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# Coexistence of bulk superconductivity and charge density wave in $\text{Cu}_x\text{ZrTe}_3$

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We report coexistence of bulk superconductivity with  $T_c = 3.8$  K and charge density wave (CDW) in Cu intercalated quasi two-dimensional crystals of  $\text{ZrTe}_3$ . The Cu intercalation results in the expansion of the unit cell orthogonal to the Zr - Zr metal chains and partial filling of CDW energy gap. We present anisotropic parameters of the superconducting state. We also show that the contribution of CDW to the scattering mechanism is anisotropic in  $\hat{a} - \hat{b}$  plane. The dominant scattering mechanism in the normal state for both  $\text{ZrTe}_3$  and  $\text{Cu}_{0.05}\text{ZrTe}_3$  along the  $\hat{b}$ -axis is the electron - electron Umklapp scattering.

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Peierls distortion results in the periodic modulation of electron density in solids and generates an energy bandgap at the Fermi surface [1]. It can be observed as a charge density wave (CDW) superstructure in many low dimensional materials [2]. The continuous suppression of CDW order brings about superconductivity (SC) in  $\text{Cu}_x\text{TiSe}_2$  [3]. This is reminiscent of SC in heavy fermion and the cuprate oxide phase diagram when the magnetic order is tuned by pressure ( $P$ ) or doping to  $T \rightarrow 0$  [4–6]. Superconducting mechanism in such electronic systems is likely to be mediated by the magnetic fluctuations [7, 8]. Similarly, the dome-like structure of  $T_c(x)$  and the pairing mechanism in  $\text{Cu}_x\text{TiSe}_2$  is argued to stem from the type of quantum criticality related to fluctuations in CDW order [9]. Quantum phase transition is proposed to drive CDW order into a quantum nematic phase [10]. On the other hand, the positive slope of the dome could be explained via the shift of the Fermi level caused by Cu intercalation and the negative slope by the enhanced scattering for the high Cu concentration [11]. This is also supported by the evidence for a single gap s-wave order parameter, implying conventional mechanism despite the dome - like evolution of  $T_c(x)$  [12]. However, a dome - like structure of  $T_c(P)$  was also discovered using  $P$  as a tuning parameter and suggesting that impurity effects may not be responsible for the dome closure [13].

Chalcogenide superconductors represent a weak coupling side of the smectic order, akin to stripe order in cuprates [10]. There is a mounting evidence that in such systems CDW states transform into Fermi liquid through an intermediate phase [14]. Therefore it is of interest to study the melting of CDW order parameter and possible nematic phases in a superconductor with highly related and tunable two-dimensional electronic system.

$\text{NbSe}_3$ , exhibits two CDW transitions at 145 K and 59 K, and becomes a superconductor under pressure [15]. Another trichalcogenide,  $\text{ZrTe}_3$ , accommodates a layered structure, where the metal - metal distances are 0.39 nm, 0.58 nm and 0.71 nm along the  $\hat{a}$ ,  $\hat{b}$  and  $\hat{c}$  - axis respectively [16]. The shortest Zr - Zr distances define two sets

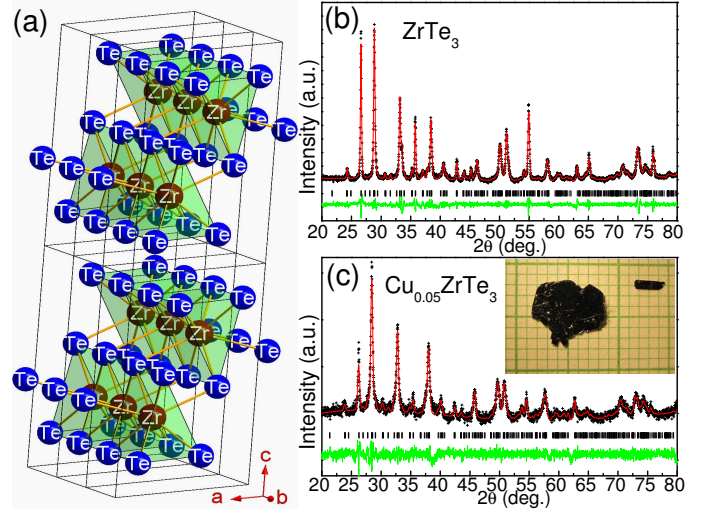


FIG. 1. (a) The crystal structure of  $\text{ZrTe}_3$  with blue (brown) symbols for Te (Zr) atoms. Crystallographic  $\hat{b}$  - axis runs along the shortest Zr - Zr distances and the  $\hat{c}$  - axis is along the vertical. Comparison of the observed (crosses) and calculated (solid line) powder X ray patterns of  $\text{ZrTe}_3$  (b) and  $\text{Cu}_{0.05}\text{ZrTe}_3$  (c). The bars (black) correspond to the Bragg reflections and the lowest solid line is the difference between the observed and the calculated patterns.

