Superconducting state in (Eu$_{1-x}$Ca$_x$)RbFe$_4$As$_4$ with 1144-type Structure

K. Kawashima$^{1,2}$, S. Ishida$^2$, K. Oka$^2$, H. Kito$^2$, N. Takeshita$^2$, H. Fujihisa$^2$, Y. Gotoh$^2$, K. Kihou$^1$, H. Eisaki$^2$, Y. Yoshida$^2$, and A. Iyo$^2$

$^1$IMRA Material R&D Co., Ltd., Kariya, Aichi 448-0032, Japan
$^2$National Institute of Advanced Industrial Science and technology (AIST), Tsukukba, Ibaraki 305-8568, Japan
E-mail: kenji.kawashima@aisin.co.jp

Abstract. We report the Ca substitution effect of the Fe-based superconductor EuRbFe$_4$As$_4$ with 1144-type structure (crystal system: tetragonal, space group: P4/mmm (No. 123)), in order to elucidate the relationship between the superconductivity and the magnetic order. The lattice constant systematically changed with the Ca concentration $x$. By Ca-substitution, the magnetic order is suppressed, while $T_c$ is almost unchanged. The results indicate that the superconductivity of EuRbFe$_4$As$_4$ is not sensitive to the magnetic order.

1. Introduction

Since the superconductivity in La(O,F)FeAs has discovered$^{11}$, variety of Fe-based superconductors have been reported. Recently discovered $AeAFe_4As_4$ ($Ae = Ca, Sr, Ba, Eu, A = K, Rb, Cs$), which is so-called 1144-type compounds, is one of the Fe-based superconductors$^{2-5}$. $AeAFe_4As_4$ has a tetragonal structure (space group: P4/mmm (No. 123)) that consists of alternate stacking of two inequivalent ThCr$_2$Si$_2$ structures, namely, $AeFe_2As_2$ and $AFe_2As_2$ (inset of Fig. 1(a)) and shows the superconductivity with superconducting transition temperature: $T_c = 31 \sim 36$ K. The $T_c$ values of 1144 compounds are closed to that of 122-type superconductors, $Ae_1,AFe_2As_2$ ($Ae = Ca, Sr, Ba, Eu, A = Na, K$)$^{7-9}$. However, the $Ae : A$ ratio in the 1144-type crystal structure is fixed to be 1 : 1, because the $Ae$ and the $A$ ions do not occupy crystallographically equivalent sites in the 1144-type crystal structure. In the case of $EuAFe_4As_4$ ($A = Rb, Cs$), besides the bulk superconductivity with $T_c = 36$ K, the magnetic transition takes place at $T_m = \sim 15$ K, indicating the coexistence of the superconductivity and the magnetic order. The magnetic order comes from the localized spin on Eu$^{2+}$ ions$^{10}$. The magnetic transition was only confirmed in the magnetic susceptibility data. In the case of the related 122-type compound, $EuFe_2As_2$, it is known that the antiferromagnetic order plays an important role$^{11}$.

In this paper, we investigate the physical properties of the Ca-substituted samples of (Eu$_{1-x}$Ca$_x$)RbFe$_4$As$_4$ to clarify the competition between the superconductivity and the magnetic order in the 1144 system.

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2. Experimental details
Polycrystalline samples of Eu_{1-x}Ca_{x}RbFe_{2}As_{4} (x = 0.0, 0.25, 0.5, 0.75, 1.0) were synthesized by a conventional solid state reaction using the stainless steel (SUS) pipe and cap method as described in Ref. 7. Details of the synthesis condition are given in Ref. 2. A powder x-ray diffraction (PXRD) pattern was measured at room temperature using CuKα radiation to evaluate the composition dependence of the lattice parameters. Intensity data were collected over a 2θ range from 5 to 80° at 0.01° step width. Magnetic susceptibility measurements were performed under a magnetic field H of 10 Oe using a magnetic-property measurement system (MPMS) (Quantum Design, MPMS-XL7). Data were collected during warming after zero-field cooling (ZFC) and then during field cooling (FC).

3. Results and discussions
Figure 1(a) shows the PXRD pattern of the Eu_{0.5}Ca_{0.5}RbFe_{2}As_{4} sample. The main peaks can be indexed by employing a primitive tetragonal structure with space group P4/mmm (No. 123), indicating that Eu_{0.5}Ca_{0.5}RbFe_{2}As_{4} possesses the 1144-type crystal structure. There are extra reflections due to 122-type RbFe_{2}As_{4} and (Eu,Ca)Fe_{2}As_{4} impurity phases. Similar characteristic diffraction patterns were also observed for other synthesized samples, ensuring that the samples have the 1144-type crystal structure. The calculated lattice constants a and c are plotted in Fig. 1(b), which decrease linearly with increasing x, as expected from the Vegard’s law. No structural phase transition is recognized by substituting Ca for Eu.

