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BNL-111655-2015-JA

^{119}Sn-NMR investigations on superconducting $Ca_3Ir_4Sn_{13}$: Evidence for multigap superconductivity

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(Dated: August 20, 2015)

We report bulk superconductivity (SC) in $Ca_3Ir_4Sn_{13}$ by means of ^{119}Sn nuclear magnetic resonance (NMR) experiments. Two classical signatures of BCS superconductivity in spin-lattice relaxation rate $(1/T_1)$, namely the Hebel-Slichter coherence peak just below the T_c, and the exponential decay in the superconducting phase, are evident. The noticeable decrease of ^{119}Sn Knight shift below T_c indicates spin-singlet superconductivity. The temperature dependence of the spin-lattice relaxation rate $^{119}(1/T_1)$ is convincingly described by the multigap isotropic superconducting gap. NMR experiments do not witness any sign of enhanced spin fluctuations.

PACS numbers:

I. INTRODUCTION

The interplay between superconductivity (SC), charge, and spin (magnetic) fluctuations is the central topic of research in the field of unconventional SC.[1–6] $Ca_3Ir_4Sn_{13}$ is a member of the material class of superconducting and/or magnetic ternary intermetallic compounds.[7] This compound was first synthesized more than 30 years ago. However, it received very recently considerable attention in the condensed matter physics community because of its interesting physical properties.[8]

In early studies superconducting transition at $T_c = 7$ K, and quasi-skutterudite crystal structure were reported. More recent thermodynamic and transport measurements indicate an anomaly at $T^* = 38$ K, well above the superconducting transition.[9] At the beginning Yang *et al.* proposed that this anomaly is the result of ferromagnetic spin fluctuations which are coupled to SC.[9] Nevertheless μSR experiments do not find any evidence of enhanced spin fluctuations.[13–15] In addition Wang *et al.* attributed that the anomaly is due to a significant Fermi surface reconstruction, and the opening of a charge density wave gap at the super-lattice transition.[10,11] While they classified $Ca_3Ir_4Sn_{13}$ as a weakly correlated nodeless superconductor, recent μSR investigations reveal that the electron-phonon pairing interaction is in the strong-coupling limit. Furthermore μSR and macroscopic measurements may indicate the presence of multiple isotropic gaps with different magnitudes.[12–14] However, so far the true nature of the superconducting gap, and the presence or absence of the spin fluctuations in $Ca_3Ir_4Sn_{13}$ are not completely understood.

In order to investigate the symmetry of the superconducting order parameter, and to prove/disprove the presence of spin (magnetic) fluctuations, and its possible impact on SC, we have carried out NMR experiments on $Ca_3Ir_4Sn_{13}$. Here we report ^{119}Sn NMR results, and discuss the symmetry of the superconducting order parameter together with the normal state properties. The NMR studies, in particular the spin-lattice relaxation rate $^{119}(1/T_1)$, indicate that $Ca_3Ir_4Sn_{13}$ is a BCS superconductor. The temperature dependence of the $^{119}(1/T_1)$ can be described by the multiple isotropic gaps. This multigap fit gives the gap values of $\frac{2\Delta_1(0)}{k_B T_c} = 7$ and $\frac{2\Delta_1(0)}{k_B T_c} = 1.5$, respectively. So far NMR experiments do not find any evidence of enhanced spin fluctuations. These results are in good agreement with the reported μSR studies.[13,15]

II. EXPERIMENTAL DETAILS

Single crystals of $Ca_3Ir_4Sn_{13}$ were grown and characterized as described elsewhere.[10] The NMR measurements were carried out using a conventional pulsed NMR technique on ^{119}Sn (nuclear spin $I = 1/2$) nuclei in the temperature range $1.5\,\mathrm{K} \leq T \leq 60\,\mathrm{K}$ at a frequency of 33 MHz in polycrystalline sample. For this purpose we have crushed the single crystal into powder, and mixed them in paraffin. The field sweep NMR spectra were obtained by integrating the spin-echo in the time domain, and plotting the resulting intensity as a function of the field. The spin lattice relaxation rate $(1/T_1)$ experiments were performed at a frequency of 33 MHz following the standard saturation recovery method.

