Heat capacity of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, $x=0$ and 0.41

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Abstract. Heat-capacity measurements on exceptionally high-quality samples of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ give the values of a number of parameters relevant to the electronic structure, the structural/magnetic transition in the undoped parent compound, and the superconducting transition in the nearly optimally doped, $x=0.41$ sample. In $\text{BaFe}_2\text{As}_2$ the changes in the lattice and magnetic structure appear as a single, sharp first-order transition at 140 K; the Sommerfeld coefficient is $\gamma = 5.1 \text{ mJ K}^{-2} \text{ mol}^{-1}$. For the superconducting, $x=0.41$, sample, the residual density of electron states in the superconducting states is essentially zero. The specific-heat anomaly at $T_c$ suggests extreme strong coupling, with $\Delta(0)/k_B T_c \approx 2.6$, and a normal-state Sommerfeld coefficient $\gamma_n \approx 45 \text{ mJ K}^{-2} \text{ mol}^{-1}$.

1. Introduction
The structural/magnetic transition in the 122 series of Fe pnictide superconductors, e.g. $\text{BaFe}_2\text{As}_2$, takes various forms in different samples and different measurements, and has been described as both first and second order. Superconductivity is produced by doping with electrons, e.g., by substitution of Co or Ni on the Fe sites, or holes, e.g., by substitution of K or Na on the Ba sites. The superconducting samples have also shown a great variety of behavior, leading to different conclusions about the symmetry of the order parameter. Complications in the analysis of the low-temperature data associated with the presence of paramagnetic impurities are one obvious factor in these discrepancies, and the presence of a residual density of electron states, "non superconducting material" is another. Since the hole-doped materials are more difficult to prepare, most measurements have been made on the electron-doped materials. There is good reason, however, to think that there may be significant differences between the two and for that reason measurements on the hole-doped materials are of interest. Here we report annealing studies on $\text{BaFe}_2\text{As}_2$ that are relevant to the order of the structural/magnetic transition, and measurements on a sample of $\text{Ba}_{0.59}\text{K}_{0.41}\text{Fe}_2\text{As}_2$ that has an unusually low concentration of paramagnetic centers and essentially zero residual density of states in the superconducting state.
2. Experimental Details
Measurements on the parent sample were made on a 10.3 mg piece from a larger crystal grown by a modified self-flux method, on which we reported neutron results earlier [1]. All the measurements were made on the same sample after successive annealing periods of time. Potassium doped samples were prepared by standard self-flux (FeAs) method [2]. The stoichiometry and the potassium doping was checked by both inductively coupled plasma (ICP) and electron microprobe analysis WDS (wavelength-dispersive X-ray spectroscopy). Measurements on both samples were made in Quantum Design apparatus, heat-capacity, resistivity and AC-magnetization measurements in a PPMS, and DC-magnetization in a MPMS.

3. Results and Discussion
3.1. BaFe$_2$As$_2$: the annealing study
The heat capacity of the as-grown BaFe$_2$As$_2$ sample is shown in Fig. 1. The structural/magnetic transition occurs at 135.4 K, with an entropy of 0.84 J K$^{-1}$ mol$^{-1}$. Annealing the sample for 30 days at 700°C sharpened the transition and shifted it to 140.2 K (as shown in the inset) with essentially no change in the entropy. For both the as-grown and annealed samples the transition was slightly hysteretic (as shown for the as-grown sample in Fig. 2) and unchanged in a magnetic field of $\mu_0 H = 14$ T (as shown for the annealed sample in Fig. 2).

![Figure 1](image1.png)  
**Figure 1.** The specific heat of the as-grown sample of BaFe$_2$As$_2$. The anomaly at the structural/magnetic transition is compared with that of the annealed sample in the inset.

![Figure 2](image2.png)  
**Figure 2.** Examples of the effects of magnetic field and hysteresis on the specific heat at the structural/magnetic transition in BaFe$_2$As$_2$.

