Journal of Alloys and Compounds 609 (2014) 150–155

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Electric field gradient wave (EFGW) in iron-based superconductor $Ba_{0.6}K_{0.4}Fe_2As_2$ studied by Mössbauer spectroscopy

A.K. Jasek [a], K. Komędera [a], A. Błachowski [a], K. Ruebenbauer [a,*], Z. Bukowski [b], J.G. Storey [c,d], J. Karpinski [e,f]

[a] Mössbauer Spectroscopy Division, Institute of Physics, Pedagogical University, ul. Podchorążych 2, PL-30-084 Kraków, Poland
[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, PL-50-422 Wrocław, Poland
[c] Cavendish Laboratory, University of Cambridge, CB3 0HE Cambridge, United Kingdom
[d] School of Chemical and Physical Sciences, Victoria University, P.O. Box 600, Wellington, New Zealand
[e] Laboratory for Solid State Physics, ETH Zurich, CH-8093 Zurich, Switzerland
[f] Institute of Condensed Matter Physics, EPFL, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 28 March 2014
Accepted 18 April 2014
Available online 28 April 2014

Keywords:
Iron-based superconductors
Mössbauer spectroscopy
Strongly correlated electrons

ABSTRACT

The optimally doped '122' iron-based superconductor $Ba_{0.6}K_{0.4}Fe_2As_2$ has been studied by ^{57}Fe Mössbauer spectroscopy versus temperature ranging from 4.2 K till 300 K with particular attention paid to the superconducting transition around 38 K. The spectra do not contain magnetic components and they exhibit *quasi*-continuous distribution of quadrupole split doublets. A distribution follows the electric field gradient (EFG) spatial modulation (wave) – EFGW. The EFGW is accompanied by some charge density wave (CDW) having about an order of magnitude lesser influence on the spectrum. The EFGW could be modeled as widely separated narrow sheets with the EFG increasing from small till maximum value almost linearly and subsequently dropping back to the original value in a similar fashion – across the sheet. One encounters very small and almost constant EFG between sheets. The EFGW shape and amplitude as well as the amplitude of CDW are strongly affected by a superconducting transition. All modulations are damped significantly at transition (38 K) and recover at a temperature being about 14 K lower. The maximum quadrupole splitting at 4.2 K amounts to about 2.1 mm/s, while the dispersion of CDW seen on the iron nuclei could be estimated far away from the superconducting gap opening and at low temperature as 0.5 el./a.u.^{3}. It drops to about 0.3 el./a.u.^{3} just below transition to the superconducting state.

1. Introduction

There are several reports on the sensitivity of Mössbauer spectroscopy to the superconducting transition [1–7] in particular for the iron-based superconductors [8,9]. Variation in the lattice dynamics due to the superconducting transition has been predicted as well [10]. Generally some variation in the recoilless fraction is observed across the transition and is sometimes accompanied by variation in the second order Doppler shift (SOD), but many reports are inconsistent. Some changes of the lattice stiffness have been observed e.g. by the neutron scattering in iron pnictides [11–13]. Mössbauer spectroscopy is generally insensitive to the superconducting transition in classical superconductors [14,15]. However, for unconventional superconductors where some very short-range pairing mechanisms could apply everything depends on the coherence length of the composite boson (Cooper pair) as long as local effects are considered. One has to note that superconductivity drastically modifies density of the electronic states at the Fermi surface, and the latter has influence on the hyperfine interactions. Hence, a search by the Mössbauer spectroscopy is justified – a method does not perturbing superconducting state.

We have chosen an optimally doped iron-based superconductor of the '122' family – namely $Ba_{0.6}K_{0.4}Fe_2As_2$. It has a relatively high critical temperature of $T_{sc} = 38$ K [16] and the magnetism is completely suppressed at optimal doping making analysis of the spectra much easier [17]. High-quality samples and large single crystals are available for the '122' family in contrast to other families of iron-based superconductors. One can observe for the sample in question hyperfine parameters, i.e. the quadrupole splitting and the total shift. Some auxiliary information is contained in the absorber line width. The area under the absorption cross-section monitors the recoilless fraction on the resonant atoms. Hence, one can look at the variation of the above parameters across a transition to the superconducting state.

