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LiFeP: A nodal superconductor with an unusually large $\frac{\Delta C}{T_c}$

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The specific heat of improved quality polycrystalline LiFeP, $T_c \approx 5$ K, was measured down to 0.4 K. The results indicate that this is another iron-based nodal superconductor (in addition to KFe_2As_2, $T_c \approx 4$ K) where the discontinuity in the specific heat ΔC at T_c violates the global trend in $\Delta C/T_c$ with T_c for the iron-based superconductors (IBSs), first pointed out by Bud'ko, Ni, and Canfield [Phys. Rev. B **79**, 220516(R) (2009)]. Thus, it may be possible that there exists a minimum of two different kinds of IBSs distinguished by their low T_c, nodal, and $\Delta C/T_c$ behavior.

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I. INTRODUCTION

The low temperature iron pnictide superconductor LiFeP, $T_c \approx 6$ K, was discovered[1] shortly after the higher transition temperature analog, LiFeAs, $T_c \approx 18$ K.[2] In addition to having the same crystal structure, both compounds have been found[3,4] to have similar Fermi surface shapes. However, various interesting contrasts have also been pointed out. For example, LiFeP has[5] a factor of 70 smaller magnetic upper critical field H_{c2} as well as weaker electronic correlations (with a factor of 3 times smaller A coefficient in $\rho = \rho_0 + AT^2$) than LiFeAs. The most interesting contrast, however, is the report[6] that single crystals of LiFeP, $T_c = 4.5$ K, display a penetration depth λ that is linear in temperature down to $T/T_c = 0.03$ while the penetration depth for LiFeAs has been reported[7] to vary as T^3. The dependence $\lambda \propto T^1$ as found for LiFeP is conclusive[8,9] evidence for nodes in the superconducting gap while the behavior $\lambda \propto T^3$ found for LiFeAs, on the other hand, is characteristic of fully gapped behavior.

To date, the only reported specific heat data were those down to 2 K of the discovery work[1] on a rather small mass of polycrystalline material. The results gave $T_c^{\text{onset}} = 4.5$ K, $T_c^{\text{peak}} \approx 3.3$ K, and a specific heat γ, proportional to the electronic density of states at the Fermi energy of 16 mJ/mol K^2. The single crystal samples available to date have been too small for specific heat characterization, e.g., the single crystals studied in the penetration work[6] had masses in the 1–2 μg range.

The present specific heat work is on a pressed pellet of higher quality material (higher T_c^{onset} with a narrow transition width) than previously available, although it is only polycrystalline. The reason for this study is to investigate the fundamental properties of this nodal iron pnictide superconductor in light of the global trend found[10] by Bud'ko, Ni, and Canfield (BNC). They found that the discontinuity in the specific heat ΔC follows approximately T_c^3. In a later study,[11] the number of iron-based superconducting samples that obey this trend (including LiFeAs) was almost doubled, and it was pointed out that this is a different behavior than electron-phonon coupled BCS superconductors, which follow approximately $\Delta C \propto T_c^2$. As has been observed,[8,11] comparing a particular iron-based superconductor's (IBS's) ΔC with the BNC-discovered unusual behavior is a definitive metric for determining if the compound in question has the same superconducting pairing mechanism as the typical IBS. There are several examples[8] of low T_c IBSs that are simply BCS-like in their ΔC vs T_c values, e.g., $RbFe_2As_2$, $T_c = 2.6$ K. Most importantly, we have previously pointed out[11,12] that KFe_2As_2, another low ($\approx$4 K) T_c IBS with nodal behavior,[13,14] does not obey the BNC global trend for ΔC at all (ΔC for KFe_2As_2 is almost two orders of magnitude larger than the BNC prediction) and is therefore likely not properly comparable to the common (presumably unconventional) iron pnictide or iron chalcogenide superconductors.

II. EXPERIMENT

The sample was prepared by the solid reaction method as described in Ref. 1. The precursor Li_3P was presynthesized by sintering the mixture of Li lumps and P powder at 600 °C for 10 h. Li_3P, Fe, and P powders were mixed according to the stoichiometric LiFeP. The powder mixture was pressed into a pellet in an alumina tube and in turn sealed in a Nb tube under 1 atm of Ar gas before it was sealed in an evacuated quartz tube. The evacuated quartz tube was heated to 700 °C for 20 h. The thus obtained LiFeP polycrystals were pressed into a dense pellet with good internal thermal conductivitiy by using a high pressure pellet press. Specific heat was measured on a pressed pellet of mass 19.87 mg using established techniques.[15] The pellet was attached to the sample platform with GE7031 varnish to assure excellent thermal contact. No sign of a second time constant indicative of poor thermal contact was present down to 0.4 K. The dc magnetic susceptibility of the sample was measured before and after application of the varnish to check if the sample degraded upon contact with it. No change in the superconducting transition, either in T_c^{onset} or in the width of the transition, was observed.

