# Point-contact tunneling spectroscopy measurement of Cu_{x}TiSe_{2}: Disorder-enhanced Coulomb effects

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# Point-contact tunneling spectroscopy measurement of $Cu_xTiSe_2$: disorder-enhanced Coulomb effects

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We performed point-contact spectroscopy tunneling measurements on $Cu_xTiSe_2$ bulk with $x = 0.02$ and 0.06 at temperatures ranging from $T = 4 - 40$ K and observe a suppression in the density of states around zero-bias that we attribute to enhanced Coulomb interactions due to disorder. We find that the correlation gap associated with this suppression is related to the zero-temperature resistivity. We use our results to estimate the disorder-free transition temperature and find that the clean limit $T_{c0}$ is close to the experimentally observed $T_c$ at optimal doping.

PACS numbers:

Copper intercalated titanium diselenide ($Cu_xTiSe_2$) is a fascinating system offering a unique opportunity to study the interplay of two collective phenomena, namely superconductivity and charge density waves (CDW).[1–5] The parent compound $TiSe_2$ has been classified as either a CDW semi-metal or excitonic insulator,[6] and upon the addition of Cu, superconductivity arises with a maximum transition temperature $T_c = 4.15$ K near $x \approx 0.08$. Several experiments have already been conducted to probe the relationship between these two states. Photoemission studies have shown that the CDW order parameter microscopically competes with superconductivity in the same band.[3] In addition, previous work suggests that the CDW is suppressed by increasing the chemical potential, while superconductivity is enhanced by the increasing density of states (DOS).[7]

With an increase in the chemical potential combined with the observation of the rapidly varying DOS near the Fermi energy, $E_F$, the question of the impact of disorder on this system is relevant.[8] Band structure calculations suggest that disorder may play an important role in moderating the large DOS. The effects of disorder then would allow for increased orbital hybridization, effectively increasing electron-phonon coupling $\lambda$ despite a reduced total DOS.

In this paper we report our findings of point-contact spectroscopy (PCS) measurements on $Cu_xTiSe_2$ and analyze our results in the context of disorder. Our measurements show that disorder-enhanced Coulomb interactions are present in the superconducting and non-superconducting crystals, providing evidence that disorder plays a role in these materials. A very likely source of the disorder is the random intercalation of Cu between the $TiSe_2$ layers. In contrast to other superconducting systems, such as $BaPb_{1-x}Bi_xO_3$ (BPBO)[9], where disorder reduces the observed superconducting transition temperature, $T_c$, from the clean limit, disorder in $Cu_xTiSe_2$ is important for disrupting the CDW, and allowing superconductivity to emerge. We show that the $T_c$ of the optimally doped system is close to that expected from a strong coupling theory that explicitly takes disorder into account.

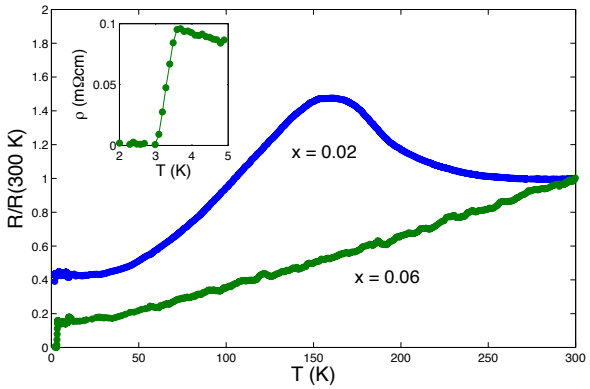


FIG. 1: Residual resistance ratio versus temperature for $x = 0.02$ (blue curve) and $x = 0.06$ (green curve) samples. The inset shows the superconducting transition with $T_c = 3$ K for the $x = 0.06$ sample. The hump at roughly 150 K in the $x = 0.02$ sample is a signature of the CDW.

