE sites (maximum $T_c = 38$ K) [2] and isovalent P doping at As sites (maximum $T_c = 31$ K) [8]. However, indirect electron doping of AEF$_2$As$_2$ by substituting the AE sites with trivalent rare earth (RE) ions was difficult to perform by conventional solid-state reactions; only Ba [9] and Sr [10] have been reported. This difficulty was attributed to electronic instability arising from the high localized density of states at the Fermi level, as predicted for La-doped AEF$_2$As$_2$ [(AE$_{1-x}$La$_x$)Fe$_2$As$_2$] by density functional theory calculations [11, 12].
Under such circumstances, indirect RE doping of AEFe$_2$As$_2$ was achieved by applying a high-pressure synthesis process for (Sr$_{1−x}$La$_x$)Fe$_2$As$_2$ polycrystals [10] and a melt-growth process using a flux agent for (Ca$_{1−x}$RE$_x$)Fe$_2$As$_2$ (where RE = La–Nd) single crystals [13–16]. Among these materials, it should be noted that a Pr-doped CaFe$_2$As$_2$ single crystal demonstrated a maximum $T_c$ of 49 K [14], which is the highest reported $T_c$ among the 122-type AEFe$_2$As$_2$ series, although their shielding volume fractions (SVFs) are as low as <1% at 40 K [13].

In contrast to the AE = Ca and Sr systems, there have been no reports on RE-doped BaFe$_2$As$_2$, probably because of the large difference between the ionic radii of Ba$^{2+}$ (142 pm for eight-fold coordination) and RE$^{3+}$ (111–116 pm) [17]. However, we recently succeeded in indirect La doping at the Ba sites in BaFe$_2$As$_2$ by using a film-growth process [18]. This success was attained by using the highly non-equilibrium nature of thin film deposition via the vapor phase. The maximum $T_c$ (22.4 K) of the (Ba$_{1−x}$La$_x$)Fe$_2$As$_2$ films was much lower than that of the RE-doped CaFe$_2$As$_2$ single crystal, and its electronic phase diagram was almost the same as that of directly doped Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$. On the other hand, according to the scenario in (Ca$_{1−x}$RE$_x$)Fe$_2$As$_2$ crystals where a smaller RE dopant than La, such as Pr, leads to a higher $T_c$, we expected that substitution of smaller RE ions with open-shell 4f electrons for the Ba sites would provide a higher $T_c$ than that attained for (Ba$_{1−x}$La$_x$)Fe$_2$As$_2$.

In this paper, we examined the indirect electron doping of open 4f shell RE ions (Ce, Pr, Nd and Sm) at the Ba sites in BaFe$_2$As$_2$ epitaxial films by pulsed laser deposition (PLD). It was confirmed that three open 4f shell RE dopants (Ce, Pr and Nd) were successfully substituted at the Ba sites by the PLD process, similar to the case for La doping. The Ce doping induced bulk superconductivity at a maximum onset $T_c$ ($T_c^{\text{onset}}$) of 13.4 K. On the other hand, although zero resistivity and the distinct Meissner effect were not observed down to 2 K, resistivity drops caused by superconducting transitions were observed at 6.2 K for the Pr doping and at 5.8 K for the Nd doping. The relationship between the 4f electron configuration and the superconducting properties is discussed and comparison is made with the results of the non-magnetic La-doping case.

2. Experimental

(Ba$_{1−x}$RE$_x$)Fe$_2$As$_2$ thin films were grown directly on MgO (001) single crystals with a PLD system using a second harmonic of a Nd:YAG laser as the excitation source [19]. Bulk polycrystalline samples of RE (La, Ce, Pr, Nd and Sm)-containing BaFe$_2$As$_2$ were used as PLD targets (see supplementary figure S1 available from stacks.iop.org/NJP/15/073019/mmedia for the synthesis of the bulk polycrystals). Powder x-ray diffraction (XRD, using CuKα anode radiation) analyses confirmed that the crystalline phases of the bulk polycrystals were mixtures of BaFe$_2$As$_2$ and REAs impurity phases, i.e. the RE ions were not incorporated in the BaFe$_2$As$_2$ phases [18]. Film growth was carried out at the previously optimized substrate temperature ($T_s$) of 850°C (note that the REAs impurity phases appeared in the films at higher values of $T_s$ > 850°C) [18–20]. Each film was 150–250 nm thick, as measured with a stylus profiler. The net doping concentrations in the (Ba$_{1−x}$RE$_x$)Fe$_2$As$_2$ films ($x_{\text{film}}$) were measured using an electron-probe microanalyzer (EPMA). The high homogeneity of the RE distribution was confirmed by the EPMA for all of the fabricated samples (see supplementary figure S2(a) for mapping images of the RE concentrations). It was also confirmed that $x_{\text{film}}$ was controlled by changes in the nominal RE concentration (nominal $x$) of the RE-containing BaFe$_2$As$_2$ PLD targets (see supplementary figure S2(b) for the relationship between nominal $x$ and $x_{\text{film}}$).
The film structures and their crystalline qualities were characterized by high-resolution XRD using Cu Kα1 anode radiation at room temperature. The temperature dependence of the electrical resistivity (\(\rho - T\)) was measured by the four-probe method in a temperature range of 2–300 K with a physical property measurement system. The temperature dependence of the magnetic susceptibility (\(\chi - T\)) was measured with a vibrating sample magnetometer after zero-field cooling (ZFC) and during field cooling (FC).