III. RESULTS AND DISCUSSION

The low temperature specific heat is shown in Fig. 1. The data present several aspects for discussion. First, the extrapolation of the normal state specific heat from above the superconducting transition temperature T_c obeys the requirement for a second order phase transition that the measured superconducting state entropy (=integral from $T = 0$ to T_c of $C^{\text{measured}}/T\,dT$) is equal to the extrapolated normal state entropy (=integral from $T = 0$ to T_c of $C^{\text{extrap}}/T\,dT$) over the same temperature range. This results in a specific heat γ

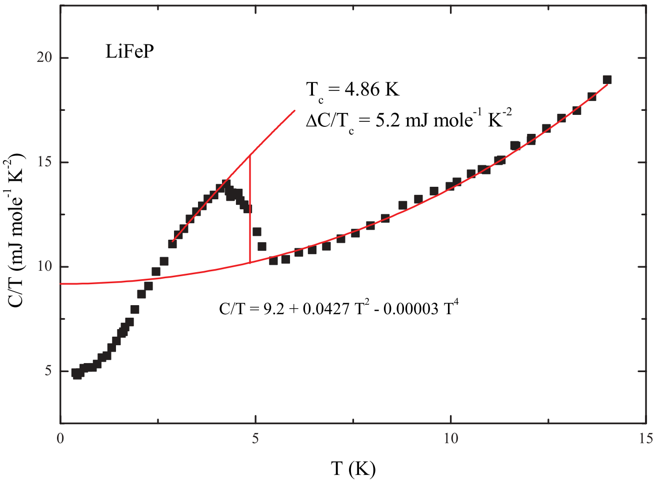

FIG. 1. (Color online) Low temperature specific heat divided by temperature C/T vs temperature of polycrystalline LiFeP between 0.4 and 14 K. The extrapolation of the normal state data that agrees with entropy balance $[S_{\mathrm{normal}}(T_c) = S_{\mathrm{sc}}(T_c)]$ results in a γ value of 9.2 mJ/mol K^2, while the idealized sharp ΔC jump at the superconducting transition gives $\Delta C/T_c = 5.2$ mJ/mol K^2. Various means of fitting the data below 3.5 K result in a residual γ, γ_r, of 4.9 $\pm$ 0.2 mJ/mol K^2 with no apparent evidence for an upturn in C/T as $T \rightarrow 0$. Although it could be argued that this residual γ is consistent with the existence of the nodes determined from the penetration depth measurements (Ref. 6), as has been pointed out in Ref. 8, line nodes in the well known $\mathrm{YBa_2Cu_3O_{7-x}}$ (YBCO) nodal superconductor result in a γ_r of at most 6% of the normal state γ. The large γ_r reported here for LiFeP is therefore not primarily due to nodal behavior.

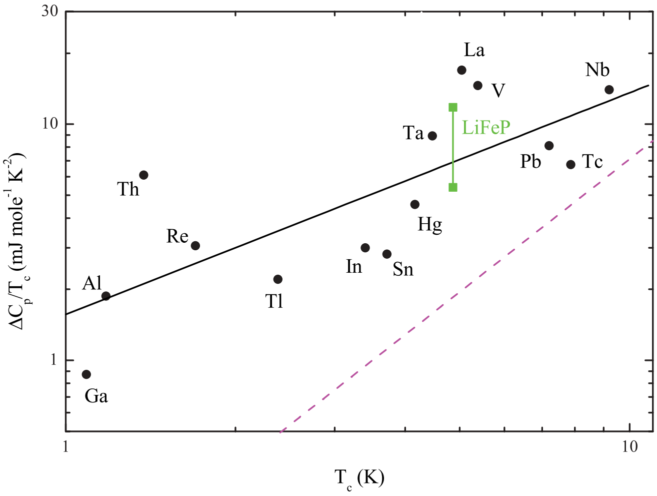

FIG. 2. (Color online) A plot of log $\Delta C/T_c$ vs log T_c after Ref. 11, with the dashed line corresponding to the BNC trend for the iron-based superconductors and the solid black line (notice the factor of 2 lower slope) representing the trend for all the elemental superconductors with $T_c > 1$ K. The solid green squares connected with a vertical line are the range of $\Delta C/T_c$ values derived from the specific heat data in Fig. 1. Even for the unscaled value of $\Delta C/T_c = 5.2$ mJ/mol K^2 at $T_c^{\mathrm{mid}} = 4.86$ K, this value is a factor of 3 larger than the BNC dashed line fit.

