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^{57}Fe nuclear resonant inelastic scattering of $Fe_{1.1}Te$

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Abstract This study reports results of ^{57}Fe Mössbauer spectroscopy and nuclear resonant inelastic scattering (NRIS) in $Fe_{1.1}Te$. The Fe-specific partial phonon densities of states (PDOSs) were extracted from the observed spectra. No detectable change at the tetragonal-monoclinic phase transition around 65 K was observed. Therefore the variations in lattice constants and/or distortion in $FeTe_4$ tetrahedron through the structural transition was minute. From the observed Fe-PDOS, the Lamb-Mössbauer factor was 0.90(3) at 10 K and the Debye temperature was evaluated as 300(10) K. In ^{57}Fe Mössbauer spectroscopy, the clear magnetic spittings of spectra were measured below Néel temperature. The obtained values of isomer shifts showed characteristics of Fe^{2+} species and clear difference with the phase transition was observed in temperature dependence of quadrupole splitting (QS). The change of QS must be caused by substantial change of the charge density distribution around the Fe site. This suggests that the band structure or the nature of the Fe-Te bonds becomes highly anisotropic. These results might provide additional information about the respective mechanisms for $FeTe_{1-x}Se_x$ superconductivity.

Keywords Nuclear resonant inelastic scattering · Synchrotron radiation · Iron based superconductors

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1 Introduction

Until today, detailed studies of the phonon density of states (PDOSs) have been performed using inelastic scattering of neutrons and X-rays. Nevertheless, the nuclear resonant inelastic scattering (NRIS) is more suitable technique to study the lattice dynamics, since partial PDOS can be extracted selectively for specific Mössbauer nuclei.

The phonon interactions plays an important role in superconducting mechanism. However, high transition temperatures (T_c) of copper oxide and iron-based superconductors cannot be explained by conventional Bardeen-Cooper-Schrieffer (BCS) theory based on the electron-phonon interaction. Iron-based superconductors include iron oxypnictide, such as $LaFeAsO_{1-x}F_x$ [1], and iron chalcogenide, such as $FeTe_xSe_{1-x}$ [2]. The iron oxipnictides have layered structures with conducting FeAs layers sandwiched between blocking layers, while the iron chalcogenides do not have blocking layers. Consequently, their simple structure is suitable for understanding the lattice dynamics of the conductive layers. The parent compound, $Fe_{1+y}Te$, does not show superconductivity but performs antiferromagnetic order at Néel temperature (T_N, 65 K) with tetragonal-to-monoclinic structural phase transition. We report results of NRIS of ^{57}Fe performed on the parent compound, $Fe_{1.1}Te$.

2 Experimental

In this study, the single crystal of ^{57}Fe-enriched $Fe_{1.1}Te$ was synthesized by slow cooling and low-temperature annealing [3]. In the typical process, H_2-reduced ^{57}Fe powder (99.89%, ^{57}Fe enrichment 95.38%), distilled Te grains (99.9999%) were mixed in an alumina crucible and sealed in an evacuated silica tube. All procedures were performed in a glovebox with a protective Ar atmosphere. The mixture was heated to a temperature of 1070 °C for 24 hours and then slowly cooled down to 710 °C at a cooling rate of 3 °C/ hour. Subsequently, the sample was annealed in vacuum at 400 °C for 240 hours. The obtained single crystal was characterized by X-ray powder diffraction, which confirmed the formation of $Fe_{1.1}Te$ with a tetragonal PbO-type structure at room temperature. The magnetic susceptibility measurements of $Fe_{1.1}Te$ indicate a magnetic phase transition at T_N of approximately 65 K.

The ^{57}Fe Mössbauer spectroscopy measurements were performed by conventional transmission methods. The velocity scale of each spectrum was calibrated using an α-Fe foil at room temperature and the isomer shift (IS) was presented relative to α-Fe. The single crystal of $Fe_{1.1}Te$ were ground into powder and formed a pellet with a diameter of 7 mm. The samples were placed in a He flow cryostat to measure the temperature dependence of Mössbauer spectra.

