Detailed Study of the Phase Diagram of Fe-based Superconductor Ba(Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}As\textsubscript{2} by Super High-Resolution Neutron Diffraction Measurements

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Abstract. Temperature (T) dependence of Bragg reflections of Ba(Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}As\textsubscript{2} (x = 0, 0.02) have been measured in detail on assembled mm-size crystallites to avoid effects of surface and/or externally induced strains with the high-resolution neutron powder diffractometer, where we have found that the profile width of the (400)\textsubscript{0}/(040)\textsubscript{0} reflections with the orthorhombic indexing begin to increase, as T decreases, at ~270 K, much higher than the tetragonal (Tet)-orthorhombic (Ort) second order transition temperature T\textsubscript{S} (~147.5 K) without showing any indication of a phase change above T\textsubscript{S}. The coexistence of two Ort phases with different orthorhombicity exists in the region of ~140 K < T < 143 K). The profile widths of (hhl)\textsubscript{0} reflections are nearly T-independent in the entire temperature region studied here (130 K ≤ T ≤ 350 K). An additional broadening due to the Co-doping is clearly found. We discuss these results in relation to the breakdown of the 4-fold symmetry of static physical quantities found in the electrical resistivity and band splitting of the 3d\textsubscript{xy} and 3d\textsubscript{yz} orbitals and conclude that the disappearance of the 4-fold symmetry even in the macroscopically tetragonal phase can be understood by the existence of orthorhombic domains induced by crystal defects and/or impurities.

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1. Introduction

In order to clarify the microscopic origin of the superconductivity of the Fe-based systems, it is important to understand their phase diagram, and because the superconductivity is found near the antiferromagnetic phase as shown in Fig. 1 for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, for example [1], the spin-fluctuation mechanism has been considered as the possible candidate [2]. On the other hand, the existence of the tetragonal (Tet)-orthorhombic (Ort) transition at temperature $T = T_S$ slightly above the magnetic transition temperature $T_N$ suggests that the orbital fluctuation (the electron occupancy fluctuation between the 3$d_{yz}$ and 3$d_{zx}$ orbitals) can be an alternative mechanism [3].

To distinguish which of the spin and orbital fluctuations is primary relevant to the superconductivity, it seems to be important to study the origin of the “nematic state” characterized by the breakdown of the four-fold symmetry ($C_4$) of static physical quantities below $T^*$, where $T^* = T_S + \eta$ ($\eta \sim 30$ K at $x \sim 0.02$) (see Fig.1), observed by transport and other experiments [4-6]. Because the in-plane anisotropy of the static quantities can be induced not by the dynamical fluctuation of the orthorhombic structure but by the static orthorhombic structure, $T^*$ should be considered to be a transition temperature to a phase without the $C_4$ symmetry, unless some local static orthorhombicity is realized. Actually, theoretical calculations carried out on the basis of the orbital-fluctuation model have pointed out that local orthorhombic domains are formed in the Tet phase through the pinning of the orbital-fluctuation by lattice imperfections such as defects and/or impurities [7]. The fact that the softening of the in-plane TA-phonons corresponding to the elastic constant $C_{66}$ is found at $T_S$ not $T^*$ seems to have a meaning in this consideration.

In order to answer the question whether $T^*$ is a well-defined transition point or induced by other extrinsic effects, we have carried out a high-resolution neutron diffraction study of the structural and magnetic transition. In this paper, we discuss what induces the nematic state and approach the issue of “spins or orbitals?”.

![Fig.1 Phase diagram of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$.](image)

2. Experiments

We used samples consisting of mm-size single crystallites of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, $x = 0$ and 0.02 to avoid external stress from (1) surface effects, which may exist in finely pulverized sample, and (2) effects of grease or other glues used to fix a single crystal sample to a holder. Using the crystallites assemblies by 10 g each, we have studied the structural transitions measuring the detailed temperature dependence of Bragg reflections related to the Tet-Ort transition. Under the stress-free conditions, we also considered effects of impurities doped to FeAs planes using samples both with and without Co dopants. The samples were grown using the flux method. Furthermore, to avoid the surface effects, we performed neutron diffraction experiments. The data were collected using a time-of-flight type diffractometer SuperHRPD (Super High-Resolution Powder Diffractometer, BL-08) at J-PARC [8]. Especially, we mainly utilize the position-sensitive detectors set near the backscattering angle to
achieve high resolution, i.e. \( \Delta \rho / \rho \sim 0.035 \% \). Throughout this paper, we used orthorhombic notation: The \((400)_0/(040)_0\) Bragg reflections, with the suffix O indicating orthorhombic notation, split below \( T_s \), for example.

