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Specific heat versus field for $LiFe_{1-x}Cu_xAs$

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Abstract

LiFeAs is one of the new class of iron superconductors with a bulk T_c^{onset} in the 15–17 K range. We report on the specific heat characterization of single crystal material prepared by self-flux growth techniques with significantly improved properties, including a much decreased residual gamma, γ_r ($\equiv C/T$ as $T \rightarrow 0$), in the superconducting state. Thus, in contrast to previous explanations of a finite γ_r in LiFeAs being due to *intrinsic* states in the superconducting gap, the present work shows that such a finite residual γ in LiFeAs is instead a function of sample quality. Further, since LiFeAs has been characterized as nodeless with multiple superconducting gaps, we report here on its specific heat properties in zero and applied magnetic fields, to compare to similar results on nodal iron superconductors. For comparison, we also investigate $LiFe_{0.98}Cu_{0.02}As$, which has the reduced T_c of ≈9 K and an H_{c2} of 15 T. Interestingly, although presumably both LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ are nodeless, they clearly show a non-linear dependence of the electronic density of states ($\propto$ specific heat γ) at the Fermi energy in the mixed state with the applied field, similar to the Volovik effect for nodal superconductors. However, rather than indicating nodal behavior, the satisfactory comparison with a recent theory for $\gamma(H)$ for a superconductor with two isotropic gaps in the presence of impurities argues for nodeless behavior. Thus, in terms of specific heat in a magnetic field, LiFeAs can serve as the prototypical multiband, nodeless iron superconductor.

(Some figures may appear in colour only in the online journal)

1. Introduction

The iron superconductor LiFeAs, with T_c reportedly varying between 15 and 19 K, was discovered by Wang *et al* [1]. Successive characterization by a variety of techniques reveals that LiFeAs can be well described [2] as nodeless. ARPES data reveals four [3] or five [4] Fermi surface pockets, although such a multiplicity of bands is at present beyond the ability of most theories describing physical measurements. A simplified two gap model has been used to fit penetration depth [5] and NMR and NQR [6] measurements.

Since the consensus is that LiFeAs is nodeless, it was of interest to examine the field dependence of the specific-heat-determined electronic density of states $\propto \gamma$, where γ is the coefficient of the linear-with-temperature term in the low temperature specific heat, $C = \gamma T + \beta T^3$. In nodal superconductors in the superconducting state, $\gamma(H) \propto H^{1/2}$ at low fields, followed by $\gamma \propto H^1$ (Volovik behavior) as has been recently seen [7] in $BaFe_2(As_{0.7}P_{0.3})_2$ and overdoped $Ba(Fe_{1-x}Co_x)_2As_2$ [8]. Thus, in nodeless LiFeAs, we would *a priori* expect qualitatively different $\gamma(H)$ behavior.

A further reason to investigate LiFeAs concerns the correlation between the discontinuity in the specific heat at T_c, ΔC, and T_c first discovered by Bud'ko *et al* [9] (hereafter 'BNC'), where they found $\Delta C/T_c \propto T_c^2$ for 14 different compositions of 122 structure iron based superconductors. LiFeAs samples that have been characterized to date, despite having similar $T_c^{midpoint}$ determined from bulk specific heat, of 14.7–16 K, had large variations in both $\Delta C/T_c$ and residual γ_r ($\equiv C/T$ as $T \rightarrow 0$). Specifically, $\Delta C/T_c$ ranges from 7.65 mJ mol^{-1} K^{-2} [10], to 12.4 mJ mol^{-1} K^{-2} [11], to

