Lower symmetrical behaviour of electronic state in the FeAs plane of $Ba(Fe_{1-x}Co_x)_2As_2$ -^{75}As NMR study-

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Abstract. To investigate the anisotropy within the FeAs plane in the tetragonal phase of $Ba(Fe_{1-x}Co_x)_2As_2$, ^{75}As NMR measurements on the electric field gradient (EFG) at the As site have been carried out for a $Ba(Fe_{1-x}Co_x)_2As_2$ single crystal of $x\sim0.08$ with the superconducting (SC) transition temperature of $T_c\sim23$ K. We present a method how to analyse the ^{75}As NMR spectra and deduce the anisotropic parameter of the EFG, η, that shows the electric in-plane anisotropy at the As site. The EFG of the As site with no Co atoms at the nearest and next nearest Fe sites has the η value of 0.08-0.10 similar to that in the non-SC samples of $x\sim0.02$ in the tetragonal phase. The in-plane anisotropy in the $x\sim0.08$ sample remains even near T_c. We discuss the relationship between the in-plane anisotropy and local physical properties.

1. Introduction

   In most Fe-based superconductors such as $LaFeAsO_{1-x}F_x$, $Ba(Fe_{1-x}Co_x)_2As_2$, and $NaFe_{1-x}Co_xAs$, an antiferromagnetic (AFM) phase with an orthorhombic structure, a paramagnetic one with a tetragonal structure, and paramagnetic and superconducting (SC) ones with a tetragonal structure appear in the phase diagram of temperature T vs. doped carrier concentration or pressure. The SC phases are located in the proximity of the AFM phases, which led on to the proposal that the AFM spin fluctuation plays a key role for making the SC pairing. Then superconducting order parameters Δ's on the different Fermi surfaces have opposite sign ($s_\pm$ symmetry of Δ) [1, 2]. However, from the early stage of studying the Fe-based superconductors, it was pointed out that Δ's with same sign (s_{++} symmetry of Δ) are realized, because the superconductivity is fairly strong against non-magnetic impurity scattering as found in $RFeAsO_{1-x}F_x$ (R =La, Nd) [3, 4], $Ca_{10}Pt_4As_8(FeAs)_{10}$ [5], and the $BaFe_2As_2$ system [6]. Kontani *et al*. suggested that the orbital fluctuation leads to the superconductivity with the s_{++} symmetry [7]. Although the orbital fluctuation is difficult to be observed directly, characteristic properties such as drastic T-dependences of elastic constants in the tetragonal phase, the impurity

effects on T_c above mentioned, and so on can be explained by taking the orbital fluctuation and its ordering into account [8-10]. In addition to the superconducting mechanism, the effects of the spin and orbital fluctuations on the electronic states appear in the tetragonal phase of the samples with the structural transition or the SC transition.

Based on the in-plane anisotropy of electrical resistivities in $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals, it was reported first that a lower symmetry in the FeAs plane than that of the crystal structure emerges even in the tetragonal phase [11]. This in-plane anisotropy has attracted much attention as a new phenomenon in a nematic electronic state and was discussed from theoretical aspects based on the spin [12] or orbital [7] fluctuation/order. To microscopically confirm whether there is the in-plain anisotropy or not, we studied the in-plane symmetry of the electronic field gradient (EFG) tensor at the As sites in $Ba(Fe_{1-x}Co_x)_2As_2$ with $x\sim0.02$, using the ^{75}As NMR technique [13]. We found that the EFG has the in-plane anisotropy with the same symmetrical axes as those of the orthorhombic structure even in the tetragonal phase. This anisotropy gradually decreases with increasing T and remains finite even near room temperature. However, it has not been elucidated whether the in-plain anisotropy remains in the SC region.