The samples were grown by the method described previously[1,10]. Four-terminal resistance versus temperature measurements for the crystals studied here are shown in Fig. 1. The $x = 0.02$ sample (upper curve), with a resistivity $\sim$ 1-2 $m\Omega$cm at low temperature, is not superconducting, while the resistivity of the sample with $x = 0.06$ is on the order of 0.1 $m\Omega$cm just above the superconducting transition at $T_c = 3$ K. The $x = 0.02$ sample displays a pronounced bump near 150 K, a signature of the CDW. This feature is not evident in resistivity curves for the superconducting sample, consistent with the suppression of the CDW below 0.4 K when $x > 0.04$.[1]

To further understand the gap structure, we performed PCS measurements on these two samples using an oxidized Aluminum tip of diameter 0.5 mm. The apparatus is a home built point contact setup designed to work in a Quantum Design Physical Property Measurement System (PPMS). Temperature control is achieved with the PPMS software, and point contact measurements were performed at temperatures ranging from $4 - 40$ K. A Keithley 6221A and 2184 instrument was used to perform

the differential conductance measurement. The junctions were prepared by cleaving the sample and Al wire in air, and then bringing the sample in contact with the Al tip at room temperature. The apparatus was then inserted into the PPMS for measurements. Previous studies using these tips demonstrate that they provide a tunneling contact, and the normalized differential conductance, $G/G(25mV)$, shown in Fig. 2 allows for a direct measure of the normalized DOS $N(E)$[9,11]. For the superconducting sample, we are essentially probing the behavior in the normal state in this temperature range.

We observe a suppression in the DOS near zero-bias as indicated by the cusps in Fig. 2 in the normal state. These cusps are reminiscent of those observed in amorphous Nb-Si alloys,[12] which is one of the classic cases of a disorder driven metal-insulator transition, and more recently such cusps were observed in BPBO and alkali-doped tungsten bronzes.[9,11] In disordered metals, the reduction of $N(E)$ due to disorder-enhanced Coulomb interactions is well established. In three dimensions theory predicts that

$$N(E) = N(0)[1 + (E/\Delta)^{1/2}], \quad (1)$$

where $N(0)$ is the normalized DOS at zero temperature, $\Delta$ is the correlation gap and $E = V_{sd}$ is the source drain voltage.[13]

To aid in the analysis, in Fig. 2 we show the normalized differential conductance versus the square root of the source drain voltage in units of $(mV)^{1/2}$ for $Cu_xTiSe_2$ with (a) $x = 0.02$ and (b) $x = 0.06$. Clearly, our data follows the energy dependence in Eq. 1 relatively well. The black dashed lines in both panels are fits to the data at the lowest temperature measured. From this fit, we determine both the correlation gap $\Delta$, which corresponds to the inverse slope of the line and the zero-temperature reduction in the normalized DOS at zero-bias, N(0), corresponding to the zero voltage intercept of the dashed line. For $x = 0.02$, we find $N(0) = 0.82$ and $\Delta = 0.52$ eV at $T = 4$ K. For $x = 0.06$, we find $N(0) = 0.95$ and $\Delta = 8.6$ eV.

The linear fit shown was done for the lowest temperature trace for each Cu doping. For low Cu doping (i.e. $x = 0.02$ here), N(0) and $\Delta$ is much more strongly temperature dependent, with a jump in the data around 11 K. Although it is not known why, we note that for low Cu doping, the resistance, Hall coefficient and thermopower shows non-monotonic temperature dependence[1,4]. For large Cu doping, $CuTiSe_2$ becomes a metal, and the temperature dependence of the physical properties is less strong. For $x = 0.06$, N(0) and $\Delta$ shows monotonic, essentially constant behavior throughout the temperature range studied here.

