Superconducting Transition Temperatures of up to 47 K from Simultaneous Rare-Earth Element and Antimony Doping of 112-Type CaFeAs$_2$

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The effects of simultaneous Sb doping on the superconductivity of 112-type Ca$_{1-x}$RE$_x$FeAs$_2$ ($RE = \text{La, Ce, Pr, and Nd}$) were studied through measurements of the magnetization and electrical resistivity. In Sb-free materials, the superconducting transition temperature $T_c$ of the La-doped sample was 35 K, while those of the Pr- and Nd-doped samples were $\sim$10 K; no superconductivity was observed in the Ce-doped sample. Sb doping increased the $T_c$ of all RE-doped samples: $T_c$ increased to 47, 43, and 43 K for $RE = \text{La, Ce, Pr, and Nd}$, respectively. We also found that the enhanced superconductivity results from the increase in the lattice parameter $b$, which increases the As-Fe-As bond angle to be closer to the ideal tetrahedron value. These observations provide insight for further increasing the $T_c$ of the 112 phase.

The discovery of iron-based superconductors has stimulated the development of novel superconducting materials such as $REFeAsO$ ($1111$ type),$^4$ $AFe_2As_2$ ($122$ type),$^5,6$ $AFeAs$ ($111$ type),$^7$ and FeSe ($11$ type)$^8$ that contain rare-earth ($RE$), alkali-earth ($AE$), and alkali ($A$) elements, as well as the development of compounds with perovskite- and/or rocksalt-type$^9,12$ and pyrite-type spacer layers.$^{13-18}$ For this class of materials, the maximum superconducting transition temperature $T_c$ is 55 K,$^{19}$ and new iron-based superconducting materials will need to be developed to further increase $T_c$.

To this end, novel 112-type iron arsenides of Ca$_{1-x}$La$_x$FeAs$_2$, Ca$_{1-x}$Pr$_x$FeAs$_2$, and Ca$_{1-x}$RE$_x$FeAs$_2$ ($RE = \text{Ce, Nd, Sm, Eu, and Gd}$) reported by Katayama et al.,$^{20}$ Yakita et al.,$^{21}$ and Sala et al.,$^{22}$ respectively, have received considerable attention, and it has been recognized that the $RE$ substitution is necessary for stabilizing the 112 phase.$^{20-22}$ These compounds crystallize in a monoclinic structure with a space group of $P2_1$ (No. 4)$^{20}$ or $P2_1/m$ (No. 11)$^{21,22}$ and consist of alternately stacked FeAs and arsenic zigzag bond layers, which are a notable feature. The arsenic zigzag bond layers are considered to be composed of As$^-$ ions with a $4p^4$ configuration as found in $RETAs_2$ ($T = \text{Ag, Au}$).$^{23}$ Thus, the chemical formula for these compounds can be written as (Ca$_{2+x}$$RE^{1+x}$)(Fe$_2$As$_3$)$_{2-x}$ where $x$ is an integer. Most 112-type iron arsenides exhibit superconductivity: La-doped compounds show bulk superconductivity at 35 K,$^{24}$ while Pr-, Nd-, Sm-, Eu-, and Gd-doped compounds show superconductivity at 10–15 K with a small shielding volume fraction (VF) of 5–20%.$^{21,22}$ Ce-doped compounds rarely exhibit superconductivity.$^{22}$

Recently, it was reported that the simultaneous doping of isovalent P or Sb drastically improves the superconductivity in the La-doped 112 phase: $T_c$ increased to 41 and 43 K as a result of 0.5% P and 1% Sb doping, respectively.$^{24}$ In this Letter, we report that a large amount of Sb doping further increases the $T_c$ of Ca$_{1-x}$La$_x$Fe(As$_{1-y}$Sb)$_y$ to 47 K, which is the second highest $T_c$ after 1111-type iron-based superconductors. Moreover, we show that bulk superconductivity at 43, 43, and 43 K is induced by the simultaneous Sb doping of Ca$_{1-x}$RE$_x$FeAs$_2$ with $RE = \text{Ce, Pr, and Nd}$, respectively, and that an increase in the lattice parameter $b$, which modifies the As-Fe-As bond angle, is important for optimizing the superconductivity in the 112 phase.