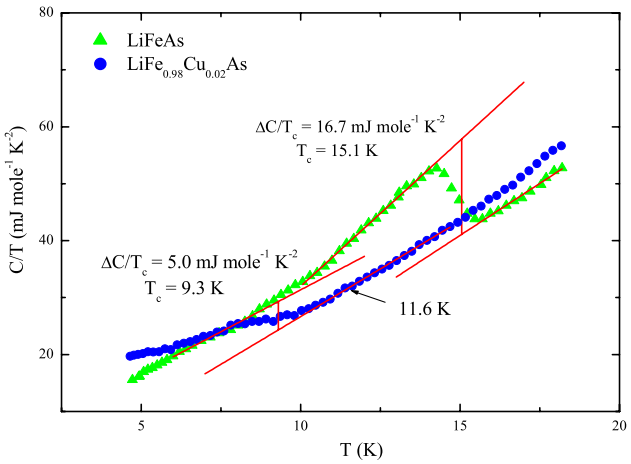

Figure 1. Specific heat divided by temperature, C/T, versus temperature for single crystal LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ expanded around T_c to show the discontinuity at the superconducting transition, ΔC. The equal area constructions shown in red are discussed in [2] and represent idealized sharp transitions. The bulk transition width, ΔT_c, for the undoped LiFeAs is as narrow or narrower than previously seen.

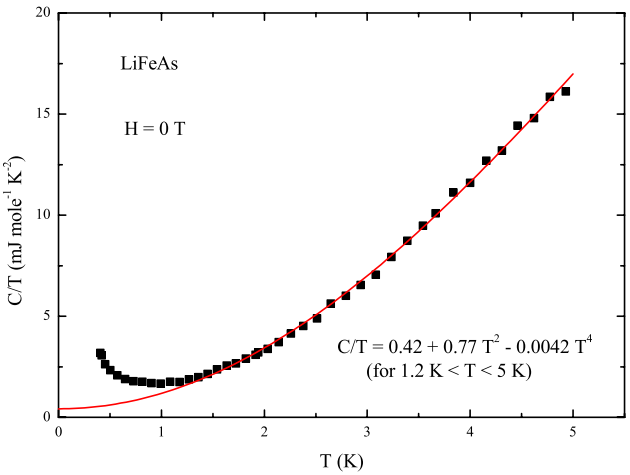

Figure 2. Low temperature C/T versus temperature for single crystal LiFeAs. The low temperature upturn below 1.3 K is an unknown minority phase Schottky anomaly as seen in other iron based superconductors [15, 16]. Note the extremely low extrapolated residual gamma value, γ_r, of 0.4 mJ mol^{-1} K^{-2}.

≈20 mJ mol^{-1} K^{-2} in [12] while residual γ_r values (instead of $\gamma_r \approx 0$ in a 100% gapped superconducting sample) range from 7.7 to 0.9 to 18.7 mJ mol^{-1} K^{-2} respectively in the three references. (Note that specific heat data were only taken down to 2 K in [11] resulting in some inaccuracy to their γ_r value.)

The samples made from self-flux characterized in the present work have almost vanishing γ_r. Thus it was considered valuable to determine $\Delta C/T_c$ for these higher quality LiFeAs crystals. $\Delta C/T_c$ for $LiFe_{0.98}Cu_{0.02}As$, $T_c^{mid} = 9.3$ K, was also measured for comparison.

2. Experimental details

Single crystals of LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ were prepared by self-flux methods. FeAs and $Fe_{0.98}Cu_{0.02}As$ were pre-synthesized by reacting the mixture of elemental powder at 750 °C for 20 h in an evacuated quartz tube; Li_3As by reacting Li lumps with As powder at 600 °C for 10 h. The Li_3As, FeAs (or $Fe_{0.98}Cu_{0.02}As$), and As powders were mixed according to the element ratio of $Li(Fe_{1-x}Cu_x)_{0.3}As$ ($x = 0, 0.02$). The powder mixture was then pressed into a pellet in an alumina oxide tube and sealed in a Nb tube under 1 atm of argon gas and then sealed in an evacuated quartz tube. The sealed quartz tube was heated up to 1100 °C for 10 h and then cooled down to 700 °C at a rate of 5 °C h^{-1}. Crystals with a size up to 10 mm × 6 mm × 0.5 mm were obtained. The whole preparation work was carried out in a glove box protected with high purity Ar gas.

A study was done as to what attachment method would react least with the known-to-be-reactive LiFeAs crystals. Both GE7031 and Wakefield grease were found to give minimal degradation in T_c^{onset} and transition width if applied within 1 day or less of cooling down to low temperatures. After a slight degradation after one day (comparable to the result of [12] which used GE7031), further storage at room temperature showed stable T_c^{onset} and ΔT_c.

