Analysis of local chemical and structural inhomogeneities in $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$ single crystals

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(Received 2 September 2011; accepted 17 October 2011; published online 8 November 2011)

Co-existence of superconductivity and magnetism has been reported in certain regions of the $\text{Fe}(\text{Se},\text{Te})$ phase diagram. Here, we address the key question of whether these different properties occur simultaneously within a homogeneous crystal or whether a “two-phase” description is more appropriate. Extensive microstructural analysis suggests that a Te-rich sample exhibiting both bulk superconductivity and magnetic order contains significant chemical and structural inhomogeneity, suggesting that the “two-phase” explanation may be valid in this sample. The high-resolution electron backscatter diffraction (HR-EBSD) technique has been used to map local changes in lattice parameter very precisely in these compounds. © 2011 American Institute of Physics. [doi:10.1063/1.3659302]

Since the discovery of superconductivity in F-doped LaFeAsO in 2008,¹ several other families of iron-based superconductors have been discovered.^{2–4} The FeSe phase is interesting because it has the simplest crystal structure of this series of compounds. It consists of planes of Fe atoms tetrahedrally co-ordinated with planes of Se atoms in the tetragonal PbO -type structure, making it an attractive system for studying relationships between electromagnetic properties and structure. The superconducting transition temperature (T_c) can be increased from 8 K in FeSe to a maximum of ≈ 15 K by substitution of $\approx 50\%$ Se by Te.^{5,15} Whilst binary Fe_yTe is not superconducting, ternary compounds with up to 90% Te substitution for Se have been found to exhibit superconductivity.

Increasing the proportion of large Te atoms on the chalcogen site results in an increase in the c-axis lattice parameter, with much smaller change in the a-axis lattice parameter. Therefore, the c/a ratio is sensitive to the Te concentration and is found experimentally to be linked to the superconducting properties, with a peak in T_c value corresponding to a c/a ratio of ≈ 1.59 .^{6,15,19} This is consistent with the theoretical prediction that the height of the chalcogenide atoms above the Fe-plane, h_z , influences the magnetic ordering in $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$.⁷ However, recent studies by Joseph *et al.*⁸ suggest that in the $\text{Fe}_y\text{Se}_{0.5}\text{Te}_{0.5}$ compound, the Fe-Se and Fe-Te bond lengths are close to the values in their respective binary compounds rather than taking some intermediate value, resulting in different h_z positions for Se and Te atoms. They have attributed this to local chemical inhomogeneities in the crystal.

Recent studies have shown that the superconducting and magnetic properties of $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$ are strongly influenced by Fe content as well as the Se-Te ratio. Excess Fe is found to occupy the interstitial 2c sites in the crystal,⁹ influencing

not only the structural parameters but also the magnetic ordering in $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$.^{9–12}

A series of single crystal samples of $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$ has been grown using a Bridgman growth technique from melts with Te content of $x = 0.75$ and iron content ranging between $0.95 < y < 1.07$.¹³ The Fe-rich starting compositions were found to yield crystals displaying incommensurate magnetism,¹² but the Fe-deficient starting composition with 0.95 exhibits bulk superconductivity with an onset T_c of 10.5 K co-existing with incommensurate magnetism. However, x-ray diffraction (XRD) analysis did not reveal any evidence of multiple phases, and moreover, the lattice parameters found by full-pattern refinement did not vary systematically with starting composition. This paper investigates local structural and compositional variations in three of these crystals with different initial Fe concentrations of $y = 0.95$ (sample A), 1.03 (sample B), and 1.07 (sample C) in order to examine whether phase separation is responsible for the differences in the previously reported superconducting and magnetic behaviour.¹²

We performed extensive energy dispersive x-ray (EDX) point analysis in a scanning electron microscope (SEM) to investigate the chemical homogeneity in this series of samples. Figure 1 shows that Fe content is related to Te content. A similar linear trend between Te and Fe content has been observed previously in both bulk^{14,15} and thin film^{6,16} samples. Sample A, grown from the most iron-deficient starting composition, contains considerable variability in composition not only on the macro-scale between different flakes cleaved from the crystal but also on the smaller scale (25–50 μm in size) within the $150 \times 150 \mu\text{m}$ test areas studied in this work. In contrast, the iron-rich samples B and C are found to be much more chemically homogeneous. This suggests that the Fe-deficient starting composition of sample A is not stable, with Te and Fe co-segregating during crystal growth resulting in regions low in Te and Fe within a matrix richer in these elements. Samples B and C do not show the same

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FIG. 1. (Color online) Composition variations within samples A, B, and C measured by EDX point analysis. The filled symbols indicate point measurements taken in square arrays from two $150 \times 150 \mu\text{m}$ test areas on each sample. The open symbols are additional point measurements taken from different macroscopic locations within each crystal. Linear fits to the entire dataset (black online) and samples A (blue) and B (green) and notional starting compositions (star symbols) are also shown.

extent of chemical segregation, presumably as loss of volatile Se during the growth process allows the formation of relatively stable compositions. The modal composition taken from data collected over two $150 \times 150 \mu\text{m}$ test areas on each sample are found to have Te contents of $x = 0.765$, 0.760 , and 0.770 with surprisingly little difference in Fe content at $y = 1.030$, 1.025 , 1.030 , for samples A, B, and C, respectively (where x and y values are given to the nearest 0.005). Powder XRD studies have shown that the average values of c/a ratio for samples A, B, and C are 1.6180 , 1.6165 , and 1.6200 (± 0.0005), respectively, indicating by comparison with the EDX data that as Te (and Fe) content increases, the c/a ratio also increases as expected.