3. Results

3.1. Growth of \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) thin films

Figure 1 shows the out-of-plane XRD patterns for films of (a) \((\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2\), (b) \((\text{Ba}_{1-x}\text{Pr}_x)\text{Fe}_2\text{As}_2\), (c) \((\text{Ba}_{1-x}\text{Nd}_x)\text{Fe}_2\text{As}_2\) and (d) Sm-containing \(\text{BaFe}_2\text{As}_2\) with various values of \(x_{\text{film}}\). In the cases of (a) Ce, (b) Pr and (c) Nd doping, the \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) films obtained were grown epitaxially on MgO substrates with the epitaxial relationship of [001] \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2 || [001] \text{MgO}\) for the out-of-plane case and [100] \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2 || [100] \text{MgO}\) for the in-plane case, which is the same as that of \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) films [18]. The 00\(l\) diffraction angles of the undoped \(\text{BaFe}_2\text{As}_2\) film are indicated by the dotted lines to clearly show the peak shift caused by the RE substitutions. Sharp 00\(l\) diffractions of the \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) phases, along with those from a small amount of the Fe impurity phase (indicated by the asterisks), were observed in the low \(x_{\text{film}}\) regions. The 00\(l\) diffraction peaks shifted systematically to higher angles from the diffraction peaks of the undoped \(\text{BaFe}_2\text{As}_2\) film as \(x_{\text{film}}\) increased. The intensities of the Fe impurity diffractions were almost the same in all the samples. Segregation of the impurity phases of REAs started to be observed at the high \(x_{\text{film}}\) values of 0.30, 0.28 and 0.20 for the Ce-, Pr- and Nd-doped films, respectively, from which we determined the solubility limits to be lower than these values. Because the formation enthalpies of the REAs impurity phases are almost the same (−288 kJ mol\(^{-1}\) for CeAs, −307 kJ mol\(^{-1}\) for PrAs and −304 kJ mol\(^{-1}\) for NdAs) [22], the different solubility limits are attributed to the differences in the ion size mismatch between \(\text{Ba}^{2+}\) and \(\text{RE}^{3+}\) in each case, and in the consequent instability among the \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) phases. In contrast, in the case of Sm doping with \(x_{\text{film}} = 0.1\) and 0.17, no peak shift of the 00\(l\) diffractions was detected, and only the segregation of SmAs impurities was observed (figure 1(d)), indicating that the incorporation of the smaller Sm ions into \(\text{BaFe}_2\text{As}_2\) was unsuccessful.

3.2. Structural characterization

Figure 2(a) summarizes the evolution of the lattice parameters \(a\) and \(c\) and the unit cell volume \(V\) at room temperature as a function of \(x_{\text{film}}\) for \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) (RE = Ce, Pr and Nd) epitaxial films. Note that those films having the segregated REAs phases in figure 1 are not plotted because \(x_{\text{film}}\) exceeds the solubility limits and the lattice parameters remain almost unchanged from those of the highest \(x_{\text{film}}\) films in figure 2. The \(c\)-axis and \(a\)-axis lattice parameters were determined by out-of-plane and in-plane XRD, respectively. In all of the dopant cases, systematic shrinkages of the \(c\)-axis length were observed (the largest \(\Delta c/c\) was \(\sim -2.3\%\) for \((\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2\) films with \(x_{\text{film}} = 0.28\), while the shrinkage of the \(a\)-axis length was very small (the largest \(\Delta a/a\) was \(\sim -0.3\%\)). Consequently, \(V\) decreases monotonically as \(x_{\text{film}}\) increases. These results, which are similar to those obtained for \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) [18],
Figure 1. High-resolution out-of-plane XRD patterns for films of
\((\text{Ba}_{1-x}\cdot\text{Ce}_x)\text{Fe}_2\text{As}_2\) (a), \((\text{Ba}_{1-x}\cdot\text{Pr}_x)\text{Fe}_2\text{As}_2\) (b), \((\text{Ba}_{1-x}\cdot\text{Nd}_x)\text{Fe}_2\text{As}_2\) (c) and
\((\text{Ba}_{1-x}\cdot\text{Sm})\text{Fe}_2\text{As}_2\) (d) with various \(x_{\text{film}}\) values. The \(x_{\text{film}}\) value is shown on the upper right of each panel. The vertical dashed lines indicate the 00\(l\) diffraction angles of the undoped \(\text{BaFe}_2\text{As}_2\) phase. The asterisks show the 110 diffraction peaks from the Fe impurity phase.

