Probing the superconducting ground state near the charge density wave phase transition in $Cu_{0.06}TiSe_2$

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We have investigated the nature of the superconducting ground state of $Cu_{0.06}TiSe_2$ using muon spin rotation and muon spin relaxation measurements. The temperature dependence of the magnetic penetration depth of $Cu_{0.06}TiSe_2$ is consistent with a single gap *s*-wave BCS superconductor in the clean limit. The gap energy is $\Delta(0)=0.27(1)$ meV, which corresponds to a gap to T_C ratio of $[2\Delta(0)/k_BT_C]=2.5$. The estimated magnetic penetration depth, λ, and the coherence length, ξ, are 660(10) and 15(5) nm, respectively. Furthermore, we observe an irreversibility line in the temperature dependence of the superconducting part of the muon relaxation rate, $\sigma_{sc}(T)$, indicating the presence of strong pinning in $Cu_{0.06}TiSe_2$. Interestingly, at low temperatures we have found clear evidence of the presence of low-energy spin fluctuations that coexist with superconductivity and have an Arrhenius temperature dependence.

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The discovery of the coexistence of superconductivity and a charge density wave (CDW) in Cu_xTiSe_2 has generated considerable interest both in theoretical and experimental condensed-matter physics.[1] This is because there are only a handful of materials that exhibit CDW and superconductivity.[2–7] One of the original materials to exhibit a CDW is $TiSe_2$ and has, therefore, been extensively studied. In this material, the CDW has a commensurate wave vector of $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ occurring at ~200 K and does not show an intermediate incommensurate phase.[8–10] However, upon intercalation of Cu in $TiSe_2$ the CDW transition is suppressed and a superconducting state appears with a maximum transition temperature of 4.15 K with $x\sim0.08$ (Ref. 1) (see Fig. 1). This phase diagram for Cu_xTiSe_2 is analogous to the phase diagram of the high-temperature superconductors (HTSCs), many heavy fermion superconductors (HFSCs), and the new Fe-based superconductors which show a crossover from a magnetic ground state to superconducting state with doping; for examples, see Ref. 11. The properties of the Cu_xTiSe_2 system provide a unique opportunity to study the CDW-superconductivity transition in detail through easily controllable chemical substitution. Magnetization and heat capacity measurements have been used to study the superconducting state of $Cu_{0.06}TiSe_2$.[1,12] These results have shown that $Cu_{0.06}TiSe_2$ is a type-II superconductor with a Ginzburg-Landau value, κ, of 100. The value of the Sommerfeld constant, γ, is low ≈ 4 mJ mol^{-1} K^{-2}, suggesting that $Cu_{0.06}TiSe_2$ is a conventional superconductor. This is corroborated by the value of the ratio $\Delta C/\gamma T_C=1.68$, where ΔC is the jump in the specific heat, which is close to the BCS value of 1.43. Indeed, thermal conductivity measurements, despite Cu_xTiSe_2 having a very similar phase diagram to that of HTSC and HFSC as mentioned above, have suggested that Cu_xTiSe_2 is a single gap dirty *s*-wave superconductor.[13] In order to investigate the superconducting ground state with an aim to determine the fundamental superconducting constants, namely, the magnetic penetration depth, λ, and coherence length, ξ, we have employed the transverse field muon spin rotation (TF-μSR) technique. As the muons probe the flux line lattice directly, λ can be accurately determined. In the limit of $\lambda \gg \xi$, λ is directly related to the superconducting energy gap, therefore the nature of the superconductivity itself can be investigated. Furthermore, using muon spin relaxation any magnetic fluctuations can be investigated. Zero-field muon spin relaxation (ZF-μSR) is extremely sensitive to small magnetic moments and low-energy fluctuations. Indeed, μSR can easily measure fields of 0.1 G which corresponds to a moment value of $0.01\mu_B$ meaning that ZF-μSR can reveal whether time-reversal symmetry (TRS) is broken as shown in $PrOs_4Sb_{12}$,[14] Sr_2RuO_4,[15] *B* phase of UPt_3,[16] $(U,Th)Be_{13}$,[17] and $LaNiC_2$.[18]

In this Brief Report we present the results of our μSR investigation of the superconducting parameters and magnetic fluctuations of Cu_xTiSe_2 where $x=0.06$. This is close to the CDW quantum critical point in the magnetic phase diagram. We show that $Cu_{0.06}TiSe_2$ is a conventional clean, not dirty as reported through the thermal conductivity[13] type-II superconductor with a single BCS gap, and there exists low-energy spin fluctuations in the superconducting state.