The ^{57}Fe NRIS experiments were performed at the Nuclear Resonant Scattering beam line (BL09XU) and the National Institutes for Quantum and Radiological Science and Technology beam line (BL11XU) of SPring-8. The temperature dependence of NRIS spectra was measured by a He flow cryostat. A nested channel-cut Si(975) and Si(511) crystals were used as the high-resolution monochromator with an energy resolution of 2.5 meV at the ^{57}Fe resonance energy of 14.41 keV [4]. A Si avalanche photodiode detector was used to distinguish the nuclear resonant signal from the electronic scattering signal by selecting an appropriate time window. The single crystal of $Fe_{1.1}Te$ which had been cleaved perpendicular to the c-axis was used for NRIS measurements. The glancing angle of the monochromatized X-ray beam with respect to the surface of the $Fe_{1.1}Te$ is approximately 2°. In the measurement of single crystal, the obvious difference in PDOS was reported

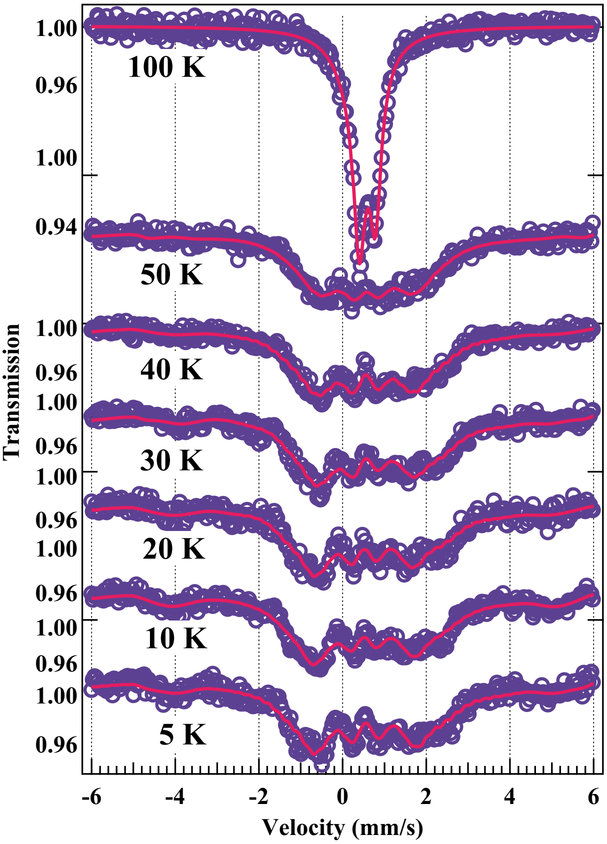

Fig. 1 ^{57}Fe Mössbauer spectra of $Fe_{1.1}Te$ at 5, 10, 20, 50, 100, and 200 K. The solid line shows the fit spectrum

by the anisotropy of phonon vibration [5]. Therefore, it is likely that the intensity of some modes, especially perpendicular to the X-ray are affected in our experimental setting.

3 Results and discussion

^{57}Fe Mössbauer spectra of $Fe_{1.1}Te$ at 5, 10, 20, 50, and 100 K are shown in Fig. 1. The clear spittings of spectra were measured below T_N. Vertical scales are transmission rate, that is, signal counts normalized by the background counts. Each Mössbauer spectra were analyzed by MossWinn program [6]. Parameters of the $Fe_{1.1}Te$ spectra are sumarized in Table 1. In $Fe_{1.1}Te$, obtained values of IS showed characteristics of Fe^{2+} species. On the values of quadrupole splitting (QS), clear difference below and above the structural transition temperature near T_N was observed. The reduction of QS with structural phase transition is also reported in 122 family of the iron-based superconductors, $EuFe_2As_2$ and $CaFe_2As_2$ [7]. In monoclinic phase, large orbital polarization between d_{xz} and d_{yz} orbitals is observed by angle-resolved photoemission spectroscopy study [8]. However, the lattice distortion, $(a - b)/(a + b)$ is approximately 0.5% in monoclinic phase of $Fe_{1.068}Te$ and the large