In this paper, we have studied the in-plane anisotropy of the EFG tensor at the As sites in a $Ba(Fe_{0.92}Co_{0.08})_2As_2$ single crystal which has the SC transition temperature $T_c\sim23K$ and does not exhibit structural and AFM transitions. We present the analysis method of the ^{75}As NMR spectrum obtained for the As sites without Co impurities at the nearest and the next nearest neighbor Fe sites to obtain the in-plane anisotropy of the EFG tensor. To discuss the x dependence of the in-plane anisotropy in the EFG tensor, we compare that in the SC sample of $x\sim0.08$ with those in the $x\sim0.02$ samples with the structural and AFM transitions. Finally, we discuss the relationship between the in-plane anisotropy and the physical properties.

2. Experiments

$Ba(Fe_{1-x}Co_x)_2As_2$ single crystals with $x\sim0.08$ were prepared by a flux method [13]. The Co concentration x was estimated by comparing the c lattice parameter ~12.9761 Å with the c-x curve reported for $Ba(Fe_{1-x}Co_x)_2As_2$ [14]. T_c was found to be 23 K from the T dependence of the superconducting diamagnetism shown in Fig. 1.

A single crystal cut in the size of $2.0 \times 2.0 \times 0.1$ mm^3 was inserted in an NMR coil. Then we did not use an adhesive bond such as GE 7031, commonly used to fix a crystal, to avoid possible effects of different thermal contractions between the sample and the bond, because the Fe-based system is considered to be very sensitive to external stresses [15, 16]. ^{75}As NMR measurements were carried out using a coherent pulsed spectrometer and a superconducting magnet with a magnetic field H of 7.6966 T, where the single crystal was rotated using a two-axis goniometer. We measured Fourier-transformed (FT) spectra of spin-echo signals by changing the frequency stepwise and obtained the whole ^{75}As NMR spectra by superposing the FT spectra at various frequencies.

3. Results and Discussion

The tensor of the nuclear electric quadrupole frequency ν_Q^{ij}, ($i, j = x, y$, and z), which is proportional to the EFG tensor, is useful for investigating the in-plain anisotropy of the electronic state in the Fe-based superconductors. In general, ν_Q^{ij} has no in-plane anisotropy in the tetragonal symmetry, whereas it shows the twofold in-plane anisotropy in the orthogonal symmetry. The principal axes of the EFG were reported to be parallel to the symmetrical axes, the a_O, b_O, and c axes, in the orthorhombic phase of $Ba(Fe_{1-x}Co_x)_2As_2$ with $x=0$ [17]. Note that the a_O and b_O axes within the Fe-plane are located at $\sim45°$ from the a_T axis, one of the symmetrical axes in the tetragonal phase above T_s. The in-plane anisotropy of ν_Q^{ij} with the twofold symmetry was clearly observed in the orthorhombic phase below T_s.
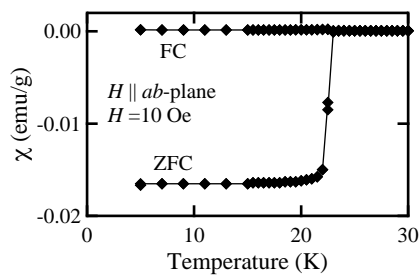
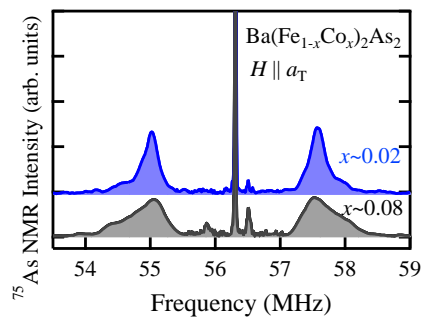Fig. 1 Temperature dependence of superconducting diamagnetic susceptibility in $Ba(Fe_{0.92}Co_{0.08})_2As_2$.

Fig. 2 ^{75}As NMR spectra at 180 K in $Ba(Fe_{1-x}Co_x)_2As_2$ of x ~0.02 and 0.08 with H parallel to the aT axis in the FeAs plane.