Single crystals of Ca$_{1-x}$RE$_x$Fe(As$_{1-y}$Sb)$_y$ ($RE = \text{La, Ce, Pr, and Nd}$) were grown by heating a mixture of Ca, $RE$, FeAs, and Sb powders with nominal compositions of $x = 0.10$ and $0.00 \leq y \leq 0.10$ (grown quantities of the 112 phase drastically decrease for $y \geq 0.20$). A stoichiometric amount of the mixture was then placed in an aluminum crucible and sealed in an evacuated quartz tube. Samples were prepared in a globe box filled with argon gas. The ampules were heated at 700 °C for 3 h, heated to 1100 °C at a rate of 46 °C/h, and then cooled to 1050 °C at a rate of 1.25 °C/h before furnace cooling. The obtained samples were characterized by powder X-ray diffraction (XRD) using a Rigaku RINT-TTR III X-ray diffractometer with CuK$_\alpha$ radiation and by single-crystal XRD using a Rigaku Single Crystal X-ray Structural Analyzer (Varimax with Saturn). Ca$_{1-x}$RE$_x$Fe(As$_{1-y}$Sb)$_y$ samples were obtained together with a powder mixture of $REAs$, FeAs, FeAs$_2$, and CaFe$_2$As$_2$. The single crystals of Ca$_{1-x}$RE$_x$Fe(As$_{1-y}$Sb)$_y$ separated from the
were determined from the onset of the diamagnetism, which is characteristic of the superconducting transition. Electrical resistivity \( \rho_{ab} \) parallel to the \( ab \) plane was also measured using a standard DC four-terminal method in a Quantum Design physical property measurement system (PPMS).

The enhancement in the superconductivity of the Sb-doped Ca\(_{1-x}\)La\(_x\)FeAs\(_2\) can be observed in the temperature dependence of \( M \) shown in Fig. 1(a). Previous studies\(^{20,24}\) have reported that La-doped samples with \( y = 0.00 \) show diamagnetic behavior below \( T_c = 34 \) K\(^{20}\) and \( T_c \) increased to 43 K for \( y = 0.01\)\(^{24}\). The values of VF at the lowest temperatures were previously estimated to be 66% and 78% for \( y = 0.00\)\(^{20}\) and 0.01,\(^{24}\) respectively, indicating bulk superconductivity. We found that a large amount of Sb doping leads to a further increase in \( T_c \) to 47 K. As shown in Fig. 1(a), the La-doped sample with \( y = 0.10 \) exhibits clear diamagnetic behavior below \( T_c = 47 \) K, and the VF at 2 K was estimated to be approximately 100%, which supports the emergence of bulk superconductivity. Further evidence of the enhanced superconductivity was obtained from the temperature dependence of \( \rho_{ab} \), as shown in Fig. 1(b). We found that \( \rho_{ab} \) for the La-doped \( y = 0.10 \) sample exhibited a sharp drop below 49 K, and zero resistivity was observed at 47 K; both these temperatures are much higher than those of the \( y = 0.00\)\(^{20}\) and 0.01\(^{24}\) samples.

The increased \( T_c \) of Ca\(_{1-x}\)La\(_x\)Fe(As\(_{1-y}\)Sb\(_y\))\(_2\) can be explained by two effects originating from the simultaneous Sb doping: a decrease in the La content and an increase in the cell volume. In Ca\(_{1-x}\)La\(_x\)FeAs\(_2\), it is known that \( T_c \) increases with decreasing \( x \) and exhibits a maximum value of 35 K at the lowest \( x \) of 0.15,\(^{24}\) as shown in Fig. 2(a); a sample with a lower \( x \) could potentially have a higher \( T_c \). Simultaneous Sb

![Figure 1](image1.png)

**Fig. 1.** (Color online) (a) Temperature dependence of the magnetization \( M \) of Ca\(_{1-x}\)La\(_x\)Fe(As\(_{1-y}\)Sb\(_y\))\(_2\) measured at a magnetic field \( H \) of 30 Oe parallel to the \( ab \) plane under zero-field-cooling and field-cooling conditions. (b) Temperature dependence of the electrical resistivity \( \rho_{ab} \) of Ca\(_{1-x}\)La\(_x\)Fe(As\(_{1-y}\)Sb\(_y\))\(_2\) parallel to the \( ab \) plane.

![Figure 2](image2.png)

**Fig. 2.** (Color online) Dependence of the (a) \( T_c \), (b) cell volume, (c) \( a \) and \( b \) parameters, (d) \( c \) parameter, and (e) \( \beta \) angle of Ca\(_{1-x}\)La\(_x\)Fe(As\(_{1-y}\)Sb\(_y\))\(_2\) on \( x \).
doping allows the La content to be reduced to $x = 0.12$, and as expected, $T_c$ increased to 47 K. In general, chemical substitution modifies the number of charge carriers and induces a chemical pressure. The primal role of La doping is charge carrier modification because the cell volume [Fig. 2(b)] and lattice parameters$^{24}$ [Figs. 2(c), (d), and (e)] of Ca$_{1-x}$La$_x$FeAs$_2$ exhibit no significant changes upon La doping owing to the similar ionic radii of Ca$^{2+}$ and La$^{3+}$. Thus, a decrease in the La content corresponds to a reduction in the number of charge carriers. Secondly, simultaneous Sb doping applies a negative chemical pressure that increases the cell volume, as shown in Fig. 2(b), because the ionic radius of Sb$^{3+}$ (Sb$^-$) is larger than that of As$^{3-}$ (As$^-$). The increased cell volume is a result of an increase in the in-plane lattice parameters $a$ and $b$, as shown in Fig. 2(c); in contrast, the $c$ parameter hardly changes, as shown in Fig. 2(d). In iron-based superconductors, the expansion can effectively optimize the superconductivity, which is sensitive to modifications in the crystal structure. $^{25-28}$ Note that the enhancement of $T_c$ by 0.5% P doping in the La-doped system, which was reported in our previous article,$^{24}$ should be attributed to a different mechanism because the small amount of P doping$^{29}$ neither reduced the La content nor changed the lattice parameters.$^{24}$ However, the exact mechanism is still unclear.