A comparison of the two samples with different Cu doping shows that the superconducting sample, $x = 0.06$ has a larger $N(0)$ than the non-superconducting sample. At the lowest measured temperature, $N(0) = 0.95$ for $x = 0.06$ and $N(0) = 0.82$ for $x = 0.02$. This trend is consistent with angle resolved photoemission studies showing that Cu doping increases the DOS[3] while also raising the chemical potential, which is seen with the significantly reduced resistivity of the $x = 0.06$ sample compared to $x = 0.02$. The one order of magnitude larger correlation gap of $\Delta = 8.6$ eV in the superconducting sample $x = 0.06$ provides experimental evidence for the greater role of disorder-induced Coulomb interactions. That disorder plays an important role is not entirely surprising as previous works suggested that the disorder induced from the random intercalation of Cu atoms between the $TiSe_2$ layers plays an important role in suppressing the CDW state[1,4]. The CDW state, characterized by the bump seen at T $\sim$ 150-200 K in the $x = 0.02$ sample, is intimately related to the structure of the $TiSe_2$ layers, which undergoes a structural transition to a 2x2x2 lattice just below 200 K. When the Cu atoms are intercalated between the layers, the 2x2x2 lattice of the $TiSe_2$ is destroyed, preventing the CDW state. Our PCS studies provide direct tunneling evidence showing that disorder is present in this system.

Disorder can play different roles depending on the material system and has been shown to be important in several distinct superconducting systems recently[9,11]. For comparison, in Fig. 3, we plot the correlation gap, $\Delta$, as a function of the zero-temperature resistivity, $\rho_0$, of various samples and concentrations. The solid black line is the relationship found for $Nb_xSi_{1-x}$.[12] The magnitude of the correlation gap and its dependence on $\rho_0$ in $Cu_xTiSe_2$ are qualitatively consistent with the other materials. Thus, although the disorder manifests in different ways for each system, we find phenomenologically similar behavior for disorder in relation to the zero temperature resistivity, suggesting universality of disordered enhanced Coulomb interactions in these distinct classes of metals.

Although disorder can be parametrized by the zero-temperature resistivity for these different materials, it is not obviously clear what effect disorder has on the superconducting transition temperature, $T_c$. As an example, in BPBO, disorder is found to reduce $T_c$ from its theoretical clean limit (which is close to the experimentally observed value in its cleaner cousin, $BaKBiO_3$). In $Cu_xTiSe_2$, the disorder seems to play a different role, that is it suppresses the CDW and allows $T_c$ to occur. In order to provide a theoretical framework to address this question, we apply the same formalism as was used previously in[9,11]. Briefly, from the work of Belitz,[14] we have a modified McMillan equation for $T_c$ valid for strong coupling and relatively strong disorder.

$$T_c = \frac{\Theta_D}{1.45} \exp\left[\frac{-1.04(1 + \tilde{\lambda} + Y')}{\tilde{\lambda} - \tilde{\mu}^*[1 + 0.62\tilde{\lambda}/(1 + Y')]}\right]. \quad (2)$$

Here $\Theta_D$ is the Debye temperature, $\tilde{\lambda}$ is the disorder dependent electron-phonon coupling, and $\tilde{\mu^*}$ is the disorder dependent Coulomb pseudopotential. Conveniently, the disorder is parameterized by the fractional reduction of the DOS at the Fermi energy.