Figure 2 shows ^{75}As NMR spectra of $Ba(Fe_{1-x}Co_x)_2As_2$ with x~0.08 at 180K together with those of $Ba(Fe_{1-x}Co_x)_2As_2$ with x~0.02 at 180 K, for comparison. Both the samples are in the tetragonal phase at 180 K, and H is parallel to the tetragonal axis a_T. The spectra split by the nuclear electric quadrupole interaction between the ^{75}As nuclear spin I (=3/2) and EFG at the As site into the central line at ~56.3 MHz and two satellite ones at ~55.0 and ~57.5 MHz as seen in Fig. 2. Satellite spectra in the x ~0.08 sample can be decomposed into the three Gaussians as denoted by As00, As01, and As02 in Fig. 3 which shows for example the satellite spectrum at ~57.5 MHz and 30 K. The intensity ratio of the As00, As01, and As02 spectra, 17:12:4, is well reproduced by the calculation based on the binominal distribution for the Co impurities, if it is assumed that the As00, As01, and As02 spectra may come from the three As sites, which have no, one, and two Co atoms, respectively, at the eight next nearest neighbor Fe sites, without Co at the four nearest neighbor Fe sites. On the other hand, the small peaks observed at ~55.9 and ~56.5 MHz in Fig. 2 are central lines coming from the As1 site which is surrounded by one Co and three Fe at the four nearest neighbour Fe sites [13, 18]. From the analysis on the angular dependence of the NMR frequency of the central lines (Fig. 4) based on the second-order electric quarupole effect, we found that the As1 site has the ν_Q^{ij} tensor with the principal axis almost parallel to the As1-Co directions, where the tensor has the maximum value ν_Q of 14.9 MHz much larger than 2.22-3.81 MHz of the As00-As02 spectra, and the asymmetry parameter of the EFG tensor η=0.63. Almost the same result was obtained for the x~0.02 sample [13]. These facts show that the As1 satellite spectra do not overlap the As00-As02 ones in both the samples. Thus we can separately monitor the local As sites using the ^{75}As NMR technique.

We have measured the angular dependence of the ^{75}As NMR spectrum with H rotated in the FeAs plane for the x~0.08 sample at 50 K, and show the result in Fig. 4. The satellite spectra for H tilted from the a_T axis can be reproduced by assuming not the three Gaussians due to one group of the As00, As01, and As02 spectra but the four Gaussians coming from a set of two As00, one As01 and one As02 spectra with the intensity ratio of As00:As00:As01:As02=8.5:8.5:12:4 following the binominal distribution for x~0.08. The angular dependences of the Gaussians coming from the As00 site show the twofold anisotropy with the orthogonal symmetry axes, a_O or b_O, parallel to the Fe-Fe direction as denoted by the red and blue spectra in Fig. 4. This means that the As00 sites are located in two sample regions with the local symmetry axes orthogonal to each other, clearly showing the presence of the in-plane anisotropy even in the tetragonal phase. The difference between the NMR frequencies of the red
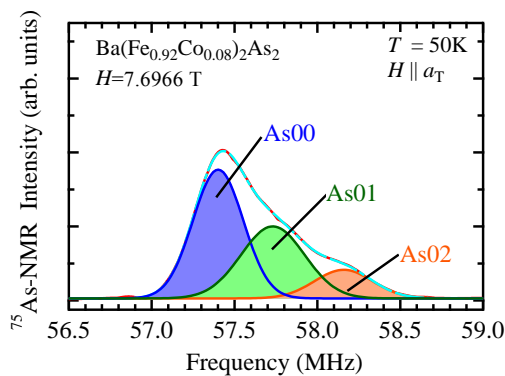
Fig.3 ^{75}As satellite spectrum at 50 K in Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ with H (=7.6966 T) parallel to the a_T axis in the FeAs plane. The spectrum is composed of the three Gaussians coming from the As00, As01, and As02 sites.

