



Evaluation of isomer shifts via ^{57}Fe nuclear forward scattering technique with α -Fe under external magnetic field

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Abstract

The isomer shift of the ^{57}Fe nuclei is an important ^{57}Fe hyperfine interaction parameter to discuss the electronic states of the Fe atoms. To evaluate the isomer shift of the ^{57}Fe nuclei in materials, we have measured ^{57}Fe nuclear forward scattering spectra of a sample with and without an α -Fe foil in which its magnetic hyperfine field was aligned by external magnetic field. Since the ^{57}Fe nuclear transitions in the α -Fe foil are selected in these experimental conditions, we precisely evaluate the absolute center shift of the ^{57}Fe nuclei in the sample. The performance of this method was demonstrated using paramagnet stainless steel, sodium nitroprusside and antiferromagnet EuFe_2As_2 at ambient pressure and 1.4 GPa.

Keywords Nuclear forward scattering · Isomer shift

1 Introduction

Nuclear forward scattering (NFS) technique is a powerful tool to investigate the electronic states of Mössbauer atoms in materials under pressure. In NFS experiment, Mössbauer nuclei are excited by a monochromatized x-ray pulse of synchrotron radiation (SR) and the γ -ray scattered along the forward direction is observed in the time domain. The decay rate in the collectively excited Mössbauer nuclei is modulated by quantum beats owing to the interferences of γ -rays emitted from the various nuclear levels with different energies. Thus, a magnetic hyperfine field H_{hf} and an electrical quadrupole splitting ΔE_Q are refined in the NFS spectrum only using a sample since the frequencies of quantum beats reflect the energy differences related to the nuclear transitions. On the other hand, we need to measure absolute

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Mössbauer transition energies in materials to estimate a center shift δ , in other word, the measurement of a sample with a reference material is required in the NFS technique.

In ^{151}Eu NFS experiment, Eu^{3+}F_3 and Eu^{2+}S have been used to evaluate δ of Eu compound [1]. This is because each compound has a single absorption line in the conventional Mössbauer spectrum at room temperature and the difference of δ between two compounds is -11.5 mm/s [2]. Among EuF_3 and EuS , we can choose the best reference material to evaluate δ , namely, the valence state of Eu ion in the sample. For ^{57}Fe NFS experiment, stainless steel (SS) and $\text{K}_4[\text{Fe}(\text{CN})_6]$ have been reported as reference materials [3, 4]. Although these ^{57}Fe Mössbauer spectra show a single absorption line, the δ values of SS and $\text{K}_4[\text{Fe}(\text{CN})_6]$ are -0.09 and -0.045 mm/s, respectively, relative to that of α -Fe at room temperature [2], indicating difficulty to evaluate δ (≈ 0 mm/s) such as paramagnetic metal samples with small ΔE_Q by ^{57}Fe NFS measurements using these reference materials. Therefore, other reference materials to refine δ of all Fe compounds are needed for ^{57}Fe NFS technique.

In this paper, we propose α -Fe with an external magnetic field (H_{ex}) as a reference material of ^{57}Fe NFS experiment. Since the ^{57}Fe NFS spectrum of a polycrystalline α -Fe at room temperature without H_{ex} shows the complex quantum beat patterns owing to its ferromagnetic state with domain structure, a polycrystalline α -Fe without H_{ex} is not a satisfactory reference material for ^{57}Fe NFS experiment. To obtain a simple quantum beat pattern in the spectrum, ^{57}Fe Mössbauer transitions in α -Fe at room temperature are restricted by the polarization of SR pulses and the direction of H_{hf} limited by H_{ex} . Two ΔI^z ($= I_g^z - I_e^z$) = 0 nuclear transitions are selected in our proposed experimental conditions [5–7], and the energy difference is about 6.2 mm/s.

2 Experimental procedure

^{57}Fe NFS experiments were conducted at the NE1 beamline on the accumulation ring of the High Energy Accelerator Research Organization. To evaluate δ of the ^{57}Fe nuclei in the sample, after passing through the sample, the monochromatized x-ray pulse encountered a polycrystalline α -Fe foil at room temperature with H_{ex} which was produced by permanent magnets and was perpendicular to the propagation k_0 and the polarization e_σ vectors of the monochromatized x-ray pulse. The performance of this method was testing on paramagnet SS, sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{II})(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (SNP), and antiferromagnet EuFe_2As_2 at ambient pressure and 1.4 GPa. Single crystals of SNP are a commercial product (Wako Co.) and the purities are 99 %. On the other hand, we grew single crystals of EuFe_2As_2 enriched with 97 at.% ^{57}Fe by a tin flux method [8, 9], and the thin single crystal was mounted in a diamond anvil cell (DAC) for applying pressure with Daphne7474 as a pressure-transmitting medium. The observed NFS spectra were analyzed by the MOTIF package [10].