![Figure 1(a): PXRD pattern of Eu_{0.5}Ca_{0.5}RbFe_{2}As_{4}](image)

Fig. 1 (a) Powder X-ray diffraction pattern of Eu_{0.5}Ca_{0.5}RbFe_{2}As_{4}. Open and filled triangles show the impurity phases of RbFe_{2}As_{4} and (Eu,Ca)Fe_{2}As_{4}, respectively. Inset shows the crystal structure of AcFe_{2}As_{4} (Program VESTA was used). (b) Ca concentration x dependence of the a- and c-axis lattice constants of Eu_{1-x}Ca_{x}RbFe_{2}As_{4}.

Figure 2(a) shows the temperature dependence of the magnetic susceptibility χ of Eu_{1-x}Ca_{x}RbFe_{2}As_{4}. The magnetic susceptibility data of all samples exhibits a large Meissner diamagnetic signal at approximately 36 K in both ZFC and ZC data, indicating the occurrence of bulk superconductivity. Because Tc of the RbFe_{2}As_{4} and (Eu,Ca)Fe_{2}As_{4} impurity phase is below 2.6 K under ambient pressure, these impurity phases do not contribute for Tc as high as 36 K. The kink behaviour in the magnetic susceptibility is observed below Tc at T = 15K for x = 0.0, T = 12K for x = 0.25, and T = 7K for x...
=0.5, respectively. These features are the signatures of the magnetic phase transition and the transition temperature, \( T_m \), decreases with increasing Ca concentration \( x \) (Fig. 2(b)). For the \( x = 0.25 \) sample, the magnetic susceptibility slightly increases near the lowest temperature. Observed \( T_m \) values of Eu\(_{1-x}\)Ca\(_x\)RbFe\(_4\)As\(_4\) are different from those of Eu\(_{1-x}\)Ca\(_x\)Fe\(_2\)As\(_2\) (\( x \leq 0.5 \))\(^{12,15} \), indicating that the behaviour is not due to the Eu\(_{1-x}\)Ca\(_x\)Fe\(_2\)As\(_2\) impurity phase.

Fig. 2 (a) Magnetic susceptibility \( \chi \) of Eu\(_{1-x}\)Ca\(_x\)RbFe\(_4\)As\(_4\) as a function of temperature \( T \). Enlarged view of the F.C. data and near \( T_c \) are shown in Fig. 2(b) and Fig. 2(c), respectively.

Fig. 3 \( T_c \) and \( T_m \) of Eu\(_{1-x}\)Ca\(_x\)RbFe\(_4\)As\(_4\) as a function of Ca concentration \( x \). \( T_c \) and \( T_m \) were defined from the \( \chi \)-\( T \) data of Fig. 2(a).

Figure 3 shows \( T_c \) and \( T_m \) as a function of \( x \). Although \( T_m \) monotonously decreases with increasing \( x \), \( T_c \) is almost unchanged. This behaviour is in contrast to the case of Eu\(_{1-x}\)Ca\(_x\)Fe\(_2\)As\(_2\), in which pressure-induced superconductivity shows up at lower pressures in the Ca-substituted samples. It is noted that the \( c \)-axis length of EuFe\(_2\)As\(_2\) sublattice in EuRbFe\(_4\)As\(_4\) is larger compared to EuFe\(_2\)As\(_2\)\(^{41} \). The longer distance between the Eu layer and the FeAs-layer in EuRbFe\(_4\)As\(_4\) would weaken the influence of the Eu\(^{2+} \) magnetic order to the superconductivity compared to EuFe\(_2\)As\(_2\).
4. Summary

We synthesized the polycrystalline sample of Eu$_{1-x}$Ca$_x$RbFe$_4$As$_4$ and characterized their properties. The lattice constants show the linear Ca concentration $x$ dependence. Superconductivity was confirmed at around 36 K in all synthesized samples. The magnetic order shows up below 15 K for EuRbFe$_4$As$_4$, which decreases with increasing $x$. On the other hand, $T_c$ does not change with $x$. These behaviors suggest that the magnetic order in the Eu-layer have little influence on the superconductivity in the 1144 system.

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