and blue satellite spectra parallel to the a_O and b_O axes provides the ν_Q^{ao} and ν_Q^{bo} values as 0.98 and 1.24 MHz, respectively. Using ν_Q^{ao} and ν_Q^{bo}, the in-plane anisotropy can be described by η defined as $\eta = \left| (\nu_Q^{ao} - \nu_Q^{bo})/\nu_Q^c \right|$ with $\nu_Q^{ao} + \nu_Q^{bo} + \nu_Q^c = 0$. Figure 5 shows the temperature dependence of η at the As00 site in the $x{\sim}0.08$ sample. It should be noted that the η value of 0.08-0.10 for $x{\sim}0.08$ is ${\sim}1/10$ times as large as the value of $\eta{\sim}1.2$ at ${\sim}5$ K in the orthorhombic phase of the $x{=}0$ sample [17]. Also the η value for $x{\sim}0.08$ without structural and AFM transitions is comparable to that for $x{\sim}0.02$ with $T_s{\sim}100$ K and $T_N{\sim}96$ K. The non-zero η value in the wide temperature range above T_s of the non-SC sample and above T_c of the SC one gradually decreases with increasing T.

Thus we observed the in-plane anisotropy of ν_Q at the As00 site in the SC sample with $x{\sim}0.08$ in addition to the non-SC one with $x{\sim}0.02$. The in-plane anisotropy, which indicates that the electronic state and/or the crystal structure are locally distorted with the orthorhombic symmetrical axes in the tetragonal phase of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, is induced by Co impurities introduced in the Fe plane [19]. Also the emergence of the in-plane anisotropy around room temperature is consistent with this picture.

4. Conclusion

We have made ^{75}As NMR measurements to study the in-plane anisotropy in the tetragonal phase of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ of $x{\sim}0.08$ with the superconducting transition temperature of $T_c{\sim}23$ K. We obtained the asymmetry parameter of the EFG tensor, η, at the As00 site with no Co atoms at the nearest and next nearest Fe sites, clearly showing the presence of the electric in-plane anisotropy above T_c. The
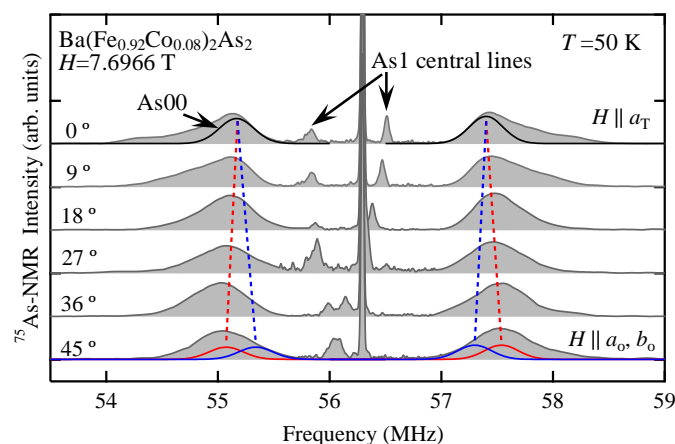

Fig. 4 Angular dependence of the ^{75}As NMR spectrum at 50 K in Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ with H (=7.6966 T) rotated in the FeAs plane. The red and blue spectra, whose angular dependences are presented by the dashed red and blue curves, respectively, come from the As00 sites in the two sample regions with the symmetry axes orthogonal to each other. The As1 spectra are central lines coming from the As1 site.
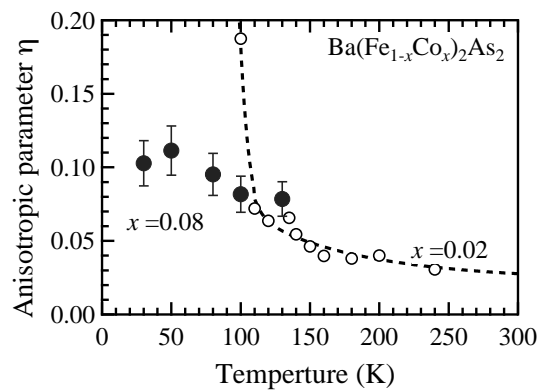
Fig.5 Temperature dependence of the asymmetry parameter of the electric field gradient tensor, η, at the As00 site in $Ba(Fe_{1-x}Co_x)_2As_2$ with $x \sim 0.02$ and 0.08.

EFG was found to have the η value of 0.08-0.10 comparable to those in the non-SC samples of $x\sim0.02$. Also the in-plane anisotropy was found to remain even near T_c.

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