Determination of the Nature of the Structural Phase Transitions in 122 Pnictide Systems

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Abstract. Transmission electron microscopy was used to investigate the tetragonal-to-orthorhombic phase transitions in SrFe$_2$As$_2$ and Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$ which are members of the recently discovered iron-based superconductors. We use a method which measures the spatially-resolved order parameter and show that whereas the transition in SrFe$_2$As$_2$ is a first-order martensitic phase change, Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$ shows a continuous change of the order parameter as the phase transition takes place. This would normally indicate a second order phase transition but the situation seems to be more complicated as, during the transition, different regions of the sample had different values of the order parameter: something which should only happen in a first order change.

1. Introduction

Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ are iron-based superconductors, discovered in 2008 [1,2]. Superconductivity occurs for a range of cobalt concentrations as shown by the phase diagram in Fig. 1. The non-superconducting compositions show a paramagnetic-to-antiferromagnetic transition accompanied by a change of crystal structure from tetragonal to orthorhombic. It has been postulated that the superconducting phase is the result of a quantum critical point [3] and this implies that the tetragonal to orthorhombic transition should be second order close to the superconducting phase. However, determining the order of the transition is no easy matter. For example, both Tegel et al. [4] and Jesche et al. [5] used x-ray diffraction to determine the order of the phase transition in SrFe$_2$As$_2$ and the first group found it was second order and the second group first order. We believe that part of the reason for such disagreements is the macroscopic nature of the measurements used and so introduce a technique to measure the spatially-resolved order parameter on a scale of tens of nanometres using transmission electron microscopy. Here we examine the phase transitions in SrFe$_2$As$_2$ and Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$. 
The room temperature tetragonal unit cell of Sr(Fe,Co)$_2$As$_2$ or Ba(Fe,Co)$_2$As$_2$ is shown in Fig. 2(a). Both compounds have space group $I\overline{4}/mmm$ with SrFe$_2$As$_2$ having lattice parameters $a_T = b_T = 3.92$ Å and $c_T = 12.36$ Å and BaFe$_2$As$_2$, $a_T = b_T = 3.96$ Å, $c_T = 12.99$ Å. Fig. 2(b) shows that in the orthorhombic phase, the right angle between $a_T$ and $b_T$ is lost (dashed lines). The orthorhombic phase has space group $Fmmm$ with lattice parameters $a_O = 5.58$ Å, $b_O = 5.52$ Å, $c_O = 12.30$ Å for SrFe$_2$As$_2$ at 90 K and $a_O = 5.62$, $b_O = 5.57$ Å, $c_O = 12.94$ Å for BaFe$_2$As$_2$ at 5 K [4,7].

To track the progress of the transition we define the order parameter, $Q$, such that $Q = \frac{a_O - b_O}{a_O}$.

3. Sample Preparation and Experimental Methods

We used single crystals of SrFe$_2$As$_2$ and Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$ synthesised as described in ref [6] and these were argon ion-thinned to electron transparency as described in ref. [8]. The local order parameter was measured using large-angle convergent beam electron diffraction (LACBED) which produces an image with dark contours running across it which correspond to specific crystallographic planes (Fig. 1(a)). Twins form in the orthorhombic phase and the change in orientation of the crystal planes on moving from one twin to the next gives a broken contour (Fig. 1(b)). The spacing between the breaks in the LACBED contours is proportional to the order parameter, $Q$. LACBED patterns were recorded as videos on warming and cooling through the phase transition. Further details are given in ref. [8].
The results of the investigation of the phase transition in SrFe₂As₂ are reported fully in ref. [8] but we summarise our findings here. The phase transition takes place by the growth of the orthorhombic twins along their length. At the end of the twins is a needle tip which is surrounded by transformation dislocations and it is the passage of these dislocations through the material which effects the transformation. The orthorhombic twins move across the specimen one at a time in a series of jumps so that the local order parameter changes faster than the time between video frames (1/25 s). The phase transition can be described as a first-order Martensitic transition.

The transition in Ba(Fe₀.₉₈₅Co₀.₀₁₅)₂As₂ was very different so that rather than jumping abruptly to zero as the specimen was warmed, the order parameter varied continuously as shown in Fig. 5(a). This suggests a second order phase transition but it appears the situation is more complicated as some of the video frames such as that shown in Fig. 5(b) clearly show twins with different values of the order parameter coexisting at the same temperature: something which should only happen in a first order change.
Summary

Transmission electron microscopy was used to investigate the tetragonal-to-orthorhombic phase transitions in SrFe$_2$As$_2$ and Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$, by mapping the spatially resolved order parameter. This showed that the transition in SrFe$_2$As$_2$ was a first-order martensitic phase change whereas Ba(Fe$_{0.985}$Co$_{0.015}$)$_2$As$_2$ showed a continuous change of the order parameter as the phase transition took place. This would normally indicate a second order phase transition but the situation seems to be more complicated than this as, during the transition, different regions of the sample had different values of the order parameter: something which should only happen in a first order change.

Acknowledgments

This work was funded by the Royal Society and the EPSRC, grant number EP/E027903/1.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H J. Am. Chem. Soc. 2008 130 3296.
[2] Sasmal K, Lv B, Lorenz B, Guloy AM, Chen F, Xue Y-Y and Chu C-W Phys. Rev. Lett. 2008 101 107007.
[3] Ning FL, Ahilan K, Imai T, Sefat AS, Jin RY, McGuire MA, Sales BC and Mandrus D J. Phys. Soc. Jpn. 2009 78 013711.
[4] Tegel M, Rotter M, Weiβ V, Schappacher FM, Pöttgen and Johrendt D J. Phys.: Condens. Matter. 2008 20 452201.
[5] Jesche A, Caroca-Canales N, Rosner H, Borrmann H, Ormeci A, Kasisnathan D, Klauss HH, Luetkens H, Khasanov R, Amato A, Hoser A, Kaneko K, Krellner C and Geibel C Phys. Rev. B 2008 78 180594(R).
[6] Gillett J, Das SD, Syers P, Ming AKT, Espeso JI, Petrone CM, Sebastian SE 2010 Preprint arXiv:1005.1330.
[7] Huang Q, Qiu Y, Bao W, Green MA, Lynn JW, Gasparovic YC, Wu T, Wu G, Chen XH Phys. Rev. Lett. 2008 101 257003.
[8] Loudon JC, Bowell CJ, Gillett J, Sebastian SE and Midgley PA Phys. Rev. B 2010 81 214111.

Figure 5. (a) The order parameter, $Q$, versus temperature from one of the twins in the region of interest. (b) A frame from the video of LACBED patterns showing two different values of the order parameter, 0.3% and 0.9% coexisting at the same temperature.