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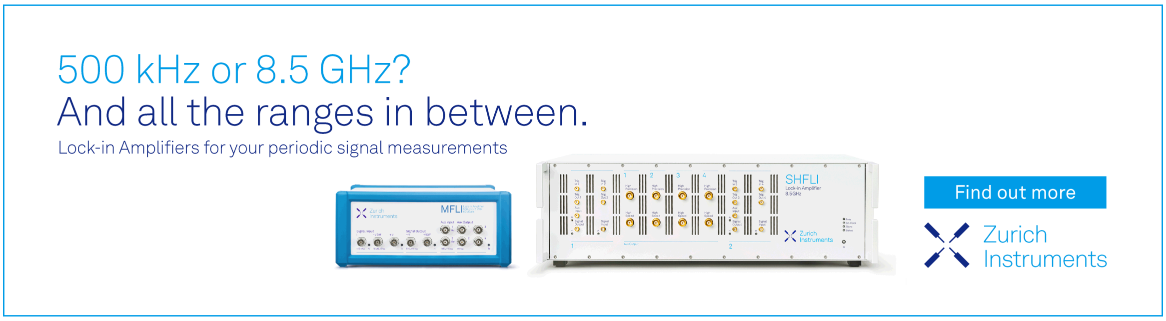

Nuclear Resonant Small-Angle Scattering for Investigation of Microstructures in Electronic States

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Abstract. The measurement of the nuclear resonant small-angle scattering was achieved by scanning the position of a multi-element avalanche photodiode detector, detecting delayed nuclear resonant signal to investigate microstructures of the electronic states. The nuclear resonant small-angle scattering has been attempted to study the coexisting phase of superconductivity and magnetic order in an under-doped Fe-based superconductor, $Ba_{0.8}K_{0.2}Fe_2As_2$. Clear change was not observed in the exponent of the angular profile of the nuclear resonant small-angle scattering in the coexisting temperature. This fact implies the microstructure in the coexisting phase does not have an obvious typical scale but a complex spatial texture. Another attempt was performed for the microstructure in the magnetic properties in an anti-invar fcc Fe-Ni-C alloy to investigate mechanism of the anti-invar properties. An enhancement of the angular profile in a few tens of nm range was observed as decreasing the temperature down to a little below the Curie temperature. This fact implies the existence of the inhomogeneity of magnetically-ordered phase in this range of size, which may related to the anti-invar properties.

INTRODUCTION

The small-angle scatting is a well-established method for various application to investigate the morphology of microstructures[1]. In the case of the small-angle x-ray scattering, the microscopic feature of electronic density, that is, element composition is concerned. On the other hand, the nuclear resonant small-angle scattering is able to detect some microstructure in the electronic states or magnetic properties[2]. The nuclear resonant scattering of synchrotron radiation contains the information of electronic states or magnetic properties corresponding to Mössbauer parameters by measuring delayed emission from resonant nuclei discerned by timing technique. By combining methods of the nuclear resonant scattering and the small-angle scatting, the microstructure in the electronic states or magnetic properties even for same element composition is detectable. The small-angular profile of the nuclear resonant scattering can be analyzed similarly to the small-angle x-ray scattering. In this study, the nuclear resonant small-angle scattering has been attempted to investigate the coexisting phase of the superconductivity and the magnetic order in an under-doped Fe-based superconductor. In addition, the microstructure in the magnetic properties in an anti-invar fcc Fe-Ni-C alloy was also studied to investigate the mechanism of the anti-invar properties.

In general, it is thought that the superconductivity cannot coexist with magnetic order, since the local magnetic fields in the magnetic order would break the Cooper pairs of the superconductivity. Because of this reason, the discovery of Fe-based superconductors surprised many researchers[3]. In the case of firstly-discovered $LaFeAsO_{1-x}F_x$, the superconducting phase appears by suppression of antiferromagnetic order without coexisting phase[4]. Besides such 1111 series, another main group of Fe-based superconductors, 122 series of Fe-based superconductors such as $Ba_{1-x}K_xFe_2As_2$ were found[5]. For the case of $Ba_{1-x}K_xFe_2As_2$, there is a specific region where superconductivity and magnetic order coexist at about $x \sim 0.2$ in the phase diagram[6]. Investigations by Mössbauer spectroscopy were performed for these compounds suggested the competition of two phases, which could not be understood by

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mesoscopic phase separation[7]. Moreover, the interplay between the magnetic order and the superconductivity was found in the coexisting phase by muon spin rotation[8] and Mössbauer spectroscopy[9]. However, since a certain spatial size of the phase separation, if any, in the coexisting phase is not directly measurable in Mössbauer spectra. Therefore, microscopic picture of the coexisting phase is still not well identified.