of chains along the crystallographic  $\hat{b}$  - axis (Fig. 1 (a)). This results in a Peierls instability and a CDW transition at  $T_{CDW} \sim 63$  K with a  $\vec{q} \equiv (\frac{1}{14}, 0, \frac{1}{3})$  [17, 18]. As opposed to the poor conductivity values of  $\text{TiSe}_2$  [3], resistivity values of  $\text{ZrTe}_3$  are up to two orders of magnitude smaller and quasi two-dimensional ( $\rho_a \sim \rho_b \sim \rho_c/10$ ) [17]. The  $\rho(T)$  is strongly affected by CDW along the crystallographic directions perpendicular to  $\hat{b}$  - axis [17]. A giant Kohn anomaly associated with a soft phonon mode and a two-dimensional order parameter have been identified, as well as CDW fluctuations (pseudogap) that extend well above 100 K [19–21]. The CDW vector  $\vec{q}$  agrees with the nesting vector from the calculated Fermi surface [16, 22]. This is in contrast to chiral CDW [23] in  $\text{TiSe}_2$  and semimetallic or semiconducting ground state

with no signature of CDW fluctuation above  $T_{CDW}$  [24–26]. The Fermi surface of  $ZrTe_3$  contains one quasi one-dimensional electron like sheet (pocket) of states of  $5p$  Te chain origin that is responsible for CDW distortion and pseudogap formation at  $T \gg T_{CDW}$  [16, 22]. There is in addition a more isotropic hole sheet that makes up to 90 % of the Fermi surface and that remains ungapped below 10 K [20]. With further decrease in temperature,  $ZrTe_3$  exhibits filamentary SC below 2 K with no diamagnetic response in  $H = 10$  Oe [27]. The origin of filamentary SC is still unclear, and it can be suppressed with  $P \sim 0.8$  GPa [28]. Cu has been intercalated in  $ZrTe_3$  with  $x = 1.9$  in  $Cu_xZrTe_3$ , though no SC was discovered [29].

In this Letter, we report coexistence of CDW and bulk SC in  $Cu_xZrTe_3$ , grown via chemical vapor transport. The Cu content  $x$  varied within the batch, and the results shown here are on crystals with optimum  $T_c$  for  $x \approx 0.05$ .

Single crystals of  $Cu_xZrTe_3$  ( $x = 0, 0.05$ ) with typical size of  $1 \times 3 \times 0.06$  mm<sup>3</sup> elongated along the  $\hat{b}$ -axis were grown from pure elements in a mole ratio of Cu:Zr:Te = (0, 0.1):1:3 with 5 mg cm<sup>-3</sup> iodine sealed in an evacuated quartz tube. The furnace gradient was kept between 1023 K and 923 K after heating at 973 K for 2 days. Elemental analysis was performed by using energy-dispersive X-ray spectroscopy in an JEOL JSM-6500 scanning electron microscope. Resistivity and magnetization were measured in Quantum Design PPMS-9 and MPMS-XL-5, respectively. The observed (Cu  $K\alpha$  radiation of Rigaku Mini-flex) and calculated [30] (Rietica software) powder X ray diffraction (XRD) patterns for  $ZrTe_3$  and  $Cu_{0.05}ZrTe_3$  are shown in Fig. 1 (b) and (c), respectively. Both can be indexed to  $ZrTe_3$ . The unit cell refinement yields lattice parameters  $a = 0.586(3)$  nm,  $b = 0.392(7)$  nm,  $c = 1.009(5)$  nm and  $\beta = 97.75(1)^\circ$  for  $ZrTe_3$ , whereas for  $Cu_{0.05}ZrTe_3$  we obtained  $a = 0.588(2)$  nm,  $b = 0.392(8)$  nm,  $c = 1.011(1)$  nm, and  $\beta = 97.75(1)^\circ$ . The Cu intercalation leads to slight expansion of the  $\hat{a}$  and  $\hat{c}$ -axis parameters. It should be noted that Zr - Zr distances along the  $\hat{b}$ -axis chains are unchanged [16].

