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^{57}Fe Mössbauer spectroscopy study of the 37 K superconductor $Sm_{0.85}Ba_{0.15}FeAsO$ doped with fluorine

V. O. Pelenovich · Y. L. Chen · R. Z. Xiao · S. Y. Liu · D. J. Fu · Z. T. Yang

Abstract Mössbauer spectroscopy investigation of superconducting $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ (T_c = 37 K) has been performed. The spectra appear to be a singlet pattern throughout the temperature range of 20–290 K. The value of Debye temperature is obtained ($\theta_D \sim 390$ K). Unusual behavior of the central shift as a function of temperature is observed below 60 K. Unlike cuprate superconductors, phonon softening is not observed near T_c of the iron pnictide.

Keywords Pnictide oxide · Mossbauer spectroscopy · Superconductivity

1 Introduction

Recent discovery of high-T_c superconductivity in iron arsenide oxides ReFeAsO (Re: rare earth element) doped with fluorine has excited interest in the research into superconductors beyond high-T_c superconducting cuprates [1]. At present the highest T_c has reached 56 K in $SmFeAsO_{1-x}F_x$ [2]. Without fluorine doping SmFeAsO does not show superconductivity, but has antiferromagnetic ordering below 130 K. This magnetic order can be suppressed by fluorine doping and superconductivity appears [3]. Having Fe-ions in their composition the new superconductors are

V. O. Pelenovich (✉) · S. Y. Liu
Department of Physics and Technology, Huazhong Normal University, Wuhan 430070, China
e-mail: pelenovich@yahoo.com

V. O. Pelenovich · Y. L. Chen · R. Z. Xiao · D. J. Fu
Key Laboratory of Artificial Micro- and Nano-Materials of Ministry of Education and Accelerator Laboratory, School of Physics and Technology, Wuhan University, Wuhan 430072, China

Z. T. Yang
CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

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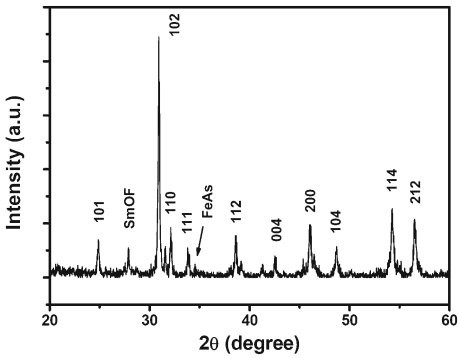

Fig. 1 Powder XRD pattern of the $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ sample

convenient tests for Mössbauer spectroscopy. Mössbauer effect investigations have been performed for $LaO_{0.89}F_{0,11}FeAs$ [4], $LaO_{0.9}FeAs$ [5], $SmO_{0.85}FeAs$ [6], and SmCoAsO [7]. However, there are only a few works devoted to detailed investigation of Mössbauer spectra in a wide temperature region and especially in the region near T_c. This temperature region is interesting because phonon softening may take place near T_c. Such phenomenon was observed in cuprate superconductors $EuBa_2Cu_3O_{7-\delta}$ [8, 9] and $YBa_2Cu_3O_{7-\delta}$ [10]. In the first case the authors observed also an anomaly in the temperature dependence of the central shift in the vicinity of T_c [8].

In the present study ^{57}Fe Mössbauer spectroscopy was applied to F-doped $Sm_{0.85}Ba_{0.15}FeAsO$ superconductor (T_c = 37 K) in the temperature range of 20–290 K.

SmAs, FeO, Fe_2As, and BaF_2 were selected as precursors according to the composition of $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$. To avoid the formation of foreign phases, two-step synthesis procedure was used. At the first step the pellets were sealed, annealed at 800 K for 0.5 h in evacuated silica tubes and cooled to room temperature. Then the annealed pellets were ground and the procedures were repeated at annealing temperature of 1150 K.

The crystal structure of the samples was determined by X-ray diffraction (Bruker D8 Focus) using Cu Kα radiation. The electrical resistivity was measured on a Physical Property Measurement System (PPMS-9T, Quantum Design). The Mossbauer spectra were recorded using a conventional spectrometer in transmission geometry. A ^{57}Co(Rh) source with activity of 25 mCi was used. The velocity calibration was done with a room temperature α-Fe absorber. Absorbers of the samples were made to a thickness of ~20 mg/cm^2. The signal-to-noise ratio was higher than 50. Fitting of the spectra was performed by Lorenz lines using the Recoil program.