III. RESULTS AND DISCUSSION

A. Sn NMR Spectra and Shift

Sn-field sweep NMR spectra are shown in Fig. 1 collected at a temperature of 10 K. Two Sn isotopes namely, ^{119}Sn and ^{117}Sn are clearly resolved. Here on we shall

only focus on the ^{119}Sn NMR investigations. Figure 2 shows the temperature dependence of the ^{119}Sn Fourier transformed NMR spectra as indicated. Individual spectrum represents a single isotropic line as expected for $I = 1/2$ nuclei in cubic crystal structure. The full width of half maximum (FWHM) is found to be 55 kHz indicating very good sample quality. While lowering the

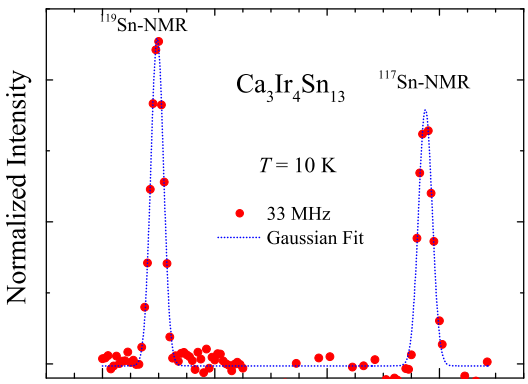

FIG. 1: $^{117/119}$Sn NMR field sweep spectrum collected at the temperature $T = 10$ K, and at the frequency of 33 MHz. The dotted lines indicate a multipeak Gaussian fit.

temperature the shape of the spectra does not change significantly, however they are shifted towards the low frequency side. The Knight shift was determined straightforwardly from the peak of the spectra. The estimated Knight shift ($^{119}K(\%)$) as a function of temperature is plotted in Fig. 3 revealing a significant drop at T_c. The NMR shift gives the information of the local susceptibility. For a spin singlet superconductor it decreases in the superconducting state. In the normal state the Knight shift is constant without any anomaly around 38 K (Fig. 3) suggesting simple metallic state of $Ca_3Ir_4Sn_{13}$. A small change is observed around 20 K (Fig. 3), however, this is not really reproduced at low-field (1 T) ^{119}Sn Knight shift measurements. This rules out the possibility of an intrinsic nature of the small change at 20 K. The ^{119}Sn Knight shift decreases in the superconducting state below 4.5 K. Even though no orbital contribution has been subtracted, the significant decrease of the Knight shift in the superconducting state indicates that $Ca_3Ir_4Sn_{13}$ is a spin-singlet superconductor.

B. ^{119}Sn NMR spin-lattice relaxation rate $^{119}(1/T_1)$

To investigate the symmetry of the superconducting order parameter, we have carried out NMR spin-lattice relaxation rate $^{119}(1/T_1)$ experiments. Spin-lattice recovery data are described by the following equation in the whole temperature range,

$$1 - \frac{M(t)}{M(\infty)} = Ae^{-t/T_1}, \qquad (1)$$

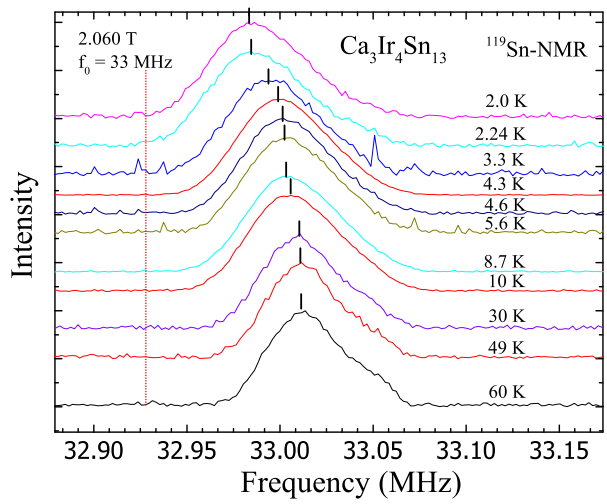

FIG. 2: Temperature dependence of the ^{119}Sn spectra. The vertical dotted line indicates the diamagnetic reference position.

