Specific heat anomalies for $T \ll T_c$ in superconducting single crystal doped $BaFe_2As_2$: comparison of different flux growth methods

2009 J. Phys.: Condens. Matter 21 252201

(http://iopscience.iop.org/0953-8984/21/25/252201)

IOP FTC
IOP Publishing — Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **21** (2009) 252201 (3pp) doi:10.1088/0953-8984/21/25/252201

FAST TRACK COMMUNICATION

Specific heat anomalies for $T \ll T_c$ in superconducting single crystal doped $BaFe_2As_2$: comparison of different flux growth methods

J S Kim, E G Kim and G R Stewart[1]

Department of Physics, University of Florida, Gainesville, FL 32611-8440, USA

E-mail: stewart@phys.ufl.edu

Received 21 May 2009
Published 2 June 2009
Online at stacks.iop.org/JPhysCM/21/252201

Abstract
One way to address the nature of the superconductivity in the new iron pnictides is to measure the low temperature specific heat in the superconducting state, where the temperature, field, and angular dependences of the specific heat each give important information. We report on an initial study of the specific heat down to 0.4 K in single crystals of $Ba_{0.6}K_{0.4}Fe_2As_2$, $T_c = 32$ K, prepared via Sn-flux and In-flux methods and compare to literature data for samples prepared using the self-flux method. We also report on the specific heat in zero and 1 T applied magnetic fields of $Ba(Fe_{0.926}Co_{0.074})_2As_2$, $T_c = 22$ K, prepared via the In-flux method. All samples show upturns in the specific heat divided by temperature below 2 K, with the upturn in the Sn-flux sample starting already at 4 K. These upturns, which are strongly dependent on the preparation method, impede determination of the intrinsic properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of superconductivity in the iron pnictides, and the rapid developments [1] in increasing the superconducting transition temperature, T_c, have caused significant interest [2] in the scientific community. After a T_c of 55 K was achieved [3] in $SmFeAsO_{1-x}F_x$, in the so-called '1111' iron arsenic structure, superconductivity was found [4] in a new class of compounds (the '122' structure) at 38 K in $Ba_{0.6}K_{0.4}Fe_2As_2$. This result was followed by the first production [5] of single crystals of these new superconductors, using growth of $Ba_{1-x}K_xFe_2As_2$ from a molten Sn metal flux. Many dopants other than K have since been found to suppress the spin density wave transition in the 122 parent compound, MFe_2As_2 (M = Ba, Sr, Ca, Eu), and cause superconductivity including, surprisingly enough, doping [6] of Co on the Fe site.

[1] Author to whom any correspondence should be addressed.

Determination of the nature of the superconductivity, whether BCS ('conventional') or not, in a new class of superconducting compounds is always important. In the iron pnictides, there have been several, conflicting experimental reports [7–10] on this subject, as well as numerous theoretical predictions [2, 11]. Likely, measurements will need to made not only on each structure (1111 versus 122), but also for each dopant and maybe even for various concentrations of dopant as concentration tunes T_c across the superconducting 'dome' in the phase diagram.

One way to gather information on the nodal structure of a superconductor is to measure the temperature dependence of the low temperature specific heat, C, or its field dependence ($C/T \sim H^{1/2}$ for [12, 13] unconventional superconductors), or its angular dependence in field [14]. In the first step to performing such thorough specific heat studies, we have prepared single crystalline samples of both K-doped and Co-doped $BaFe_2As_2$, using different growth methods, and measured their specific heats down to 0.4 K.

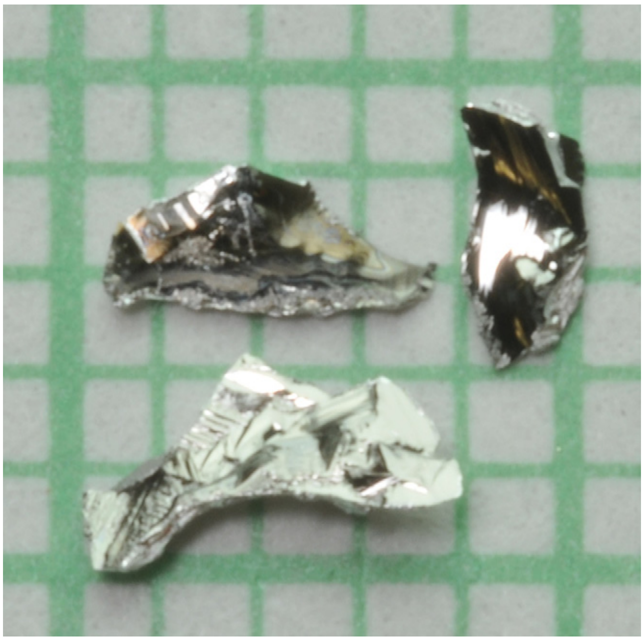

Figure 1. $Ba(Fe_{0.926}Co_{0.074})_2As_2$ single crystals, $T_c^{onset} = 22$ K, In-flux, harvested from the surface of the growth crucible, shown on mm paper.