Specific heat in zero and applied magnetic fields up to 12 T was measured down to 0.4 K according to established techniques [13]. The sample platform was reinforced to increase the strength of the support wires by the addition of two crossed hollow cylinders of kapton, 0.0065″ OD, 0.000 75″ wall, attached to the platform with epoxy[3]. Due to the existence of an unknown magnetic impurity phase the pure LiFeAs sample experienced a large magnetic force in magnetic fields >9 T. Such technical difficulties in determining $\gamma(H)$ have been seen in other systems, e.g. Co-doped $BaFe_2As_2$ [8]. This force caused the sample to fly off the Wakefield grease bonding to the sample platform. The sample was reattached with the more secure GE7031 varnish, and then further measured up to 12 T. At some larger field, the force would exceed the support platform's failure strength and thus data collection was halted after 12 T.

3. Results and discussion

Figure 1 shows the $\Delta C/T_c$ determinations for both LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ and figure 2 shows the low temperature specific heat down to 0.4 K to determine γ_r. The previous values for $\Delta C/T_c$ for LiFeAs were 7.65 mJ mol^{-1} K^{-2}, ($T_c^{midpoint} = 15$ K from the specific heat, transition width $\Delta T_c \cong 3$ K, $\gamma_r \cong 7.7$ mJ mol^{-1} K^{-2}) [10]; 12.4 mJ mol^{-1} K^{-2} ($T_c = 14.7$ K, $\Delta T_c \cong 1.3$ K, $\gamma_r \cong 0.9$ mJ mol^{-1} K^{-2}) [11] and ≈20 mJ mol^{-1} K^{-2} ($T_c = 16.8$ K, $\Delta T_c \cong 2.5$ K, $\gamma_r = 18.7$ mJ mol^{-1} K^{-2}) [12]. These results compare to the present work's (see figure 1) $\Delta C/T_c = 16.7$ mJ mol^{-1} K^{-2}, with a transition width ΔT_c of ≈1 K while figure 2 shows that $\gamma_r = 0.4$ mJ mol^{-1} K^{-2}.

[3] This is similar to the sample platform in the Quantum Design PPMS® P850 DR system.

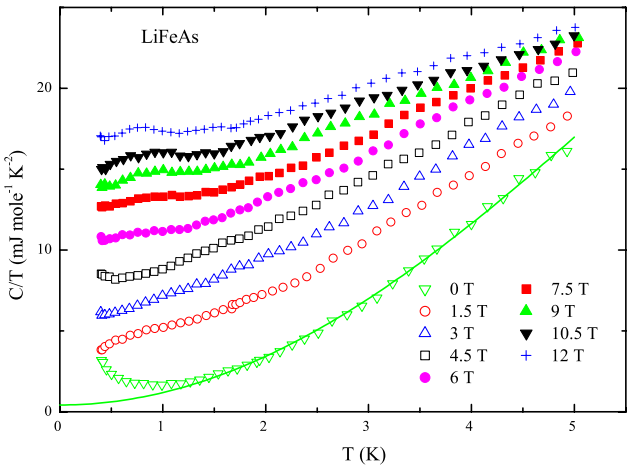

Figure 3. C/T versus temperature in fields up to 12 T of single crystal LiFeAs with field aligned in the c-axis direction. γ values ($\equiv C/T$ as $T \to 0$) are determined by fitting the data from 2 to 5 K, avoiding the small anomaly in C/T around 1 K that grows with increasing field. For comparison to $\gamma(H)$, smoothed values of C/T (2 K, H) are also determined by fitting the data in the vicinity of 2 K as discussed in the text and [7, 8].