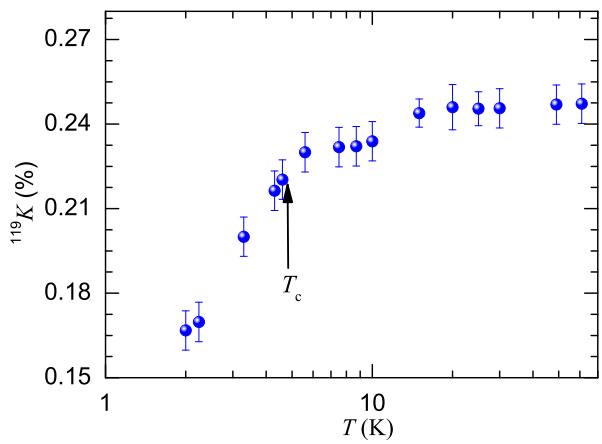

FIG. 3: Temperature dependence of the Knight shift $^{119}K(\%)$ measured at 33 MHz.

where $M(t)$ is the nuclear magnetization at a time t after the saturation pulse, and $M(\infty)$ is the equilibrium magnetization. The recovery curves are well described by the single T_1 component. This indicates that the $Ca_3Ir_4Sn_{13}$ is a very homogeneous system. In the inset of the Fig. 4 two recovery curves in the superconducting state are shown. The temperature dependence of $^{119}(1/T_1)$ is presented in Fig. 4. In the temperature range 4.5 - 60 K, $^{119}(1/T_1)$ follows a linear relation with temperature indicating the validity of the Korringa law, and implying a simple metallic state for $Ca_3Ir_4Sn_{13}$. However with lowering the temperature, just below $T = 4.5$ K, $^{119}(1/T_1)$ displays a Hebel-Slichter coherence peak, and followed by this $^{119}(1/T_1)$ sharply decreases with two different slopes. To model the superconducting ordered state we use two

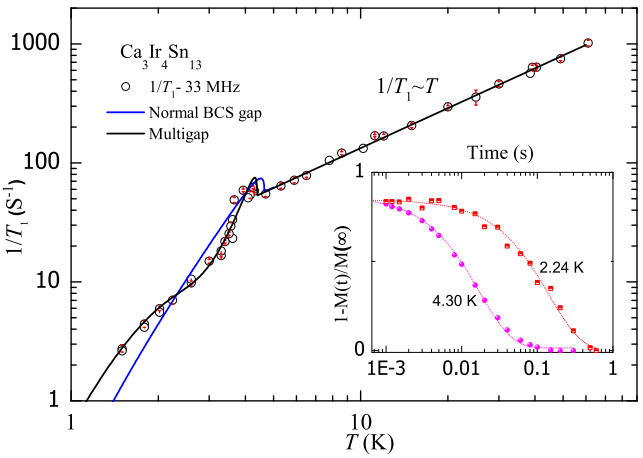

FIG. 4: (main panel)^{119}Sn spin-lattice relaxation rate $^{119}(1/T_1)$ vs T plot at frequency 33 MHz, and magnetic field 2.06 T for $Ca_3Ir_4Sn_{13}$. Lines represent different theoretical model as described in the text. Inset shows the recovery curves for the spin lattice relaxation rate $^{119}(1/T_1)$ measurements.