3 Results and discussion

As seen in Fig. 1a, a simple quantum beat pattern was observed in the ^{57}Fe NFS spectrum of the α -Fe foil at room temperature with H_{ex} . Since the magnetic anisotropy of α -Fe is not so large, the magnetic moments of the polycrystalline α -Fe foil are easily aligned along the direction of H_{ex} . In this experiment, the direction of H_{hf} was perpendicular to both k_0 and e_σ of the incident x-ray pulse. Accordingly, two ΔI^z ($= I_g^z - I_e^z$) = 0 nuclear

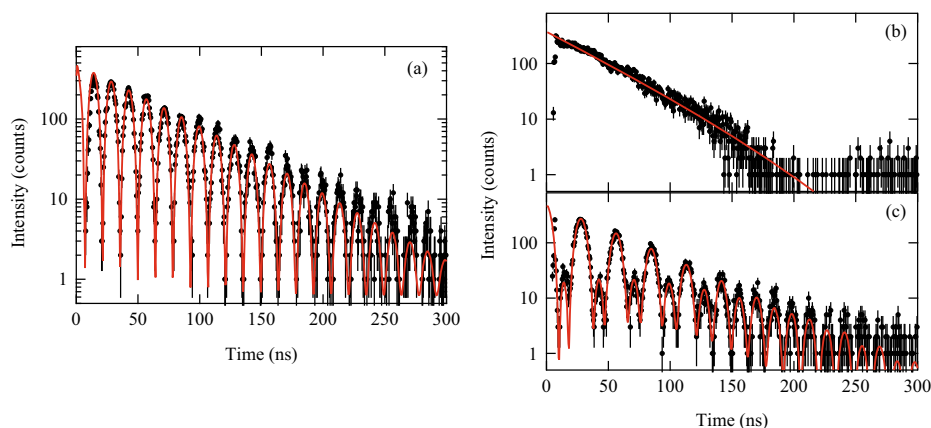


Fig. 1 ^{57}Fe nuclear forward scattering spectra of **a** α -Fe foil at room temperature with external magnetic field $H_{\text{ex}} \sim 5$ kOe and stainless steel **b** without and **c** with the α -Fe foil at room temperature in H_{ex} . The closed circles with error bars indicate the observed spectrum, and the solid line represents the fitting curve obtained by MOTIF[10]

transitions are selected in the six $M1$ nuclear transitions of the ^{57}Fe Mössbauer resonance, and the scattered γ -rays have the perfect σ -polarization [5–7]. As shown in Fig. 1a, the ^{57}Fe NFS spectrum was well reconstructed using the package MOTIF applying the full dynamical theory of nuclear resonant scattering and including the diagonalization of the complete hyperfine interaction Hamiltonian [10]. The H_{hf} value was evaluated to be 325(1) kOe, indicating that the effective H_{ex} value was approximately 5 kOe.

To verify the effectiveness of α -Fe with H_{ex} as the reference material, we have measured δ of SS at room temperature by this method. A single absorption line was observed in conventional ^{57}Fe Mössbauer spectrum at room temperature using SS in this study and the position was $-0.104(9)$ mm/s relative to that of α -Fe at room temperature (not shown). Thus, the ^{57}Fe NFS spectrum of SS shown in Fig. 1b indicates a dynamical beat pattern with no interference due to H_{hf} or ΔE_Q . On the other hand, from Fig. 1c, we obtained the clear interference between photons emitted from SS and α -Fe with H_{ex} . The spectrum is analyzed by $|\delta| = 0.110(3)$ mm/s of SS which is in good agreement with that estimated by conventional ^{57}Fe Mössbauer spectroscopy. Accordingly, this method using α -Fe with H_{ex} as the reference material is effective for metallic Fe samples without ΔE_Q and H_{hf} .

