Physical properties of the layered oxypnictide Sr$_2$ScFeAsO$_3$: a Mössbauer study down to 1.7 K

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Abstract
A polycrystalline sample of Sr$_2$ScFeAsO$_3$ was studied by $^{57}$Fe Mössbauer spectroscopy down to 1.7 K. In contrast to the earlier Mössbauer data, the obtained in this work results indicate that Sr$_2$ScFeAsO$_3$ is in paramagnetic state down to 10 K, while the spectra recorded at 4.6 K and 1.7 K show a weak magnetic order of Fe moments in the Fe$_2$As$_2$ layers. Temperature dependences of isomer shift and quadrupole splitting/shift are compared with specific heat and electrical resistivity data from earlier investigations revealing different local Debye temperatures for the Fe$_2$As$_2$ and perovskite-related Sr$_2$ScO$_3$ layers. Finally, a fast decrease of the carrier density was observed below 80 K and this effect seems to be responsible for the absence of superconductivity in the studied compound.

Keywords: magnetism, Mössbauer spectroscopy, iron-based superconductors

1. Introduction
The Sr$_2$ScFeAsO$_3$ belongs to the family of oxypnictides Sr$_2$AFeAsO$_3$ where A denotes Sc, Ti, Cr, V, and other transition metal atoms. These compounds crystallize in the tetragonal $P4/nmm$ space group and their structure consists of the perovskite Sr$_2$AO$_3$ blocks and the Fe$_2$As$_2$ layers, alternatively stacking up along the $c$-axis [1–4]. Their transport and magnetic properties have been systematically studied over recent years. It was found that Sr$_2$VFeAsO$_3$ undergoes superconducting (SC) transition at $T_c \approx 37.2$ K [3, 5] under ambient pressure and at $T_c = 46$ K under high pressure [6]. The Sr$_2$CrFeAsO$_3$ compound is not superconducting but exhibits antiferromagnetic order of the Cr$^{3+}$ moments [1, 4, 7]. In the case of Sr$_2$ScFeAsO$_3$, the literature reports are controversial [1, 2, 8–10]. The temperature dependences of the magnetic susceptibility presented in works [1, 2, 10] show paramagnetic behaviour down to 1.7 K without any anomaly which would ascribe to magnetic ordering or superconductivity. At the same time, the magnetoresistivity study suggests the formation of the spin density wave (SDW) at around 125 K [10], while the combined $^{57}$Fe transmission Mössbauer spectroscopy (TMS) and muon spin relaxation measurements demonstrated static magnetic order of the Fe sublattice in the Sr$_2$ScFeAsO$_3$ compound below 35 K [9]. According to this work, the TMS spectrum recorded for polycrystalline Sr$_2$ScFeAsO$_3$ at room temperature shows a simple paramagnetic doublet. At 35 K the TMS spectrum splits into two components, remaining paramagnetic doublet but exhibits antiferromagnetic order of the Fe$^{3+}$ moments [1, 4, 7]. In the case of Sr$_2$ScFeAsO$_3$, the literature reports are
Moreover, a visual inspection of the TMS spectra presented in work [9] indicates that the studied sample may contain some amount of magnetic impurities or structural inhomogeneities since the shape of Zeeman sextet observed at 4.3 K deviates significantly from the corresponding one measured at 4.2 K for antiferromagnetically ordered Sr₂CrFeAsO₃ compound [4]. Its broad and irregular shape indicates a high magnetic disorder or the presence of SDW which was never been reported in the Sr₂AFEAsO₃ systems. Additionally, values of isomer shift determined from Sr₂ScFeAsO₃ spectra tend to decrease with decreasing temperature (IS = 0.465(3) mm s⁻¹ at 300 K and IS = 0.426(4) mm s⁻¹ at 4.3 K) [9]. This result is rather surprising and unexpected because in the case of iron pnictides, the IS(T) dependence is dominated by a second-order Doppler shift [4, 5, 11, 12]. In general, the second-order Doppler shift is a temperature-dependent effect on the center shift of the Mössbauer spectrum according to which the IS of a sample with no phase transition increases and saturates at low temperatures [13]. Therefore, to resolve the aforementioned controversies, in this paper, we present new results of ⁵⁷Fe transmission Mössbauer spectroscopy measurements on a polycrystalline Sr₂ScFeAsO₃.

In contrast to the results presented by Munevar et al [9], our measurements clearly show that the Sr₂ScFeAsO₃ compound is in paramagnetic state down to 10 K, while spectra measured at 4.6 K and 1.7 K indicate a weak magnetic order of Fe moments in the Fe₂As₂ layers. Additionally, temperature dependences of isomer shift and quadrupole splitting/shift are discussed in details.