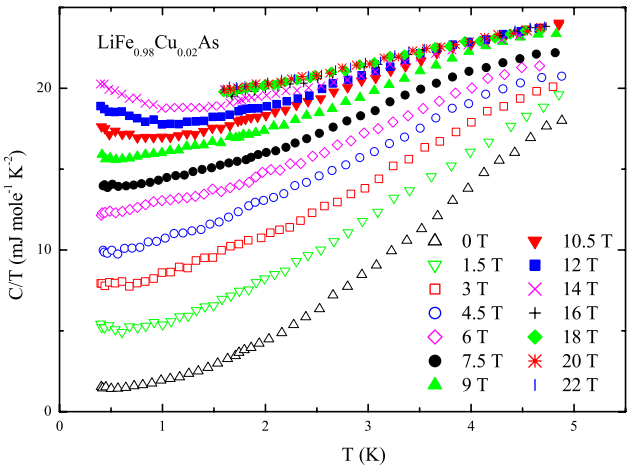

Figure 4. C/T versus temperature in fields up to 22 T of $LiFe_{0.98}Cu_{0.02}As$, field $\parallel$ c-axis. γ values ($\equiv C/T$ as $T \to 0$) are determined by fitting the data from 2 to 5 K to $C/T = \gamma + \beta T^2 + \delta T^4$, avoiding the upturn at low temperatures due to field splitting of the nuclear levels that grows with increasing field. Note the larger upturn for the Cu-doped sample in 12 T compared to pure LiFeAs in figure 3. This is not just due to the extra contribution to $C/T(H)$ from the 2% Cu, but is presumably (see an exhaustive discussion in [8]) primarily due to the lower electronic density of states at the Fermi energy, $N(0)$, in LiFeAs at 12 T. This $N(0)$ is responsible for coupling the nuclear levels to the rest of the lattice, and is larger at 12 T in the smaller H_{c2} $LiFe_{0.98}Cu_{0.02}As$. For comparison to $\gamma(H)$, smoothed values of C/T (2 K, H) are also determined by fitting the data in the vicinity of 2 K as discussed in the text and [7, 8].

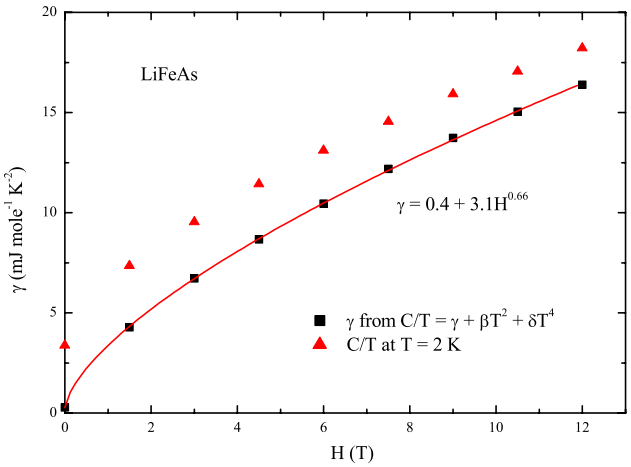

Figure 5. Specific heat γ from a three term polynomial fit to the 2–5 K data in figure 3 versus H for LiFeAs, as well as C/T (2 K) versus H for comparison. The two metrics for the field dependence of γ agree very well, and result in $\gamma \propto H^{0.66}$.

Thus, we can draw two conclusions from these results. First, as clear from the data in figures 1 and 2 (considering the narrowness of the transition and the low, 0.4 mJ mol^{-1} K^{-2} γ_r for the parent LiFeAs compound), the correct $\Delta C/T_c$ value for pure LiFeAs is close to 17 mJ mol^{-1} K^{-2}. $\Delta C/T_c$ for the lower transition temperature, somewhat broader ΔT_c Cu-doped sample is 5 mJ mol^{-1} K^{-2}. These values agree well with the overall $\Delta C/T_c \propto T_c^2$ trend for the iron based superconductors established [9] by Bud'ko *et al* and later confirmed [14] by Kim *et al* for a wider spectrum of samples.

A second conclusion that can be drawn from figure 2 is that a large γ_r such as reported by [10, 12] is not intrinsic to LiFeAs. Although there is a low temperature Schottky anomaly upturn in C/T in figure 2 (as has been seen in other iron based superconductors, see e.g. [15, 16]), this does not affect the accuracy of the extrapolation of γ_r to only 0.4 mJ mol^{-1} K^{-2}. Thus, we suggest that in LiFeAs in particular, and in other iron based superconductors in general, that the size of the residual gamma is proportional to the sample quality. This is consistent with the evidence in [16, 17] that γ_r decreases with annealing in $Ba(Fe_{1-x}Co_x)_2As_2$. Thus, the correct explanation of this residual gamma is that it is more likely due to a non-superconducting fraction rather than states in the gap due to strong unitary scattering (which might be expected to depress T_c) as has been proposed by some works to explain the presence of substantial γ_r values.