The orthorhombic paramagnet SNP is one of the standard reference materials with the relatively large ΔE_Q . Figure 2 shows the ^{57}Fe NFS spectra of SNP at room temperature without and with the α -Fe foil, where the [001] and [100] axes of the single crystal were aligned along k_0 and e_σ of the incident x-ray, respectively. The nitroprusside ion is a basic structural unit in SNP with an orthorhombic $Pnmm$ symmetry and approximately has the $4mm$ symmetry although the local symmetry at the Fe site is $\dots m$ in this orthorhombic structure [11]. The Fe=N=O portion of the nitroprusside ion is along the fourfold rotational axis within the $4mm$ symmetry approximation and is in the c -plane strictly because the local symmetry at the Fe site is $\dots m$ in SNP[11]. The directions of the Fe=N=O portions of four nitroprusside ions in the primitive cell of SNP are different, and the angles θ between the fourfold rotational and the [010] axes are same in these four nitroprusside ions. Therefore, one crystallographically equivalent Fe site in the primitive cell gives four spectroscopically nonequivalent Fe sites. As shown in Fig. 2, the ^{57}Fe NFS spectrum observed using the

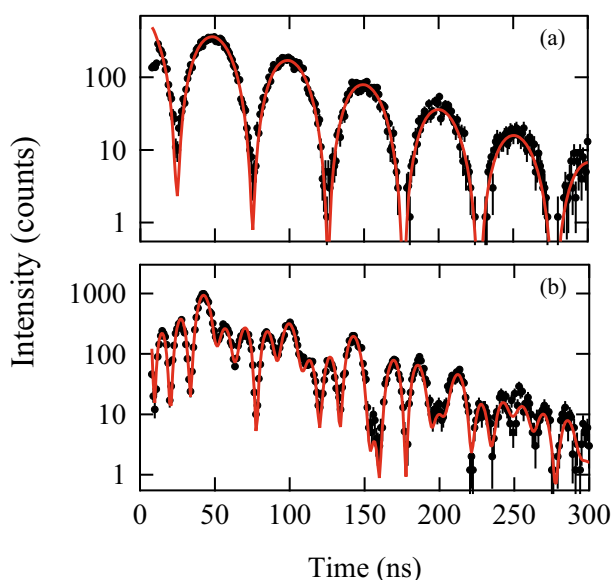


Fig. 2 ^{57}Fe nuclear forward scattering spectra of $\text{Na}_2[\text{Fe}(\text{II})(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ at room temperature: **a** without and **b** with the α -Fe foil at room temperature in external magnetic field. The closed circles with error bars and the solid lines indicate the observed spectra and the fitting curves obtained by MOTIF [10], respectively

single-crystalline sample was reconstructed with four spectroscopically nonequivalent Fe sites within the assumption of the axial symmetric EFG tensor by MOTIF [10], and $|\delta|$, ΔE_Q and θ were refined to be 0.262(1), 1.700(3) mm/s and 56(1) deg, respectively, which consists with previous results within the experimental accuracy [11, 12].

As an example measured a magnetic material, the ^{57}Fe NFS experiment of tetragonal antiferromagnet EuFe_2As_2 has been conducted at 4 K and ambient pressure, where the [001] axis of the single crystal was aligned along k_0 of the incident x-ray. The Fe sublattice of EuFe_2As_2 exhibits a simple-Q commensurate stripe-type antiferromagnetic (sAFM) order below 190 K accompanied by a structural change from the tetragonal $I4/mmm$ to the orthorhombic $Fmmm$ symmetries [13]. The magnetic moments of Fe sublattice are oriented along the orthorhombic [100] direction in the sAFM state, and thus the direction of H_{hf} in the Fe sublattice are perpendicular to k_0 . As shown in Fig. 3a and b, the ^{57}Fe NFS spectrum observed without and with the α -Fe foil was well analyzed by assuming the sAFM structure with a structural twinning effect caused by the structural change. The detailed analysis procedure for the ^{57}Fe NFS spectrum without the α -Fe foil has been described in Refs [8, 9]. The refined $|\delta|$, ΔE_Q and H_{hf} values were 0.546(2), 0.217(6) mm/s and 84.4(1) kOe, respectively, which are in good agreement with those extracted by previous our conventional ^{57}Fe Mössbauer spectroscopy [8]. Consequently, we also precisely evaluate the δ value of ^{57}Fe nuclei in a sample with a magnetic order using this method.