(linear temperature term coefficient, or $\gamma \equiv C/T$ as $T \rightarrow 0$) of 9.2 mJ/mol K^2. This is significantly smaller than the value of approximately 16 mJ/mol K^2 obtained from the rather scattered data reported down to 2 K in the discovery paper.[1]

Second, the C/T data in Fig. 1 down to 0.4 K show a significant finite intercept, or "residual" γ (γ_r) in the superconducting state, of approximately 5 mJ/mol K^2. There does not seem to be an upturn due to an impurity phase, as has been found[16,17] in numerous IBSs—usually starting above 1 K. Instead, this finite γ_r may be evidence[18] for defect-caused states in the superconducting gap or nanoscale inhomogeneity. In any case, this finite γ_r in the superconducting state implies that only a fraction of the sample contributes to the discontinuity in the specific heat ΔC at the superconducting transition.

Lastly, this discussion leads to considering the ΔC value shown in Fig. 1 for an idealized transition of $\Delta C/T_c = 5.2$ mJ/mol K^2. Ideally,[18] this $\Delta C/T_c$ value should be scaled to the amount of superconducting sample, i.e., increased by the fraction $\gamma_{\mathrm{normal}}(\gamma_{\mathrm{normal}} - \gamma_r)$. Thus, 5.2 mJ/mol K^2 might better be scaled to 11.4 mJ/mol K^2 for a 100% superconducting sample. These two possible values for $\Delta C/T_c$ for LiFeP are shown in Fig. 2, which shows the low T_c end of the most recent update[11] of the BNC plot along with values for the elemental superconductors with $T_c > 1$ K. Although the results for LiFeP of $\Delta C/T_c$ are not as far from the BNC line as that for the nodal superconductor $\mathrm{KFe_2As_2}$, certainly the range of values of 5.2–11.4 mJ/mol K^2 plotted in Fig. 2 appears to agree more with the elemental BCS superconductors than with the IBSs, where the BNC trend would suggest a γ of less than 2 mJ/mol K^2 for this T_c of 4.86 K. In addition, the value of $\Delta C/\gamma T_c$ is—based on the discussion of the limits on $\Delta C/T_c$ based on either the raw data ($\Delta C/T_c = 5.2$ mJ/mol K^2) or on the value scaled for the 100% superconducting sample ($\Delta C/T_c = 11.4$ mJ/mol K^2)—somewhere between 0.6 and 1.3. This is certainly more consistent with weak-coupled BCS behavior, where $\Delta C/\gamma T_c = 1.43$, than IBS. For example, the recent result[18] for optimally doped, annealed $\mathrm{Ba(Fe_{0.92}Co_{0.08})_2As_2}$ for $\Delta C/\gamma T_c$ is over 3.

IV. SUMMARY AND CONCLUSIONS

The specific heat of an improved quality sample of polycrystalline LiFeP has been measured. The normal state γ value is 9.2 mJ/mol K^2, a factor of 2 smaller than that recently reported[17,19,20] for LiFeAs. The specific heat discontinuity at T_c, ΔC, is significantly larger than would correspond to the trend established for the IBSs by Bud'ko, Ni, and Canfield.[10] This is the second example of an IBS with nodes[13] (the first being $\mathrm{KFe_2As_2}$, also a low T_c, $\approx$4 K, material) where $\Delta C/T_c$ is much too large for its T_c compared to the other IBS. In the present case of LiFeP, $\Delta C/T_c$ as well as $\Delta C/\gamma T_c$ are instead similar to values that are characteristic of the BCS elemental superconductors. Although it is theoretically possible for an electron-phonon coupled superconductor to have nodes, experimental examples are still missing. Thus, the more likely explanation for the disagreement of the $\Delta C/T_c$ for LiFeP (and $\mathrm{KFe_2As_2}$) with the trend established[10] for the IBS is that there exist subtypes of superconducting behaviors in these presumably unconventional superconductors. It is worth noting that $\Delta C/T_c$ for $\mathrm{BaFe_2(As_{0.7}P_{0.3})_2}$, $T_c \approx 30$ K, where nodes have also been shown via penetration depth measurements[21] as well as by other techniques,[8] agrees[11] with the BNC trend.[10]

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