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Evidence of Nematicity in $K_{0.8}Fe_{1.7}Se_2$

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Abstract It has been proposed that the superconducting state of $K_{0.8}Fe_{1.7}Se_2$ is phase separated from a non-superconducting magnetic state. The results from a recent neutron diffraction study on a single crystal of $K_{0.8}Fe_{1.7}Se_2$ provide evidence for a continuous transition between the $I4/mmm$ high temperature phase in which the Fe vacancies are randomly distributed and the $I4/m$ vacancy ordered phase in the temperature range between T_C and T_S. Upon cooling, the $I4/m$ phase becomes more populated, increasing the $\sqrt{5} \times \sqrt{5} \times 1$ superlattice structure, resulting in an enhancement of the (101) superlattice peak. The same temperature dependence is observed for the magnetic peak as well. Moreover, due to the Fe site splitting with the transition, its z-coordinate fluctuates, and so must the d_{xz} and d_{yz} orbitals. The orbital fluctuations couple to the magnetic ordering as seen here and may lead to a realization of nematic order in this system.

Keywords Superconductivity · Neutron scattering · Vacancies · Nematic phase

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1 Introduction

The intercalation of potassium, K, into the tetragonal lattice of the chalcogenide $Fe_{1-y}Se$ superconductor as in $K_xFe_{2-y}Se_2$ drives the system to a fourfold increase in the transition temperature, T_C[1]. The new compound has K and Fe vacancies. At temperatures much higher than T_C, both a structural and a magnetic transition occur. The structural transition, T_S, is observed around 578 K[2], from the $I4/mmm$ high temperature phase where the K and Fe sites have vacancies randomly distributed in the lattice, to a phase in which the Fe vacancies order in several possible superlattice patterns[2][3][4][5][6][7]. Among the reported patterns, the $\sqrt{5} \times \sqrt{5} \times 1$ superlattice structure with space group $I4/m$[2][6][7] is the most common one. The structural transition is followed by a magnetic transition to a collinear antiferromagnetic structure with the Fe spins aligned in an up-up-down-down arrangement along the c-axis[2].

In the superconducting state, the symmetry of the crystal has been widely debated because of the possibility of phase separation[5][8]. It has been suggested that upon cooling, the $I4/mmm$ phase coexists with the $I4/m$, but vacancies are only present in the latter symmetry[8]. What happens at intermediate temperatures, between the magnetic and superconducting transition, is critical to understand the possible origin of phase separation in the superconducting phase.

The results from the neutron diffraction measurement on a $K_{0.8}Fe_{1.7}Se_2$ single crystal show that upon cooling, a continuous transition between $I4/m$ and $I4/mmm$ occurs. This suggests that the Fe vacancies gradually order without resorting to phase separation. The superlattice peak intensity arising from the $I4/m$ phase continuously increases with cooling along with

the magnetic peak and both saturate upon entering the superconducting phase. Moreover, the Fe z-coordinate shows a different dependence to temperature, that most likely has an effect on the d_{xz} and d_{yz} orbitals and their degree of hybridization with the Se p-orbitals.

2 Experimental Details

The single crystal of $K_{0.8}Fe_{1.7}Se_2$ was made by the self-flux method. The first step involved the preparation of high-quality tetragonal FeSe powder. Stoichiometric quantities of iron pieces and selenium powder were heated to $1075°C$ for 50 hours in a sealed vacuum quartz tubes, then quenched in liquid nitrogen. The second step involved placing the potassium grain and the FeSe powder with a nominal composition ratio of 0.8 : 2 in an alumina crucible, double sealed in quartz tubes, and partially backfilled with ultra-high purity argon gas. It was then heated at $1030°C$ for 2 hours, cooled down to $750°C$ at a rate of $6°C/hour$, then cooled down to room temperature by switching off the furnace. Finally, the sample was further annealed at $350°C$ for 2 hours and quenched in liquid nitrogen.

The neutron scattering experiment was carried out at the Corelli Spectrometer at the Spallation Neutron Source of Oak Ridge National Laboratory. The sample was coated using a hydrogen-free fluoropolymer, Cytop, to avoid exposure to air. The incident neutron was a white beam with wavelengths ranging from 0.64 Å to 2.86 Å. The diffracted neutron was detected by 91 detectors, which covered a 2θ angle from 10° to 190°.