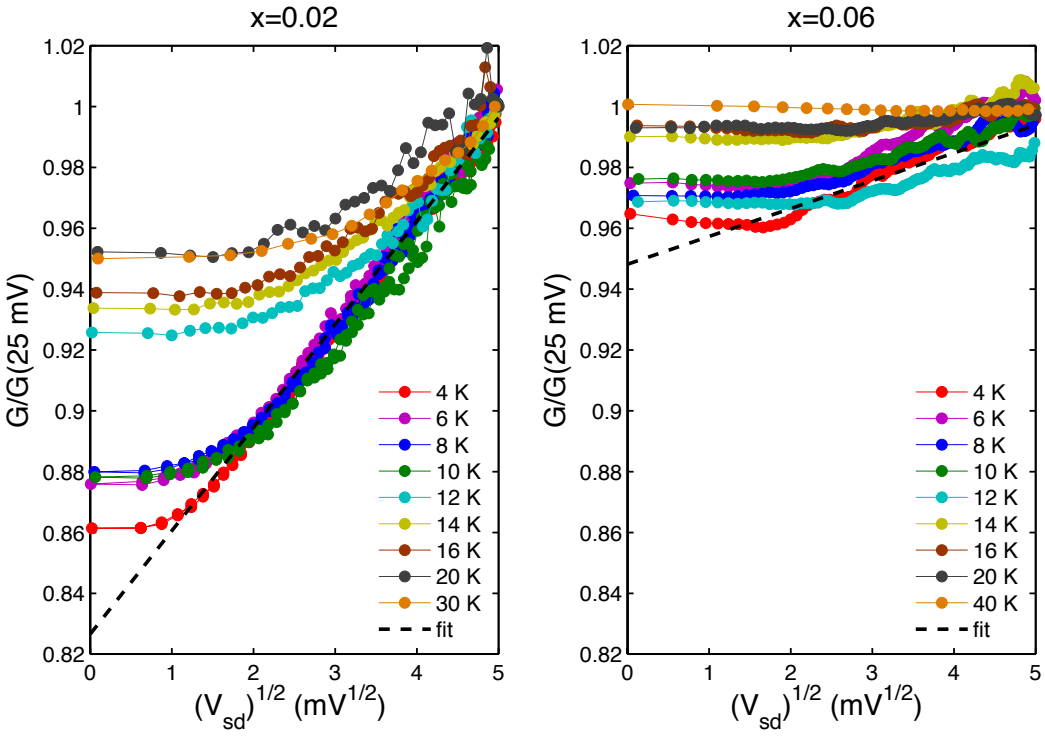


FIG. 2: Normalized differential conductance G versus square root of the source drain voltage $V_{sd}$ in units of $(mV)^{1/2}$ for $Cu_xTiSe_2$ with (a) $x = 0.02$ and (b) $x = 0.06$. The black dashed lines are fits used to extract the normalized zero temperature DOS and correlation gap.

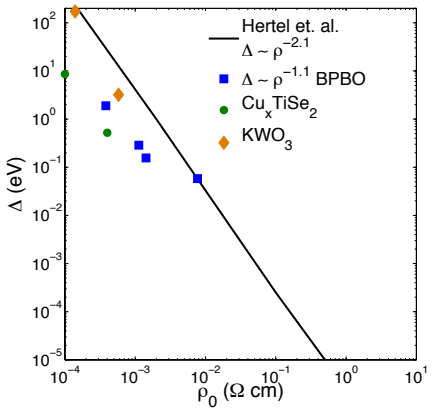


FIG. 3: Correlation gap as a function of the zero-temperature resistivity for $Nb_xSi_{1-x}$ (black line), $BaPb_{1-x}Bi_xO_3$ (blue squares), $K_{0.33}WO_3$ thin films with different thicknesses (orange diamonds) and $Cu_xTiSe_2$ (green circles) for Cu concentration $x = 0.02$ and 0.06.

$$Y' = N(E_F)/N(0) - 1 \tag{3}$$

where $N(E_F)$ is the DOS at the Fermi level.

$Y'$ enters in the equation for the reduction of $T_c$ both explicitly as shown in Eq. 1 and implicitly through $\tilde{\lambda}(Y') > \lambda$ and $\tilde{\mu}^*(Y') > \mu^*$.

In order to determine $\mu^*$, we use the Morel-Anderson equation $\mu^* = \mu/[1 + \mu\ln(E_F/k_B\Theta_D)]$[15] as described in Ref.[9,11]. Experimental results of the Debye temperature $\Theta_D = 137$ was extracted from Fig. 1 of Ref.[16] for $x = 0.08$, using the low temperature limit assumption where $\beta = (12/5)\pi^4 R\Theta^{-3} = 3/4$ mJ/mol K. In addition, we used the value of the carrier density $n = 8.1 \times 10^{19}$ cm$^3$ from Ref.[17] for $1T-TiSe_2$. The Fermi energy was taken to be $E_F = 1eV$, where this value does not affect the result appreciably. This procedure produces the value $\mu^* = 0.15$.