Figure 1 shows the powder X-ray diffraction (XRD) pattern of the $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ sample. It is found that the peaks can be well indexed to the tetragonal ZrCuSiAs-type structure except for some tiny peaks from impurity phases which were identified as FeAs and SmOF. The temperature dependence of electrical resistivity $\rho(T)$ in zero magnetic field gave an onset of superconductivity at 37 K, i. e., $T_c = 37$ K.

Figure 2 shows the Mössbauer spectra of $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ measured at the temperatures from 290 K down to 20 K. The spectra appear to be a singlet pattern throughout the temperature range, except for a doublet corresponding to a foreign phase. Hyperfine parameters of the singlet at room temperature are

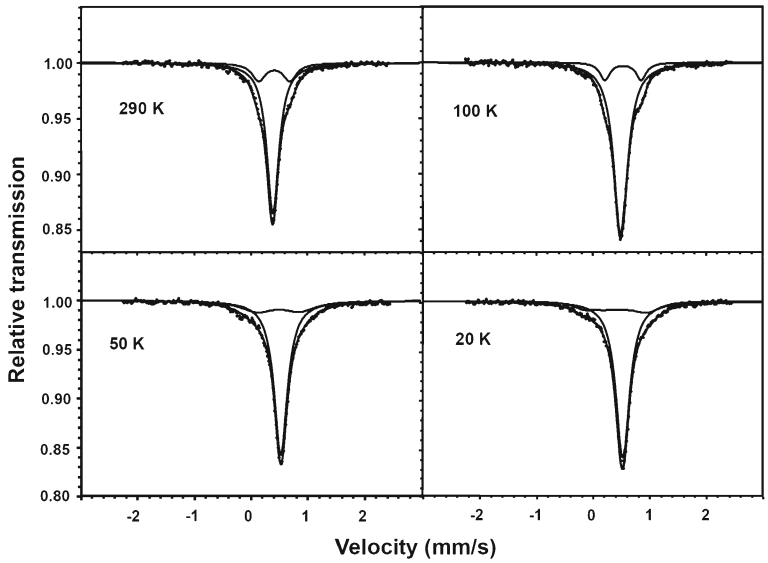

Fig. 2 Mössbauer spectra of $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ at various temperatures

$\delta_{CS} = 0.400 \pm 0.0015$ mm/s and $\Gamma = 0.27 \pm 0.01$ mm/s and correspond to the Fe^{3+} ions in SmFeAsO crystal lattice in accordance with previous studies [4–7]. The fact that the spectra remain singlet throughout the temperature range clearly shows that no magnetic order occurs both in superconducting and normal phases.

The temperature dependence of area under the singlet line is given in Fig. 3. Within the Debye model, this dependence can be fitted with:

$$\ln f = -\frac{E_\gamma^2}{Mc^2 k_B \theta_D}\left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)\int_0^{\theta_D/T}\frac{x dx}{e^x - 1}\right] \tag{1}$$

where f is the recoilless fraction, E_γ is the gamma-ray energy, M is the mass of a Mössbauer atom, c is the velocity of light, k_B is Boltzmann constant, θ_D is Debye temperature, T is temperature, and x is θ_D/T ratio. The fitting is given as a solid line in Fig. 3. The expression (1) allows estimation of Debye temperature: 390 ± 10 K. Phonon softening in the temperature dependence of area near T_c was also observed in $Ba_2EuCu_3O_{9-x}$. But for the present case, it is not observed for $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ within experimental uncertainty (see Fig. 3).

Figure 4 shows the central shift δ_{CS} of the singlet as a function of the temperature. Theoretically this function is given by the expressions:

$$\delta_{CS} = \delta_{IS} + \delta_{SOD}\ \delta_{IS} = const\left\{|\Psi_a(0)|^2 - |\Psi_s(0)|^2\right\}$$

$$\delta_{SOD} = -\frac{3k_B\theta_D}{2Mc}\left[\frac{3}{8} + 3\left(\frac{T}{\theta_D}\right)^4\int_0^{\theta_D/T}\frac{x^3 dx}{e^x - 1}\right] \tag{2}$$