2. Experimental details

Polycrystalline samples of Sr₂ScFeAsO₃ were prepared by solid phase reaction in a manner similar to reported in [1]. The starting components Sr, SrO, Sc₂O₃ and FeAs (previously obtained by the reaction of As and Fe at 700 °C) were mixed in molar proportions of 0.6:1.5:0.5:1 and pressed into pellets. Weighing, mixing and pressing of the ingredients was carried out in a glove box in a protective Ar atmosphere with moisture and oxygen levels below 1 ppm. The pellets were sealed in evacuated quartz ampoules and annealed at 1050 °C for 50 h. It is worth noting that a 5% excess of Sr was necessary to compensate Sr losses and to prevent sample contamination with FeAs, which was particularly important for Mössbauer spectroscopy.

The quality of the obtained sample was checked by x-ray powder diffraction (XRD) at room temperature using an X’Pert PRO diffractometer with CuKα radiation. The recorded x-ray diffraction pattern of the studied sample is shown in figure 1. The analysis of the obtained XRD data, using Rietveld refinement method, revealed that the sample crystallize in the tetragonal \textit{P4/nmm} space group. The determined lattice parameters of the studied compound \(a = b = 0.40491(2) \text{ nm}\) and \(c = 1.5789(1) \text{ nm}\) are in agreement with those reported before for Sr₂ScFeAsO₃ [1, 2].

Magnetic measurements in magnetic fields up to 70 kOe were performed in the temperature range of 2–300 K using a superconducting quantum interference device magnetometer (Quantum Design MPMS XL-7). The presented values of magnetization have an uncertainty of less than 5%.

The ⁵⁷Fe Mössbauer spectra were measured in transmission geometry with a conventional constant-acceleration spectrometer, using a ⁵⁷Co-in-Rh standard source with a full width at half maximum (FWHM) of 0.22 mm s⁻¹. The powdered samples were placed in thin PVC foils and their temperature in the range of 1.7–300 K was controlled using a variable-temperature insert in an Oxford Instruments Spectromag cryostat. The obtained TMS spectra were analysed using a least-squares fitting procedure which allows to determine the hyperfine interactions parameters such as isomer shift (IS), quadrupole splitting/shift (QS) and hyperfine field (B) as well as the absorption spectral areas (C) and linewidths (Γ). The IS values presented in this paper are related to the α-Fe standard.

3. Results and discussion

Figure 2 presents the temperature dependence of the magnetic susceptibility measured for Sr₂ScFeAsO₃ sample at \(\mu_0H = 1 \text{ T}\). The inset shows field dependence of magnetisation at 2 K.

![Figure 1. X-ray powder diffraction pattern of the Sr₂ScFeAsO₃ sample. Experimental (circles) and calculated (solid line) profiles and differences between them (solid line in the bottom). Lower bars show diffraction peak positions of Sr₂ScFeAsO₃.](image1.png)

![Figure 2. The temperature dependence of the magnetic susceptibility measured for Sr₂ScFeAsO₃ sample at \(\mu_0H = 1 \text{ T}\).](image2.png)
can notice, the \(M(H)\) curve shows non-linear magnetization response to applied magnetic field and the magnetic saturation is not reached even at \(\mu_0 H = 7\) T. Moreover, no spontaneous magnetization as well as magnetic hysteresis were observed for the studied system. Therefore, this observation cannot be explained by the presence of a small amount of ferromagnetic impurities as it was suggested in the case of the \(M(H)\) curve obtained for the same system at 10 K [10]. In fact, the behaviour of \(M(H)\) curve reveals a weak magnetic correlations between Fe in the Fe\(_2\)As\(_2\) layers at 2 K.

The TMS spectra recorded for Sr\(_2\)ScFeAsO\(_3\) in the temperature range 1.7–300 K are presented in figure 3 together with transmission integral fits. The selected Mössbauer parameters derived from the fitting procedure of these spectra are listed in table 1. As expected from the crystal structure (one single iron site), all measured spectra consist of one component over the whole temperature range. The lack of additional subspectra indicates a high purity of the prepared sample. All measured TMS spectra could be fitted by using paramagnetic doublet which points out the presence of electric quadrupole interaction associated with the non-cubic site symmetry of the iron atoms. However, below 10 K, the spectra display a distinct broadening of the doublet. The obtained line widths \(\Gamma\) are equal to 0.38, 0.42 and 0.45 mm s\(^{-1}\) at 10, 4.2 and 1.7 K, respectively. Since relaxation effects on the low-temperature TMS spectra are unlikely with Fe in such system [14], this broadening could be explained assuming that it is a consequence of the appearance at around 4.6 K of a very small hyperfine field \(B\) connected with a weak magnetic order of Fe in the Fe\(_2\)As\(_2\) layers. The assumption is in agreement with \(M(H)\) data obtained at 2 K as well as is commonly used to interpret doublet broadening at low temperatures in various Mössbauer works [15–17]. Therefore, the spectra recorded at 4.6 K and 1.7 K could also be fitted by using Zeeman sextet. Figure 4 presents the comparison between mentioned above spectra fitted by doublet or sextet with the same \(\Gamma\). As one can notice, especially in the case of spectrum measured at 1.7 K, a slightly better fitting could be achieved by using sextet. Regardless of the accepted interpretation (paramagnetic state down to 1.7 K or weak magnetic order of Fe at 4.6 and 1.7 K), it is clear that the obtained TMS results are different than those presented in work [9]. The previous Mössbauer study of Sr\(_2\)ScFeAsO\(_3\) revealed that below 40 K, the TMS spectrum splits into two phases, remaining paramagnetic doublet and magnetic sextet. With decreasing temperature, the paramagnetic doublet fraction diminishes while the hyperfine magnetic field increases and reaches a saturation value of \(B = 1.65\) T at 4.3 K [9]. In contrast to those findings, the results obtained in