We observe onset of SC at  $T = 3.8$  K in  $\hat{b}$ -axis resistivity  $\rho_b$  (Fig. 2 (a)). The transition width (10-90%) is 0.28 K. Fig. 2 (b,c) show magnetic properties of  $Cu_{0.05}ZrTe_3$  in the superconducting state. The shape of the magnetic hysteresis loop (Fig. 2 (b)) is typical of type - 2 inhomogeneous superconductors with some electromagnetic granularity. This is in agreement with the transition from the real part of ac susceptibility ( $\chi'_{ac}$ ) curve (Fig. 2 (c)), and is similar to data in  $SmFeAsO_{0.85}F_{0.15}$  [31]. The  $\chi'_{ac}$  becomes diamagnetic around  $T = (4.0 \pm 0.2)$  K (Fig. 2 (c)), confirming SC. The  $\chi'_{ac}$  decreases gradually with the decrease in temperature, showing no sign of saturation down to 1.8 K. The large estimated superconducting volume fraction at  $T = 1.8$  K ( $4\pi\chi'_{ac} \sim 94\%$ ) reveals the bulk nature of SC in  $Cu_{0.05}ZrTe_3$ , as opposed to the pure material [27].

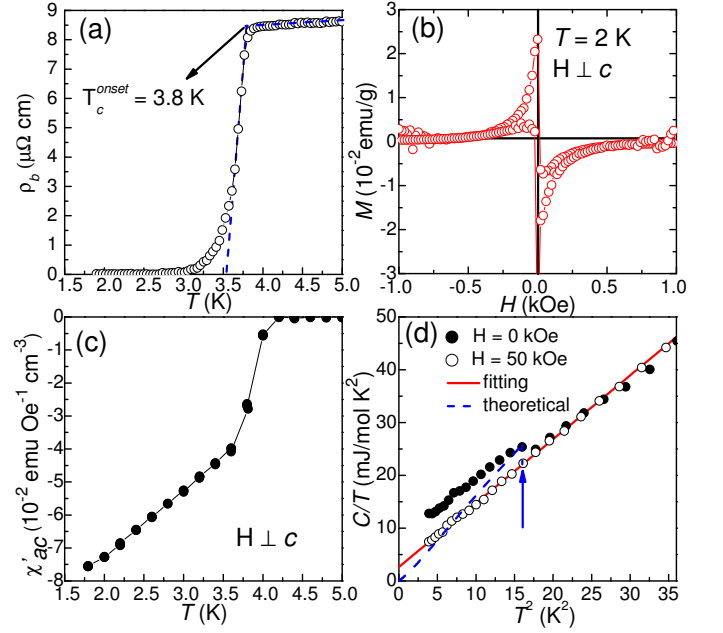


FIG. 2. (a)  $\rho_b$  ( $T$ ) of  $Cu_{0.05}ZrTe_3$  near  $T_c$ . (b) The magnetic hysteresis loop measured at  $T = 2$  K for  $H \perp c$ . (c) The temperature dependence of the real part of  $\chi_{ac}$ . (d)  $(C/T)$  of  $Cu_{0.05}ZrTe_3$  as a function of  $T^2$  for  $H = 0$  (solid circles) and  $H \parallel c = 50$  kOe (open circles). The solid line represents the fitting of the  $C/T$  vs.  $T^2$  curve for  $H \parallel c = 50$  kOe. The dashed line represents the theoretical curve (see text). The arrow marks the specific heat jump.

Figure 2 (d) depicts the specific heat divided by  $T$  ( $C/T$ ) as a function of  $T^2$  of  $Cu_{0.05}ZrTe_3$  in  $H = 0$  kOe and  $H \parallel c = 50$  kOe. Superconducting transition is suppressed in 50 kOe and from the linear fit  $C/T = \gamma + \beta T^2$  we obtain  $\gamma = 2.64 \pm 0.12$  mJ/molK<sup>2</sup> and  $\beta = 1.21 \pm 0.01$  mJ/molK<sup>4</sup>. A Debye temperature  $\Theta_D = 186(1)$  K can be estimated using  $\Theta_D = [ \frac{1.944 \times 10^6 \times N}{\beta} ]^{1/3}$  where  $N$  is the number of atoms per formula unit. From the McMillan formula [32]

$$\lambda = \frac{\mu^* \ln(\frac{1.45T_c}{\Theta_D}) - 1.04}{1.04 + \ln(\frac{1.45T_c}{\Theta_D})(1 - 0.62\mu^*)}, \quad (1)$$

we estimate the electron-phonon coupling constant  $\lambda \sim 0.68$  by assuming  $\mu^* = 0.13$  for the Coulomb pseudopotential. This is a typical value of an intermediate coupled BCS superconductor. A specific heat jump ( $\Delta C/\gamma T_c$ ) around  $T = 4$  K (Fig. 2 (d)) confirms bulk SC. The dashed curve depicted in Fig. 2 (d) is the calculated result of the isotropic BCS gap with  $2\Delta/k_B T_c = 3.53$  and  $\Delta C/\gamma T_c = 1.43$ . The  $C/T$  vs  $T^2$  curve of  $Cu_{0.05}ZrTe_3$  does not follow the calculated result in the superconducting state, most likely due to the sample inhomogeneity. Yet, a  $\Delta C/\gamma T_c$  larger than 1.43 can be estimated from the Fig. 2 (d), suggesting the intermediate or strong phonon-electron coupling.