The Fe-Ni alloys are known to have typical invar properties, which shows minimal thermal expansion coefficient at room temperature at around 36 wt% of Ni. For general use of steel materials, trace amount of carbon or other metallic elements is added to promote hardness or toughness for various purposes by controlling the doping amount and the process of heat treatment. The properties of these controlled steel materials are related to the microstructures of precipitation of carbide and/or partial structural transformation such as Martensitic transformation. The Fe-Ni invar alloys can also be controlled by C doping to control not only the mechanical properties but also the invar properties. In the fcc Fe-Ni-C alloys, thermal expansion coefficient increases in the vicinity of the Curie temperature of about 180K, which is known as anti-invar property[10]. To understand the mechanism of anti-invar property, it is important to understand not only the microstructures of structural or component inhomogeneity but also the microstructure of magnetic property. The Mössbauer and small-angle neutron scattering experiments of fcc Fe-Ni-C alloys suggested the evolution of magnetic order with changing temperature resulted in anti-invar properties[11].

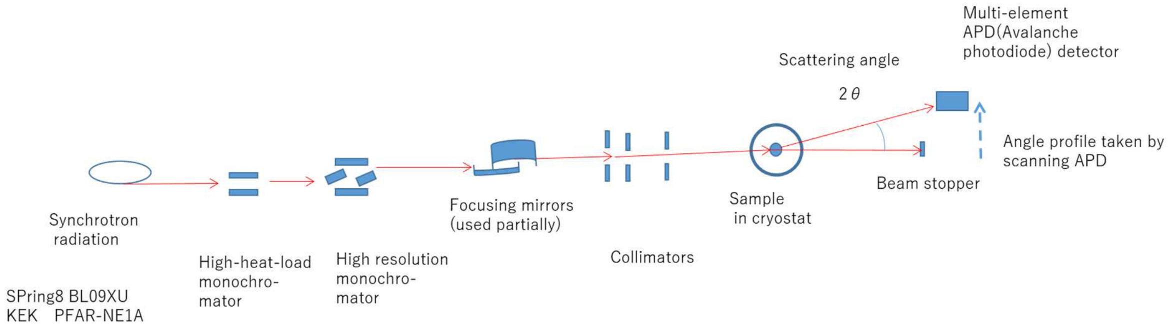


FIGURE 1. Experimental setup of nuclear resonant small-angle scattering.

EXPERIMENTAL

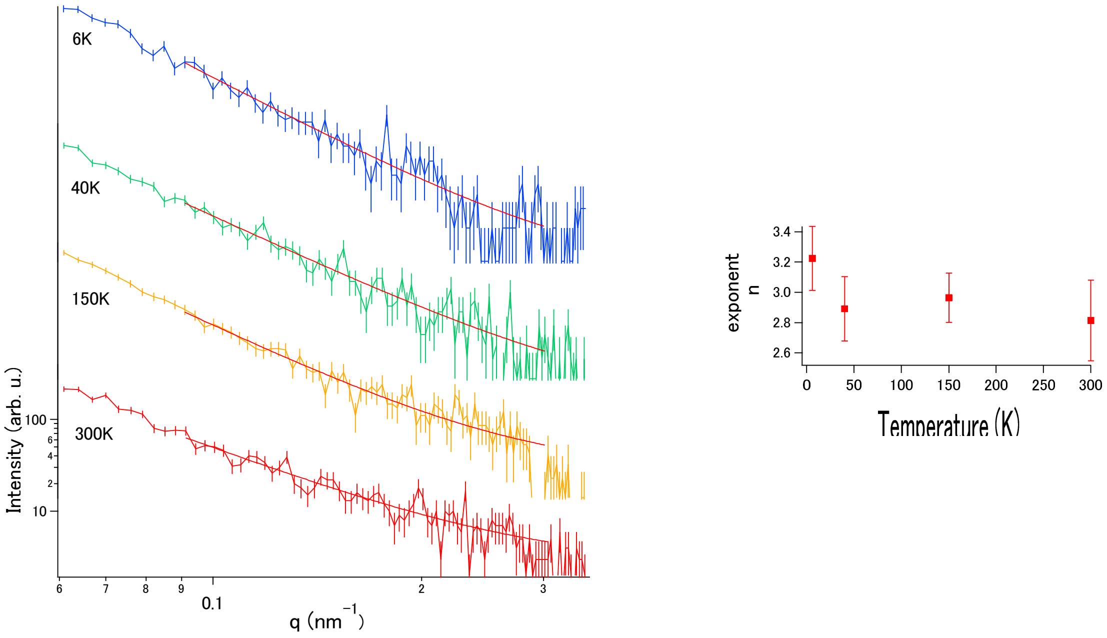
The experiment of the nuclear resonant scattering was performed at BL09XU undulator beamline at SPring-8. Typical experimental setup is shown in Fig.1. The x-rays of synchrotron radiation were monochromatized by the Si(111) high-heat-load monochromator and the Si(511)-Si(975) high-resolution monochromator with an energy width ΔE of about 3.5 meV. The x-rays were collimated by several slits and led to the sample in a He-flow cryostat. The nuclear resonant small-angle scattering were obtained by delayed scattering in a multi-element avalanche photodiode(APD) detector. The amplitude of the scattering vector q was changed by scanning the APD detector horizontally from the forward scattering direction. Typical scale of the setup was about 1 m for the distance between sample and the detector, and detector is scanned by a few mm. From the acceptance of each APD element, the resolution of the scattering vector Δq was evaluated as 0.007 nm^{-1}. The angular profile is obtained by adding counts of each APD element at each q position. The typical obtained q range of the angular profile was about 0.02 to 0.6 nm^{-1}. A part of experiments were performed at PFAR-NE1A beamline at High Energy Accelerator Research Organization(KEK) using a focusing mirror with ΔE of about 12 meV.