substratate the fact that the \(\text{RE}^{3+}\) ions substitute the \(\text{Ba}^{2+}\) sites in epitaxial films. It is noteworthy
that the \(c\)-axis shrinkage increases in the order of \(\text{Nd}, \text{Pr}\) and \(\text{Ce}\) dopants, when compared with
the same \(x_{\text{film}}\), but this result is inconsistent with the differences in the ionic radii of the \(\text{RE}^{3+}\) ions
(\(\text{Ce}^{3+}\) (114 pm), \(\text{Pr}^{3+}\) (113 pm) and \(\text{Nd}^{3+}\) (111 pm) because of
the lanthanide contraction) [17]. Additionally, the variation in the \(a\)-axis length was independent
of the ionic radii.
Figure 2. $x_{\text{film}}$ dependence of the structural properties of $(\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ epitaxial films. (a) $a$-axis and $c$-axis lattice parameters and unit cell volume $V$, (b) FWHM values of rocking curves for 004 ($\Delta \omega$) and 200 ($\Delta \phi$) diffractions and (c) FWHM values of 004 diffractions ($\Delta 2\theta$). The solid lines in the middle figure of (a) are indicators of changes in the $c$-axis lattice parameters. Open pentagon symbols and dotted lines show the results for undoped BaFe$_2$As$_2$ films. The diamonds, circles, squares and triangles indicate values for La-, Ce-, Pr- and Nd-doped films, respectively.

Figure 2(b) shows the $x_{\text{film}}$ dependence of the crystalline quality of the $(\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ epitaxial films. Here, the full-width at half-maximum (FWHM) values of rocking curves for 004 ($\Delta \omega$, out-of-plane) and 200 ($\Delta \phi$, in-plane) diffractions were used to evaluate the crystalline quality. The $\Delta \omega$ and $\Delta \phi$ values scatter to an extent but remain almost unchanged at $\sim 1.0^\circ$, regardless of $x_{\text{film}}$ for all dopants. Figure 2(c) shows the $x_{\text{film}}$ dependence of the FWHM values of 004 diffractions ($\Delta 2\theta$). $\Delta 2\theta$ gradually increases as $x_{\text{film}}$ increases, which may originate from the structural strains and/or distortions in the films, probably because of large ion-size mismatches between the Ba$^{2+}$ ion and the doped RE$^{3+}$ ions. However, it is safely concluded that the structural quality is similar for all RE dopants.

3.3. Transport and magnetic properties

Figure 3 summarizes the $\rho$–$T$ curves for epitaxial films of (a) $(\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2$, (b) $(\text{Ba}_{1-x}\text{Pr}_x)\text{Fe}_2\text{As}_2$ and (c) $(\text{Ba}_{1-x}\text{Nd}_x)\text{Fe}_2\text{As}_2$ for various values of $x_{\text{film}}$. The inset figures are magnified views that show the resistivity drops more clearly. The $\rho$–$T$ curve of an undoped BaFe$_2$As$_2$ epitaxial film is shown in the top panel of figure 3(a) for comparison. The $\rho$ of an
undoped BaFe$_2$As$_2$ film decreases with decreasing $T$ from 300 K, and falls rapidly from $\sim$150 K, whose resistivity anomaly is associated with magnetic/structural transitions [23]. As seen in supplementary figure S3 (available from stacks.iop.org/NJP/15/073019/mmedia), a $d\rho/dT$–$T$ curve provides a clear peak and resistivity anomaly temperatures ($T_{\text{anom}}$). It should be noted that the anomalous temperature range around $T_{\text{anom}}$ for the undoped BaFe$_2$As$_2$ epitaxial film is broader than that of a single crystal [24]. However, the crystalline quality of this film ($\Delta\omega$ of the 002 diffraction $\sim$1$^\circ$) is almost the same as that of the single crystal ($\Delta\omega$ of the 002 diffraction = 0.7$^\circ$) [24]. Further, it is reported that a sharp $d\rho/dT$ curve similar to that of the single crystal is observed even in a polycrystal [25]. These results indicate that the broader
magneto-structural transition of this film does not originate from a crystalline quality issue. It is reported that a small in-plane stress applied to the BaFe$_2$As$_2$ single crystal broadens the structural transition due to the de-twinning of the crystals [26]; therefore, we speculate that a lattice-strain effect at the epitaxial film–substrate interface would be an origin of the broadening. In all dopant cases, $\rho$ at 300 K gradually decreased, and $T_{\text{anom}}$ shifted to lower temperatures as $x_{\text{film}}$ increased.