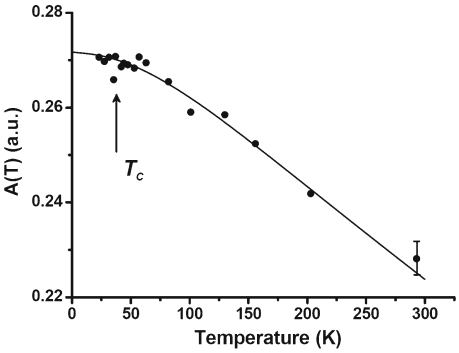

Fig. 3 Temperature dependence of the area under the singlet for $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$. The *solid curve* represents fitting of the experimental $A(T)$using the Debye model

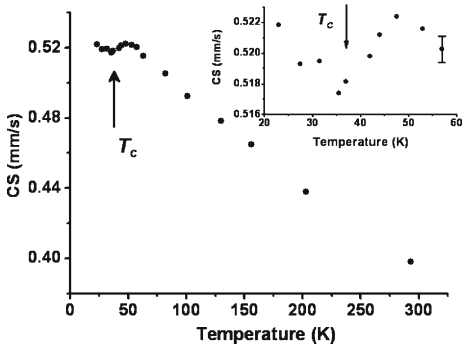

Fig. 4 Temperature dependence of the central shift of the singlet for $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$

Where δ_{IS} is the isomer shift, $\Psi_a(0)$ and $\Psi_s(0)$ are wave functions of the s-electrons near the nuclei in the absorber and source, respectively, and δ_{SOD} is the second-order Doppler shift. The value of Debye temperature estimated by the latter formula is equal to 380 ± 10 K. It is seen the Debye values estimated by formulas (1) and (2) are in rather close agreement.

Aberrant behavior in the temperature dependence of the central shift is observed in the temperature range below 60 K (Fig. 4). Such deviation can be explained by changing of Debye temperature θ_D near the phase transition into superconducting phase or by temperature dependent δ_{IS}. However, the change of Debye temperature seems not to be the reason of such behavior of the central shift. There is no any deviation in the temperature dependence of the area under the curve (see Fig. 3). But as the area also is a function of Debye temperature (1), this means its constancy within experimental uncertainty. Moreover as it is known that the temperature derivative of δ_{SOD} can be expressed as:

$$\frac{\partial}{\partial T}\left(\frac{\delta\nu}{\nu}\right) = \frac{C_p}{2c^2} \tag{3}$$

where ν is the frequency of incident γ-quanta, $\delta\nu$ corresponds to δ_{SOD}, and C_p is isobaric specific heat capacity. Hence δ_{SOD} can be obtained by integration of $C_p(T)$. Ding et al. [3] studied specific heat of a similar system—$SmFeAsO_{1-x}F_x$ in a wide temperature region. A clear specific heat peak near the zero resistivity T_c was observed. Using that result of the specific heat measurement the value of

$\delta v/v$ could be estimated and it was three orders less than the value in the present experiment. Hence one can assume that the aberrant behavior in δ_{CS} may be caused by temperature change of δ_{IS}, i.e., by change of s-electron density $|\Psi_a(0)|^2$ at the iron nuclei below 60 K. Similar temperature dependence of δ_{CS} was observed in ^{151}Eu Mössbauer spectroscopy study of $Ba_2EuCu_3O_{9-x}$ compounds near T_c and explained by the same mechanism [8].

Hyperfine parameters of the doublet are $\delta_{CS} = 0.42 \pm 0.01$ mm/s, QS $= 0.55 \pm 0.03$ mm/s, $\Gamma = 0.29 \pm 0.02$ mm/s and $\delta_{CS} = 0.55 \pm 0.01$ mm/s, QS $= 0.64 \pm 0.03$ mm/s, $\Gamma = 0.25 \pm 0.02$ mm/s at room temperature and 80 K, respectively. All of these parameters are close to those of FeAs [11]. The relative abundance of this phase is 21 %. The same foreign phase was also observed in SmFeAsO though with smaller different hyperfine parameters [12]. At the lower temperature the doublet disappears, instead a broadened structure is observed, that also corresponds to FeAs, as FeAs is antiferromagnetic below 77 K [11].

In conclusion, the superconductor $Sm_{0.85}Ba_{0.15}FeAsO_{0.7}F_{0.3}$ samples with $T_c = 37$ K have been studied by Mossbauer spectroscopy, throughout the temperature range of 20–290 K. Within the Debye model framework the Debye temperature value evaluated is $\theta_D \sim 390$ K. Unusual behavior of the central shift as a function of temperature was observed below 60 K and has been interpreted by the change of s-electron density at the iron nuclei. Phonon softening near T_c was not observed.

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