The sample was prepared by mixing stoichiometric amounts of the elemental powders together in a mortar and pestle, pressed into pellets and placed in an evacuated silica tube. The sample was then heated from room temperature to 350 °C, held for 1 h and heated to 650 °C, held for 20 h before cooling down to room temperature. The pellets were reground and pressed into pellets again, resealed in a silica tube under vacuum and annealed at 650 °C for 50 h. The sample was heated and cooled at a rate of 1 °C/min for all operations. Once prepared, the sample was characterized by x-ray diffraction, using a STOE Stadi P transmission diffractometer (Cu $K_{\alpha1}$, $\lambda=1.5406$ Å) and heat capacity, using a Quantum design PPMS with an ^{3}He insert. A x-ray diffraction study shows that the sample is single phase and that the lattice parameters are in close agreement with the published literature.[1] The heat-capacity measurements show a superconducting transition at 2.5 K again in close agreement with the published literature.[1] The muon spin relaxation and rotation (μSR) experiments were conducted on the MuSR spectrometer at the ISIS facility, U.K., in both longitudinal and transverse geometry. The sample was mounted onto an Ag

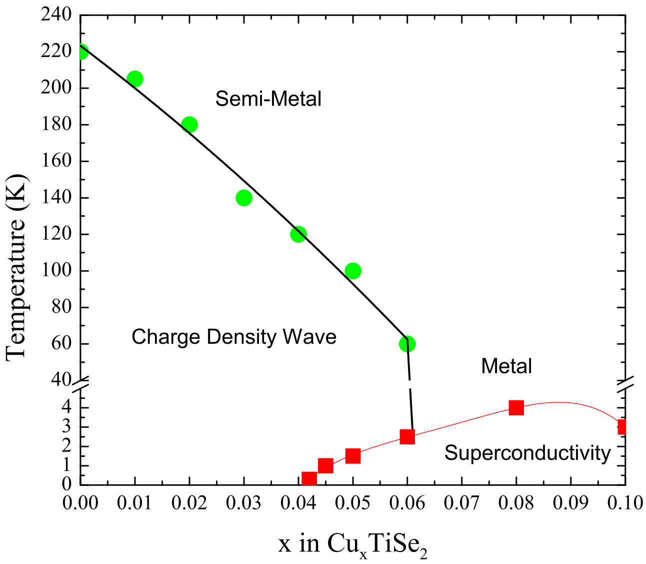

FIG. 1. (Color online) The phase diagram of Cu_xTiSe_2 taken from Ref. 1. The line through the points is a guide to the eyes.

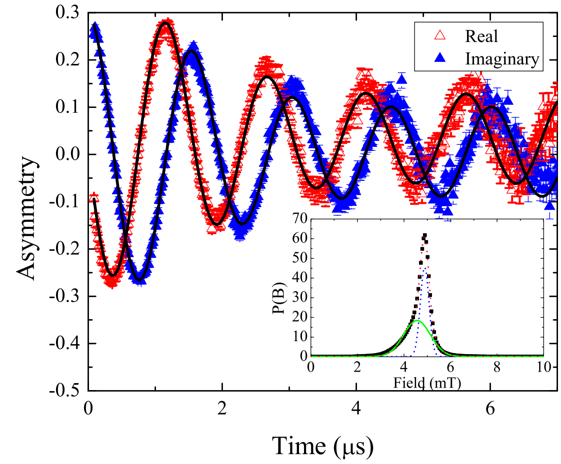

FIG. 2. (Color online) A typical muon asymmetry spectra in $Cu_{0.06}TiSe_2$ taken in a transverse field of 5 mT at 0.1 K. The line is a fit to the data using Eq. (1). The inset is the field distribution as determined using a Maximum Entropy technique. The points are the results from the maximum entropy and the lines are the Gaussian line shapes. This shows that the data can be well described using two Gaussian field profiles.

plate and a small amount of diluted GE varnish was added to aid thermal contact. The sample and mount were then inserted into a dilution fridge with a temperature range of 50 mK to 4 K. Any Ag exposed to the muon beam would give a flat time independent background or a nondecaying sine wave for longitudinal or transverse geometry measurement respectively. The amount of GE varnish was so small such it did not contribute to a μSR signal.

