Possible evidence of a two-gap structure for the Cu$_x$TiSe$_2$ superconductor

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We report a comprehensive transverse-field μSR study of Cu$_x$TiSe$_2$. The magnetic penetration depth was found to saturate at low temperature as expected in an *s*-wave superconductor. As *x* is increased we find that the superfluid density increases and the size of the superconducting gap, calculated from the temperature dependence of the superfluid density, is approaching the BCS value. However, for low values of *x*, the gap is smaller than the weak-coupling BCS prediction suggesting that two superconducting gaps are present in the sample.

The transition-metal dichalcogenides (TMDCs) exhibit a variety of interesting physical phenomena.[1] Many of the TM-DCs have a charge-density wave (CDW) modulation in the ground state and many others show superconductivity (SC) in the ground state. There are few examples of systems having both CDW and SC, which raises interesting questions regarding the way the Fermi-surface accommodates these, apparently, competing orders. The interplay between CDW and SC is regaining attention, mainly in the context of the newly discovered pnictide high-temperature superconductors.[2]

Recently, superconductivity was discovered in Cu intercalated TiSe$_2$.[3] The addition of Cu gradually suppresses the CDW transition temperature and above 4% Cu a superconducting phase emerges. T_c increases with the Cu concentration up to 4.15 K for $x=0.08$ and decreases for higher concentrations. This compound provides an opportunity to study in detail the interplay between CDW and SC by simply changing *x*.

We report a detailed study of the SC state in Cu$_x$TiSe$_2$, using muon spin rotation (μSR). μSR allows us to measure the magnetic penetration depth, λ, as a function of the Cu doping and the temperature dependence of λ, which is intimately related to the SC gap.[4]

Pressed powder samples of Cu$_x$TiSe$_2$ with different Cu amounts, ranging from $x=0.02$ to $x=0.081$, were prepared as described in Ref. 3. Copper concentration was calculated using x-ray diffraction (XRD) and the known *c*-axis calibration.[3] XRD patterns show no signs of foreign phases.

The resistivity as a function of the temperature for all the samples is presented in Fig. 1(a). All the samples show metallic behavior at high temperatures. The $x=0.044$ sample has, in addition, a broad hump at around 100 K. This is related to the formation of the CDW in the sample. Above $x=0.044$ this broad hump cannot be observed anymore, consistent with the CDW phase ending at around 4% Cu.

A zoom in on the low-temperature part for three of the samples is shown in Fig. 1(b). In Fig. 1(c) T_c vs the Cu doping can be seen. The T_c of the $x=0.044$ sample was measured using μSR, since we cannot measure resistivity below 1.8 K. So far, the preparation of Cu$_x$TiSe$_2$ was reported by two groups;[3,5] they find very similar phase diagrams. In Ref.

3 superconductivity emerges just above $x=0.04$. Both groups report $x=0.11$ to be the solubility limit of Cu. We find that the $x=0.044$ sample is superconducting with a transition temperature of about 1.5 K; samples with lower Cu concentration are not superconducting down to 50 mK as revealed by μSR. The maximal T_c is 4.17 K, for $x\approx0.08$, similar to the maximal T_c reported previously.[3]

In Fig. 2 we show thermoelectric-power (TEP) data taken at room temperature for the samples. The results indicate an increase in the carrier density as Cu is added. The Seebeck coefficient is negative for all the samples at all temperatures as expected for negative charge carriers (electrons). This is in agreement with previous results.[3,5]

