Mössbauer Study of BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$

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1. Introduction

The discovery of high-temperature superconductivity $T_c = 26$ K in fluorine-doped LaFeAsO$_{1-x}$F$_x$[1] has resulted in widespread interest and exploration of related materials. Recently, the first electron-doped double-Fe$_2$As$_2$-layer Fe-based superconductor, BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ with the superconducting transition temperature of $T_{c\text{onset}} = 30$ K was synthesized.[2]

This 12442-type compound can be viewed as the result of intergrowth of ThCr$_2$Si$_2$-type (122-type) BaFe$_2$As$_2$ and ZrCuSiAs-type (1111-type) ThFeAsN$_{0.7}$O$_{0.3}$. The latter phase is also superconducting with a slightly lower $T_c$. As the phase contains iron, $^{57}$Fe Mössbauer spectra can be used for recording presence of local magnetic and electric interactions, as well information about the Fe valence and possible changes in the vibrational spectrum of Fe, which was the aim for this work. To the best of our knowledge, there are not yet any Mössbauer studies on BaTh$_2$Fe$_4$As$_4$(N$_{1-x}$O$_{x}$)$_2$.

2. Results and Discussion

2.1. XRD

The phase composition of the BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ sample was checked by X-ray powder diffraction. The tetragonal space group $I4/mmm$, No. 139 was used for BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ to confirm the origin of the observed peaks in the diffraction pattern. The room-temperature powder XRD pattern of the BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ sample is shown in Figure 1. All observed peaks can be indexed with reflections of the main phase and the ThFeAsN$_{1-x}$O$_x$ impurity. The latter phase contains some oxygen judging by the value of lattice parameter $a = 3.98659$ Å.[3] The fitted lattice parameter values for the BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ were $a = 3.9886$ Å and $c = 29.853$ Å. From the Rietveld refinement analysis of the XRD spectrum the weight percentage of the main component BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ was 88.24 and for ThFeAsN$_{0.7}$O$_{0.3}$, 11.76, respectively. The Rietveld result can be converted (assuming perfect interelemental stoichiometry) into Fe mass portions using the molar mass and iron mass percent for each component. Although BaFe$_2$As$_2$, due to the detection limit for XRD of $\approx$5%, is “invisible” in the Rietveld analysis, the following sample composition is assumed

$$[\text{ThFeAsN}_{0.7}\text{O}_{0.3}]_{2x} + [\text{BaFe}_2\text{As}_2]_x + [\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_{0.7}\text{O}_{0.3})]_{1-x}$$

where $x$ denotes the concentration of impurities. The conversion is based on the molar masses of the three phases: 376.81, 398.86, and 1153.68 g mol$^{-1}$ for ThFeAsN$_{0.7}$O$_{0.3}$, BaFe$_2$As$_2$, and BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$, respectively. The corresponding mass percentages of Fe are 14.82, 28.00, and 19.36 in the three phases. In accord with this we expect that 4.04%, 7.65%, and 88.31% of the signal in the Mössbauer measurements arise from the three phases.

2.2. Mössbauer Spectra

At all temperatures, the $^{57}$Fe Mössbauer spectra are dominated by a singlet-like resonance line (see Figure 2). They can be fitted using one to two components in addition to the main singlet drawn in red. Absence of magnetic interaction for the dominating component indicates that possible spin density wave magnetism is suppressed down to 5 K. According to the literature, ThFeAsN gives rise to a singlet-like line with a small unresolved quadrupole splitting,[4] seemingly identical to the main-phase component we observe, and consequently they are indistinguishable from each other. While the Rietveld analysis revealed only two phases, BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ and ThFeAsN$_{0.7}$O$_{0.3}$, in the

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In addition, a small paramagnetic doublet (green), due to traces of Fe in the beryllium window of the detector, present at all temperatures and the velocity of light, $c$, is $9.3 	imes 10^5$ m/s. The isomer shift was constrained equal to that of the main singlet. The internal field was constrained to be $\geq 3.8$ T and for the quadrupole interaction we constrained $|eQV_{zz}| < 0.3$ mm s$^{-1}$. Finally, the intensity was constrained to be $\leq 5.0\%$. Below 25 K none of these constraints were actually needed, but at higher temperatures some of them were.

Owing to the fact that the main component and the parent component ThFeAsN$_{0.7}$O$_{0.3}$ merge at all temperatures and the component due to BaFe$_2$As$_2$ also merges upon passing its Néel temperature, it is neither possible to separately obtain the absorption area nor the isomer shift values for the main component. Therefore, the total absorption area for the whole spectrum, except that of the detector window, and the isomer shift values of the main component are shown in Figure 4 and 5 as functions of the temperature.