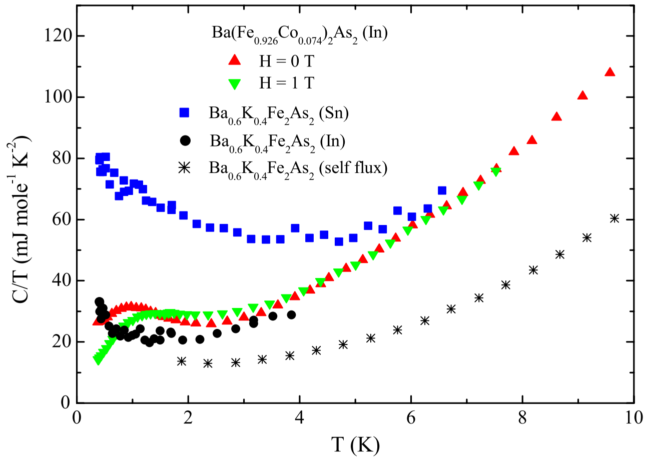

Figure 2. Low temperature specific heat, C, divided by temperature, T, in zero field vs temperature for single crystals of superconducting $Ba_{0.6}K_{0.4}Fe_2As_2$ grown by Sn-, In- and (from the literature [19]) self-flux methods as well as for single crystals of superconducting $Ba(Fe_{0.926}Co_{0.074})_2As_2$ grown from In-flux in zero and 1 T magnetic fields. The superconducting transition temperature for the sample grown by self-flux is 36.5 K [19].

2. Experimental details

Single crystals of $Ba_{0.6}K_{0.4}Fe_2As_2$ were prepared using the Sn-flux method [5], where the constituent elements are heated in a Sn-flux to 850 °C and then cooled at 5 °C h^{-1} to 500 °C. Also, we prepared the same composition using our new In-flux technique [15], where the constituent elements are heated to 1100 °C and then cooled at 5 °C h^{-1} to 600 °C in an In-flux, followed by cooling to room temperature at 75 °C h^{-1}. Rather than centrifuging at 500 °C (as is done [5] for the Sn-flux samples) to remove the samples from the In-flux, crystals that have formed on top of the flux (with a flux-free top surface) are removed while heating the reaction crucible on a hot plate slightly above the melting point of In at 157 °C. This is then followed by centrifuging the remaining material to obtain the crystals that formed below the surface. In addition, crystals of $Ba(Fe_{0.926}Co_{0.074})_2As_2$ [6] (see figure 1) and pure $BaFe_2As_2$ were grown using the In-flux method.

Sample quality and impurity effects will be seen below to play an important role in the low temperature specific heat. We note that the amount of In inclusion due to the flux growth process in the undoped $BaFe_2As_2$ single crystals is 0.4 at.%, measured via electron microprobe using a JEOL Superprobe 733. This may be compared to ~1% Sn found [5] to be in $BaFe_2As_2$ grown using Sn-flux. Resistivity and magnetic susceptibility measurements show that the temperature of the spin density wave transition in $BaFe_2As_2$ grown in In-flux is 137 ± 1 K, comparable to the result [16, 17] for self-flux grown samples. A further measure of the quality of crystals from the In-flux growth process is the residual resistivity ratio ($\equiv\rho(300\ \text{K})/\rho(T \to 0\ \text{K})$) for In-flux grown $BaFe_2As_2$, which is 5.0, compared to around 3 for self-flux grown crystals [16, 17].

Samples were characterized using magnetic susceptibility in a commercial MPMS™ Quantum Design machine, 4 probe dc resistivity, and specific heat in zero and applied magnetic fields using established [18] techniques. The T_c^{onset} of the K-doped samples, both for Sn- and In-flux growth, was 32.5 K, while T_c^{onset} for the Co-doped crystals was 22 K determined by resistive and susceptibility measurements.

3. Results and discussion

The specific heat of the Sn-flux and In-flux crystals is shown in figure 2, with literature data [19] for $Ba_{0.6}K_{0.4}Fe_2As_2$ crystals grown by self-flux shown for comparison.

Focusing first on the data for $Ba_{0.6}K_{0.4}Fe_2As_2$, we see that the literature data [19] for the self-flux grown crystal, measured only down to 2 K, show the beginning of an upturn in C/T below 2 K. There is a similar upturn in the low temperature In-flux grown $Ba_{0.6}K_{0.4}Fe_2As_2$ C/T data starting at a slightly lower temperature. Also, the In-flux sample C/T data are approximately 30% larger at 2 K. In contrast, the Sn-flux grown $Ba_{0.6}K_{0.4}Fe_2As_2$ C/T data show an upturn starting at approximately 4 K, and a much larger magnitude at low temperature—about a factor of four larger at 2 K than the self-flux data.