The TF-μSR experiment was conducted with applied fields between 5 and 60 mT, which ensured that the sample was in the mixed state. Each field was either applied above the superconducting transition and the sample was then cooled to base temperature [field cooled (FC)] or the sample was first cooled to base temperature and then the field was applied [zero field cooled (ZFC)]. The MuSR spectrometer comprises 64 detectors. In software, each detector is normalized for the muon decay and reduced into a real and imaginary component. The resulting two spectra were simultaneously fitted with a sinusoidal oscillating function with the relaxation Gaussian component,

$$G_{xx}(t) = \sum_{i=1}^{2} A_i \exp\left(-\frac{\sigma_i^2 t^2}{2}\right)\cos(2\pi\nu_i t + \varphi_{real,imag}) \quad (1)$$

where the ith index denotes the contribution from the superconducting and background phases, respectively, A_i is the initial asymmetry, σ_i is the Gaussian relaxation rate, ν_i is the muon spin precessional frequency, and φ is the phase offset. Figure 2 shows typical spectra for $Cu_{0.06}TiSe_2$ with an applied field of 5 mT at 0.1 K after being FC. The inset in Fig. 2 is the field distribution as determined using a maximum entropy technique.[19] This shows that the data can be well described using two Gaussian field profiles. Such an asymmetric line shape could be the result of a highly anisotropic superconductor. However, a simpler explanation, consistent with the size of the sample can be given. The sharper peak centered at the applied field is the Ag contribution and the broader peak shifted from the applied field is the contribution associated with the flux line lattice. It is likely that the Ag peak has probably been broadened due to the inhomogeneous field from flux exclusion in the superconductor.

The σ_1 value measured while in the superconducting state, σ_{sc} is a convolution of both the flux line lattice and the nuclear moments. The contribution from the nuclear moments has been determined at a temperature just above T_C and has been assumed to be constant. This assumption is justified later by the longitudinal zero field μSR experiment. Figure 3 shows the field dependence of σ_{sc} at 0.1 K. Each data point was collected after field cooling the sample from above T_C. As the field is increased σ_{sc} decreases, this is caused by the overlapping of the flux lines. The data can be well described using the modified London model,

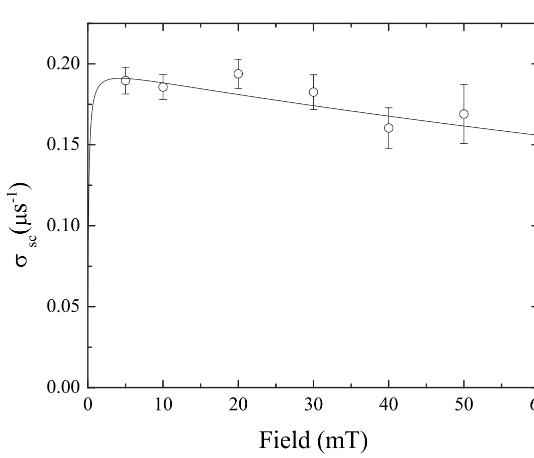

FIG. 3. The field dependence of σ_{sc} at 0.1 K. The line is a fit to the data using the modified London model (see text [Eq. (2)]). The results of the fit give $\lambda = 660(10)$ nm and $\xi = 15(5)$ nm.

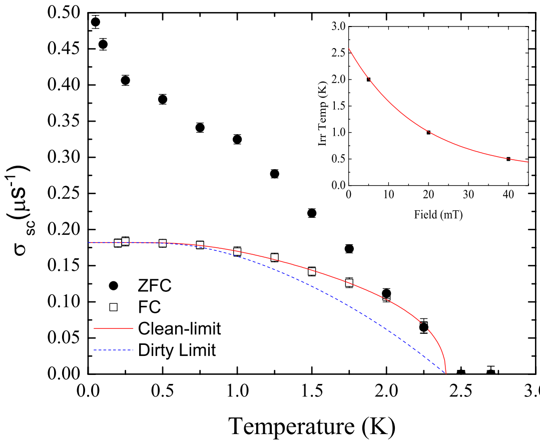

FIG. 4. (Color online) The temperature dependence of σ_{sc} in an applied field of 5 mT. The filled symbols show the data after cooling the sample in zero field and applying 5 mT while at base temperature. The hollow symbols show the data after cooling in 5 mT. The lines are fits to the data using the dirty limit and clean limit. The inset shows the field dependence of the irreversibility temperature where the line is a guide to the eyes.

