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Magnetic and structural transitions in the iron-chalcogenide high- T_c superconductor: $K_{0.8}Fe_{1.76}Se_{2.00}$

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⁵⁷Fe Mössbauer spectroscopy was used to study single-crystals of $K_{0.8}Fe_{1.76}Se_{2.00}$ from 6 K to 673 K. At 6 K, the hyperfine field (B_{hf}) is canted away from the c -axis by $18 \pm 3^\circ$. The temperature dependence of B_{hf} follows a spin wave model with a spin excitation gap of 9 ± 1 meV. A sudden increase in the linewidth and a corresponding drop in $(1/2)eQV_{zz}$ at $T_N = 532$ K are indications of strong coupling between the magnetic and structural transitions. © 2012 American Institute of Physics. [doi:10.1063/1.3673848]

I. INTRODUCTION

The iron chalcogenide $K_{0.8}Fe_{1.8}Se_2$ is superconducting up to $T_{sc} = 30$ K (Ref. 1) and antiferromagnetic up to $T_N \sim 559$ K.^{2,3} Neutron diffraction suggested that the $3.3 \mu_B$ iron moments are oriented parallel to the c -axis,² while single-crystal Mössbauer data demonstrated a slight canting of the moments away from the c -axis.³ Single-crystal x-ray diffraction showed that superconducting $K_yFe_{2-x}Se_2$ adopts an $I4/m$ structure below T_N , with a $(\sqrt{5} \times \sqrt{5} \times 1)$ iron vacancy ordering and that iron atoms fully occupy the 16i site.⁴ The collapse of the magnetism is associated with the loss of this vacancy ordering at a first order $I4/m \rightarrow I4/mmm$ magnetostructural transition.^{2,3}

Single-crystal Mössbauer studies of $A_yFe_{2-x}Se_2$ ($A = K, Rb$)^{3,5,6} all show a clear asymmetry in the intensity of the absorption peaks and a failure to account for this may lie behind the disagreement on the ordering direction with angles of 0° ,² 18° ,³ and $40\text{--}45^\circ$ (Ref. 7) between the moments and the c -axis all being proposed. Li *et al.*⁵ have also claimed that the temperature dependence of the hyperfine field [$B_{\text{hf}}(T)$] exhibits evidence for a spin excitation gap (SEG) and that there is a drop in absorption associated with the superconducting transition. All of these issues are addressed here by analyzing the single-crystal Mössbauer spectra using a full Hamiltonian solution to the spectral shape.

II. EXPERIMENTAL METHODS

Single-crystals of $K_{0.80}Fe_{1.76}Se_{2.00}$ were grown and characterized as previously described.⁸ The crystals were cleaved and mounted into spectrometers with the γ beam aligned along the c -axis of the crystal mosaic.³ The Mössbauer spectra were collected using 50 mCi ⁵⁷CoRh sources and electromechanical drives using both constant acceleration

and sine modes in conventional spectrometers. Calibration was done using an α -Fe foil as a reference. Two closed-cycle He refrigerators were used in addition to a furnace for the high temperature data. One sample was cycled through the Néel temperature twice and another was cycled three times, spending over a week above 550 K. Contrary to reports by Nowik *et al.*,⁷ we observed no degradation of the samples below 673 K and the $I4/m \rightarrow I4/mmm$ structural transition appeared to be reversible.

The Mössbauer spectra were fitted using a nonlinear least squares minimization routine for ⁵⁷Fe single-crystal spectra employing the general static Mössbauer solution⁹ using a full Hamiltonian code.

III. RESULTS

The Mössbauer spectrum at 6 K (Fig. 1) was fitted using two components. The magnetic sextet, accounts for $86 \pm 1\%$ of the spectrum and a paramagnetic impurity, the doublet, represents $14 \pm 1\%$ of the spectrum. The deviation of the magnetic peak intensities from the 3:2:1:1:2:3 ratio and the paramagnetic peaks from the 1:1 ratio, is due to the use of oriented single-crystals as opposed to powder samples. The magnetic component has a clear asymmetry between the lines that correspond to the same Δm_I . This can best be seen in lines 2 and 5, where line 2 is more intense than line 5. This is an indication of a nonzero asymmetry parameter (η). At 6 K $B_{\text{hf}} = 28.3 \pm 0.1$ T, $(1/2)eQV_{zz} = 1.3 \pm 0.1$ mm/s, $\eta = 0.11 \pm 0.09$ and the angle, θ , between V_{zz} and B_{hf} , $= 45 \pm 1^\circ$. For the paramagnetic component, we find that V_{zz} is parallel to the γ -beam. These results are all consistent with values obtained for $Rb_{0.8}Fe_{1.6}Se_{2.0}$.⁶