![Figure 3](image3.jpg)

Figure 3. The TMS spectra recorded for Sr\(_2\)ScFeAsO\(_3\) in the temperature range 1.7–300 K fitted with one doublet.

| \(T(K)\) | IS (mm s\(^{-1}\)) | QS (mm s\(^{-1}\)) | \(B(T)\) (mm s\(^{-1}\)) | \(\Gamma\) (mm s\(^{-1}\)) |
|-------|-----------------|-----------------|-----------------|-----------------|
| 300   | 0.453(2)        | −0.202(2)       | 0               | 0.34(1)         |
| 250   | 0.481(2)        | −0.202(2)       | 0               | 0.36(1)         |
| 180   | 0.517(4)        | −0.201(5)       | 0               | 0.39(2)         |
| 120   | 0.552(2)        | −0.187(6)       | 0               | 0.40(2)         |
| 80    | 0.567(2)        | −0.176(6)       | 0               | 0.41(2)         |
| 40    | 0.582(2)        | −0.183(4)       | 0               | 0.38(2)         |
| 20    | 0.581(4)        | −0.188(6)       | 0               | 0.36(2)         |
| 10    | 0.580(3)        | −0.201(4)       | 0               | 0.38(2)         |
| 4.6 (doublet) | 0.579(4)       | −0.230(5)       | 0               | 0.42(2)         |
| 4.6 (sextet) | 0.581(4)        | −0.238(6)       | 0.19(6)         | 0.39(3)         |
| 1.7 (doublet) | 0.576(4)       | −0.244(5)       | 0               | 0.45(2)         |
| 1.7 (sextet) | 0.579(4)        | −0.256(6)       | 0.38(4)         | 0.40(3)         |
Figure 4. The TMS spectra recorded for Sr₂ScFeAsO₃ at 4.6 K and 1.7 K fitted with one doublet with fixed \( \Gamma \) (left panel) and one sextet (right panel). Solid lines in the bottom show differences between experimental and calculated values.

Figure 5. Temperature dependences of (a) IS and (b) QS obtained from TMS spectra of Sr₂ScFeAsO₃. The solid line represents the fit to equation (1).

This work shows that the temperature at which the Zeeman sextet probably appears is much lower and it is close to 5 K. The estimated \( B \) values are much lower than those reported in work [9] and increase with further lowering temperature. Alternatively, one may neglect the small broadening of the spectral lines at 4.6 and 1.7 K. In this scenario, the differences between results presented in this work and in work [9] are much more significant since the absence of sextet at low temperatures indicates that Sr₂ScFeAsO₃ is in paramagnetic state down to 1.7 K. Another important difference is the absence of spectra which are composed simultaneously with doublet and sextet as it was in the case of Sr₂ScFeAsO₃ spectra recorded in the temperature range of 35–10 K [9]. This finding suggests that the sample studied in this work is much more homogeneous since all Fe atoms are in the same magnetic phase. At the same time, the coexistence of two phases observed by Munevar et al [9] may be attributed to the presence of various domains in their sample for which ordering temperature lies between 35–4.6 K. This effect may be caused by the presence of various number of oxygen vacancies in the different regions of the polycrystalline Sr₂ScFeAsO₃ sample. Such explanation is very plausible since in the case of Sr₂VFeAsO₃–\( \delta \), the oxygen deficiency leads to significant changes in electronic and magnetic properties of this compound [5].