$$\sqrt{\overline{\Delta B^2}} = 2\sigma_{sc}^2/\gamma_\mu^2 = B_0 \sqrt{\sum_{h,k} \frac{\exp(-\xi^2 q_{h,k}^2)}{\left(1+\frac{q_{h,k}^2\lambda^2}{1-b}\right)^2}}, \tag{2}$$

where B_0 is the mean internal field, $b=B_0/B_{C2}$, and the sum is over all nonzero reciprocal-lattice vectors, $q_{h,k}$ of the hexagonal flux line lattice. The results of the fit gives $\lambda=660(10)$ nm and $\xi_0=15(5)$ nm and thus yields a Ginzburg-Landau parameter, $\kappa=\lambda/\xi=44$ indicating that $Cu_{0.06}TiSe_2$ is an extreme type-II superconductor. Using these results together with the heat capacity then we find that n_s and m^*/m_e of 4.8×10^{26} m^{-3} and 7.5, respectively. For further details on these calculations see Ref. 20.

Figure 4 shows the temperature dependence of σ_{sc} for both ZFC and FC. As is clearly seen σ_{sc} for the ZFC and FC separates at 2.0 K. A similar effect [see Fig. 4 (inset)] is seen if the field is increased to 20 and 40 mT where the separation temperature is 1.0 and 0.5 K. This suggests that there is an irreversibility line in $Cu_{0.06}TiSe_2$ indicating the presence of strong pinning in $Cu_{0.06}TiSe_2$. A similar irreversibility has also been observed in the μSR depolarization rate of Mo_3Sb_7 (T_C=2.2 K), which reveals two BCS-type superconducting gaps.[21]

Now we present a detailed analysis of the FC σ_{sc} and, as we can be sure of a stable flux line lattice, the data have been analyzed within the dirty- and the clean-limit approaches. In the dirty-limit theory $1/\lambda^2(T)$ has the form[22]

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = \frac{\sigma(T)}{\sigma(0)} = \frac{\Delta(T)}{\Delta(0)}\tanh\left[\frac{\Delta(T)}{2k_BT}\right], \tag{3}$$

whereas in the clean limit it has the form

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = \frac{\sigma(T)}{\sigma(0)} = 1 + 2\int_{\Delta(T)}^{\infty}\left(\frac{\partial f}{\partial E}\right)\frac{E}{\sqrt{E^2-\Delta(T)^2}}dE, \tag{4}$$

where $f=[1+\exp(E/k_BT)]^{-1}$ which is the Fermi function. For both models, the temperature dependence of the gap was approximated by[23]

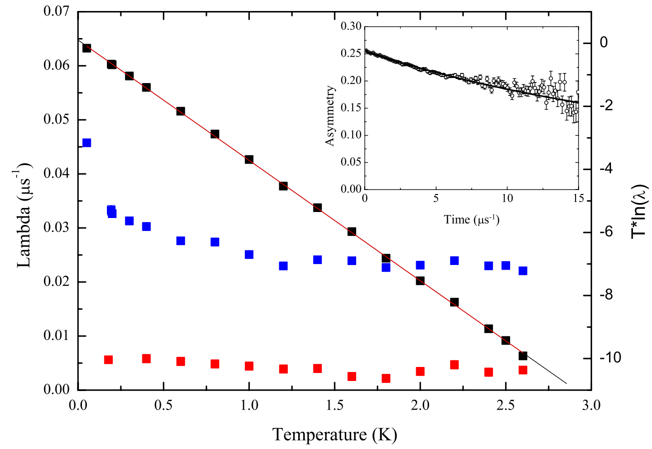

FIG. 5. (Color online) The temperature dependence of Λ in both zero field (△) and a longitudinal field of 5 mT (▽). The solid squares are the Arrhenius plot of the zero field Λ and the line is a fit to the data. The inset shows the data and fit at 50 mK in zero field.

$$\Delta(T) = \Delta(0)\tanh\{1.82[1.018(T_c/T-1)]^{0.51}\}. \tag{5}$$

As can be seen from Fig. 4 the FC data are best described by the clean-limit theory and not the dirty limit, (as seen in the thermal conductivity[13]), which does not have the correct temperature dependence. The results of the fit to the clean limit give a $\Delta(0)=0.27(1)$ meV which corresponds to a gap to T_C ratio of $[2\Delta(0)/k_BT_C]=2.5$, which is significantly less than the predicted BCS value of 3.5. This implies that $Cu_{0.06}TiSe_2$ is a weakly coupled superconductor. It is possible for superconductors, in particular HTSC,[24,25] with impurities to appear s-wave but actually have a different symmetry, however, we do not have any detectable impurities in our sample and therefore conclude that our data are consistent with $Cu_{0.06}TiSe_2$ being a weakly coupled s-wave superconductor in the clean limit.