In the Ce-doping case (a), a resistivity drop without zero resistivity was observed for $x_{\text{film}} = 0.09$, but the resistivity anomaly was still observed at $T_{\text{anom}} = 70$ K. With a further increase in $x_{\text{film}}$, the resistivity anomaly was not detected in the $\rho - T$ curves, and $T_{c}^{\text{onset}}$ for a superconductivity transition appears at $x_{\text{film}} \geq 0.09$. $T_{c}^{\text{onset}}$ reached a maximum value of 13.4 K at $x_{\text{film}} = 0.15$. The resistivity transition width (defined by $\Delta T_{c} = T_{c}^{\text{onset}} - T_{c}^{\text{offset}}$, where $T_{c}^{\text{offset}}$ is the offset critical temperature determined by extrapolating a $\rho - T$ curve to zero resistivity) of this film is 4.5 K, which is doubly larger than $\Delta T_{c} = 2.7$ K of La-doped films [18] although the crystalline qualities are almost the same as seen in $\Delta\phi$, $\Delta\omega$ and $\Delta\theta$ in figures 2(b) and (c), and the dopant distribution is homogeneous, which is confirmed by both EPMA (see supplementary figure S2(a), available from stacks.iop.org/NJP/15/073019/mmmedia) and XRD (peak shift and broadening are not observed by Ce doping). Thus, the broad resistivity transition reflects a wide vortex liquid phase due to strong vortex pinning centers, similar to that of the Co-doped BaFe$_2$As$_2$ epitaxial film [27, 28]. The wide liquid phase is due to disorder in the films, which may also be the case in the Ce-doped films. $T_{c}^{\text{onset}}$ then decreased as $x_{\text{film}}$ increased further, and the resistivity drop finally disappeared at $x_{\text{film}} = 0.29$. Also, in the case of Pr doping (b), $T_{\text{anom}}$ shifted to lower $T$ values as $x_{\text{film}}$ increased and the resistivity drop was observed at $x_{\text{film}} = 0.11$. However, although $T_{\text{anom}}$ disappeared at $x_{\text{film}} = 0.18$, clear zero resistivity was not observed at least down to 2 K. On the other hand, in the Nd-doping case (c), the resistivity drop was observed at $x_{\text{film}} = 0.13$, but larger values of $x_{\text{film}}$, where the resistivity anomaly is completely suppressed, could not be obtained because of the low solubility limit of the Nd dopant. The maximum transition temperatures of the resistivity drop are 6.2 and 5.8 K for Pr and Nd doping, respectively, but each film did not get into a clear superconducting state.

To confirm that the observed resistivity drops originate from superconducting transitions, we measured the magnetic field dependence of the $\rho - T$ curves and the temperature dependence of the magnetic susceptibilities ($\chi - T$) for epitaxial films of (Ba$_{0.85}$Ce$_{0.15}$)Fe$_2$As$_2$ (a), (Ba$_{0.82}$Pr$_{0.18}$)Fe$_2$As$_2$ (b) and (Ba$_{0.87}$Nd$_{0.13}$)Fe$_2$As$_2$ (c), whose chemical compositions were chosen to have the maximum $T_{c}^{\text{onset}}$ for each dopant (figure 4). For both measurements, the external magnetic field was applied parallel to the c-axis of the epitaxial films. For all dopants, shifts of $T_{c}$ to lower $T$ were observed under application of magnetic fields. This result strongly suggests that all the low-temperature resistivity drops originate from superconducting transitions. A clear diamagnetic signal with an SVF of up to 10% at $< 4$ K was observed only in the case of Ce doping. Note that the Meissner effect starts to appear at a temperature of $T_{c}^{\text{Meissner}} \sim 7.8$ K, which is almost the same as $T_{c}^{\text{zero}} \sim 8.0$ K where the resistivity reaches zero. However, the SVFs of the superconducting phases in the Pr- and Nd-doped films are very low because no Meissner effect is observed in their $\chi - T$ curves. This observation suggests the possibility that the observed resistivity drops in the Pr- and Nd-doped films come from a superconducting transition from impurity phases; however, the impurity phase detected by XRD (figure 1) was only Fe, which does not show superconductivity at $T \geq 2$ K. It is hard to consider that an amorphous impurity caused the superconductivity-like resistivity drops; therefore, we consider that the Meissner effect was not observed for the Pr- or Nd-doped film because $T_{c}^{\text{Meissner}}$ would be lower than the temperature range examined in this study (i.e. $< 2$ K). As a consequence,
we conclude that the resistivity drops are caused by superconducting transitions of the Pr- and Nd-doped BaFe$_2$As$_2$ phases. Considering that perfect diamagnetism with an SVF of 100% at $T < 7 \, \text{K}$ was obtained in the case of non-magnetic La-doped (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$ epitaxial films with maximum $T'_{\text{onset}} = 22.4 \, \text{K}$ [18], it seems that the doping of RE with 4f electrons decreases the SVF of its superconducting phases in the extreme. This result is markedly different from that in the case of the (Ca$_{1-x}$RE$_x$)Fe$_2$As$_2$ crystals because the maximum $T'_{\text{onset}}$ of the RE-doped CaFe$_2$As$_2$ single crystal increases in the order of RE = La, Ce, Pr and Nd, which is opposite to the present (Ba$_{1-x}$RE$_x$)Fe$_2$As$_2$ case [13–16].

