Magnetization Properties and Vortex Phase Diagram in Cu$_x$TiSe$_2$ Single Crystals

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We have investigated the magnetization properties and flux dynamics of superconducting Cu$_x$TiSe$_2$ single crystals within wide range of copper concentrations. We find that the superconducting anisotropy is low and independent on copper concentration ($\gamma \sim 1.7$), except in the case of strongly underdoped samples ($x \leq 0.06$) that show a gradual increase in anisotropy to $\gamma \sim 1.9$. The vortex phase diagram in this material is characterized by broad region of vortex liquid phase that is unusual for such low-$T_c$ superconductor with low anisotropy. Below the irreversibility line the vortex solid state supports relatively low critical current densities as compared to the depairing current limit ($J_c/J_0 \sim 10^{-7}$). All this points out that local fluctuations in copper concentration have little effect on bulk pinning properties in this system.

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1T$^\prime$ − TiSe$_2$, a quasi-2D layered material with a trigonal symmetry, has been studied for over 30 years due to the unconventional nature of its charge density wave (CDW) state.$^{1,2}$ Recently, the superconductivity was discovered in this system below 4.15 K by intercalating copper between the van der Waals - coupled Se-Ti-Se trilayers.$^2$ Subsequently, superconductivity was also induced by palladium intercalation,$^2$ as well as by hydrostatic pressure in pristine 1T$^\prime$ − TiSe$_2$. Despite the low superconducting critical temperature $T_c$, the material has attracted significant attention due to the peculiar nature of the emergent superconductivity from a semimetallic state above $T_c$, as well as the coexistence of the superconductivity with the chiral CDW state.$^{2,3}$ The initial studies probing the superconducting phase in Cu$_x$TiSe$_2$ have yielded diverging results ranging from multiple superconducting energy gaps,$^4$ to weakly coupled superconductivity and the presence of spin fluctuations.$^5$ ARPES measurements near the superconducting transition have shown $d$ - like character of the emergent density of states near the $L$ point of the Brillouin zone at Cu concentrations $x > 0.04$ with competing nature of CDW and superconducting order parameters.$^6$ On the other hand, detailed specific heat measurements of superconducting Cu$_x$TiSe$_2$ have shown that the system behaves as a conventional s-wave superconductor with $2\Delta/k_BT_c \sim 3.7^{17,18}$ It is remarkable that for such a simple compound as TiSe$_2$, there are diverging explanations about the origin of the emergent superconductivity. The phase diagram of the Cu-doped TiSe$_2$ is similar to the one of high-temperature superconductors, pnictides, and heavy fermions, in that the superconducting phase at the specific doping interval coexists with other correlated electron states (charge or spin ordering). Considering the relatively simple lattice structure of the parent compound 1T$^\prime$ − TiSe$_2$, the system should be suitable for detailed studies of emergent superconductivity and the evolution of competing order parameters, CDW and superconductivity.

Besides the intriguing electronic properties very little is known about the Abrikosov vortex configurations in this superconductor. The static and dynamic behavior of the vortex lattice, anisotropy of the superconducting order parameters and vortex lattice phase diagram could provide further insight into the superconducting state in Cu$_x$TiSe$_2$ and the specific role that copper plays in facilitating superconductivity. In this work we study anisotropic superconducting properties of Cu$_x$TiSe$_2$ single crystals via bulk magnetization measurements for a range of copper concentrations spanning from the highly underdoped regime to the overdoped one. We establish fundamental superconducting parameters of this system such as upper critical field, coherence length, and superconducting anisotropy. We establish the vortex phase diagram of Cu$_x$TiSe$_2$ and we find that the reversibility region is unexpectedly broad for an extended range of Cu doping values. Despite the atomic disorder created by intercalated copper atoms, we observe very low bulk pinning in this material even far from $T_c$. This points to a uniform amplitude of the superconducting order parameter across the sample and vortex liquid-like behavior of the vortex lattice.

Cu$_x$TiSe$_2$ single crystals were grown by means of iodine vapor transport method in evacuated silica ampoules in a gradient furnace with the lower temperature part set to 720°C and the temperature gradient of 80°C/m. An average crystal size was on the order of few mm$^2$ with thickness of several tens of micrometers. Energy dispersive X-ray spectroscopy (EDS) was used to establish the quantitative elemental content of the crystals. The selected single crystals were analyzed for spatial uniformity of copper concentration by performing EDS analysis at several points across the sam-
The crystals with good spatial uniformity of copper and sharp superconducting transition were selected for detailed studies of magnetization properties. The magnetization measurements were conducted within few weeks from the single crystal growth as copper tends to migrate with time. Magnetization measurements were performed in a vibrating sample magnetometer of PPMS, as well as SQUID magnetometer (Quantum Design PPMS w/VSM option and MPMS, respectively).