This upturn in C/T for $Ba_{0.6}K_{0.4}Fe_2As_2$ becomes an actual rounded transition centered at 1 K for the In-flux grown crystals of $Ba(Fe_{0.926}Co_{0.074})_2As_2$. This transition moves to higher temperature in magnetic field, indicating that the transition is ferromagnetic-like in origin. The fact that the transition *increases* in temperature with the application of low magnetic fields offers the prospect that at higher fields, and at dilution refrigerator temperatures down to 0.05 K, we indeed can investigate the low temperature C/T as $T \to 0$ (see figure 2) in order to investigate the nature of the nodes [12–14] in the superconducting state as discussed above in section 1.

However, until progress is made in preparing $Ba_{0.6}K_{0.4}Fe_2As_2$ without the upturns in C/T shown in figure 2, such specific heat methods for determining the nodal superconductivity in this material have definite problems. Since the C/T of the three types of $Ba_{0.6}K_{0.4}Fe_2As_2$ samples at low temperatures shows a progression in magnitude (smallest to largest) from the self-flux grown crystal to the In-flux crystal (0.4 at.% inclusions) to the Sn-flux crystal (∼1% inclusions), the conclusion for future direction in sample preparation seems clearly to improve upon the self-flux prepared methodology. The higher RRR values obtained for our In-flux grown crystals of $BaFe_2As_2$ than for self-flux grown crystals holds out hope that the self-flux method can indeed be improved.

Acknowledgments

The authors gratefully acknowledge helpful discussions with Professor Peter Hirschfeld. Work at Florida performed under the auspices of the United States Department of Energy, contract no. DE-FG02-86ER45268.

References

[1] Hosono H 2008 *J. Phys. Soc. Japan* **77** (Suppl.) C 1–8
[2] Norman M R 2008 *Physics* **1** 21
[3] Ren Z A, Lu W, Yang J, Yi W, Shen X L, Li Z C, Che G C, Dong X L, Sun L L, Zhou F and Zhao Z X 2008 *Chin. Phys. Lett.* **25** 2215
[4] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
[5] Ni N, Bud'ko S L, Kreyssig A, Nandi S, Rustan G E, Goldman A I, Gupta S, Corbett J D, Kracher A and Canfield P C 2008 *Phys. Rev.* B **78** 014507
[6] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 *Phys. Rev. Lett.* **101** 117004
[7] Chen T Y, Tesanovic Z, Liu R H, Chen X H and Chien C L 2008 *Nature* **453** 1224
[8] Dubroka A, Kim K W, Roessle M, Malik V K, Drew A J, Liu R H, Wu G, Chen H and Bernhard C 2008 *Phys. Rev. Lett.* **101** 097011
[9] Fletcher J D, Serafin A, Malone L, Analytis J, Chu J-H, Erickson A S, Fisher I R and Carrington A 2008 arXiv:0812.3858
[10] Gordon R T, Ni N, Martin C, Tanatar M A, Vannette M D, Kim H, Samolyuk G, Schmalian J, Nandi S, Kreyssig A, Goldman A I, Yan J Q, Bud'ko S L, Canfield P C and Prozorovar R 2009 *Phys. Rev. Lett.* **102** 127004
[11] See also Mishra V, Boyd G, Graser S, Maier T, Hirschfeld P J and Scalapino D J 2009 *Phys. Rev.* B **79** 094512 and references therein
[12] Moler K A, Baar D J, Urbach J S, Liang R, Hardy W N and Kapitulnik A 1994 *Phys. Rev. Lett.* **73** 2744
Moler K A, Sisson D L, Urbach J S, Beasley M R, Kapitulnik A, Baar D J, Liang R and Hardy W N 1997 *Phys. Rev.* B **55** 3954
[13] Volovik G E 1993 *JETP* **58** 469
[14] For a review see Park T and Salamon M B 2004 *Mod. Phys. Lett.* B **18** 1205
[15] Kim J S and Stewart G R, unpublished
[16] Tanatar M A, Ni N, Samolyuk G D, Bud'ko S L, Canfield P C and Prozorov R 2009 arXiv:0903.0820
[17] Sun G L, Sun D L, Konuma M, Popovich P, Boris A, Peng J B, Choi K Y, Lemmens P and Lin C T 2009 arXiv:0901.2728
[18] Stewart G R 1983 *Rev. Sci. Instrum.* **54** 1
[19] Mu G, Luo H, Wang Z, Shan L, Ren C and Wen H-H 2009 *Phys. Rev.* B **79** 174501