The near vanishing of lines 2 and 5 indicates that the γ -beam and B_{hf} are nearly, but not quite, fully aligned, as has been previously reported.^{3,5,6} This contradicts the claim by Nowik *et al.*⁷ that the iron moments in $A_{0.8}Fe_{2-y}Se_2$ ($A = K,$

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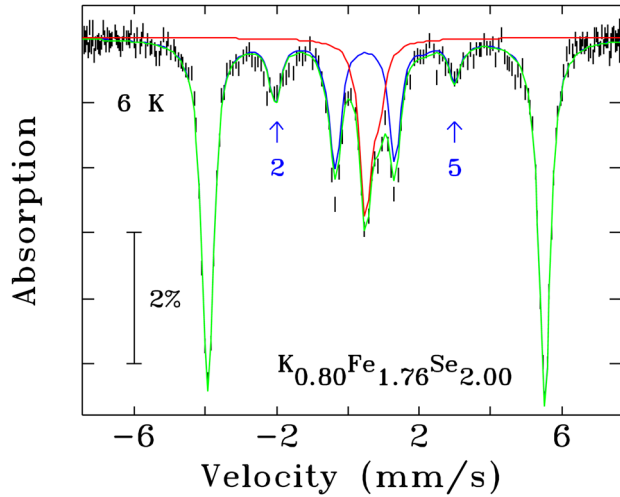


FIG. 1. (Color online) Mössbauer spectrum at 6 K of $K_{0.80}Fe_{1.76}Se_{2.00}$. The spectrum was fitted using a full Hamiltonian code. The blue sextet is the magnetic component, the red doublet is an impurity and the solid green line through the data is the sum of the two components. Lines 2 and 5 of the magnetic sextet are marked.

Rb and K/Tl) are tilted by $40\text{--}45^\circ$ away from the c -axis. A conclusion arrived at by using powders and assuming that V_{zz} points along the c -axis. However, the low point symmetry of the 16i site (1) allows V_{zz} to make an arbitrary angle with the c -axis. Using single-crystals, unlike powders, permits the direct measurement of the $18 \pm 3^\circ$ angle between the γ -beam and B_{hf} . This angle comes from three independent mosaics run on different spectrometers and exceeds any possible misalignment. While we cannot distinguish between uniaxial canting and some form of conical spin arrangement, there is definitely a small canting of B_{hf} , and hence the iron moments, away from the c -axis. This same canting has now been seen in both the potassium³ and rubidium⁶ compounds and suggests that the neutron diffraction results^{2,10} need to be re-evaluated.

The low temperature dependence of the hyperfine field is shown in Fig. 2. A $T^{3/2}$ spin wave model shown by the dotted red line in Fig. 2 fails to reproduce adequately $B_{\text{hf}}(T)$ so we included a spin excitation gap:

$$B_{\text{hf}}(T) = B_{\text{hf}}(0) \left(1 - CT^{3/2} \sum_{k=1}^{\infty} \frac{e^{-\Delta E/k_B T}}{k^{3/2}} \right), \quad (1)$$

where $B_{\text{hf}}(0)$ is the hyperfine field at 0 K, C is the spin stiffness constant, ΔE is the energy of the SEG and k_B is Boltzmann's constant.¹¹ A previous study claimed a gap of ~ 5 meV;⁵ here the gap was found to be 9 ± 1 meV with a spin stiffness constant of $18 \pm 1 \times 10^{-6} \text{ K}^{-3/2}$. The summation was limited to the first 19 terms of the series. The difference between the infinite series and our limited summation is less than 0.001%.