We can determine the clean limit transition temperature without disorder, $T_{c0}$, by first plotting an array of curves for the variation of $T_c$ with the disorder parameter $Y'$, as shown in Fig. 4. We can then triangulate the particular curve of interest, as we know the measured $T_c$ and can estimate $Y'$ using the DOS from PCS measurements. Tracing back the selected curve, corresponding to the intersection point, to the clean limit when $Y' = 0$ yields for $x \approx 0.06$, $(T_c, T_{c0}) = (3\text{K}, 3.2\text{K})$, $(\lambda, \tilde{\lambda}) = (0.76, 0.8)$, $(\mu^*, \tilde{\mu^*}) = (0.15, 0.16)$.

Using this formalism, we find that the observed $T_c = 3$ K is not significantly different from the clean limit $T_{c0} = 3.2$ K, in contrast to BPBO or $KWO_3$.[9,11] This calculated clean limit value is very close to the $T_c = 4.15$ K at optimal doping. Beyond optimal doping, the additional Cu and disorder leads to more scattering and then begins to negatively affect $T_c$. There are some differences between

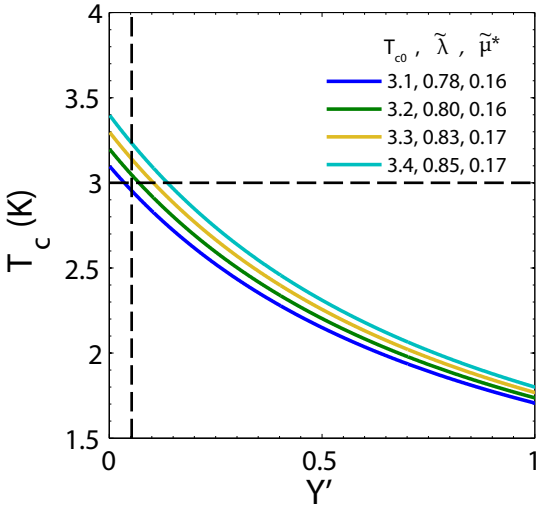


FIG. 4: Calculated $T_c$ as a function of the disorder parameter $Y'$ for different values of $\tilde{\mu^*}$ and $\tilde{\lambda}$. From the intersection of the measured $T_c$ and $Y'$ for $x \approx 0.06$, $T_{c0}$ where $Y' = 0$ can be backtracked.

$Cu_xTiSe_2$ and BPBO which might account for the possible effects disorder has on $T_c$. In $Cu_xTiSe_2$, the CDW partially gaps the Fermi surface[7] whereas in BPBO, for example, the negative-U CDW insulator affects the entire Fermi surface, so the effect of disorder on $T_c$ in BPBO is more pronounced.[18,19]

We note that in addition to providing an estimate for $T_c$, the triangulation method allows to extract the disorder dependent $\tilde{\mu^*}$ and $\tilde{\lambda}$ compared to the clean limit $\mu^*$ and $\lambda$. Band structure calculations[8] showed Cu doping brings Cu d states near the Fermi level which hybridize with the Ti d band. This increases the DOS. Disorder helps in moderating the sharp DOS and can also make $\lambda$ larger. The increased $\tilde{\lambda}$ with disorder compared to $\lambda$ supports this picture.

In summary, we performed PCS on $Cu_xTiSe_2$ and found a suppression in the DOS, a strong experimental signature of electron-electron interactions in the presence of disorder. Our results suggest that disorder-enhanced Coulomb interactions should be taken into account in this system. This is not entirely surprising considering the disorder is likely introduced by the random intercalation of Cu between $TiSe_2$ layers. We found that the correlation gap associated with this suppression is correlated with the zero-temperature resistivity, suggestive of some universal scaling result across a number of materials. Finally, we address the question of how disorder impacts $T_c$ for a sample close to optimal doping. We find that the clean limit $T_{c0}$ is close to the experimentally observed $T_c$, suggesting that the effects of disorder on $T_c$ in $CuTiSe_2$ are not very pronounced.

**Acknowledgments**

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