Now let us consider the field dependences of C/T of LiFeAs and $LiFe_{0.98}Cu_{0.02}As$, where the specific heat data versus temperature as a function of field are plotted in figures 3 and 4 respectively. As has been discussed thoroughly in [8], we present two methods to track γ (where $C/T = \gamma$ as $T \to 0$) as a function of field. The first method is a fit of the C/T data to $C/T = \gamma + \beta T^2 + \delta T^4$ in a temperature range above any anomalies or upturns (the higher field, low temperature data for $LiFe_{0.98}Cu_{0.02}As$ in figure 4 show an upturn due to field splitting of the nuclear hyperfine levels). The second method is a fit of the C/T data in the close neighborhood of 2 K, since C/T (2 K) is proportional to γ. This latter proportionality is readily apparent when both methods of tracking γ versus H are shown in figures 5, 7 and 8.

Consider first γ and C/T (2 K) versus H for LiFeAs, shown in figure 5. γ can be fit to a simple power law of field, giving a field dependence of $\gamma \propto H^{0.66}$ over the entire field range of measurement. Although these γ versus H data may

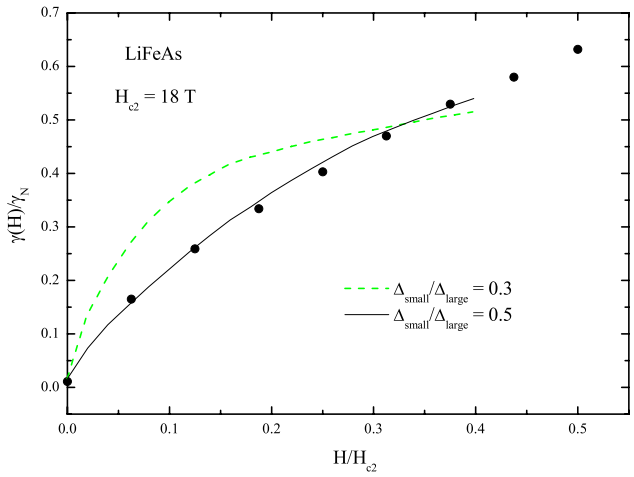

Figure 6. Shown here is a fit (obtained from [18]) to the $\gamma(H)$ data from figure 5 for LiFeAs based on a two isotropic band model, where the theory in [18] is only up to $H/H_{c2} = 0.4$. Although ARPES data find more than two bands in the iron based superconductors, the ratio of the band gaps of 0.5, $\Delta_{small}/\Delta_{large}$, is not inconsistent with the ARPES-determined band gaps [3, 4].

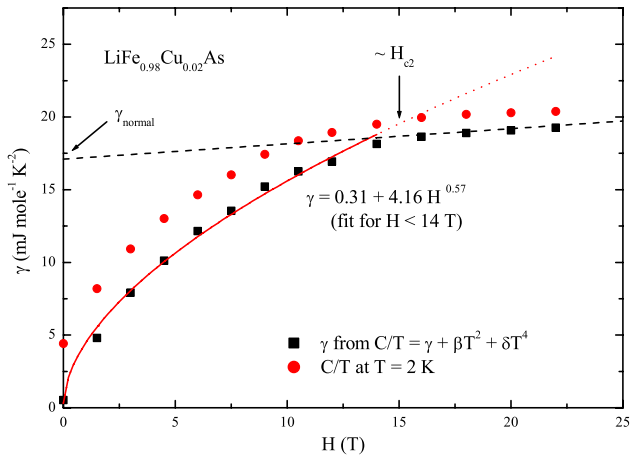

Figure 7. Specific heat γ from a three term polynomial fit to the 2–5 K data in figure 4 versus H for $LiFe_{0.98}Cu_{0.02}As$, as well as C/T (2 K) versus H for comparison. These field data are up to 22 T, well above $H_{c2} \approx 15$ T. The two metrics for the field dependence of γ, just as for LiFeAs in figure 5, agree very well, and result in $\gamma \propto H^{0.57}$. The fact that the normal state γ appears to be a slight function of field implies that the power law dependence of γ in the superconducting state could be altered by the field dependence of the specific heat of the normal state cores. This issue is addressed below in figure 8.

look 'Volovik-like' (i.e. indicative of nodes or deep minima), in fact—as shown in figure 6—a two isotropic band fit like that proposed by Bang (which in [18] only extends up to $H/H_{c2} = 0.4$ but see [10]) gives a good fit of the data.