3.4. Electronic phase diagrams

Figure 5 summarizes the electronic phase diagrams for the (Ba$_{1-x}$RE$_x$)Fe$_2$As$_2$ epitaxial films. The electronic phase diagram of (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$ epitaxial films is also shown in the figure for comparison [18]. For all RE dopants, the antiferromagnetic (AFM) transition at $T_{\text{anom}}$ is suppressed as $x_{\text{film}}$ increases, but the suppression rate of $T_{\text{anom}}$ is different for different dopants; i.e. it decreases in the order of RE = La, Ce, Pr and Nd. The vertical arrows, which indicate the extrapolated intersections at the $x_{\text{film}}$ axis by using a phenomenological fit to $T_{\text{anom}}$, indicate this trend more clearly. The extrapolated $x$-point (critical $x$), where the resistivity anomaly would disappear completely, shifts to higher $x_{\text{film}}$ values in the order of La, Ce and Pr doping (in the case of Nd doping, the extrapolation is unavailable because of the low solubility limit).

The plots of $T'_{\text{onset}}$ for the (Ba$_{1-x}$Ce$_x$)Fe$_2$As$_2$ epitaxial films form a dome-shaped structure in the $0.06 \leq x_{\text{film}} \leq 0.28$ range. Also, in the cases of Pr and Nd doping, $T_c$ appeared at $x_{\text{film}} > 0.1$ as $T_{\text{anom}}$ shifted to the lower $T$ side. However, unlike the Ce-doping case, neither of the superconducting domes extended to an over-doped region. The maximum $T'_{\text{onset}}$ values for the (Ba$_{1-x}$Ce$_x$)Fe$_2$As$_2$ and (Ba$_{1-x}$Pr$_x$)Fe$_2$As$_2$ films were obtained at their critical $x$-points of $\sim 0.15$ and $\sim 0.18$, respectively. The coexistence of superconductivity with an AFM state is stabilized only in the doping region that is lower than the critical $x$. The superconducting dome shape and the coexistence of AFM with superconductivity are qualitatively similar to those observed in the (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$ epitaxial films, but the superconducting dome is slightly shifted to higher $x_{\text{film}}$ values and the height of the dome becomes smaller than that of (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$, suggesting that the maximum $T'_{\text{onset}}$ at the critical $x$ point decreases depending on the RE dopant.
Figure 5. Electronic phase diagrams of \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) epitaxial films. The diamonds, circles, squares and triangles represent phase diagrams for the epitaxial films of \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) [18], \((\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2\), \((\text{Ba}_{1-x}\text{Pr}_x)\text{Fe}_2\text{As}_2\) and \((\text{Ba}_{1-x}\text{Nd}_x)\text{Fe}_2\text{As}_2\), respectively. \(T_{\text{anom}}\) and \(T_{\text{onset}}\) are indicated by the closed and open symbols, respectively. The vertical dashed/dotted lines indicate the solubility limits for the dopants. The dashed curves show phenomenological fits to \(T_{\text{anom}}\) as a function of \(x_{\text{film}}\), and the bottom vertical arrows indicate the critical points extrapolated to \(T_{\text{anom}} = 0\). The inset figure represents the c-axis lattice parameter dependences of \(T_{\text{anom}}\) and \(T_{\text{onset}}\).

species. The difference in the suppression rate of \(T_{\text{anom}}\) and the superconducting dome shift may relate to the different variations in the c-axis lattice parameters with respect to \(x_{\text{film}}\), as shown in figure 2(a). The inset figure in figure 5 replots \(T_{\text{anom}}\) and \(T_{\text{onset}}\) against the c-axis lattice parameters for the \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) epitaxial films. The suppression curves of \(T_{\text{anom}}\) converge to a single line, and the peak position of the superconducting dome converges to the same c-axis length of 1.285 nm. This result implies that both chemical pressure and carrier doping are effective for suppression of the AFM transition and induction of superconductivity in the \(\text{BaFe}_2\text{As}_2\) system [29].