A similar enhancement in the superconductivity was also observed in Sb-doped Ca$_{1-x}$RE$_x$FeAs$_2$ (RE = Ce, Pr, and Nd). As shown in Figs. 3(a), (b), and (c), in the Sb-free samples, the Ce-doped system shows no bulk superconductivity down to 2 K, while the Pr- and Nd-doped systems exhibit superconductivity at 10 and 11 K, respectively, with a small VF of 5%. These results are consistent with previous reports.$^{21,22}$ Sb doping resulted in higher $T_c$ values of 21 and 43 K in Ce-doped systems of $y = 0.01$ and 0.10, respectively, 26 and 43 K in Pr-doped systems of $y = 0.01$ and 0.05, respectively, and 24 and 43 K in Nd-doped systems of $y = 0.01$ and 0.05, respectively. Thus, we found that Sb-doped 112 phase samples have a $T_c$ of higher than 40 K irrespective of RE. More importantly, Sb substitution resulted in a substantial increase in the VF, indicating the emergence of bulk superconductivity. Evidence of the enhanced superconductivity was also found in the temperature dependence of $\rho_{ab}$. As shown in Figs. 3(d), (e), and (f), $\rho_{ab}$ of Ca$_{1-x}$RE$_x$Fe(As$_{1-y}$Sb$_y$)$_2$ (RE = Ce, Pr, and Nd) with $y = 0.05$ was zero at 37, 43, and 37 K, respectively; these temperatures are much higher than those (5, 9, and 13 K) of the Sb-free samples. Note that the zero resistivity observed in the Sb-free Ca$_{1-x}$Ce$_x$FeAs$_2$ sample is attributed to filamentary superconductivity because there is no visible diamagnetic signal at $T_c$. In Ca$_{1-x}$RE$_x$Fe(As$_{1-y}$Sb$_y$)$_2$ (RE = Ce,
Pr, and Nd), while we have observed the importance of the volume effect [Figs. 4(a) and (b)] in the enhanced superconductivity in the same manner as discussed for the La-doped system, the precise $x$ and $y$ dependences of the $T_c$ are still unclear.

On considering the well-known relation between $T_c$ and local structure in the iron-based superconductors, the increase in the $b$ parameter is the most important factor that determines the volume effect, which enhances superconductivity, is the increase in the $b$ parameter. In general, iron-based superconductors with high $T_c$ values are slightly larger than the ideal value: $\alpha = 109.47^\circ$.\textsuperscript{4,5,25-28} The $ab$ parameter, which improves the As-Fe-As bond angle, is a key factor for enhancing the superconductivity in the 112 phase.\textsuperscript{31} On the other hand, Sb doping does not modify $h_{pn}$ as much, because the $c$ parameter is almost insensitive to Sb doping [Fig. 4(b)]. In both Sb-free and Sb-doped samples, the $h_{pn}$ values are slightly larger than the ideal value: $h_{pn} = 1.418$ and 1.408 Å in the Sb-free\textsuperscript{20} and Sb-doped samples, respectively. We expect that the $T_c$ of the 112 phase can be increased above 50 K, if the $b$ parameter can be increased to approximately equal $a$ and, simultaneously, the $c$ parameter can be slightly decreased.

In summary, the effects of Sb doping on the $T_c$ of 112-type Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ ($RE = La, Ce, Pr, and Nd$) were studied through measurements of the magnetization and electrical resistivity. Sb-doping results in an increase in $T_c$ such that the $T_c$ values of Sb-doped Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ with $RE = La, Ce, Pr, and Nd$ were 47, 43, 43, and 43 K, respectively. We found that the increase in the $b$ parameter, which improves the As-Fe-As bond angle, is important for enhancing the superconductivity in the 112 phase.

Acknowledgments This work was partially supported by Grants-in-Aid for Scientific Research (B) (26287082) and (C) (25400572) from the Japan Society for the Promotion of Science (JSPS) and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) from JSPS.

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29) By doping $P$ in a range of more than 1%, the La doped 112 phase was not obtained.
30) The values of $\alpha$ and $h_{pn}$ were determined on the basis of the crystal structure with the space group $P2_1$ proposed by Katayama et al.\textsuperscript{29} We have checked that they are nearly unchanged even when using the space group $P2_1/m$ proposed by Yakita et al.\textsuperscript{24} The increased $\alpha$ parameter [Fig. 4(a)] results in an increased $\alpha_b$, but the nearly ideal condition of $\alpha_a$ in the Sb-free sample remains almost unchanged in the Sb-doped sample.