* Corresponding author. Tel.: +48 12 662 6317; fax: +48 12 637 2243.
E-mail address: sfrueben@cyf-kr.edu.pl (K. Ruebenbauer).

http://dx.doi.org/10.1016/j.jallcom.2014.04.129
0925-8388/

2. Experimental

The polycrystalline sample of $Ba_{0.6}K_{0.4}Fe_2As_2$ was prepared by a solid state reaction method from high-purity Ba, K, As, and Fe with natural isotopic composition, as described in Ref. [18].

The Mössbauer absorber was prepared in powder form by mixing 39 mg of $Ba_{0.6}K_{0.4}Fe_2As_2$ with the B_4C carrier. The thickness of the absorber amounted to 19 mg/cm^2 of $Ba_{0.6}K_{0.4}Fe_2As_2$. A commercial ^{57}Co(Rh) source kept at room temperature was applied. A Janis Research Co. SVT-400 cryostat was used to maintain the absorber temperature, with the long time accuracy better than 0.01 K (except at 4.2 K, where the accuracy is better than 0.1 K). A RENON MsAa-3 Mössbauer spectrometer equipped with a Kr-filled proportional counter was used to collect spectra in the photo-peak window. The geometry, count-rate and single channel analyzer window borders were kept constant during all measurements constituting a single uninterrupted series with increasing subsequent temperatures within the range 4.2–65 K. Additional spectra were collected at 80 K and 300 K. The velocity scale was calibrated by a He-Ne laser-equipped interferometer. The data were processed within the transmission integral approximation by the Mosgraf-2009 software suite applying GmfpQDW application [19].

3. Theoretical background for EFGW and data evaluation method

The Mössbauer spectroscopy is sensitive to the charge (electron) distribution around the resonant nucleus via the isomer shift and the electric quadrupole interaction. The former is possible to observe due to the fact that two nuclear levels are involved and it amounts to $S_I = \alpha(\rho - \rho_S)$, where the parameter α is the so-called calibration constant, while the symbol ρ stands for the electron density on the resonant nucleus in the absorber. The symbol ρ_S denotes corresponding electron density in the source or reference material (constant). For a resonant transition from the ground to the first excited nuclear state of ^{57}Fe one has $\alpha = -0.291$(mm/s)(a.u.)^{3}el.$^{-1}$ [20]. A total spectral shift versus some reference material like α-Fe (at normal conditions) or source involves a second order Doppler shift (SOD) S_D as well. However, the latter shift is usually the same for all resonant atoms at a given temperature and pressure provided the source is kept under constant temperature and pressure as well. Hence, a total shift versus reference material (α-Fe at room temperature and normal pressure in the present work) amounts to $S = S_D + S_I$. The electric quadrupole interaction affects solely the first excited nuclear state for aforementioned transition as the ground state has nuclear spin $I_g = 1/2$. The first excited state has spin $I_e = 3/2$ and hence, a doublet is observed with the splitting $\Delta = 2|\varepsilon|$. For isotropic recoilless fraction and completely random absorber this is symmetrical doublet composed of two Lorentzian lines having the same line width Γ. Note that aforementioned resonant transition is of the pure M1 character. It is assumed that the source is resonantly thin and emits unpolarized radiation as a single Lorentzian line having width Γ_S. The parameter ε (quadrupole coupling constant) evaluates to $\varepsilon = [(ecQ_e)/(4E_0)]V_{zz}(1+\eta^2/3)^{1/2}$. The symbol e stands for the positive elementary charge, while the symbol c denotes speed of light in vacuum. The spectroscopic electric quadrupole moment amounts to $Q_e = +0.17$b for the first excited state in ^{57}Fe [20]. The symbol E_0 denotes energy of the resonant transition (14.41 keV), while the symbol V_{zz} stands for the principal component of the electric field gradient tensor (EFG) on the resonant nucleus. The parameter $0 \leqslant \eta \leqslant 1$ is the so-called asymmetry parameter of the EFG. It equals null for the axially symmetric EFG. One can measure only the splitting Δ for a transition above mentioned in the absence of magnetic hyperfine interactions, and for the material being isotropic in the sense defined above.