4. Discussion

First, we should recall that the amounts of the Fe impurity phase in the \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) films were almost the same in all the samples with different RE dopants; therefore, the severe decrease in \(T_c\) and superconducting volume fractions cannot be explained by the impurity effects such as Fe. There are other plausible origins of the differences in the maximum \(T_{\text{onset}}\) and SVFs of the superconducting phase of \((\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2\) films with the different RE dopants. The first is structural differences, because it has been noted that the shapes and sizes of the FeAs tetrahedra critically affect the superconducting properties of iron pnictide superconductors; i.e. deviation of the As-Fe-As bonding angle from a regular tetrahedron is highly correlated with
the maximum $T_c$ values achieved [30]. Theoretical work has also shown that the Fermi surface topology is highly sensitive to the height of the As atom from the Fe sheet [31]. BaFe$_2$As$_2$ has a tetragonal crystal structure with a space group of $I4/mmm$, in which only the $z$-coordinate of the As (z$_{As}$, at the Wyckoff position 4e) site is a variable parameter. The height of the As atom from the Fe sheet (h$_{As} = c(z_{As} - 0.25)$) and the As–Fe–As angle ($\alpha = 2 \tan^{-1}(a/2h_{As})$) can therefore be estimated if the $a$-axis and $c$-axis lattice parameters and z$_{As}$ are determined. It has been reported that z$_{As}$ can be estimated from the ratio of the integrated intensities of 00l diffractions of epitaxial films in the out-of-plane XRD patterns [32]. In the Ce-doping case, it was found that z$_{As}$ only changed from z$_{As} = 0.3545$ at $x = 0$ to 0.352, even when $x_{film} = 0.29$, because the intensity ratios of the 00l diffractions showed little change, as shown in figure 1(a), which indicates that the angle $\alpha$ and h$_{As}$ primarily depend on the lattice parameters [33]. Table 1 summarizes the superconducting and structural parameters of the following optimally doped epitaxial films with critical $x$: (Ba$_{0.87}$La$_{0.13}$)Fe$_2$As$_2$ with a maximum $T_c^{onset}$ of 22.4 K, (Ba$_{0.83}$Ce$_{0.15}$)Fe$_2$As$_2$ with a $T_c^{onset}$ of 13.4 K and (Ba$_{0.82}$Pr$_{0.18}$)Fe$_2$As$_2$ with a $T_c^{onset}$ of 6.2 K. The lattice parameters and the structural parameters, such as z$_{As}$, h$_{As}$ and the $\alpha$ angles, are almost the same for each dopant. Density functional structure relaxation calculations for the models of (Ba$_{3/4}$RE$_{1/4}$)Fe$_2$As$_2$ supported this result in that there is no remarkable difference in z$_{As}$, h$_{As}$ and the $\alpha$ angles for different RE dopants. These results indicate that the difference in the maximum $T_c$ and the SVFs of the superconducting phases cannot be explained in terms of the difference in the local structure.

Another plausible origin is the different electronic properties that originate from the different numbers of RE 4f electrons. It should be noted that the resistivity upturn at $< T_{min} $ is residual resistivity, for breaking of the superconducting electron pair is the interaction between the localized RE 4f electrons and the Fe 3d conduction electrons [34]. The contribution of the magnetic RE ions to the electron scattering can be estimated by comparing the electronic properties of the RE-doped samples with those of the non-magnetic reference (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$ epitaxial films, because their structural differences are negligible, as shown in figure 2 and table 1.

The excess resistivity caused by magnetic scattering should give rise to a negative magnetoresistance (MR), because a high magnetic field suppresses spin inversion and scattering [35]. To clarify the magnetic scattering behavior, the field dependence of MR, which is defined as $[\rho(\mu_0 H) - \rho(0)]/\rho(0) \times 100$, was measured at 30 K under fields of up to $\mu_0 H = 9$ T applied parallel to the $c$-axis and at the dc current in the $ab$-plane of the epitaxial film. Figures 6(a)–(c) show the MR for epitaxial films of (Ba$_{1-x}$La$_x$)Fe$_2$As$_2$ with $x_{film} = 0.06–0.29$, (Ba$_{1-x}$Ce$_x$)Fe$_2$As$_2$ with $x_{film} = 0.06–0.29$, and (Ba$_{1-x}$Pr$_x$)Fe$_2$As$_2$ with $x_{film} = 0.06–0.18$. No
The MR observed on the La-doped films is explained very well by the MR \(\text{SDW} \pm \alpha H^2\) model, as shown by the fitting curves in figure 6(a). The fitted parameters are summarized in table 2. The \(\beta\) values

### Table 1. Summary of the superconducting and structural properties of optimally doped epitaxial films of \((\text{Ba}_{0.87}\text{La}_{0.13})\text{Fe}_2\text{As}_2\), \((\text{Ba}_{0.85}\text{Ce}_{0.15})\text{Fe}_2\text{As}_2\) and \((\text{Ba}_{0.85}\text{Pr}_{0.18})\text{Fe}_2\text{As}_2\).

