Relation between superconductivity and tetragonal phase stabilized by uniaxial pressure in CaFe$_2$As$_2$

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Abstract. We report on neutron diffraction experiments on high quality CaFe$_2$As$_2$ single crystals performed under uniaxial pressure and combined with in-situ electrical resistance measurements. We conclude that the superconductivity is associated with the high-temperature tetragonal phase that is stabilized down to the lowest temperatures by a small uniaxial pressure of at least 0.075 GPa applied along the c-axis.

1. Introduction

Despite a century of intensive efforts in the field of superconductivity (SC), this phenomenon remains one of the most active research areas of the condensed matter physics. Especially large families of superconducting compounds allow us to draw more general conclusions regarding the relation between the crystal structure (and underlined magnetic properties) on one side and superconductivity on the other. Much that we understand about unconventional high temperature superconductivity comes from our knowledge of the cuprate family [1]. The parent phase of those materials is an antiferromagnetic (AF) Mott insulator and when doped chemically with holes, ordered magnetism is suppressed and SC emerges. In the newly discovered RFeAsO ($R = \text{rare earth}$) [2] and A$\text{E}$Fe$_2$As$_2$ ($A\text{E} = \text{Ca, Sr, Ba}$) [3] families, the situation is quite similar. SC emerges when the non-SC parent compounds, are chemically doped much in the same fashion as in the cuprates. These compounds undergo a structural and AF transitions that are, at least in some instances, intimately linked [4-5]. Both, structural transition and magnetism is suppressed with doping and eventually the SC appears at low temperatures. It seems that both, AF and SC coexist, in some cases. Surprisingly, unlike the cuprates, the application of pressure on these parent compounds leads to SC as high as ~50 K [6-7]. There have been several studies to unravel the question which phase in A$\text{E}$Fe$_2$As$_2$ compounds when subjected to pressure hosts SC. At ambient pressure, CaFe$_2$As$_2$ undergoes a first order transition from a high temperature tetragonal ($T$) phase ($\text{ThCr}_2\text{Si}_2$ structure) to a structure with orthorhombic ($O$) symmetry at $T_{TO} = 172$ K connected with an AF transition [5]. Upon the application of modest pressures, using liquid media clamping cells, the structural and AF transition is rapidly suppressed and SC was observed for $P > 0.23$ GPa and $T_{SC} \sim 12$ K [7]. SC has also been observed in electrical resistance measurements of samples under uniaxial pressure [8]. In that material initial bulk property
measurements under less than ideal hydrostatic conditions showed superconductivity above 0.1 GPa, while measurements close to ideal hydrostatic pressure showed no evidence of SC. The later result is consistent with a previously known non-magnetic phase $T$ phase with a significantly reduced unit cell volume, the so-called collapsed tetragonal ($cT$) phase. In this contribution we report on our recent neutron diffraction experiments on high quality CaFe$_2$As$_2$ single crystals performed under uniaxial pressure combined with in-situ electrical resistance measurements.

2. Experimental

Several high quality single crystals of CaFe$_2$As$_2$ with dimensions of 2-3mm x 3-4mm x 0.2mm (mass between 8 and 12 mg) were grown out of a Sn flux. The crystals were carefully polished to produce parallel surfaces perpendicular to the $c$-axis and checked by neutron Laue technique that confirmed the good quality of samples. Crystals were clamped between two ZrO$_2$ cylindrical pistons that comprise a small uniaxial pressure cell. A force up to 1 kN was applied on the sample and the corresponding pressure calculated from the calibrated displacement of the clamping screws and the measured sample cross section. Several different single crystals at several pressures between ambient pressure and 0.3 GPa were studied.

The neutron diffraction experiments were performed at two different diffractometers: on the E4 double-axis diffractometer at the Helmholtz-Zentrum Berlin using a neutron wavelength of $\lambda = 2.45$ Å using a standard cryostat and on the D10 diffractometer at the Institute Laue-Langevin (ILL) with a wavelength of 2.36 Å using a four-circle closed cycle refrigerator. In both cases, two-dimensional area detectors that provide a diffraction image over a range of scattering angles ($2\theta$) as the sample is rocked over a specified angular range ($\omega$) were used. Pyrolytic graphite filters were

*Figure 1.* (Color online) Color map showing the temperature dependence of a portion of the diffraction pattern recorded using D10 in ILL that covers the (002)$_T$, (002)$_O$ and (002)$_{cT}$ reflections of CaFe$_2$As$_2$ with lowering the temperature (a). Integrated intensities of reflections shown in (a) as a function of the temperature (b) and d-spacings (c). Color map showing the temperature dependence of the diffraction range covering the (-220)$_T$ reflection that splits at lower temperatures to (-400)$_O$ and (0-40)$_O$ (with remnants of the (-2 20)$_T$ reflections is shown in panel (d). Fitted integrated intensities and d-spacings obtained from data shown in (d) are shown in (e) and (f), respectively.
employed in both sets of measurements to reduce the higher harmonic contents to less that $10^{-4}$ of the primary beam. During the E4 measurements we have measured in-situ electrical resistance using a standard 2-point or 4-point ac methods.