different fitting model. The first one represents a simple s-wave symmetry with a phenomenological distribution of gaps as described in Ref.[16], and can be interpreted as an anisotropy of the order parameter. The distribution is set to be a rectangular function in the interval $[\Delta_0(1-\delta/2), \Delta_0(1+\delta/2)]$. The anisotropy broadens the peak in the density of states. Because this model deviates significantly from the data in Fig. 4, we also tried a multigap s-wave model with two gaps Δ_1 and Δ_2.[12,13] The temperature dependence of the gap is calculated by solving the coupled gap equations as suggested by Suhl *et al.*[17] Then the relaxation rate $1/T_1$ can be evaluated with the integral

$$\frac{T_{1\mathrm{N}}}{T_{1\mathrm{S}}} = \frac{2}{k_\mathrm{B}T}\int_0^\infty \sum_{n=1,2} c_n \left\{N_\mathrm{s}^n(E)^2 + M_\mathrm{s}^n(E)^2\right\} f(E)\,(1-f(E))\,dE, \qquad (2)$$

with the anomalous density of states $N_s^n(E)$ and $M_s^n(E)$ of the band with index n, the relative weight of the density of states c_n, and the Fermi function f. This equation implies that inter-band scattering of the electrons within the relaxation process is neglected, which is motivated by the weak inter-band scattering channels necessary for significant multigap effects. The anisotropy of the particular band is covered in the same manner as in the single gap model. In the Fig. 4 blue and black lines represent the normal BCS and multigap fits, respectively. Important parameters as obtained from the multigap fit are as follows $c_1 = 0.83$, $c_2 = 0.17$, $\frac{2\Delta_1(0)}{k_BT_c} = 7$, and $\frac{2\Delta_1(0)}{k_BT_c} = 1.5$. One of the estimated gap value is $\frac{2\Delta_1(0)}{k_BT_c} = 7$ which is much larger than the weak-coupling BCS value of $\frac{2\Delta}{k_BT_c} = 3.5$, suggesting a strong electron-phonon coupling, and being consistent with the μSR results.[13]

In the present local probe NMR investigations neither the Knight shift (static susceptibility) nor the spin-lattice relaxation rate $(1/T_1)$ (dynamic susceptibility) suggests the presence of enhanced spin fluctuations. In contrast these NMR results demonstrate the simple metallic nature of $Ca_3Ir_4Sn_{13}$.

IV. CONCLUSIONS

In conclusion ^{119}Sn NMR experiments were carried out on $Ca_3Ir_4Sn_{13}$. From the NMR point of view $Ca_3Ir_4Sn_{13}$ does not possess any significant enhanced spin fluctuations in the normal state. The temperature dependence of ^{119}Sn Knight shift displays a significant decrease below T_c, suggesting a spin-singlet SC. Two classical signatures of BCS superconductors, namely 1) the Hebel-Slichter coherence peak in $^{119}(1/T_1)$ vs. T just below T_c, and 2) an exponential decay in $^{119}(1/T_1)$, are evident. The temperature dependence of $^{119}(1/T_1)$ data in the superconducting state could be described by the multigap SC in $Ca_3Ir_4Sn_{13}$ exhibiting gap values of $\frac{2\Delta_1(0)}{k_BT_c} = 7$, and $\frac{2\Delta_1(0)}{k_BT_c} = 1.5$, respectively.

Acknowledgments

R. Sarkar is thankful to DFG for the financial support through grant No. SA 2426/1-1. Work at Brookhaven is supported by the US DOE under Contract No. DE-SC00112704.