Zero-field (ZF) μSR measurements were done at the Rutherford Appleton Laboratory, using a dilution refrigerator and a flow cryostat. ZF μSR is a very sensitive local probe of magnetic field. The ZF μSR results for the $x=0.081$ sample are shown in the inset of Fig. 2. We see a very weak Gaussian relaxation for all temperatures down to 150 mK with no sign of magnetism. This suggests that probably each Cu ion contributes one electron to the sample and that the Cu ions
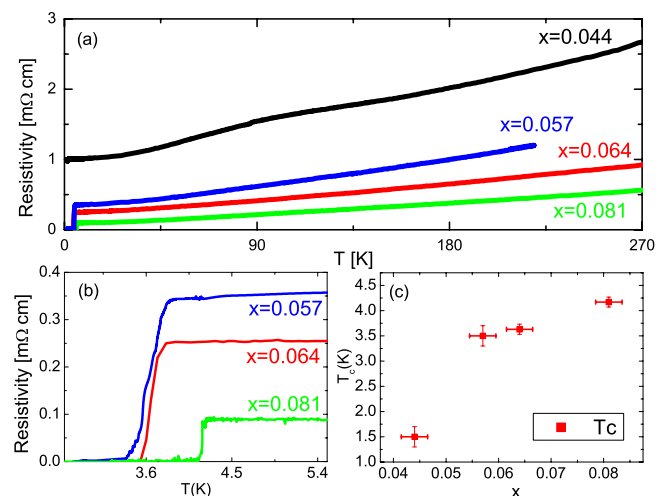

FIG. 1. (Color online) (a) The temperature dependence of the resistivity for four samples with various Cu concentration. (b) Resistivity at low temperatures. (c) T_c vs *x*.
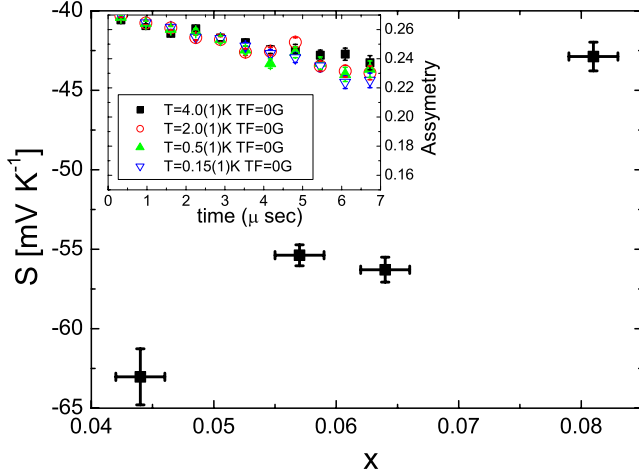
FIG. 2. (Color online) The Cu concentration dependence of the TEP at room temperature. Inset: ZF-μSR asymmetry for the $x=0.08$ sample at various temperatures.
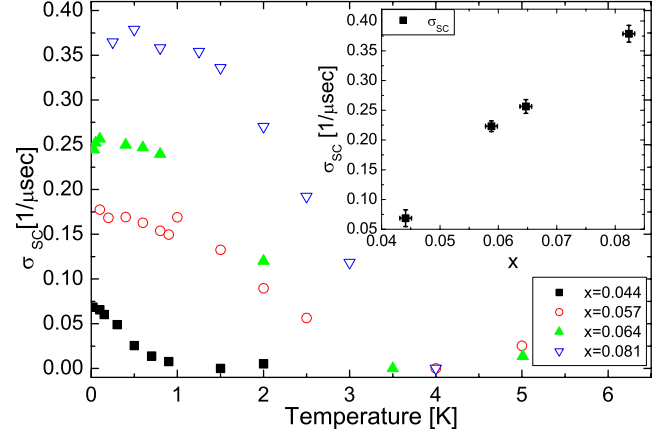

FIG. 3. (Color online) The temperature dependence of the relaxation due to the flux-lattice formation for various samples with different copper amounts. Inset: σ_{SC} at the lowest temperature vs x.

are in the Cu^{+1} configuration. Cu^{++} is magnetic and thus is ruled out.

Transverse-field (TF) μSR measurements were done at the Laboratory for Muon Spin Spectroscopy (LMU) in the Paul Scherrer Institute (PSI), using the General Purpose Surface-Muon (GPS) and the Low Temperature Facility (LTF) instruments.

For the μSR experiments the samples were mounted on silver backing plates. The samples were cooled in a magnetic field of 1000 G from above T_c down to 50 mK. The magnetic field direction was perpendicular to the muons' initial polarization direction. In addition, we measured the $x=0.081$ sample at 1.7 K in magnetic field ranging from 400 to 1500 G.