The polycrystalline sample of $Ba_{0.8}K_{0.2}Fe_2As_2$ was synthesized similarly to the referenced method[5]. The ^{57}FeAs was synthesized beforehand by heating several times the mixture of reduced ^{57}Fe powder and distilled As at 850°C. Thus, a mixture of stoichiometric Ba, ^{57}FeAs with excess amount of K were heated at 600°C, and then ground and heated again at 750°C. The resultant sample was evaluated by powder x-ray diffraction as almost a single component. By the magnetic susceptibility measurement, the onset temperature of the superconducting transition (T_c) was evaluated as about 40K. Conventional ^{57}Fe-Mössbauer spectra were measured using a pellet of ground powder of $Ba_{0.8}K_{0.2}Fe_2As_2$ using a ^{57}Co source to confirm the magnetic transition temperature (T_N) of about 90 K.

The fcc Fe-Ni-C alloy was obtained by arc-melting method from mixture of metal powder of ^{57}Fe with 25% Ni and about 1% C(wt%). The obtained alloy was annealed at 1100°C and quenched in water. The alloy was rolled to a foil with a thickness of about 20 μm and annealed at 1100°C. The fcc structure of the obtained alloy was confirmed by x-ray diffraction. The Curie temperature was measured as about 180 K by magnetic susceptibility measurement. The Mössbauer spectroscopy was performed to confirm its paramagnetic property at room temperature. The measurements for the nuclear resonant scattering were performed in controlling the temperatures not to cool the sample lower than the Martensitic transition temperature of around 120K.

RESULTS AND DISCUSSION

The obtained temperature dependence of angular profiles of the nuclear resonant small-angle scattering are shown in Fig. 2(a). Any characteristic structure was not clearly observed in the measured region. This implies that there is no characteristic spatial microstructure of a few to a few tens of nm scale, if we assume any microscopic phase separation in the coexisting region. Since the angular profile includes the information of the microstructure of the sample, the shape of the angular profile was fit by a function $aq^{-n}+c$, where a, n, c are fitting parameters. The temperature dependence of exponent n is shown in Fig. 2(b). Clear change was not observed in the exponent of the angular profile of the nuclear resonant small-angle scattering in the coexisting temperature. This fact implies the microstructure in the coexisting phase does not have an obvious typical scale but a complex spatial texture.



(a) (b)

FIGURE 2. Angular profile of nuclear resonant small-angle scattering of Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$(a) and temperature dependence of the exponent of the angular profile curves(b).