We studied Cu$_x$TiSe$_2$ single crystals with Cu concentrations of $x = 0.058, 0.062, 0.067, 0.085,$ and $0.090$ and these cover the range from electron underdoped ($x < 0.08$) to overdoped ($x > 0.08$) regimes. At normal pressure the superconductivity in Cu$_x$TiSe$_2$ emerges at Cu doping of around $x = 0.04$, reaching the maximum critical temperature of 4.15K at $x=0.08$. For copper concentrations beyond $x = 0.08$ the $T_c$ starts to gradually decrease. The data from all samples follow the empirical irreversibility in magnetization curves observed at lower fields represents the effect of vortex pinning. From the magnetization curves we extracted the temperature dependence of the upper critical field $H_{c2}$ along the two primary axes, perpendicular and parallel to the crystal planes, as shown in Fig. 2a. The linear dependence of the $H_{c2}(T)$ near $T_c$ is evident for all copper concentrations. The values of $H_{c2}(0)$ were extracted from the data in Fig. 2a using Werthamer-Helfand-Hohenberg (WHH) formula:

$$H_{c2}(0) = -0.693 \cdot T_c \left( \frac{dH_{c2}}{dT} \right)_{T_c}$$

This step assumes that the Cu$_x$TiSe$_2$ is an s-wave BCS superconductor, which is in accordance to recent results. The data from all samples follow the empirical
However, in the highly underdoped regime we found an
ξ(0) and γΦc
Ginzburg-Landau formulas
Hc2(0)= 0.76 T and Hc2ab(0)=1.31 T. Using the anisotropic
Ginzburg-Landau formula:
Hc2(0) = \frac{\Phi_0}{2\pi \xi_{ab}(0)} ; \quad Hc2ab(0) = \frac{\Phi_0}{2\pi \xi_{ab}(0) \xi_c(0)}
the superconducting coherence length along the c-axis
ξc(0) and in the ab-plane ξab(0) were obtained (here
Φ0 = 2.07 \times 10^{-7} \text{G-cm}^2 is the flux quantum). Optimally
doped sample with x =0.085 shows ξab(0) = 20.5 nm
and ξc(0)=11.9 nm. The anisotropy of the upper critical
field, γ = Hc2ab(0)/Hc2(0), was found to be 1.7 for
x ≥ 0.067 and independent on the copper concentration.
However, in the highly underdoped regime we found an
increase of the anisotropy to γ ~ 1.9 (inset of Fig. 2). It is
interesting to note that compared to other superconducting
transition metal dichalcogenides such as 2H-NbSe2,32
2H-NbSe2,31,32, NaNbSe2,31 and 2H-TaSe2,30 Cu_xTiSe2
has the lowest anisotropy of the upper critical field coinciding
to one observed in K0.6Fe2Se2 superconductors.32
The values of Hc2(0) obtained in the slightly underdoped
case (x = 0.07) that were reported earlier in28 are
consistent with our dome-like dependence in Fig. 3.
The physical origin of the deviation in the upper
critical field and anisotropy in highly underdoped samp-
les may be due to the confluence of higher electronic
anisotropy with lack of available electronic states to form
Cooper pairs. The CDW amplitude is strong in the
underdoped regime and CDW order parameter competes
with superconductivity.29 For similar Cu concentrations
(x = 0.055) an unusual behavior of magnetoresistance
has been reported recently29. Moreover, Kusmartseva et
al.29 observed a sizable suppression of the exponent n in
the temperature-dependent resistance R(T) = R_0 + AT^n
around the critical pressure of \sim 3 \text{GPa}. This deviation
was attributed to quantum fluctuations in the vicinity of
the CDW quantum critical point. Similarly, Zaberiukh et
al.29 observed a deviation from BCS model in a tempera-
ture dependence of a superfluid density for lower copper
concentrations in their muon-spin rotation experiments.
It is quite possible that at lower Cu concentrations the
amplitude of the CDW remains strong despite the pres-
ence of the superconducting order parameter, causing an
increase of the superconducting anisotropy and decrease
of available electronic states participating in supercon-
ducting pairing.
Next, we examine in detail the vortex states in
Cu_xTiSe2 using DC magnetization hysteresis measure-
ments. The bulk superconducting critical current densi-
ties are determined from the irreversible part of magnet-
ization loops using the Bean model. For H \parallel c, the
correspondence between J_c and the width of the mag-
netization loop is given by the isotropic Bean model,34
whereas for H \perp c we apply the anisotropic Bean model35
that takes into account the difference in the supercon-
ducting critical current flowing along and perpendicular
to the crystal planes. At fields of several hundred Oerst-
eds we can assume that the surface and geometrical barri-
ers do not significantly contribute to the irreversibility in
our samples. We use well established expressions for
critical current densities in anisotropic superconductors with
slab geometry.36 For H \parallel c, in the case of a rectangular
shape of crystal with b > a > c (b, a, and c are the length,
width, and thickness of the sample) the in-plane critical
current density is given by 37:
J_{cb}(H) = \frac{2\Delta M(H)}{a b (1-\gamma^2)},
where a, b are the dimensions in cm and \Delta M is a difference
between the magnetization for decreasing and increasing
branch of magnetization loop in emu/cm^3. For magnetic
field applied along the ab plane, there are two contribu-
tions to the supercurrent - parallel to the Ti-Se layers,
j_{cb}^p, and perpendicular to the Ti-Se layers, j_{cb}^p. In
the limit a, b \gg c \cdot j_{cb}^p, the former is given by
J_{cb} = \frac{2\Delta M(H)}{c}.
An example of magnetic field dependence of J_c and
J_{cb}^p for the sample with x=0.058 are shown in Fig. 4. We ob-
serve an exponential dependence that can be expressed using
\begin{equation}
J_c(H, T) = J_{c0}(T) \exp(-H/H_0(T))
\end{equation}
Extracted values of J_{c0}(T) and H_0(T) show a linear
temperature dependence shown in the inset of Fig. 4. Similar
exponential field dependence of the critical current den-
sity was observed in the rest of the samples with differ-
FIG. 3. (Color online) Dependence of the upper critical fields and
superconducting transition temperature on the Cu con-
centration x in Cu_xTiSe2.