In order to analyze the TF-μSR data we used the following fitting function:

$$A(t) = A_{SC} \exp\left(-\frac{\sigma_{dip}^2 + \sigma_{SC}^2}{2} t^2\right) \cos(\gamma_\mu B_{int} t + \phi)$$

$$+ A_{Ag} \exp\left(-\frac{\sigma_{Ag}^2}{2} t^2\right) \cos(\gamma_\mu B_{ext} t). \quad (1)$$

The first term is the contribution of the sample while the second term is the contribution of the silver holder. A_{SC} and A_{Ag} are the initial asymmetries, B_{int} and B_{ext} are the internal field inside the SC and the external applied field, respectively. $\gamma_\mu = 2\pi \times 135.5342$ MHz/T is the gyromagnetic ratio of the muon and ϕ is the initial phase. There are two contributions to the relaxation of the muons in the sample, σ_{SC}, the origin of which is the inhomogeneity of the field due to the formation of the vortex lattice in the sample, and σ_{dip}, the contribution to the dipolar relaxation due to the nuclear moments. σ_{Ag} is the very slow relaxation of the muons in silver.

The data for each sample over the entire temperature range are fitted globally. The initial asymmetries, the initial phase, σ_{dip}, and the external field are temperature independent. σ_{Ag} was measured independently. This allows us to reduce the number of free parameters and increase the accu-

racy of the fitting procedure. σ_{SC} is proportional $1/\lambda^2$, which, through the London relation, is proportional to the superfluid density of the sample.[6] For anisotropic materials with an anisotropy ratio larger than five, it was shown that the μSR linewidth is proportional to $1/\lambda_{ab}^2$, where λ_{ab} is the in-plane penetration depth.[7] As Cu$_x$TiSe$_2$ is very anisotropic,[8] all our measurements are sensitive only to the in-plane part of the penetration depth.

The temperature dependence of σ_{SC} for all the samples is presented in Fig. 3. It can be seen that the relaxation increases as the temperature decreases, and that it saturates at low temperatures. In an s-wave SC in which there is a fully gapped Fermi surface, a thermally activated behavior is expected. This leads to an almost constant superfluid density at low temperatures. In contrast, nodes in the gap lead to a linear temperature dependence at low temperatures. Our results are consistent with an s-wave order parameter in Cu$_x$TiSe$_2$, in agreement with previous work.[9]

In the inset of Fig. 3, we show the low-temperature value of the muon relaxation versus the Cu content x. We find that it increases linearly when Cu is added to the system. In a BCS SC T_c is not related to the superfluid density, in general. Here, we believe that because the changes induced by the Cu on the structure of the sample are very small, it will have a negligible effect on the electron-phonon interaction and on the pairing potential. Cu increases the amount of free carriers which will raise the Fermi energy and increase the density of states at the Fermi energy and will increase T_c. Each Cu adds one mobile electron to the system and that electron contributes to the superfluid density below T_c.

In general, extracting the penetration depth from the μSR linewidth, σ is not a simple task.[10] For the case of a perfect vortex lattice in a single-gap s-wave SC, there is a very good approximation by Brandt,[11] based on a numerical solution of the Ginzburg-Landau equations. This approximation works for $\kappa \geq 5$ and for a wide range of fields, $0.25/\kappa^{1.3} \leq B/B_{c2} \leq 1$, where κ is the Ginzburg-Landau parameter
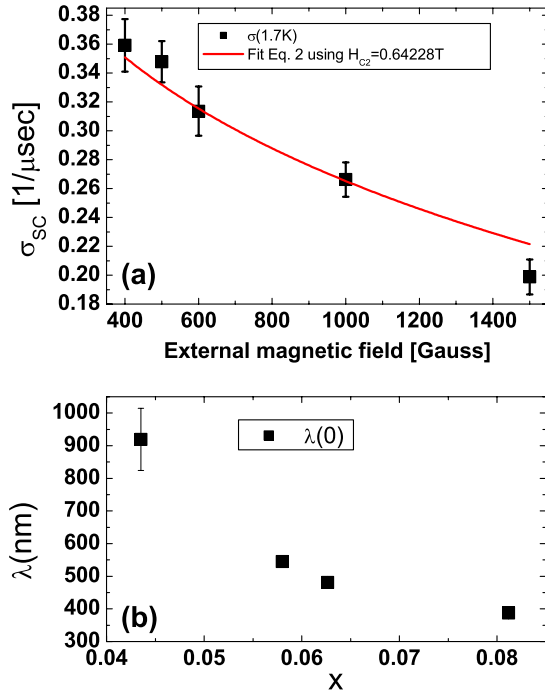
FIG. 4. (Color online) (a) The dependence of the relaxation on the external magnetic field for the $x=0.081$ sample. (b) λ vs the copper ratio (x).