The heat capacity of the as-grown sample below 10 K and in fields to $\mu_0 H = 14$ T is shown in Fig. 3. To the accuracy of the measurements the heat capacity is independent of field, which shows that the concentration of paramagnetic impurities is well below $10^{-3}$ mol mol$^{-1}$. The data in all fields were fit simultaneously with $C = \gamma T + B_3T^3 + B_5T^5 + B_7T^7$, to obtain $\gamma = 5.11$ mJ K$^{-2}$ mol$^{-1}$, $B_3 = 0.412$ mJ K$^{-4}$ mol$^{-1}$, $B_5 = 8.27 \times 10^{-5}$ mJ K$^{-6}$ mol$^{-1}$ and $B_7 = 6.22 \times 10^{-8}$ mJ K$^{-2}$ mol$^{-1}$. The experimental data are compared with the resulting fit in Fig. 4, where the data in fields other than zero are shifted in C/T by increments of 5 mJ K$^{-2}$ mol$^{-1}$ for clarity, but in each case the common fitting expression is shown.

3.2. The hole-doped Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$
The zero-field heat capacity of the Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$ sample is shown in Fig. 4. One notable feature is the absence of structure in the heat capacity near 71 K. FeAs, which is a common
impurity in superconducting samples made by doping BaFe$_2$As$_2$, has a sharp peak in the heat capacity at that temperature, and, apparently, a significant Sommerfeld coefficient [3]. A sample of Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$ that showed the 71-K FeAs feature in the heat capacity had a substantially larger residual density of states in the superconducting state and a smaller heat capacity anomaly at the superconducting transition than reported here for the Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$ sample. It seems probable that some of the discrepancies between the results reported here and other measurements are also associated with the presence of FeAs in the other samples. The feature near 37 K is the transition to the superconducting state. The corresponding feature in the susceptibility is shown in the inset. The heat-capacity anomalies at $T_c$ for fields to $\mu_0 H = 14$ T

Figure 3. The low-temperature specific heat of BaFe$_2$As$_2$. The data in magnetic fields are displaced by progressive increments of 5 mJ K$^{-2}$ mol$^{-1}$ for clarity. For each field the curve represents a simultaneous fit to all the data.

Figure 4. The specific heat of Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$. The feature in the susceptibility at the transition to the superconducting state is shown in the inset.

Figure 5. The specific heat of Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$ in the vicinity of the transition to the superconducting state.

Figure 6. Specific heat of Ba$_{0.59}$K$_{0.41}$Fe$_2$As$_2$ at low temperatures.
are shown in Fig. 5. The straight-line, entropy-conserving construction on the zero-field data gives $T_c = 37.2$ K and $\Delta C(T_c)/T_c = 153$ mJ K$^{-2}$ mol$^{-1}$. The shape of the zero-field anomaly suggests strong coupling. The assumption of a single gap in the superconducting state, and comparison with the $\alpha$ model [4] gives estimates of the normal-state Sommerfeld coefficient, $\gamma_n$, and the coupling strength, as measured by the parameter $\alpha = \Delta(0)/k_BT_c$: (The $\alpha$ model gives the ratios of the discontinuities in $C$ and $dC/dT$ to $\gamma_n$.) The straight-line construction in the figure gives $\gamma_n = 45$ mJ K$^{-2}$ mol$^{-1}$, and $\alpha = 2.61$, substantially larger than the BCS weak-coupling value, 1.764.

The low-temperature data are shown in Fig. 6 as $C/T$ vs $T^2$. The small upturns in the 0-, 0.5-, and 1-T data at the lowest temperatures, and the negative curvature in the 9-, 11-, and 14-T data indicate the presence of paramagnetic impurities. The 0-, 0.5-, and 1-T data below 6 K were fit separately with the high-temperature tail of a two-level Schottky anomaly and terms for the vortex and lattice contributions, $\gamma_v(H)T$ and $B_3T^3$, respectively. For all three fields the fits gave $2 \times 10^{-3}$ mol mol$^{-1}$ for the concentration of paramagnetic centers and $B_3 = 0.79$ mJ K$^{-4}$ mol$^{-1}$; the value of $\gamma_v(H)$ was significant in magnitude and positive only for $\mu_0H = 1$ T, $\gamma_v(1) = 0.23$ mJ K$^{-2}$ mol$^{-1}$. Thus, both the concentration of paramagnetic centers and the residual density of states are remarkably low.

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