The integrated spectral area, ζ , is shown in Fig. 3. ζ s for different samples in different spectrometers have been combined by scaling data taken at a common temperature in order to cover the full temperature range of the experiments. Li *et al.*⁵ claimed a $\sim 10\%$ drop in ζ associated with the superconducting transition and a similar one below the

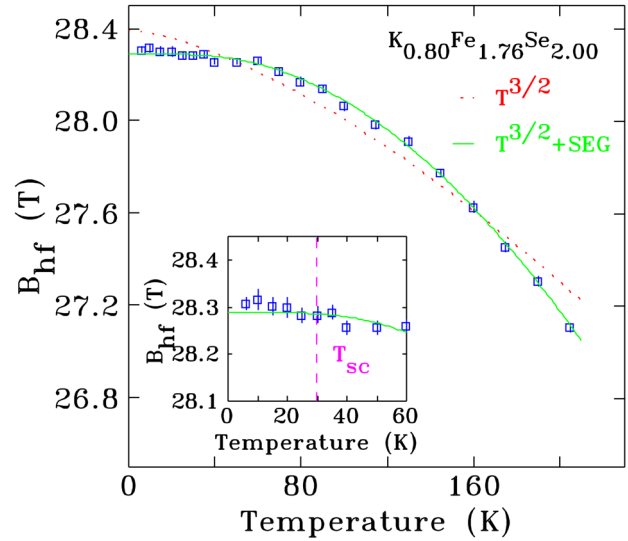


FIG. 2. (Color online) The hyperfine field (B_{hf}) of the antiferromagnetic subspectrum of $K_{0.80}Fe_{1.76}Se_{2.00}$. $B_{\text{hf}}(T)$ was fitted using a $T^{3/2}$ law (dotted red line), and a $T^{3/2}$ law with a SEG (solid green line) up to 200 K. The SEG was found to be 9 ± 1 meV. The inset shows $B_{\text{hf}}(T)$ close to the superconducting transition (T_{sc}), marked as the dashed magenta line.

transition. No such drops were observed here, as can be seen in the inset of Fig. 3. Since there is no structural transition or other behavior causing lattice softening associated with the superconducting transition, no drop in ζ is expected. Fitting of $\zeta(T)$ to a Debye-Waller model between 6 and 673 K (Fig. 3), yields θ_D of 195 ± 2 K, typical for an intermetallic.

The development of a soft phonon mode near the $I4/m \rightarrow I4/mmm$ structural transition could lead to a reduction in the f -factor.¹² However, no drop in absorption was observed. The small break near T_N in Fig. 3 is consistent with a fitting artifact (there are rapid changes in both the spectral form and linewidth near T_N) and would be followed by a recovery if it were indeed due to a soft mode.

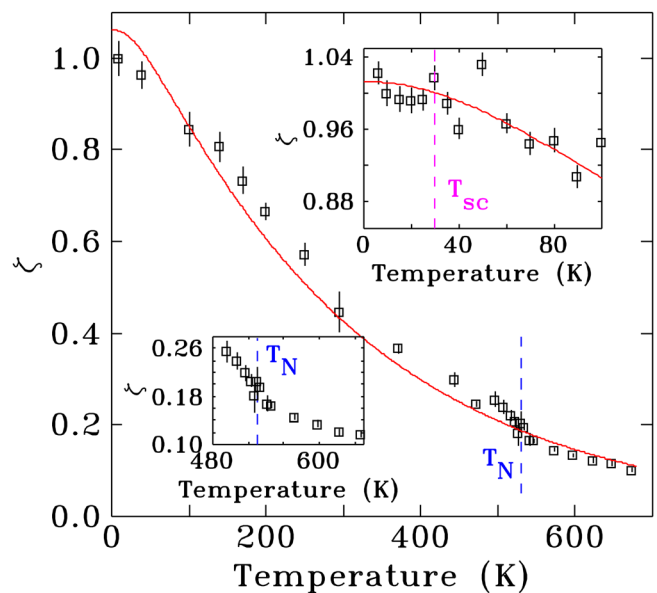


FIG. 3. (Color online) The integrated spectral area, ζ , fitted using a Debye-Waller model giving $\theta_D = 195 \pm 2$ K. The insets show ζ : (top right) near the superconducting transition, the magenta line, and (bottom left) the magnetic transition, the blue line.