$$\sigma_{SC}[\mu s^{-1}] = 4.83 \times 10^4 \times (1-b)$$
$$\times [1 + 1.21(1 - \sqrt{b})^3]\lambda^{-2}[nm], \qquad (2)$$

where $b = B/B_{c2}$.

A possible self-consistency check is to verify that the penetration depth calculated using Eq. (2) is field independent. The penetration depth measured by μSR is calculated by measuring the length scale associated with the decay of the supercurrents around the vortex core. This length scale is expected to be field independent for a single s-wave gap SC.[10] In Fig. 4(a), we show the field dependence of σ_{SC} for the $x=0.081$ sample, taken at $T=1.7$ K. The solid line is a fit to the data using Eq. (2), and $H_{c2}(T=1.7$ K$)=0.64$ T as determined from magnetoresistance data, $\rho(H)$, measured using the same sample. We get $\lambda=441\pm5$ nm, and as one can see, the agreement is reasonable, but not perfect. A possible explanation for this very weak field dependence of λ is that this sample is not a perfect single gap s-wave SC.

We use the Gorkov approximation for the temperature dependence of H_{c2} (Ref. [12]) to extrapolate $H_{c2}(T)$ to low temperatures. We obtain $H_{c2}(0)=0.85$ T for the $x=0.081$ sample; we can then estimate the zero-temperature coherence length $\xi(0)=\sqrt{\Phi_0/2\pi H_{c2}}$ to be 180 Å. The fact that λ does not depend on the field and that we get $\kappa>5$ indicates that Eq. (2) can be used for analyzing our μSR data, at least for the $x=0.081$ sample. Next, we used Eq. (2) to calculate $\lambda(T)$ using the data presented in Fig. 3 for three of our samples. It is essential to take into account the temperature dependence of H_{c2} when calculating λ. For each sample we measured H_{c2} at high temperature and used the Gorkov approximation[12] to extrapolate H_{c2} to lower temperatures.
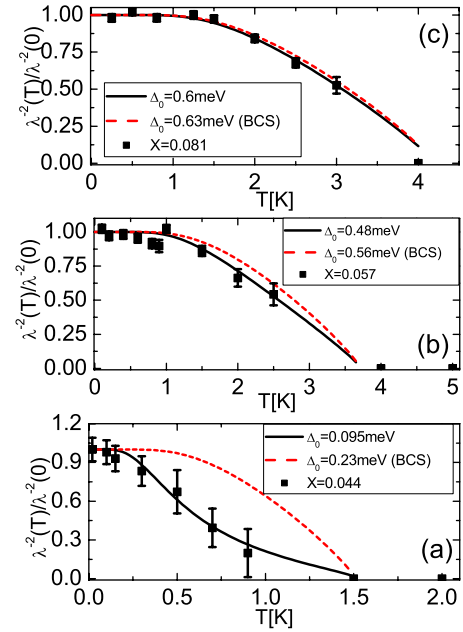

FIG. 5. (Color online) Temperature dependence of $\lambda(T)^{-2}$. The black solid lines are best fits to the data using Eq. (3). The dashed red lines are the BCS prediction. Part (a) for $x=0.044(1)$ sample, part (b) for $x=0.057(1)$ sample, and part (c) for $x=0.081(1)$ sample.

We found that H_{c2} depends rather weakly on the doping. The penetration depth at base temperature for all the samples is shown in Fig. 4(b).