| Film                        | \(T_c^\text{onset}\) (K) | \(c\) (nm) | \(a\) (nm) | \(z_{\text{As}}\) | \(h_{\text{As}}\) (nm) | \(\alpha\) (deg) |
|-----------------------------|---------------------------|------------|------------|------------------|--------------------------|-----------------|
| \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) | 0.13                      | 22.4       | 1.2872     | 0.3970           | 0.352                    | 0.13129         | 113.04         |
| \((\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2\) | 0.15                      | 13.4       | 1.2866     | 0.3962           | 0.352                    | 0.13123         | 112.95         |
| \((\text{Ba}_{1-x}\text{Pr}_x)\text{Fe}_2\text{As}_2\) | 0.18                      | 6.2        | 1.2879     | 0.3952           | 0.352                    | 0.13136         | 112.76         |

### Figure 6. Field dependence of magnetoresistance \(\text{MR} = [\rho(\mu_0H) - \rho(0)]/\rho(0) \times 100\) at 30 K for epitaxial films of (a) \((\text{Ba}_{1-x}\text{La}_x)\text{Fe}_2\text{As}_2\) with \(x_{\text{film}} = 0\)–0.44, (b) \((\text{Ba}_{1-x}\text{Ce}_x)\text{Fe}_2\text{As}_2\) with \(x_{\text{film}} = 0.06\)–0.29 and (c) \((\text{Ba}_{1-x}\text{Pr}_x)\text{Fe}_2\text{As}_2\) with \(x_{\text{film}} = 0.06\)–0.18. The \(x_{\text{film}}\) values for each MR are indicated in the figures. The solid red lines in (a) represent the fitting results with the MR\(\text{SDW}\) model, and those in (b) and (c) show the fitting results with an MR\(\text{SDW} - \alpha H^2\) model. The dotted lines in (b) and (c) indicate the fitting results with an MR\(\text{SDW} - \beta \log H + \text{const}\) and the arrows represent the transition point from a \(-\alpha H^2\) dependence to a \(-\alpha \log H\) dependence.
increase and \( \mu_0 \) decreases with increasing \( x_{\text{film}} \), while the \( \gamma \) values remain constant, which is consistent with the La-doping result that La doping increased the majority carriers (electrons) and decreased their mobilities. The MR became undetectable at higher \( x_{\text{film}} \) values of 0.13–0.44, which is similar to the behavior of \( \text{Ba(Fe}_{1-x}\text{Co}_{x})_2\text{As}_2 \) single crystals [40]. On the other hand, in the cases of magnetic Ce and Pr doping, a negative MR appeared as \( x_{\text{film}} \) increased. It has been reported that MR with magnetic scattering represents a \(-H^2\) dependence at low fields, and it then follows a \(-\log H\) dependence after sufficient suppression of the spin inversion [41, 42]. It is seen that carrier doping into the \( \text{BaFe}_2\text{As}_2 \) films by the non-magnetic La dopants generates MR_{SDW} only, while negative MR expressed by \(-H^2\) and \(-\log H\) are superimposed for the magnetic Ce- and Pr-doping cases. The fitting results are shown by the curves in figures 6(b) and (c). The coexistence of a positive MR and a weak negative MR with \(-H^2\) dependence was observed for low \( x_{\text{film}} < 0.12 \). With an increase in \( x_{\text{film}} \), the positive MR disappeared and only the negative MR was then observed. In the case of Ce doping with \( x_{\text{film}} \) up to 0.18, the negative MR showed a \(-H^2\) dependence at fields up to 9 T. The MR at larger values of \( x_{\text{film}} \) up to 0.29 deviates from the \(-H^2\) dependence at a higher value of \( \mu_0 H \) of 3 T and showed a transition to the \(-\log H\) dependence. With a decrease in temperature from 30 to 2 K, the negative MR becomes larger and the transition \( H \) value from the \(-H^2\) dependence to the \(-\log H\) dependence shifts to lower fields (see supplementary figure S4 (available from stacks.iop.org/NJP/15/073019/mmedia) for MR measured at 30, 10 and 2 K for (\( \text{Ba}_{0.72}\text{Ce}_{0.28})\text{Fe}_2\text{As}_2 \) epitaxial films). In addition, the negative MR along the \( ab\)-plane is much smaller than that along the \( c\)-axis. This result indicates that AFM spin ordering parallel to the \( c\)-axis and ferromagnetic ordering parallel to the \( ab\)-plane affect the negative MR (see supplementary figure S4). Also, in the Pr-doping case, the field dependence changed from \(-H^2\) to \(-\log H\) in the negative MR observed at a high \( \mu_0 H \) of 2.5 T, even at a low \( x_{\text{film}} \) value of 0.18. With an increase in the number of 4f electrons from the RE dopants, the negative MR increased (the observed maximum negative MR = \(-0.15\) % for Ce doping and \(-0.42\) % for Pr doping with the same \( x_{\text{film}} \) value of 0.18). No observation of the negative MR in the (\( \text{Ba}_{1-x}\text{La}_x\))\( \text{Fe}_2\text{As}_2 \) films and the enhanced negative MR in the Ce- and Pr-doping cases, which is associated with spin flip magnetic scattering of the charge carriers, indicate that the interaction between the 4f electrons and the conduction 3d electrons is enhanced in the order from Ce to Pr doping. This would cause the electron pair breaking that is responsible for the suppression of superconductivity in the magnetic RE-ion-doped (\( \text{Ba}_{1-x}\text{RE}_x\))\( \text{Fe}_2\text{As}_2 \) epitaxial films.