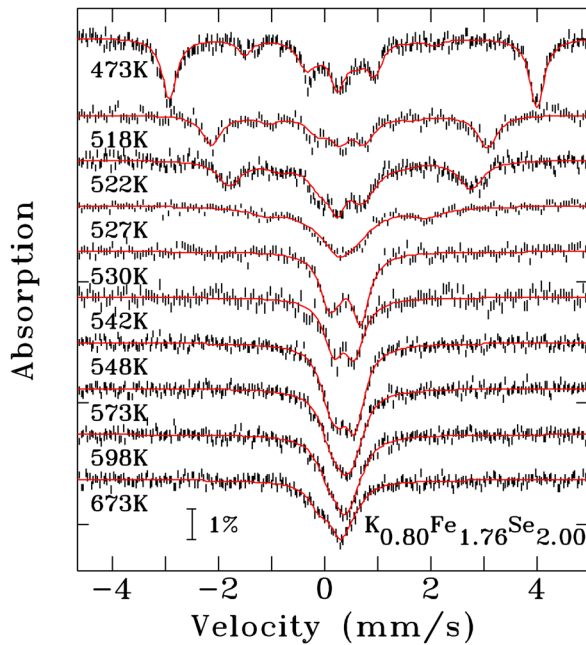


FIG. 4. (Color online) Mössbauer spectra of $K_{0.80}Fe_{1.76}Se_{2.00}$. The fits to the spectra, made using a full Hamiltonian solution, are shown as solid red lines.

The high temperature Mössbauer spectra are shown in Fig. 4. The magnetic transition is obvious from the collapse of the outer (magnetic) peaks, accompanied by the growth of a paramagnetic doublet. As we heat through T_N there is a marked reduction in $(1/2)eQV_{zz}$ (Fig. 5), the new paramagnetic component starts to appear at least 10 K below T_N and the transformation in $(1/2)eQV_{zz}$ is not complete until 10 K above T_N (upper inset to Fig. 5). The line-width, Γ , increases dramatically and then recovers (lower inset to Fig. 5). These changes indicate that the structural transition from $I4/m$ to $I4/mmm$ is closely linked to the magnetic transition. It starts *before* the magnetism collapse

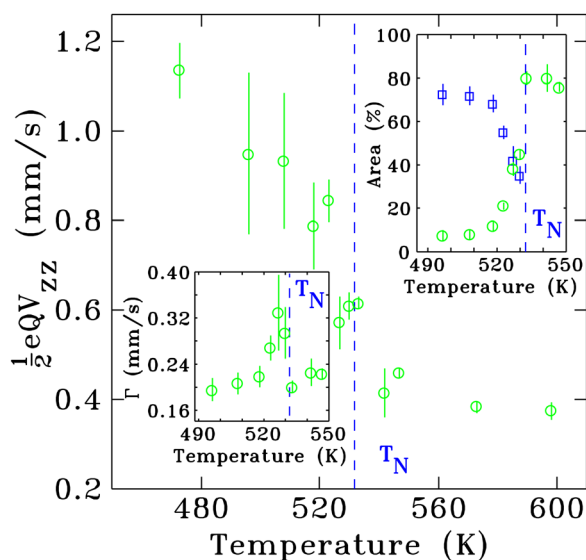


FIG. 5. (Color online) $(1/2)eQV_{zz}$ of $K_{0.80}Fe_{1.76}Se_{2.00}$ determined from the Mössbauer spectra shown in Fig. 4. The lower inset shows the spectral line-width (Γ) while the upper inset shows the fractional areas of the magnetic (blue \square) and paramagnetic (green \circ) components. The Néel temperature, $T_N = 532 \pm 2$ K, is marked by the dashed blue line.

and likely causes the collapse. The increase in line-width suggests a rapid increase in disorder at the iron site, while the reduction in $(1/2)eQV_{zz}$ is consistent with an increase in symmetry associated with the structural transition. Although neutron diffraction data have been interpreted as showing a gap of ~ 20 K between the T_N and T_S ,^{2,10} the results in Fig. 5 demonstrate that the first stages of the $I4/m \rightarrow I4/mmm$ transition start well below T_N and continue after the magnetic order is lost. The two transitions are essentially coincident and the changes in crystal structure drive the loss of magnetic order.

IV. CONCLUSIONS

The iron moments in $K_{0.80}Fe_{1.76}Se_{2.00}$ are canted away from the c -axis by $18 \pm 3^\circ$ below T_N . Below ~ 200 K, B_{hf} follows a gapped spin wave model with a SEG of $9(1)$ meV. Material degradation is not an intrinsic property of the $I4/m \rightarrow I4/mmm$ transition, rather it stems from reactions with mounting materials or contaminated vacuum. The $I4/m \rightarrow I4/mmm$ structural transition is coincident with the loss of antiferromagnetic order and likely plays a causal role in the loss of magnetic ordering.

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