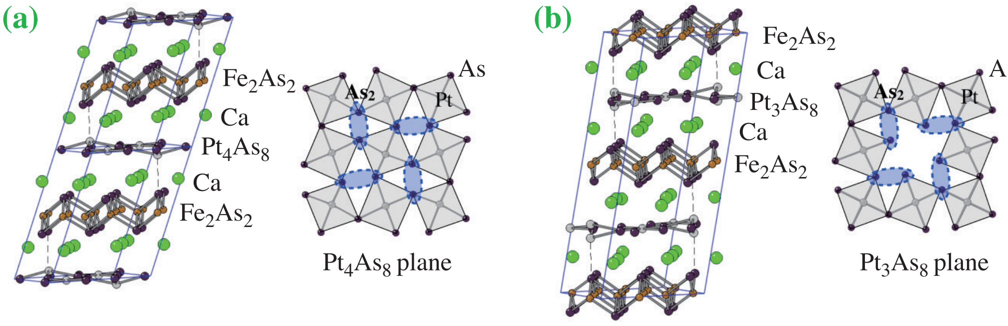
Discovery of iron-based superconductor with platinum arsenide layers

We often compare the crystal structures of copper oxide superconductors and iron-based superconductors to a sandwich. The copper oxide (CuO_2) layers of copper oxide superconductors and the iron arsenide (FeAs) layers of iron-based superconductors comprise the bread portion of the sandwich. Since we have only two types of bread at the moment, we have to be creative with the ingredients (interlayer substances) to be placed between the slices of bread to make a delicious sandwich (to raise the transition temperature of the superconductor). Three types of ingredients have been discovered for iron-based superconductors thus far. The first consists of substances made of alkaline metals and alkaline earth metals, such as lithium in LiFeAs and barium in $BaFe_2As_2$. In this group, $(Ba_{0.6}K_{0.4})Fe_2As_2$ has the highest transition temperature of 38 K. The second type consists of substances made of fluorite-type structures, such as lanthanum oxide (LaO) in LaFeAsO and calcium fluoride (CaF) in CaFeAsF. The maximum superconducting transition temperature for this group is 56 K. The third type consists of metal oxide substances; superconductivity is observed at 47 K when calcium magnesium titanium oxide $Ca_4(Mg,Ti)_3O_8$ are used. The superconductor we discovered this time —$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$— contains a fourth type of interlayer substance, $Ca_{10}(Pt_4As_8)$, which does not belong to any of the above three groups [1,2]. This ingredient shows great potential and diversity of iron-based materials, since interlayer substances with strong covalency, such as platinum arsenides, have not been available for copper oxides.

The crystal structure of α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ is shown in Fig. 1(a). This is a triclinic crystal (space group P-1) with 21 atoms in the unit cell. The interlayer substance with one less platinum, β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$, is a triclinic crystal (space group P-1) with 42 atoms in the unit cell. Synchrotron radiation X-ray diffraction experiments at beamlines **BL02B1** and **BL02B2** were essential for analyzing such complex crystal structures with low symmetry. Both α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ and β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$ have iron arsenide (FeAs) layers, with some iron (Fe) replaced by platinum (Pt). The FeAs layer, which induces superconductivity, laminates in alternating Pt_4As_8 layers in the α-phase, and Pt_3As_8 layers in the β-phase. The Ca^{2+} ions act as a glue to attach the FeAs layers and the Pt_4As_8 (Pt_3As_8) layers to each other. α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$, shown in Fig. 1(a), consists of planar quadrangles of $PtAs_4$ that are connected at a shared apex. Dimer-like As-As bonds (As_2 molecules) are formed in-plane as the $PtAs_4$ planar quadrangles rotate alternately. This kind of As_2 molecule often appears in pyrite-type structure such as $PtAs_2$. When the interlayer substance Pt is periodically absent, β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$ is obtained, as shown in Fig. 2(b).