3. Results and Discussion

Figure 2 shows example profiles of the \((400)_0/(040)_0\) reflections taken for BaFe\(_2\)As\(_2\). Their characteristics observed just below \( T \sim 143 \) K can be understood by considering the coexistence of two Ort phases with different orthorhombicity: The broad center peak consists of two nearly Lorentzian-type peaks from the parts with the smaller orthorhombicity than that of the outer peaks, as shown by the fitted curves. This is consistent with the results of Kim \textit{et al.} obtained by the x-ray diffraction measurement [9]. As \( T \) becomes higher than \( \sim 143 \) K, outer peak suddenly disappear, and at around \( 147.5 \) K (\( = T_s \)), the Ort splitting of the center peak becomes inappreaciable, suggesting that the system undergoes the second order transition to the macroscopically Tet phase.

With further increase of \( T \), the \((400)_0/(040)_0\) reflections, for example, exhibit significant \( T \) dependence in their linewidths \( \Delta d \) (FWHM) as shown in Figs. 3 and 4 even in the \( T \) region well above \( T_s \). In contrast, the \((hhl)_0\) Bragg reflections, e.g. the \((440)_0\) reflection, which do not split in the Ort phase, have almost negligible \( T \) dependence of their linewidths \( \Delta d \) in the entire \( T \) region studied here as shown in Fig. 3. Since \( T \) dependence becomes appreciable with decreasing \( T \), say, at \( \sim 270 \) K, the \( T \) dependent behavior of the linewidths should begin at \( T \) higher than 270 K, because the value we observed includes the resolution width. One more thing we note here is that the linewidth exhibits no anomalous \( T \) dependence indicative of a phase transition above \( T_s \). It is consistent with the fact that the softening amplitude of the elastic constant \( C_{66} \) reaches its maximum at \( T_s \) without showing any anomaly above \( T_s \) [10]. It is also consistent with the fact that no anomaly has been observed in the precise measurements of the specific heat around the \( T \) region corresponding to \( T^* \) [11].

However, experimental observations say that the breakdown of the \( C_4 \) symmetry surely exists in the static quantities in the region \( T_s < T < T^* \) [5, 12]. To understand this situation in a consistent way, we have to introduce static Ort domains. As \( T \) approaches the intrinsic Tet-Ort transition temperature, the domain size may become larger, which can explain the \( T \) dependence of the observed broadening of the profile width with increasing \( x \).

![Fig. 2 Example profiles obtained at (400)_0/(040)_0 Bragg reflections of BaFe_2As_2.](image-url)
We can find that, with increasing $x$, the linewidths increase in the high $T$-region (see Fig. 4). It is consistent with the results of ref. [7], which predict stabilization of the local orbital order by the pinning potential of Co impurities in high $T$ region above $T_S$. The fact that the softening amplitude of the $C_{66}$ mode becomes the largest at $x = 0$ [10] can be explained by this pinning model, because as the volume fraction of the Ort domain increases with increasing $x$, the softening amplitude at $T_S$ is expected to decrease. As $T$ approaches $T_S$, the Ort domains around the defects prevail and consequently, due to the oblong imbalance of the Ort domains along $a$- and $b$- axes the anisotropy of various physical properties appears.

4. Summary

We have investigated the Tet-Ort structural transition in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 0$ and 0.02, using high-resolution neutron diffraction experiments to study the $T$-$x$ phase diagram. From the $T$ and $x$ dependences of the linewidths shown in Figs. 3 and 4, we find that the orbital fluctuation model with the pinning by lattice imperfection present the explanation how the nematic phase appears. The fact that the nematic phase persists up to rather high temperature suggests that the coupling between the orbital fluctuation and lattice system is also large, which implies that the orbital fluctuation is primary relevant to the microscopic origin of the superconductivity.

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