3 Results and Discussion

In Fig. 1 the temperature dependence of the in-plane resistivity and shielding fraction of the crystal used in the diffraction experiment are shown. In the lower figure, the superconducting volume fraction is ∼70 %. The sample undergoes a semiconductor to metal transition, with a broad peak at 200 K in the transport measurement, prior to the superconducting transition at $T_C \sim 31$ K. The bump in the transport was reported to have a dependence on the Fe vacancy[9].

The neutron diffraction experiment at Corelli was carried out as a function of temperature, and the results are summarized in Figs. 2 and 3. Shown in Fig. 2 is five Bragg peaks at 6 K. In (a), the (002) nuclear peak, in (b), the (312) nuclear peak, in (c), the (101) superlattice peak, in (d), the (0.8 0.6 1) superlattice peak, and in (e), the (211) magnetic peak are shown. Shown in (f) is two distinct ways of forming the $\sqrt{5} \times \sqrt{5} \times 1$ superlattice pattern. The two ways of ordering differ by

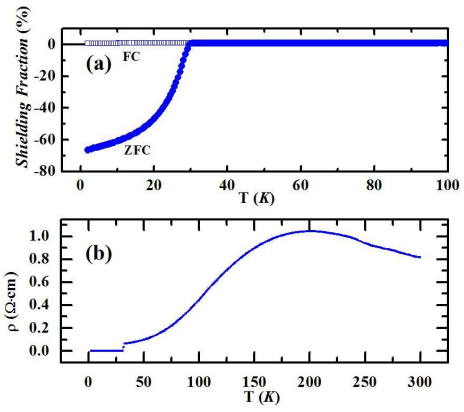

Fig. 1 (a)The temperature-dependent resistivity measurement of the sample. (b)The temperature-dependent shielding (ZFC) and Meissner fraction (FC) measurement of the sample.

a rotation of $\theta = \arccos(\frac{4}{5})$ around the c-axis that reindexes the (101) superlattice peak to (0.8 0.6 1). The two superlattice peaks arising from the two domains shown in Fig 2 (c) and (d) have the same d-spacing. The Bragg peaks are plotted in the reciprocal space where the vertical axis is intensity. The (002) and (101) peaks are shown in the h0l-plane. The (312) and (211) peaks are shown in the h1l-plane. The (0.8 0.6 1) peak is shown in the h0.6l-plane. The k-coordinate was integrated over a narrow thickness of 0.05 in reciprocal lattice units. A double-peak structure is observed in all five peaks due to the presence of two grains, a large and a small one.

The temperature dependence of the integrated intensity of the five peaks is shown in Fig. 3. Below T_C, hardly any temperature dependence is observed in all the peaks. In the superconducting phase, both the superlattice and the magnetic peaks are present. Above T_C, the nuclear (312) peak shows an inflection between $150 \sim 200$ K, but otherwise appears constant. On the other hand, the nuclear (002) peak which is mostly due to Fe shows a sharp decrease with cooling, while the

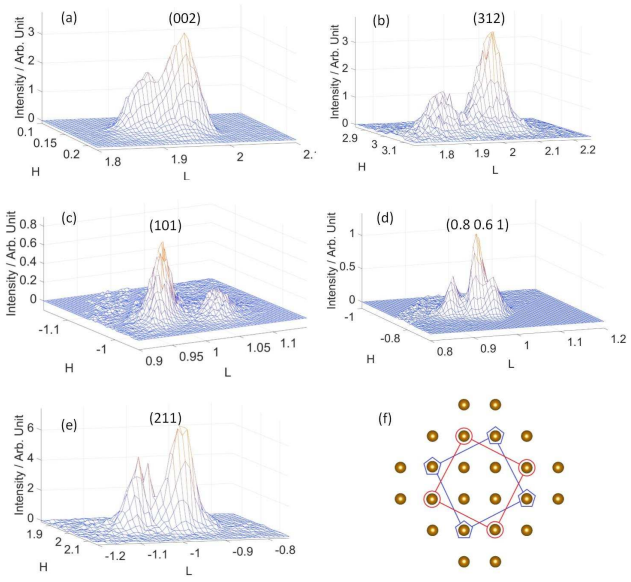

Fig. 2 (a) to (e): The neutron diffraction data measured at 6K at Corelli diffractometer are shownn in the reciprocal space. The (002) and (101) peaks are shown in the h0l-plane. The (312) and (211) peaks are shown in the h1l-plane. The (0.8 0.6 1) peak is shown in the h0.6l-plane. (f) The two distinct ways (red circle and blue pentagon) of forming $\sqrt{5} \times \sqrt{5} \times 1$ superlattice pattern. Marked Fe atoms indicated Fe vacancy.