As noted at the end of section 3.3, the variation of \( T_c \) with the RE dopant is opposite between the present (\( \text{Ba}_{1-x}\text{RE}_x\))\( \text{Fe}_2\text{As}_2 \) epitaxial films and the (\( \text{Ca}_{1-x}\text{RE}_x\))\( \text{Fe}_2\text{As}_2 \) single

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**Table 2.** Summary of the fitting parameters using the model [37] for the MR of (\( \text{Ba}_{1-x}\text{La}_x\))\( \text{Fe}_2\text{As}_2 \) epitaxial films. Errors are indicated in the values in parentheses.

| \( x_{\text{film}} \) | \( T \) | \( \beta \) | \( \gamma \) | \( \mu_0 \) (m\(^2\)V\(^{-1}\)s\(^{-1}\)) |
|-----------------|-----|-----|-----|------------------|
| 0 in (\( \text{Ba}_{1-x}\text{La}_x\))\( \text{Fe}_2\text{As}_2 \) film | 30 | 34.0 (±0.1) | 1.75 (±0.05) | 0.151 (±0.001) |
| 0.02 in (\( \text{Ba}_{1-x}\text{La}_x\))\( \text{Fe}_2\text{As}_2 \) film | 30 | 79.0 (±0.3) | 1.25 (±0.06) | 0.0740 (±0.0001) |
| 0.08 in (\( \text{Ba}_{1-x}\text{La}_x\))\( \text{Fe}_2\text{As}_2 \) film | 30 | 98.7 (±0.8) | 1.52 (±0.06) | 0.0430 (±0.0004) |
| \( \text{BaFe}_2\text{As}_2 \) single crystal [37] | 50 | 44.5 | 1.14 | 0.16 |
crystals; i.e. the maximum $T_c$ of the $(\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ epitaxial films decreases in the order of $\text{RE} = \text{La, Ce, Pr and Nd}$, while that of the $(\text{Ca}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ single crystals increases in this order [13–16]. The origins of this difference would be classified to an intrinsic effect and an extrinsic effect. To clarify the extrinsic effect originating from the different crystal structure parameters and crystalline quality between the thin films and the single crystals, we should use epitaxial films of RE-doped CaFe$_2$As$_2$ epitaxial films; however, unfortunately, epitaxial thin film growth of CaFe$_2$As$_2$ by PLD has not been attained [21]. Here, we would like to discuss plausible intrinsic origins. One possible origin of this discrepancy may be the structural transition in $(\text{Ca}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$. It should be noted that $(\text{Ca}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ transits easily to a collapsed tetragonal structure by replacing the Ca site with a smaller RE dopant, such as Pr and Nd [13]. In the thin film samples used here, the local structures of the $(\text{Ba}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ films remained almost unchanged for different RE dopants, implying that the film’s electronic structures are not changed drastically by the RE doping. Therefore, it would be possible that the structural flexibility to a collapsed structure in $(\text{Ca}_{1-x}\text{RE}_x)\text{Fe}_2\text{As}_2$ contributes to the high $T_c$.

5. Conclusions

A non-equilibrium PLD process was used to stabilize non-magnetic/magnetic RE ($= \text{La, Ce, Pr and Nd}$) dopants in BaFe$_2$As$_2$, and their superconductivities were examined with respect to the 4f electrons of RE dopants. The indirect electron doping of each RE element produced superconductivity along with suppression of the resistivity anomaly, which is associated with magnetic/structural phase transitions. The La and Ce doping induced bulk superconductivity at a maximum $T_c^{\text{onset}}$ of 22.4 K at $x_{\text{film}} = 0.13$ for La doping and 13.4 K at $x_{\text{film}} = 0.15$ for Ce doping. In the cases of Pr and Nd doping, the superconducting transitions started from $T_c^{\text{onset}} = 6.2$ and 5.8 K, respectively, while zero resistivity and diamagnetism were not observed. The severe decrease in $T_c^{\text{onset}}$ and SVFs upon RE doping from non-magnetic La to magnetic Ce and Pr is attributed to magnetic electron pair breaking, as evidence of the magnetic electron scattering and the negative MR, with interaction between the localized 4f electrons and the Fe 3d conduction electrons.

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