[Image: Graph showing dependence of the upper critical fields and superconducting transition temperature on Cu content x in Cu_xTiSe2]
FIG. 4. (Color online) Magnetic field dependence of the superconducting critical current density in Cu$_{0.058}$TiSe$_2$ for applied field $H \parallel c$ at $T$ = 1.8, 1.9, 2.0, 2.1, 2.2, and 2.3 K (upper panel) and for $H \parallel ab$ at $T$ = 1.8, 2.0, and 2.2 K (lower panel). The curves were fit with equation (3) and temperature dependence of parameters $J_{c0}$ and $H_0$ is shown in the inset.

The relative large reversible part of the magnetization curve $M(H)$ spanning up to $H_c2$ signifies the presence of a vortex liquid phase. The boundary between vortex solid and liquid phases, the irreversibility field $H_{irr}$, was inferred from the magnetization hysteresis loops as a field at which upper and lower magnetization branches merge. As an onset criterium of reversibility we used the value of $\Delta m \leq 5 \times 10^{-7}$ emu. A vortex phase diagram for samples with different copper concentrations is shown in Fig. 5. The perfect scaling of the $H_{c2}(T)$ and $H_{irr}(T)$ with $T_c$ is further evidence that the underlying nature of the vortex dynamics in samples with different Cu concentration is the same. It is remarkable to notice that the reversible region of the vortex liquid phase is so broad for such a low-$T_c$ material with relatively low superconducting anisotropy. Normally, the broad vortex liquid region in the phase diagram is associated with the existence of thermal fluctuations, a perfect example of which are the high temperature superconductors. The irrelevance of thermal fluctuations in our system can be inferred from the estimate of the Ginzburg number $G \sim 3 \times 10^{-6}$, a value much smaller than the one found in high-$T_c$ materials ($G \geq 10^{-3}$). The estimate of the ratio of the critical current density to the depairing current density $J_c/H_c3/\lambda$, where depairing current $J_{0} = 4\mu_{0}H_c3/\lambda$, $\lambda$ is London penetration depth, $H_c$ is thermodynamical critical field, and $\mu_{0}$ is permeability of vacuum). In Cu$_{x}$TiSe$_2$ this ratio is found to be $\sim 4 \times 10^{-7}$, which is much smaller than the one found typically in single crystal of low-$T_c$ dichalcogenide superconductors such as NbSe$_2$ ($\sim 10^{-3}$). From this we can conclude that the broad area of the vortex liquid phase in the phase diagram is evidence of high copper dopant spatial homogeneity that results in vanishing quenched disorder. It is possible that additional mechanisms could play a role in reducing the shear modulus of the vortex lattice, but this issue would need to be addressed through a combination of microscopic measurements of the local density of states of the individual vortex line and vortex lattice...
In conclusion, we have investigated the magnetization properties and flux dynamics of Cu$_2$TiSe$_2$ single crystals in a wide range of copper concentrations. We find that the superconducting anisotropy is independent on Cu concentration except in the case of strongly underdoped samples that show a gradual increase in anisotropy. We establish the vortex phase diagram in this material. We find a broad, doping-independent region of vortex liquid phase that is unusual for such low-$T_c$ superconductor with low anisotropy. Deep in the vortex solid phase the pinning remains very weak compared to other dicaulogenide superconductors. This leads us to believe that fluctuations in copper concentration on a nanometer scale have little effect on the pinning potential landscape.

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