The nuclear resonant small-angle scattering of an anti-invar fcc Fe-Ni-C alloy was measured similarly as shown in Fig.3. The temperature of the alloy was cooled down from room temperature to a little below the Curie temperature of 180K. According to the general analyses for the small angle scattering, the angular profiles can be analyzed by the Guinier plot, which provides a radius of gyration, that is, a measure of the size of the aggregates of the magnetic inhomogeneity. Moreover, the exponent of the angular profile shows the shape of the aggregates, and the roughness of the aggregates can be analyzed by the Porod rule. The angular profile of the spectra shows an enhancement of the intensity in a few tens of nm range as decrease in the temperature down to a little below the Curie temperature. This fact shows the existence of the inhomogeneity of magnetic ordered phase in this range of size, which may related to the anti-invar properties. This fact agrees with the results of small-angle neutron scattering[11].

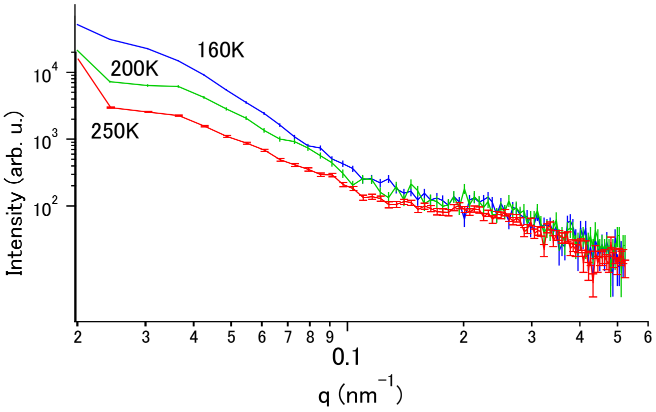


FIGURE 3. Angular profile of nuclear resonant small-angle scattering of an anti-invar fcc Fe-Ni-C alloy.

In summary, the nuclear resonant small-angle scattering experiments were attempted to evaluate microscopic feature on the angular profile in a *q* range between about 0.02 and 0.6 nm^{-1}. This method is well applicable to investigate Fe-based superconductors and Fe-Ni-C alloys. In the angular profiles, the information of the microstructures of electronic state or magnetic state was obtained. The nuclear resonant small-angle scattering must be one of the essential methods for investigating the inhomogeneity of the electronic or magnetic properties, even when the element composition is homogeneous. Moreover, the information of the electronic states can also be known by the time spectrum of the nuclear resonant scattering in a certain angle, which corresponds to a certain specific size. The experimental techniques can be improved by developments of multi-element detectors to obtain efficient count rates in the large *q* region. Moreover, by using the Bonze-Hart arrangement of the analyzer crystals, the ultra-small-angle scattering experiment is also applicable for the investigation in μm scale order as shown in the original study[2]. Thus, the nuclear resonant small-angle scattering can be a unique method for various areas in microstructure researches.

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REFERENCES

1. For example, O. Glatter and O. Kratky ed., *Small Angle X-ray Scattering* (Academic Press, 1982).
2. Yu. V. Shvyd'ko, A. I. Chumakov, A. Q. R. Baron, E. Gerdau, R. Rüffer, A. Bernhard, and J. Metge, Phys. Rev. B **54**, 14942 (1996).
3. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
4. S. Kitao, Y. Kobayashi, S. Higashitaniguchi, M. Saito, Y. Kamihara, M. Hirano, T. Mitsui, H. Hosono, and M. Seto, J. Phys. Soc. Jpn. **77**, 103706 (2008).
5. M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).
6. M. Rotter, M. Pangerl, M. Tegel, and D. Johrendt, Angew. Chem. Int. Ed. **47**, 7949(2008).

7. M. Rotter, M. Tegel, I. Schellenberg, F.M. Schappacher, R. Poettgen, G. Deisenhofer, G. Joachim, A. Guenther, F. Schrettle, A. Loidl, and D. Johrendt, New J. Phys. **11**, 025014 (2009).
8. E. Wiesenmayer, H. Luetkens, G. Pascua, R. Khasanov, A. Amato, H. Potts, B. Banusch, H.-H. Klauss, and D. Johrendt, Phys. Rev. Lett. **107**, 237001 (2011).
9. J. Munevar, H. Micklitz, J. Agüero, Guotai Tan, Chenglin Zhang,Pengcheng Dai, and E. Baggio-Saitovitch, Phys. Rev. B **88**, 184514 (2013).
10. M. Acet, T. Schneider, H. Zähres, E. F. Wassermann, and W. Pepperhoff, J. Appl. Phys. **75**, 7015 (1994).
11. V. M. Nadutov, S. G. Kosintsev, Ye. O. Svystunov, V. M. Garamus, R. Willumeit, H. Eckerlebe, T. Ericsson, and H. Annersten, J. Magn. Magn. Mater. **323**, 2786 (2011).