Now we discuss the results of our zero field μSR measurements of $Cu_{0.06}TiSe_2$. The muon spin relaxation for a metallic system that does not exhibit magnetic order will only be sensitive to the local fields associated with the nuclear spins. Normally, on the time scale of the muon, these nuclear spins are static and randomly orientated. Therefore, the μSR spectra can be described by the Kubo-Toyabe function[26]

$$G_z^{KT}(t) = \left[\frac{1}{3} + \frac{2}{3}(1-\zeta^2t^2)\exp\left(-\frac{\zeta^2t^2}{2}\right)\right], \tag{6}$$

where ζ/γ_μ is the local-field distribution width and $\gamma_\mu/2\pi=135.5$ MHz/T is the muon gyromagnetic ratio. In the magnetically ordered state, the muon polarization will precess with a frequency which is directly proportional to the ordered moment. However, if the internal field is small, or if there is a broad distribution of local fields then an increase in the relaxation rate should be observed and could be described by an exponential decay. The spectrum from $Cu_{0.06}TiSe_2$ are best described [see Fig. 5 (inset)] by

$$G_z(t) = A_0 G_z^{KT}(t)\exp(-\Lambda t) + A_{bckgrd}, \quad (7)$$

where Λ is the relaxation rate associated with the dynamic electronic spin fluctuations. The parameters from the fit show that ζ is temperature independent ($0.03\ \mu s^{-1}$), thus indicating that the muons are static in the sample. However, as can be seen in Fig. 5, Λ shows a small increase as the temperature is decreased. If a longitudinal field of 5 mT is applied, then the temperature dependence of Λ is suppressed. This behavior has often been interpreted as showing the presence of static internal fields. Interestingly, when the zero field μSR Λ is plotted in an Arrhenius form then a linear temperature dependence is observed (see Fig. 5). This indicates that in $Cu_{0.06}TiSe_2$ there is a weak fluctuating magnetic moment, with an activation energy of 0.1 K. The field at the muon site must be small and the fluctuation rate is low as this temperature dependence of Λ is decoupled in a field of 5 mT. Also, for materials that show breakdown of TRS an increase in Λ has been observed at T_C and has a temperature dependence that is similar to the order parameter. As we have not observed an order-parameter-type temperature dependence in Λ, we conclude that TRS is not broken and the observed behavior of $\Lambda(T)$ is attributed to the existence of low-energy dynamic spin fluctuations in $Cu_{0.06}TiSe_2$.

In conclusion, we have shown that $Cu_{0.06}TiSe_2$ is consistent with being a BCS superconductor with a single gap of 0.27 meV and has a penetration depth, λ, and coherence length, ξ, of 660(10) and 15(5) nm, respectively. Using these results together with heat-capacity measurements we have determined the superconducting carrier density, n_s, and effective mass, m^*/m_e, to be $4.8\times10^{26}\ m^{-3}$ and 7.5, respectively. The temperature dependence of λ is entirely consistent with a single gap s-wave BCS superconductor in the clean limit, in contrast to the dirty limit seen in the thermal conductivity.[13] The gap energy is $\Delta(0)=0.27(1)$ meV which corresponds to a gap to T_C ratio of $[2\Delta(0)/k_BT_C]=2.5$ that is less than the predicted BCS gap and therefore $Cu_{0.06}TiSe_2$ is a weakly coupled superconductor. Also, the flux line lattice shows an irreversibility and the critical temperature decreases with increasing applied field, indicating strong pinning of the flux line lattice. Moreover, at the lowest temperature there is evidence of low-energy dynamic spin fluctuations. These fluctuations have an Arrhenius temperature dependence with an activation energy of 0.1 K. The present work should spur interest, both experimentally and theoretically, in the field of CDW and superconductivity, similar to the role of quantum critical points and superconductivity in the cuprates and heavy fermions.

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