3. Results

As an example, in Fig. 1a we show the temperature dependence of the neutron diffracted intensity recorded in the vicinity of the (002) Bragg reflections at the D10 instrument with decreasing temperature. The nominal pressure applied in this case on a 5.3 mg CaFe$_2$As$_2$ single crystal was 0.092 GPa. It is seen that the pressure stabilizes the $T$ phase to temperatures far below $T'_{T0} \sim 170$ K and induces the $cT$ phase below $T_{cT} \sim 70$ K. The corresponding fitted integrated intensities and calculated d-spacings are shown in Figs. 1b and 1c, respectively. The (002)$_0$ reflection grows much faster between $T_{T0}$ and $T_{cT}$ than below $T_{cT}$. Color map showing the temperature dependence of the diffracted signal recorded under the same conditions around the (-220)$_T$ Bragg reflection is shown in Fig. 1d. The $O-T$ transition is clearly visible, although the (-220)$_T$ reflection does not split below $T_{TO}$ into (-400)$_0$ and (0-40)$_0$ completely. Part of the sample volume retains the $T$ symmetry. This is reflected in a different width of the two split reflections and different temperature dependence of the reflection positions. Resulting fitted integrated intensities and d-spacings are shown in Figs. 1e and 1f, respectively. The influence of the $T$ and $O$ phase mixing in the low-temperature limit eventually reduces and both split reflections tend to have similar intensities and also the width. Due to strong anisotropic absorption of the pressure cell it is impossible to determine all the crystallographic details of the stabilized $T'$ phase. However, smooth temperature dependence of the lattice parameters and Bragg reflection intensities give a good reason to conclude that this stabilized $T'$ phase is simply the very same $T$ phase that is stable at high temperatures in samples without influence of pressure. Although we have performed several types of reciprocal scans, no signal that could be ascribed to magnetic origin could be found. We conclude therefore that the $T'$ phase does not order magnetically.

Considering also other pressure runs at different crystals we can conclude that at pressures below a starting pressure of 0.06 GPa, the $cT$ phase is absent at all temperatures and the $T$ phase is observed only over a narrow range of temperatures below $T_{TO}$. Upon increasing the pressure, we observe that the relative fractions of the stabilized tetragonal ($T$) and $cT$ phases increase at the expense of the $O$ phase. A finite fraction of the $T$ phase extends down to the lowest temperatures measured for uniaxial pressures greater than 0.075 GPa. At even higher applied pressure, the $cT$ phase appears at progressively higher temperatures and its weight fraction increases together with that of the

![Figure 2](image-url)  
Figure 2. Triangles and half-filled diamonds show the pressure dependence of the onset of the SC transition and the temperature with the maximal $dR/dT$ value of CaFe$_2$As$_2$. Filled and open circles show the weight fraction of the pressure stabilized phase $T'$ and the collapsed tetragonal phase $cT$ as a function of pressure, respectively. Dotted lines are guides to the eye.
$T'$ phase at the expense of the $O$ phase. However, at pressures higher than $\sim 0.2$ GPa the weight fraction of the $T'$ phase does not grow anymore although the fraction of the $cT$ phase continues to increase on the expense of the $O$ phase. This trend is documented in Fig. 2, in which we show by full full (open) points the pressure dependence of the weight fraction of the stabilized $T'$ (collapsed tetragonal $cT$) phase deduced from neutron diffraction data recorded at 2 K. Unfortunately, we have not been able to determine the upper limit of the $T$ phase existence due to limitations of our pressure cell. In the same picture we show the pressure dependence of the onset of the SC transition $T_0$ deduced from the in-situ measured electrical resistance and of the temperature with the maximal temperature derivative of the electrical resistance $(dR/dT)_m$. Clearly, the $T$ phase appears to be stable in a part of the sample in the very same pressure range at which also the SC exists. The latter data are in good agreement with electrical resistivity curves obtained under uniaxial pressure by Torikachvili et al. [8].

4. Conclusions

We find that in a narrow range of uniaxial pressure applied along the c axis of CaFe$_2$As$_2$ the high-temperature tetragonal phase is stabilized down to the lowest temperatures. This tetragonal phase differs from the so-called collapsed tetragonal phase that is not found in hydrostatic measurements and appears also to be present in our measurements. Mapping out its stability in temperature and pressure and using in-situ resistivity measurements we argue that this non-magnetic, pressure-stabilized tetragonal phase is the likely host of superconductivity in CaFe$_2$As$_2$ under pressure.

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