The value of IS = 0.453(1) mm s\(^{-1}\) determined at 300 K is close to IS = 0.465(3) mm s\(^{-1}\) reported in work [9]. At the same time, in contrast to the results obtained by Munevar et al [9], in this work the IS values increase with decreasing temperature as it was expected due to the second-order Doppler effect. In terms of the Debye approximation of the lattice vibrations, the second-order Doppler shift IS\(_{\text{SOD}}\)(\( T \)) and the Debye temperature \( \Theta_D \) are connected via the below relation [13]:

\[
\text{IS}(T) = IS_0 + IS_{\text{SOD}}(T) = IS_0 - \frac{9 k_B T}{2 Mc} \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} e^{x^3} dx
\]  

(1)

where IS\(_0\) denotes the temperature-independent isomer shift, \( M \) is the mass of \(^{57}\)Fe, \( k_B \) is the Boltzmann constant and \( c \) is the speed of light in vacuum. The fit of equation (1) to experimental IS\(_0\)(\( T \)) values, which is presented in figure 5(a), yields IS\(_0\) = 0.579(2) mm s\(^{-1}\) and \( \Theta_D = 374(22) \) K. Here, it should be noted that the TMS technique is sensitive only to the immediate neighbourhood of the Mössbauer probe atom \(^{57}\)Fe and due to this, the estimated \( \Theta_D \) value from TMS spectra should be treated as a local Debye temperature of iron atoms in the Fe\(_2\)As\(_2\) layers. Nevertheless, the obtained local Debye temperature could be compared with the bulk Debye temperature \( \Theta_D^{\text{bulk}} = 305 \) K determined from specific heat measurements [10]. As one can notice the local \( \Theta_D \) is higher than the bulk one. This finding suggests that in the case of Sr₂ScFeAsO₃ compound, the Debye temperature is layer-dependent and the local \( \Theta_D \) for the perovskite-related Sr₂ScO₃ layers should be lower than corresponding one for the Fe\(_2\)As\(_2\) layers.

The temperature dependence of the QS parameter, which is directly proportional to the electric field gradient at the Fe nucleus, is presented in figure 5(b). Since the sign of the QS parameter cannot be determined from the paramagnetic doublet [13], the negative values of this parameter were deduced from the fitting of the magnetically split spectra recorded at 4.6 K and 1.7 K. In both cases a much more reasonable fit was obtained for negative QS value than the positive one. Additionally, Munevar et al also reported the negative QS value for this system [9]. In the case of many iron pnictides studied by \(^{57}\)Fe
Mössbauer spectroscopy, the magnitude of QS increases with decrease of temperature and this behaviour can be described with the empirical \( T^{3/2} \) law \([4, 11, 18, 19]\). However, as one can notice in figure 5(b), the QS(\( T \)) dependence obtained for Sr\(_2\)ScFeAsO\(_3\) cannot be described with that law. Having the knowledge that the Sr\(_2\)ScFeAsO\(_3\) compound does not undergo any structural transition down to 1.7 K, the rapid increase of the absolute QS values below 80 K can be connected with electrical resistivity data presented in works \([2, 10]\), where below \(\sim80\) K the resistivity sharply increases with decreasing temperature. Therefore, the aforementioned change of QS can be explained by a systematic localization of the formerly delocalized electrons in the Fe\(_2\)As\(_2\) layers during lowering temperature. Based on our results, we propose that a rapid loss of charge carriers with lowering temperature is probably mainly responsible for the absence of superconductivity in Sr\(_2\)ScFeAsO\(_3\).

### 4. Conclusions

The study of Sr\(_2\)ScFeAsO\(_3\) by \(^{57}\)Fe Mössbauer spectroscopy reveals interesting magnetic and electronic properties of this compound. In contrast to the previous Mössbauer data, the obtained in this work results show that Sr\(_2\)ScFeAsO\(_3\) is in paramagnetic state down to 10 K, while the broadening of TMS spectra at 4.6 K and 1.7 K indicate the weak magnetic order of Fe moments in the Fe\(_2\)As\(_2\) layers. Alternatively, one may neglect the small broadening of the spectral lines at 4.6 and 1.7 K. In this scenario, the differences between previous and current findings are much more significant since the absence of Zeeman sextet at low temperatures indicates that Sr\(_2\)ScFeAsO\(_3\) is in paramagnetic state down to 1.7 K. The local Debye temperature for the Fe\(_2\)As\(_2\) layers \(\Theta_D = 374(22)\) K calculated from the IS(\( T \)) dependence in higher than the bulk \(\Theta_D^{bulk} = 305\) K determined from specific heat measurements. This finding can be explained assuming that in the case of Sr\(_2\)ScFeAsO\(_3\) compound, the Debye temperature is layer-dependent and the local \(\Theta_D\) for the perovskite-related Sr\(_2\)ScO\(_3\) layers should be much lower than corresponding one for the Fe\(_2\)As\(_2\) layers. Finally, the rapid increase of the magnitude of QS parameter observed below 80 K is connected with the systematic localization of the formerly delocalized electrons in the Fe\(_2\)As\(_2\) layers during lowering temperature. Based on our results, we propose that a rapid loss of charge carriers with lowering temperature is probably mainly responsible for the absence of superconductivity in Sr\(_2\)ScFeAsO\(_3\).

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