Local variations in unit cell anisotropy across relatively large areas of $150 \times 150 \mu\text{m}$ have been studied using high-resolution electron backscatter diffraction (HR-EBSD) in an SEM¹⁷ on freshly cleaved (001) surfaces. This technique has the advantage over EDX of being much more sensitive to small variations, with lattice strains being measured with a precision of 1×10^{-4} . However, only relative c/a values are measured rather than absolute values. (See supplementary material²⁰ for more details about this technique.) Figure 2 shows typical maps of c/a ratio from each sample, with the absolute values estimated by setting the modal c/a value to the average value measured by powder XRD. Sample A clearly contains much more variability in c/a ratio than samples B and C as also shown in Figure 2(d), consistent with the more pronounced chemical inhomogeneity found using EDX. Sample A contains c/a variations over regions of 25 – $50 \mu\text{m}$ in size, whereas samples B and C contain a fairly uniform matrix containing isolated features, often elongated in shape, with different c/a values. These features frequently appear in pairs, with regions with increased c/a compared to the matrix average in close proximity to reduced c/a regions. Higher magnification SEM imaging has revealed that large areas of the cleaved surfaces of sample C contain a high density of much smaller linear-shaped features with widths less than $1 \mu\text{m}$. Cross-sectional transmission electron microscopy (TEM) shows that these surface features extend about 400 nm into an otherwise rather perfect crystal, accommo-

FIG. 2. (Color online) HR-EBSD maps showing variations in c/a ratio across one of the $150 \times 150 \mu\text{m}$ test areas of (a) sample A, (b) sample B, and (c) sample C. The probability distributions of c/a ratio based on EBSD data taken from two $150 \times 150 \mu\text{m}$ test areas on each sample are given in (d). Absolute values of c/a ratio have been estimated using average c/a value measured by XRD. White pixels indicate low quality EBSD patterns due to surface roughness or impurity phases.

dated by a row of dislocations at the interface. They are accompanied by slight changes in Te content measured both by EDX on the TEM cross-section and c/a ratio changes in plan view HR-EBSD (see supplementary material²⁰ for more details).

This observation of structural and chemical variations on the microscopic scale is direct evidence supporting a two phase description of the co-existence of superconductivity and magnetism in which superconducting and magnetic regions occupy spatially distinct zones within the crystal.¹⁸ According to this model, the larger degree of chemical and structural inhomogeneity in the low Fe-content sample A compared with the Fe-rich samples B and C could account for the differences in their magnetic and superconducting properties. Liu *et al.* have produced a phase diagram for the Te-rich $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$ compounds showing that, in compounds with average Fe-content of $y = 1.02$, bulk superconductivity only exists for Te-content below $x = 0.71$.¹⁸ Compounds with this Te composition are found to have a corresponding c/a ratio of about 1.614 according to experimental data from Vienneis¹¹ and Sales.¹⁹ In Figure 3, the EBSD data given in Figure 2 are reproduced with regions below certain threshold values of c/a ratio coloured light grey and regions above the threshold coloured dark grey. Hypothesising that the upper limit for superconductivity is $c/a = 1.614$, corresponding to the onset of bulk superconductivity in a compound with Fe-content of $y = 1.02$, we find that only 6% of sample A, 4% of sample B and 0% of sample C are in the superconducting region. The values for samples B and C are consistent with the SQUID data for these samples reported previously,¹² but sample A was found experimentally to exhibit bulk superconductivity co-existing with magnetic order, suggesting a larger superconducting fraction. However, the EDX data indicates that, whilst in general the Fe-content is found to be linked with Te-content, the concentration of Fe tends to be lower in sample A for a given Te concentration compared with samples B and C (see Figure 1). Since it is believed that reducing the Fe concentration

FIG. 3. HR-EBSD maps from samples A, B, and C with light grey indicating regions with c/a ratio below the given threshold value (superconducting) and dark grey indicating regions with c/a ratio above the threshold. The white pixels indicate areas from which high quality diffraction patterns could not be obtained, usually due to surface roughness.

effectively moves the phase boundary for bulk superconductivity to higher Te concentrations, it is reasonable to assume that the c/a threshold value for superconductivity increases as a result of the observed dependence of c/a ratio on Te content. From Figure 3, it can be seen that sample A requires the higher threshold value of about 1.619 to produce a well-connected network of superconducting areas, corresponding to Te-content of about 0.76.^{11,19} This hypothesis assumes that c/a ratio is most strongly influenced by Te concentration rather than by the quantity of excess iron. Since the stable Fe content increases with increasing Te content, the effect of varying Fe content independent of Te content on c/a ratio is not known. In addition, here we have assumed that the average c/a value for each EBSD map is given by the bulk value measured by x-ray diffraction. However, since chemical inhomogeneities exist on the macro-scale, particularly in crystal A, errors in the absolute c/a values in the EBSD maps may be present, although the shapes of the c/a probability distributions would remain unchanged.

In summary, the HR-EBSD technique has been used to investigate local structural variations in a series of $\text{Fe}_y\text{Se}_{1-x}\text{Te}_x$ single crystals with nominal Te content $x=0.75$ and a range of Fe contents ($0.95 < y < 1.07$). The local variations in c/a ratio and chemical composition observed on the microscopic scale and possibly also on the nano-scale provide evidence for a “two phase” model in which regions with c/a

ratio below some threshold value are superconducting, whereas spatially separated regions with c/a ratio above this value are magnetic in nature. The overall superconducting and magnetic properties depend on the volume fraction of each “phase” present in the crystal, where the term “phase” relates to the electronic properties of the material, rather than referring to discrete chemical phases. We surmise that the threshold value for superconductivity is strongly influenced by Fe concentration in these compounds.

Dr. S. Speller is supported under the RAEng/EPSC research fellowship scheme.

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