Arsenic ion favors an electron count of As^{3-} in solid to fill up 4*p* atomic orbital. Arsenic molecule prefers to



α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ **β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$**

Fig. 1. Crystal structures of **(a)** α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ and **(b)** β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$. Thin solid lines represent unit cells. Two unit cells are shown for α-$Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ along the *c* axis, while one is shown for β-$Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$. Details of Pt_4As_8 and Pt_3As_8 layers are also shown. The dashed ellipsoids represent As_2 dimers. [2]

be $[\text{As}_2]^{4-}$ in solid to fill up π^* molecular orbital. In the present compound, there exist arsenic in the form of As^{3-} in the FeAs layers and in the form of $[\text{As}_2]^{4-}$ in the Pt_4As_8 (Pt_3As_8) layers. Thus, according to the charge balance, we estimate a formal electron count of iron and platinum to be Fe^{2+} and Pt^{2+} for $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ when $x = 0.0$. Thus $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ can be regarded as a parent compound of the present material. Superconductivity emerges when platinum is partially substituted for iron in the FeAs layers to induce additional electrons in FeAs layers. Rietveld analysis from the X-ray data gives an estimate of platinum content of $x = 0.16$ for $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$. Further electron doping can be realized for $\alpha\text{-Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$, owing to one more Pt in the Pt_4As_8 layers together with an increased Pt content in the FeAs layers ($x = 0.36$) as determined by Rietveld analysis. In the latter compound, the highest superconducting transition temperature was observed.

Data on electrical resistivity and magnetization are shown in Fig. 2(a) and 2(b), respectively. Superconductivity with a transition temperature of 38 K, which was signaled by zero resistivity and shielding effects (negative magnetization), was observed in $\alpha\text{-Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ for $x = 0.36$. Superconductivity with a transition temperature of 13 K was seen for $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ for $x = 0.16$. This demonstrates the surprising discovery that despite substituting Pt for a large portion of the primary element Fe of iron-based superconductor, superconductivity occurs at a high temperature of 38 K. In contrast, when Cu, the principal element for high-temperature superconductivity in copper oxides, is partially replaced, superconductivity does not occur owing to strong pair-breaking effects. Our findings will provide clues to the occurrence mechanisms of iron-based superconductors [3].

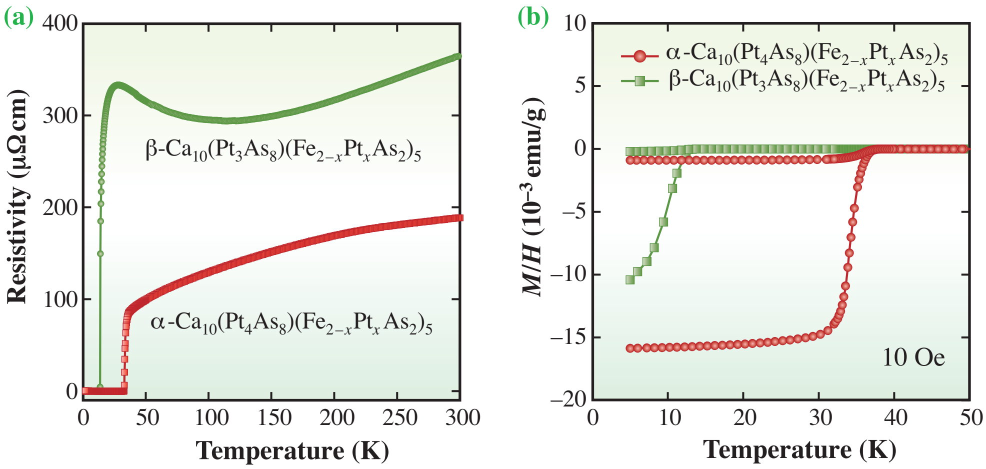


Fig. 2. Temperature dependence of **(a)** electrical resistivity and **(b)** magnetization for $\alpha\text{-Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ with $x = 0.36$ and $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ with $x = 0.16$. The former shows superconducting transition at 38 K, while the latter shows at 13 K.

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References

[1] *S. Kakiya, K. Kudo, Y. Nishikubo, K. Oku, E. Nishibori, H. Sawa, T. Yamamoto, T. Nozaka and M. Nohara: J. Phys. Soc. Jpn.* ***80*** *(2011) 093704.*
[2] *M. Nohara, S. Kakiya, K. Kudo, Y. Oshiro, S. Araki, T.C. Kobayashi, K. Oku, E. Nishibori and H. Sawa: Solid State Commun.* ***152*** *(2012) 635.*
[3] K. Ishida *et al.*: J. Phys. Soc. Jpn. **78** (2009) 062001.