Because of extremely high brilliance from SR, NFS has been performed extensively in high pressure researches using DAC. Thus, the performance of this method was testing for EuFe_2As_2 under pressure. Figure 3c and d show the ^{57}Fe NFS spectra of EuFe_2As_2 observed at 1.4 GPa and 4 K without and with the α -Fe foil at room temperature in H_{ex} , respectively. The magnetic structure in the Fe sublattice of EuFe_2As_2 maintains up to ~ 2.4 GPa at 4 K [9]. These observed ^{57}Fe NFS spectra were analyzed in the similar procedure

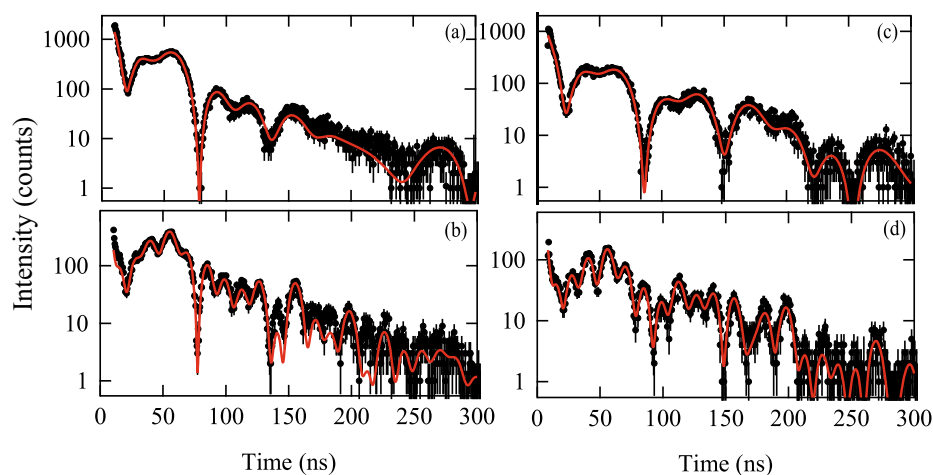


Fig. 3 ^{57}Fe nuclear forward scattering spectra of EuFe_2As_2 at 4 K : (left) ambient pressure and (right) 1.4 GPa. The closed circles with error bars indicate the observed spectra in **a** and **c** without the α -Fe foil and in **b** and **d** with the α -Fe foil at room temperature in external magnetic field. The solid lines represent the fitting curves obtained by MOTIF [10].

to the analyses of the ^{57}Fe NFS spectra at ambient pressure and 4 K. The $|\delta|$, ΔE_Q and H_{hf} values were refined to be 0.543(2), 0.249(8) mm/s and 77.0(1) kOe, respectively. These results indicate that H_{hf} decreases with increasing pressure and the δ values are independent of pressure within the experimental accuracy up to 1.4 GPa in the sAFM state of EuFe_2As_2 with the orthorhombic $Fmmm$ structure. In the previous results, the δ values of EuFe_2As_2 lineally decrease with increasing pressure at room temperature [14], where EuFe_2As_2 is in the paramagnetic state with the tetragonal $I4/mmm$ structure. Since the δ value usually decreases with increasing pressure [15], the independent of pressure in δ suggests a change in the electronic state of the Fe atom in EuFe_2As_2 with the orthorhombic $Fmmm$ structure under pressure. Consequently, it is critical to get the δ values of ^{57}Fe nuclei in materials to discuss electronic states of Fe atoms in materials under pressure. These results demonstrate that the ^{57}Fe NFS experiment using α -Fe with H_{ex} is very useful to estimate the δ value in FeAs based superconductors under pressure.

4 Summary

We have proposed α -Fe with H_{ex} as the reference material necessary for evaluating δ by ^{57}Fe NFS. Because the magnetic moments of the polycrystalline α -Fe foil are easily aligned along the direction of H_{ex} due to the small magnetic anisotropy, we have observed the simple quantum beat due to only two $\Delta I^z (= I_g^z - I_e^z) = 0$ nuclear transitions in the ^{57}Fe NFS spectrum of α -Fe with H_{ex} . The accuracies of this method have been proven using the standard reference material stainless steel and $\text{Na}_2[\text{Fe}(\text{II})(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ with the paramagnetic state for ^{57}Fe Mössbauer spectroscopy and antiferromagnet EuFe_2As_2 at ambient pressure and 4 K. Furthermore, the performance of this method under pressure has been demonstrated via the ^{57}Fe NFS experiments on EuFe_2As_2 at 1.4 GPa and 4 K. These results reveal that the ^{57}Fe NFS technique using this method allows one to accurately estimate the absolute value of δ of Fe atoms in all materials.

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