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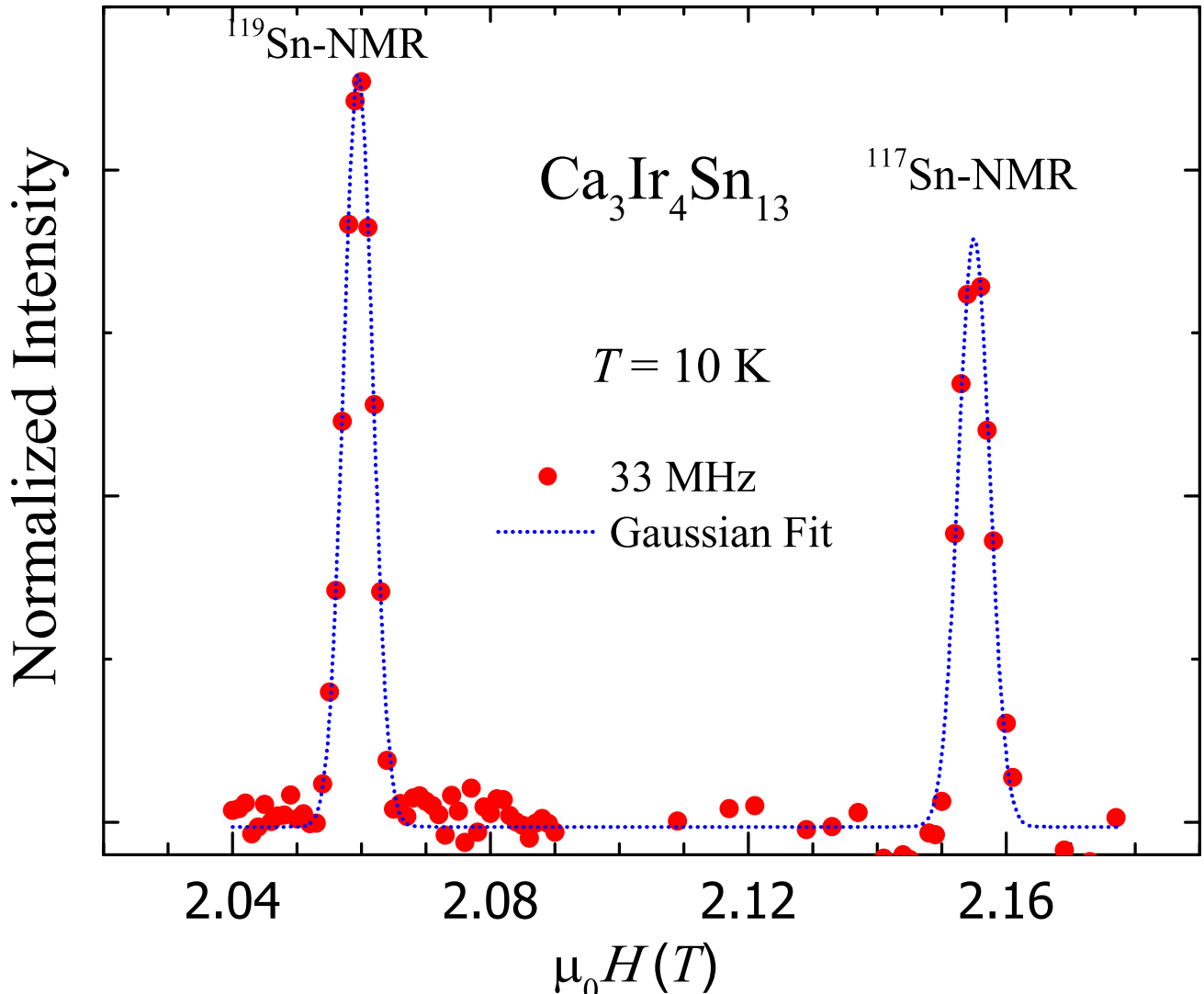
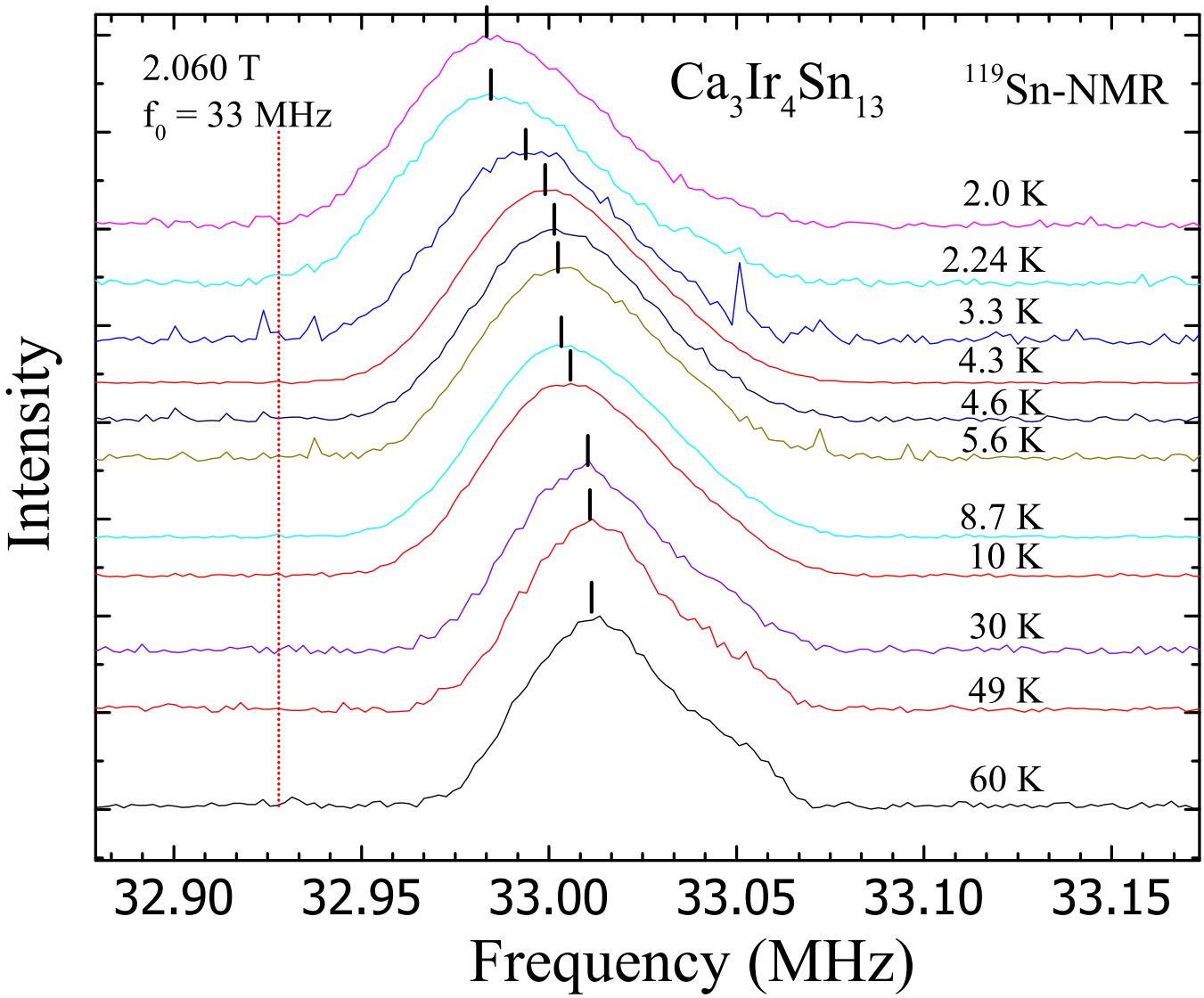