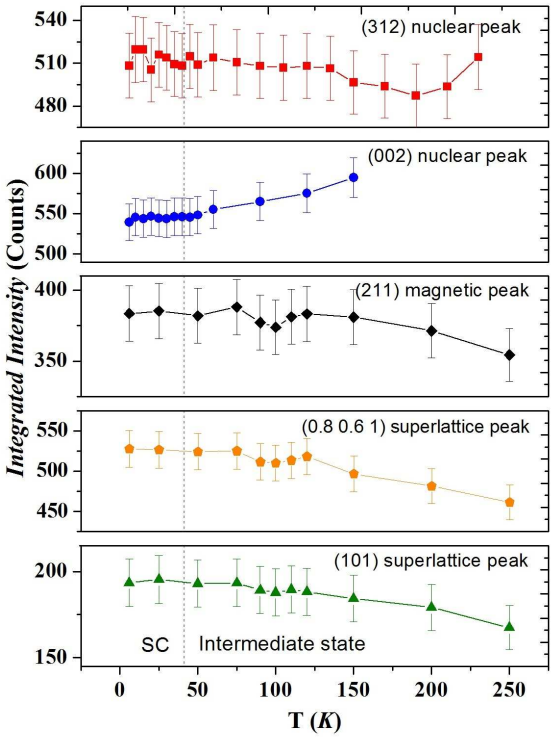

Fig. 3 The integrated intensities of the five peaks.

(211) magnetic and the two superlattice peaks increase upon cooling.

The increase of the intensity of the two superlattice peaks indicates that the fraction of iron vacancy ordering increases upon cooling in both domains. This process breaks the symmetry from the space group $I4/mmm$ to $I4/m$. In the I4/m phase, iron has two sites, one of which has a Wyckoff position of $4d$ and is partially empty (Fe1); the other with Wyckoff position $16i$ is fully occupied and magnetically ordered (Fe2). Upon cooling, more iron atoms move to the $16i$ site, resulting in an increase in the magnetic peak intensity as seen here with (211) peak. At the same time, the $16i$ site no longer has a symmetry protected z-coordinate of $\frac{1}{4}$. This implies that the vacancy order causes broadening of the spatial distribution of the lattice in the z direction, resulting in a decrease of the (002) nuclear peak intensity as seen here. The observed temperature-dependent features give strong indication that the structural phase transition of $I4/mmm$ to $I4/m$ is continuous with cooling, even when the temperature is well below the structural transition temperature $T_S \sim 578\ K$.

4 Conclusions

The transition from the $I4/mmm$ to the $I4/m$ is not first order, but is instead continuous with both phases most likely coexisting well below T_S. This indicates that the $I4/mmm$ phase below T_S has randomly distributed Fe vacancies and the same lattice constance as in $I4/m$, instead of having no Fe vacancies as suggested by the phase separation hypothesis. The onset of T_S marks the temperature at which the Fe2 site becomes more populated and continuously grows with the superlattice ordering of the $I4/m$ phase. Furthermore, as the z-coordinate of the Fe2 site fluctuates upon cooling, the d_{xz} and d_{yz} orbitals fluctuate as well. The orbital fluctuations couple to the magnetic ordering and appear to dissipate upon entering the superconducting phase. The intermediate temperature region between T_S and T_C may represent a nematic phase in $K_xFe_{2-y}Se_2$ as has been extensively described in $BaFe_2As_2$[10][11], driven

by the lattice symmetry break and the magnetic order. Even though the average symmetry is tetragonal, the orbital fluctuations can break the symmetry, leading to a lattice instability. Recent results on the local structure analysis have shown that locally the Fe environment is distorted with long and short Fe bonds, giving rise to a local orthorhombicity.[12][13]

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