The temperature dependence of λ, as already mentioned, is set by the SC gap size and momentum dependence. $\lambda(T)^{-2}$ for all the samples saturates at low temperature indicating the s-wave nature of the gap. The gap size can be extracted from the data using this relation[13]

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = 1 - 2\int_{\Delta(T)}^{\infty}\left(-\frac{\partial f}{\partial E}\right)\frac{E}{\sqrt{E^2 - [\Delta(T)]^2}}dE, \qquad (3)$$

where f is the Fermi function, $\Delta(T)$ is the temperature-dependent superconducting gap and the integration is over energy measured from the chemical potential. We used $\Delta(T)=\Delta(0)\tanh\{1.82[1.018(\frac{T_c}{T})-1]^{0.51}\}$ to describe the temperature dependence of the gap.[14] The data and the fitting curves are shown in Fig. 5. The black solid lines represent the best fit and the red dashed lines represent the expected temperature dependence for the gap size predicted by the weak-coupling BCS theory, $\Delta(0)=1.764k_BT_c$. The gap sizes we find are: $\Delta(0)=0.60(2)$ meV, $\Delta(0)=0.48(2)$ meV, and $\Delta(0)=0.095(5)$ meV for the $x=0.081$, $x=0.057$, and $x=0.044$, respectively.

We systematically get gap values that are lower than the BCS weak-coupling values, $\Delta(0)=1.764k_B$. While for the $x=0.081$ sample, $\Delta/k_BT_c=1.67\pm0.09$ is in reasonable agreement with the BCS value, for the lower T_c samples we get gap-to-T_c ratios of 1.51 ± 0.09 and 0.7 ± 0.2. The small gap values tell us that the simple single s-wave gap picture cannot explain our data. $\lambda(T)$ is controlled by thermal excitation of quasiparticles across the SC gap. In multigap systems or in systems with an anisotropic gap $\lambda(T)$ is a measure of the

smallest gap in the system. Similar results, namely, small $\Delta(0)/T_c$, have been found in MgB$_2$ (Ref. [15]) and in NbSe$_2$ (Ref. [16]) too. MgB$_2$ has two superconducting gaps as was seen, for example, using angle resolved photo emission spectroscopy (ARPES).[17] NbSe$_2$ has a multisheet Fermi surface[18] with two electronlike cylindical Fermi surface derived from the Nb band, centered around Γ and K points. In addition, there is a holelike Fermi sheet derived from the Se band around the Γ point. In this system, which is structurally similar to TiSe$_2$, two SC gaps were clearly identified on the two holelike Fermi sheets.[19]

Our case is different: we find an evolution of the $\Delta(0)/T_c$ ratio as the doping level is changed. Based on our data and the available models for analyzing μSR data, we cannot say if in Cu$_x$TiSe$_2$ there are two s-wave gaps residing on two different Fermi-surface sheets or one anisotropic s-wave gap.

Cu$_x$TiSe$_2$ ARPES data[20,21] clearly show two Fermi sheets, one holelike pocket centered around the Γ point and one electronlike pocket around the L points. The electron pocket was shown to grow with the Cu concentration while the hole pocket seems less sensitive to the amount of Cu. Combined with our result that shows that the zero-temperature superfluid density increases with the addition of Cu, this might suggest that there is a small SC gap on the hole pocket the contribution of which to the overall superfluid density is decreasing as more Cu is added to the system.

An alternative scenario is one in which there is a single anisotropic s-wave gap, probably on the large electronlike pocket, which becomes more isotropic as charge is added to the system and the CDW vanishes. Recently it was suggested, based on ARPES data in NbSe$_2$,[22] that at the CDW transition, parts of the Fermi surface which are nested are gapped out and excluded from participation in superconductivity. It is not clear to us how a situation like that would influence the temperature dependence of the penetration depth, but it might lead to an anisotropic SC gap.

In summary, we have performed TF-μSR experiments on a set of Cu$_x$TiSe$_2$ samples with different Cu concentrations. The saturation of the muon relaxation at low temperatures indicates that the Fermi surface in this system is fully gapped, but the temperature dependence of the penetration depth cannot be explained by a single isotropic s-wave gap. The data indicate that there are probably two gaps in this system the contribution to which the superfluid density changes with the Cu concentration.

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