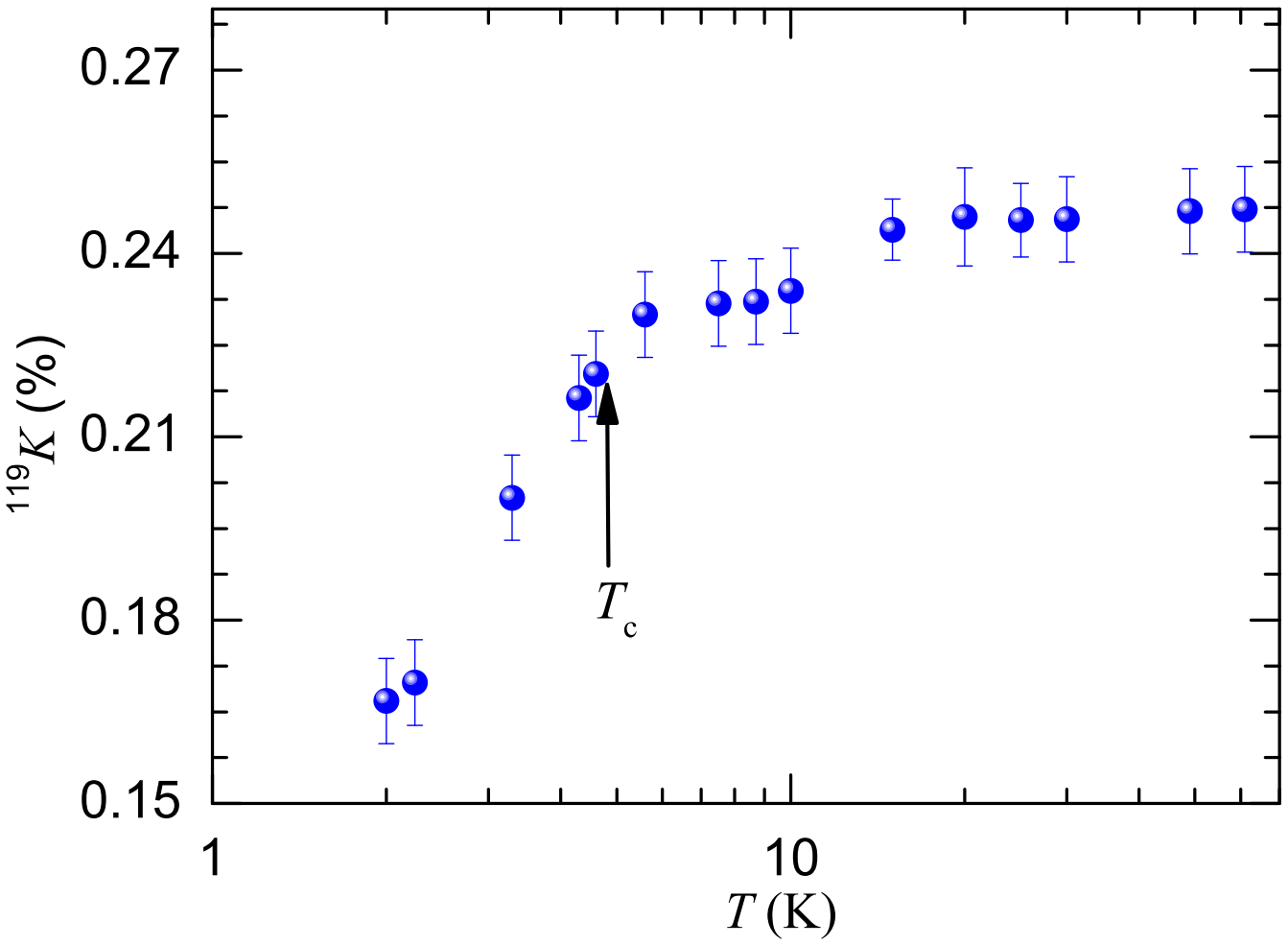
Figure