The isomer shift data of Figure 4 can be fitted using the Debye model for the second-order Doppler shift:

$$\delta(T) = \delta_0 - \frac{9k_B\theta_D}{16Mc} - \frac{9k_B T}{2Mc} \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{x^3 \, dx}{e^x - 1}$$

where $\theta_D$ is the Debye temperature, $c$ is the velocity of light, $k_B$ the Boltzmann constant, $M$ the mass of the $^{57}$Fe atom, and $\delta_0$ the
temperature-independent part, i.e., the chemical isomer shift. Fitting the data yields $\delta_0 = 0.573(1) \text{ mm s}^{-1}$, which is compatible with low-to-intermediate-spin Fe$^{2+}$. The Debye temperature value was fitted at $\theta_D = 369(5)$ K. The total area of the spectrum, Figure 5, is proportional to the recoil-free fraction $f$ of absorption and can also be fitted using the Debye model:

$$\ln f = -\frac{6E_R}{k_B\theta_D} \left[ 1 + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/2} \frac{e^x}{e^x - 1} \, dx \right]$$

(3)

where the recoil energy $E_R = 0.0019 \text{ eV}$ for the 14.4 keV $\gamma$ quantum of $^{57}$Fe. In this case, the fitted Debye temperature was 352(5) K. In the Debye model, a quadratic density of phonon states is assumed, which is necessarily not true in reality. As the integrals of Equation (2) and (3) differ in the weighting of the normalized temperature $\theta/T$, the obtained Debye temperatures may differ considerably, which is not the case here. This indicates that the vibrations of the Fe atoms are fairly harmonic.

3. Conclusion

$^{57}$Fe Mössbauer spectra of the oxypnictide BaTh$_2$Fe$_4$As$_4$(N$_{0.7}$O$_{0.3}$)$_2$ and BaFe$_2$As$_2$ (above 140 K) are practically identical. Using the...
Figure 5. Total absorption area versus temperature for $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_0.7\text{O}_0.3)_2$. The data were fitted using the Debye model (see text) and the line is the result of the fitting. Statistical errors do not exceed the size of the symbols.

Debye model for analyzing the temperature-dependent part of the isomer shift data and the sample absorption yields Debye temperatures of 352–369 K, which are similar to those obtained for other pnictide superconductors. The chemical isomer shift value indicates that Fe is divalent in low-spin state when Th valence is close to +4 and As valence close to −3. A nonzero quadrupole splitting is seen below 80 K, reflecting the deviation from a regular tetrahedral coordination of As around Fe.

4. Experimental Section

The polycrystalline $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_0.7\text{O}_0.3)_2$ sample was synthesized by a solid-state reaction method using the source materials Ba rods (99%), Fe powders (99.998%), As pieces (99.999%), and ThO$_2$ powders (99.9%). First, the intermediate materials Th, Th$_2$N$_x$, Th$_2$As$_4$, FeAs, and BaFe$_2$As$_2$ were prepared. Fe$_3$As and Th$_2$As$_4$ were prepared by heating their stoichiometric mixtures in sealed evacuated quartz ampule to 1123 K, holding for 30 h. BaFe$_2$As$_2$ was prepared by reacting the mixtures of BaS and Fe$_2$As at 1273 K for 40 h. Other intermediate materials such as Th, Th$_2$As$_4$, and FeAs were prepared as reported elsewhere.$^{[9]}$ Then, stoichiometric mixtures of Fe, ThO$_2$, Th$_2$As$_4$, Th$_2$N$_x$, FeAs, and BaFe$_2$As$_2$ were pressed into pellets, and then placed in an alumina tube and sealed in an evacuated quartz ampule which was heated to 1223 K and held at this temperature for 60 h. The solid-state reactions were repeated with intermediate grinding to improve the sample quality.

For the Mössbauer measurements, the sample was reground and 80 mg of the powder was used for making the absorber by mixing with an epoxy glue and spreading it evenly on a thin Al foil. The properties of the $\text{BaTh}_2\text{Fe}_4\text{As}_4(\text{N}_0.7\text{O}_0.3)_2$ sample were characterized using $^{57}$Fe Mössbauer spectroscopy in transmission geometry. The spectra were measured using a $^{57}$Co:Rh source (Ritverc Co. 50 mCi June 2020) at temperatures between 4.8 and 305 K using maximum Doppler velocities of 2.0 and 2.6 mm s$^{-1}$. Additional control with a Doppler velocity $\approx 10$ mm s$^{-1}$ for the detection of magnetic phases was done. The sample was cooled using an Oxford CF 506 continuous-flow cryostat with liquid helium between 4.8 and 150 K and with liquid nitrogen between 77 and 305 K. At the start of the low-temperature measurements, the test chamber was partly filled with helium gas to ensure proper thermal conduct to sample. The temperature was controlled using an Oxford Intelligent Temperature Controller ITC 4. All spectra were fitted using a home-written program with the following Mössbauer parameters for the components: the quadrupole coupling constant $eQ\lambda_z$, relative intensities, isomer shift $\delta$ relative to $\alpha$-Fe, and internal hyperfine magnetic field $B$ when present. Transmission-integral fittings with the MoSSWinn 4.0 program$^{[10]}$ of selected spectra were used to confirm that the samples could be regarded as thin and that the line shape exhibits a small quadrupole splitting.

Powder X-ray diffraction (XRD) data used for the structural identification were collected at room temperature on a PanAnalytical X'Pert Pro MPD diffractometer using Cu K$\alpha$ ($\lambda = 1.54051$) radiation. Data were analyzed by the Rietveld method using the software program FullProf$^{[11]}$.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

Debye temperature, $^{57}$Fe Mössbauer spectroscopy, pnictide superconductors

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