The charge density wave (CDW) is a spatial modulation of the charge (electron) density and for three dimensional or layered systems it is usually approximated by the time independent standing plane wave with the spatial period quite often being incommensurate with the lattice period in the same direction. The s electrons in CDW affect the isomer shift on resonant nuclei leading to the distribution of the isomer shifts. A contribution from the minor relativistic p electrons could be neglected for such light atoms like iron. Cieślak and Dubiel [21] performed detailed studies on the influence of the CDW shape on the Mössbauer spectra. For a similar modulation of the density of electrons with higher angular momentum than zero one can expect modulation of the EFG in addition to the constant EFG induced locally by some symmetry breaking below cubic. The latter effect could be much stronger than the previous one, i.e. the isomer shift modulation, (about an order of magnitude) due to the local enhancement caused by redistribution of the valence electrons. Hence, the parameter ε could be written in the form $\varepsilon = \varepsilon(\mathbf{q}\cdot\mathbf{r}) = [(ecQ_e)/(4E_0)]V_{zz}(\mathbf{q}\cdot\mathbf{r})[1+\eta^2(\mathbf{q}\cdot\mathbf{r})/3]^{1/2}$. The symbol $\mathbf{q}$ denotes wave vector of the time independent standing wave leading to the modulation, while the symbol $\mathbf{r}$ stands for a position of the particular resonant nucleus. The latter type of modulation is abbreviated further as EFGW (electric field gradient wave). One cannot fit simultaneously CDW and EFGW shapes due to the limited resolution. The parameter $\varepsilon = \varepsilon(\mathbf{q}\cdot\mathbf{r})$ could be expanded into harmonics as follows:

$$\varepsilon = \varepsilon(\mathbf{q}\cdot\mathbf{r}) = \varepsilon_0 + \sum_{n=1}^{N}(a_n\cos[n(\mathbf{q}\cdot\mathbf{r})] + b_n\sin[n(\mathbf{q}\cdot\mathbf{r})]). \quad (1)$$

The symbol ε_0 stands for a constant component. The parameters a_n and b_n denote amplitudes of subsequent harmonics. For a complex shape of EFGW ($N \gg 1$) it is virtually impossible to fit independent amplitudes of various harmonics due to the limited resolution. The situation is much better in the case of the spin density waves (SDW) as the resolution of the magnetically split spectra is much higher [22]. Hence, some approximation is necessary in the case of EFGW (and even more in the case of CDW). We have used the following approximation within the range $0 \leqslant \mathbf{q}\cdot\mathbf{r} \leqslant 2\pi$:

$$\varepsilon = \varepsilon(\mathbf{q}\cdot\mathbf{r}) = \varepsilon_0 + AF_{\max}^{-1}F(\mathbf{q}\cdot\mathbf{r}). \quad (2)$$

Here the symbol $A > 0$ stands for the amplitude of the modulation, while the symbol $F_{\max} > 0$ denotes maximum value of the function $F(\mathbf{q}\cdot\mathbf{r})$ taking on the following form:

$$F(\mathbf{q}\cdot\mathbf{r}) = \sin(\mathbf{q}\cdot\mathbf{r})\left\{\exp\left[-\beta^2\left(\frac{\mathbf{q}\cdot\mathbf{r}}{2\pi}-\frac{1}{4}\right)^2\right] + \exp\left[-\beta^2\left(\frac{\mathbf{q}\cdot\mathbf{r}}{2\pi}-\frac{3}{4}\right)^2\right]\right\}. \quad (3)$$

The shape of EFGW is described by the adjustable parameter β. This approximation works reasonably and it relies on the two adjustable parameters only A and β being therefore numerically stable. Hence, the absorption cross-section is described by a *quasi*-continuous set of symmetrical doublets having common total shift S (average total shift) and being composed of Lorentzians having all the same line width. The absorber dimensionless resonant thickness t_A is an adjustable parameter within standard transmission integral used to fit the spectrum. Another parameter describing transmission integral is the effective source recoilless fraction, i.e. a recoilless fraction of the source corrected for the detector background under the resonant γ-ray line. However, for a single series of uninterrupted measurements with approximately constant average count-rate (within the linear amplitude and frequency response range of the detector system) above parameter could be kept constant upon having measured it independently. It has been set here to $f_S/\lambda = 0.56$ with the symbol f_S denoting recoilless fraction of the source and symbol $\lambda > 1$ standing for the background counts correction. The parameter λ is defined as $\lambda = (s+b)/s$, where s stands for the number of counts due to the resonant line (both recoilless and with recoil), while b denotes number of counts belonging to the background. Both numbers of counts are those accepted within the window of the analyzer.