^{119}Sn-NMR
^{117}Sn-NMR
$Ca_3Ir_4Sn_{13}$
T = 10 K
33 MHz
Gaussian Fit
Normalized Intensity
2.04
2.08
2.12
2.16
$\mu_0 H (T)$

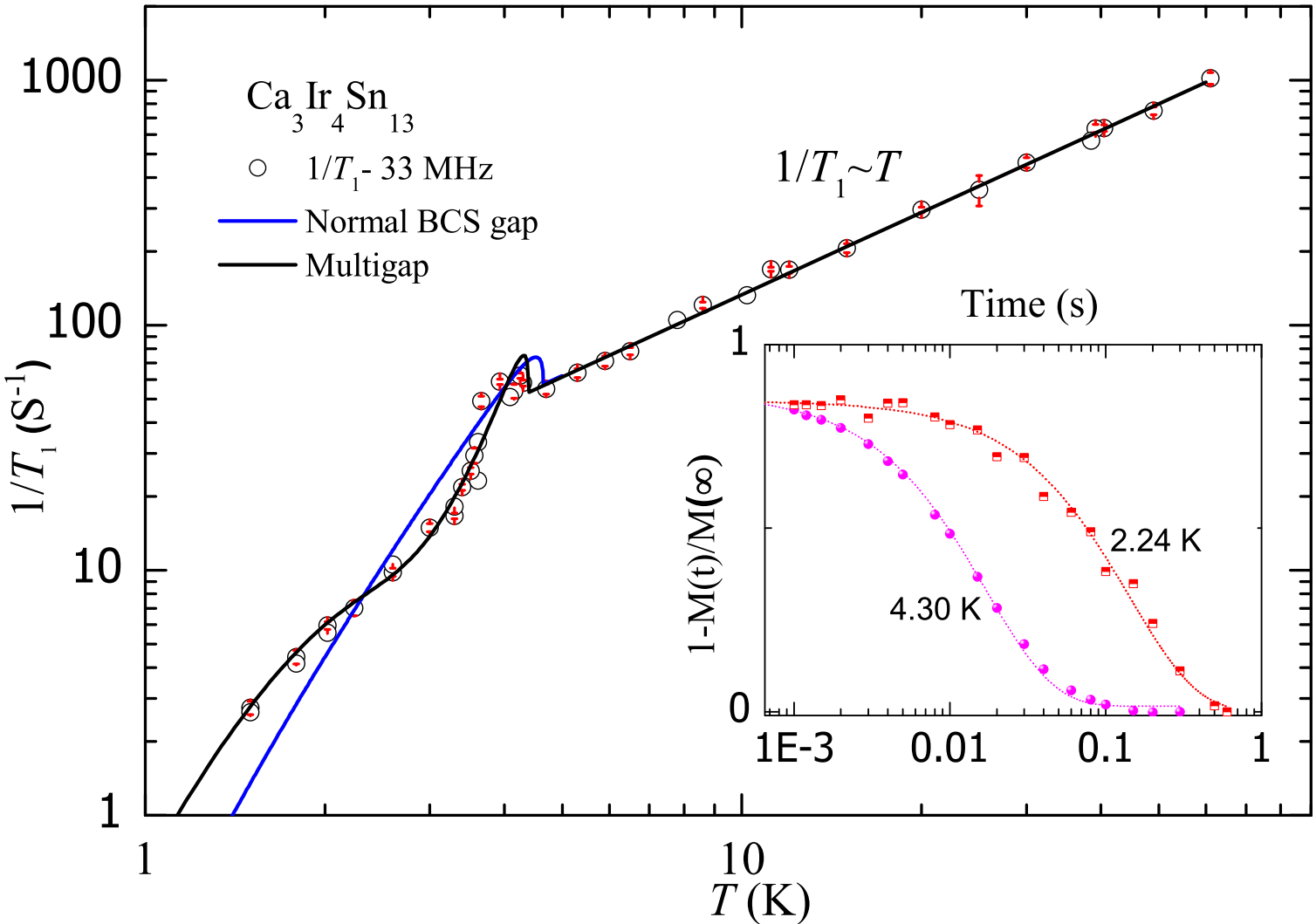
Figure


2.060 T
f0 = 33 MHz
Ca3Ir4Sn13
119Sn-NMR
2.0 K
2.24 K
3.3 K
4.3 K
4.6 K
5.6 K
8.7 K
10 K
30 K
49 K
60 K
Intensity
32.90
32.95
33.00
33.05
33.10
33.15
Frequency (MHz)

Figure



Figure


$Ca_3Ir_4Sn_{13}$
○ $1/T_1$- 33 MHz
Normal BCS gap
Multigap
$1/T_1 \sim T$
$1/T_1$ (S^{-1})
T (K)
1000
100
10
1
1
10
Time (s)
1-M(t)/M(∞)
2.24 K
4.30 K
1
0
1E-3
0.01
0.1
1