Table 1 Parameters of the $Fe_{1.1}Te$ spectra and Fe-PDOSs. IS: isomer shift, QS: quadrupole splitting, H_{hf}: hyperfine fields, f_{LM}: Lamb-Mössbauer factor

Temperature (K)	IS (mm/s)	QS (mm/s)	Averaged H_{hf} (T)	f_{LM}
5	0.63(1)	0.16(3)	11.6	
10	0.60(2)	0.19(5)	11.3	0.90(3)
20	0.61(3)	0.20(5)	11.2	0.90(3)
30	0.66(1)	0.21(1)	10.9	
40	0.60(1)	0.10(3)	10.7	
50	0.62(1)	0.09(1)	10.0	
100	0.59(1)	0.39(1)		0.82(4)

orbital polarization cannot explain by the monoclinic distortion [9, 10]. Therefore, the drastic change of QS must be caused by substantial change of the charge density distribution around the Fe sites. This suggests that the band structure or the nature of the Fe-Te bonds becomes highly anisotropic in the *ab*-plane. The distribution of hyperfine fields (H_{hf}) was sited for spectrum of magnetic hyperfine sprinting. The averaged H_{hf} in $Fe_{1.1}Te$ was 11.6 T at 5 K. This value is similar to that obtained by Błachowski et al. [11]. These distributions are reflected to the magnetic structure of $Fe_{1.1}Te$.

Fe-PDOSs were derived from the NRIS spectrum with removing the resonance peak and deconvoluting the energy resolution function [5]. Figure 2 shows the Fe-PDOSs of $Fe_{1.1}Te$ at 10, 20, and 100 K. Unlike the temperature dependence of QS, Fe-PDOSs showed any significant change above and below the structural transition temperature, although the phonon spectra could be affected by the structural phase transition. This fact suggests the variations in lattice constants and/or distortion in $FeTe_4$ tetrahedron through the structural transition was minute. In addition, no change of Fe-PDOD is consistent with the large orbital polarization in monoclinic phase is not derived from simple lattice distortion.

Unresolved Peaks around 10 meV observed in NRIS spectra are assigned transversal acoustic modes and longitudinal acoustic modes. This assignment of the acoustic modes is agreement with the PDOSs of FeSe [12]. Above 16 meV, we assign the resolved spectral features in the PDOSs to optical modes. Resolved three peaks which can be adjusted by Gaussian profiles were shown in the 10 K data of Fig. 2. The peaks at approximately 25 meV can be assigned to the Raman-active B_{1g} mode by the results of Raman scattering measurements [13–16]. The B_{1g} mode primarily involves the displacement of Fe atoms vibrating in opposite directions, parallel to the *c*-axis in the Fe-Te layers. B_{1g} modes are also observed around 25 meV in ^{57}Fe NRIS studies of the other Fe-based superconductors, $LaFeAsO_{1-x}F_x$ [17], $Ba_{1-x}K_xFe_2As_2$ [18] and FeSe [12]. In Raman studies, very similar dependence was observed [16]. We proceed to the resolved peaks in the energy region from 20 to 40 meV, consisting of combined Fe and Te optical modes. The mode with the highest energy of around 30 meV is attributed to the E_g mode and the peak at 22 meV can be attributed to the E_u mode from comparison with theoretical studies [13, 14].