Similarly, γ and C/T (2 K) versus H for $LiFe_{0.98}Cu_{0.02}As$, shown in figure 7, also follow a simple power law, where $\gamma \propto H^{0.57}$. Since there was no parasitic ferromagnetic phase to cause the sample to fly off the platform, these data were measured up past $H_{c2} \approx 15$ up to 22 T. In the high field normal state data it is apparent that the normal state γ is slightly field dependent. Figure 8 shows this normal state γ

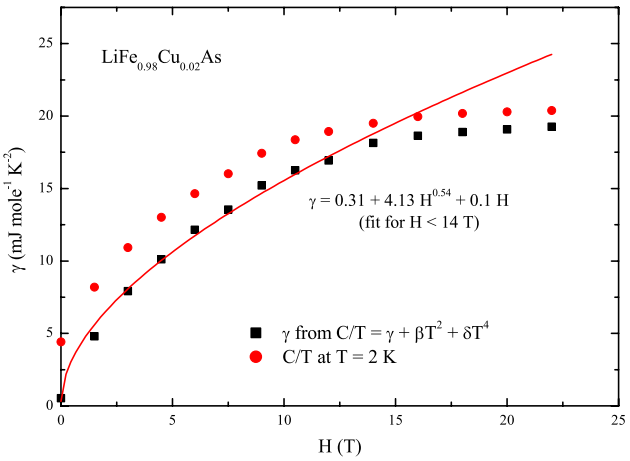

Figure 8. γ and C/T (2 K) versus field in $LiFe_{0.98}Cu_{0.02}As$, with the power law fit adjusted for the field dependence of the normal state γ determined in figure 7. As may be seen, the change in the power law exponent is within the error bar, from 0.57 without adjustment to 0.54 with.

field dependence factored into the fit of the γ versus H data in the superconducting state to give a slightly altered (0.54 versus 0.57) field exponent. This power law is reminiscent of Volovik behavior in YBCO, where [20] found that γ varied as $H^{1/2}$ indicative of nodes in the superconducting gap function. However, just as for LiFeAs, figure 6, a fit (not shown) of these γ versus H data for $LiFe_{0.98}Cu_{0.02}As$ to the two isotropic band fit of Bang [18] gives a convincingly good agreement between the fit and the data.

Thus, these specific heat data in field in a superconductor system known-to-be-nodeless serve as a warning that $\gamma \propto H^{\alpha}$, α near 0.5–0.7, is not necessarily an indication of nodal or deep minima behavior in the superconducting gap. This sub-linear behavior of γ with H has also been reported [20] in the 122 defect structure $Rb_{1-x}Fe_{2-y}Se_2$, $T_c = 32$ K, which is also believed to be nodeless.

4. Conclusions

The specific heat in zero and applied field of single crystals of LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ showed good agreement between $\Delta C/T_c$ and the published trend [9, 14] versus T_c for all iron based superconductors. The measured residual γ, γ_r, for pure LiFeAs is only 0.4 mJ mol^{-1} K^{-2}, which suggests the conclusion that previously observed larger values are not characteristic of the intrinsic properties. Thus, as a speculation, such finite residual gamma values in other iron based superconductors, e.g. in Co-doped $BaFe_2As_2$, may also be merely due to sample quality issues. The field dependence of the specific heat γ of both LiFeAs and $LiFe_{0.98}Cu_{0.02}As$ obeys approximately an $H^{0.6\pm0.05}$ power law. Although such a field dependence is reminiscent of the Volovik effect and its inference of nodal superconductivity, in these known-to-be-nodeless materials this $\gamma(H)$ behavior is instead indicative of the behavior of two (or more) approximately isotropic bands as proposed by Bang [18].

Acknowledgments

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