The value of Lamb-Mössbauer factor (f_{LM}) for $Fe_{1.1}Te$ was shown in Table 1. Calculation of the Debye temperature (θ_{D}) from values of f_{LM} was done using the formula of the Debye model [19],

$$f_{\mathrm{LM}} = \exp\left[-\frac{3E_R}{2k_{\mathrm{B}}\theta_{\mathrm{D}}}\left\{1+4\left(\frac{T}{\theta_{\mathrm{D}}}\right)^2\int_0^{\theta_{\mathrm{D}}/T}\frac{u}{e^u-1}du\right\}\right], \quad (1)$$

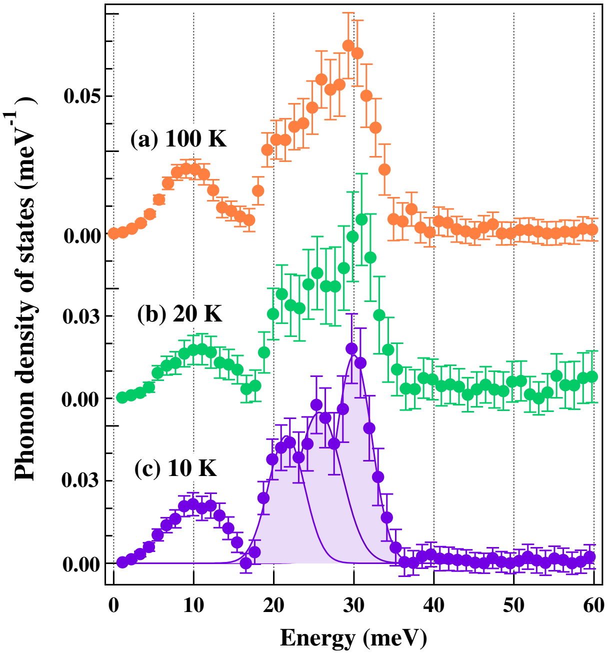

Fig. 2 The circles with err bars presents Fe-phonon densities of states of $Fe_{1.1}Te$ at (**a**)100, (**b**)20, and (**c**)10 K. At 10 K, resolved peaks are shaded with violet

where T is a temperature of sample, k_B is Boltzmann constant, and E_R is recoil energy of Mössbauer Nuclei. From this formula and temperature dependence of f_{LM}, the θ_D for $Fe_{1.1}Te$ was evaluated as 300(10) K.

From the temperature-dependent extended X-ray absorption fine structure studies of $FeTe_{1-x}Se_x$, the observation of local distortions near the superconducting onset is most relevant for the superconducting mechanism [20]. Such distortions seem to be absent in non-superconducting $Fe_{1+y}Te$. On the other hand, the phase separation at the local level results in anion heights was reported in $FeTe_{0.5}Se_{0.5}$. Near superconducting onset, anion heights show nearly opposite behaviour. Such behaviour could perhaps be due to a correlation between Fe-chalcogen hybridization and superconductivity in Fe chalcogenides. Investigation of the PDOS and local properties of Fe in iron chalcogenide might provide additional information about the respective mechanisms for superconductivity.

4 Summary

The temperature dependence of the Fe-PDOSs in $Fe_{1.1}Te$ was studied by ^{57}Fe NRIS. No detectable change at the tetragonal-monoclinic phase transition around 65 K was observed in Fe-PDOSs. This fact suggests the variations in lattice constants and/or distortion in $FeTe_4$ tetrahedron through the structural phase transition was minute. We also measured temperature dependence of ^{57}Fe Mössbauer spectra in $Fe_{1.1}Te$. The obtained values of IS showed characteristics of Fe^{2+} species. On the other hands, clear jump of QS with the phase transition was observed. The change of QS must be caused by substantial change of the charge density distribution around the Fe sites. This suggests that the band structure or the nature of the Fe-Te bonds becomes highly anisotropic in the *ab*-plane. Investigation of the PDOS and Mössbauer parameters in iron chalcogenide might provide additional information about the respective mechanisms for superconductivity.

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