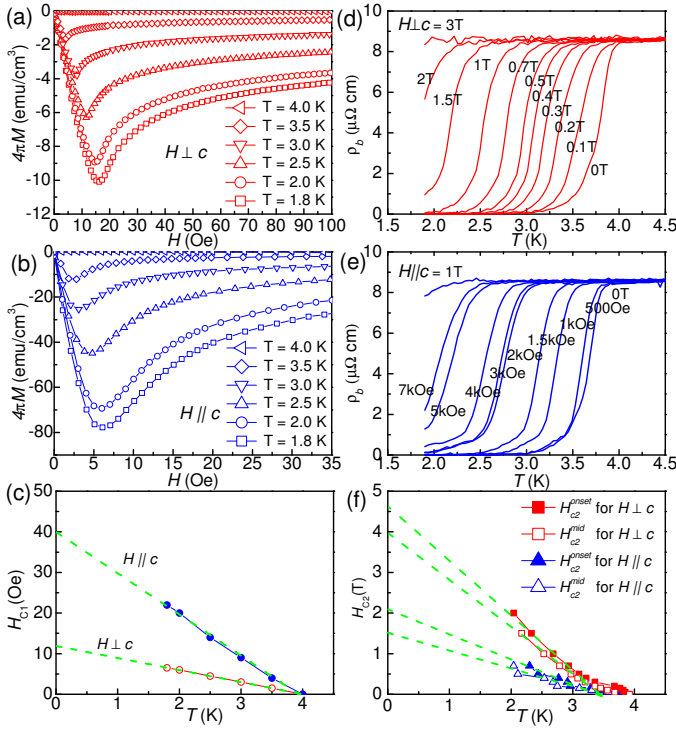


FIG. 3. (a) Field dependence of magnetization of  $\text{Cu}_{0.05}\text{ZrTe}_3$  for  $H \perp c$ . (b) Field dependence of magnetization of  $\text{Cu}_{0.05}\text{ZrTe}_3$  for  $H \parallel c$ . (c) Temperature dependence of  $H_{c1}$  for  $H \perp c$  and  $H \parallel c$ . The dashed lines are the fitted lines. (d)  $\rho_b(T)$  of  $\text{Cu}_{0.05}\text{ZrTe}_3$  for  $H \perp c$ . (e)  $\rho_b(T)$  of  $\text{Cu}_{0.05}\text{ZrTe}_3$  for  $H \parallel c$ . (f)  $H_{c2}^{\text{onset}}(T)$  and  $H_{c2}^{\text{mid}}(T)$  (see text) for  $\text{Cu}_{0.05}\text{ZrTe}_3$ .

Figures 3 (a,b) show field dependence of magnetization of  $\text{Cu}_{0.05}\text{ZrTe}_3$  measured at different temperatures for  $H \perp c$  and  $H \parallel c$ . For  $H \parallel c$ , the  $H_{c1}$  is obtained using the demagnetization correction [33]. The  $H_{c1}(T)$  shows almost linear rather than  $H_{c1} = H_{c1}(0)[1 - (T/T_c)^2]$  temperature dependence for both field orientations (Fig. 3(c), dashed lines). Thus, we estimate  $H_{c1}(0) = -0.693 \frac{\partial H_{c1}}{\partial T} T|_{T=T_c}$  from the Werthamer-Helfand-Hohenberg (WHH) equation [34] and we obtain 8.3(1) Oe ( $H \perp c$ ) and 27.7(4) Oe ( $H \parallel c$ ).

Figures 3 (d,e) show anisotropic  $\rho_b(T)$  of  $\text{Cu}_{0.05}\text{ZrTe}_3$  measured in different fields. Figure 3(f) plots the temperature dependence of  $H_{c2}^{\text{onset}}$  (onset) and  $H_{c2}^{\text{mid}}$  (midpoint, 50% of  $\rho$  in the normal state).  $H_{c2}(0)$  are estimated from the linear  $H_{c2}$ - $T$  relation with WHH equation. Due to small variance in the in plane resistivity values [17], we assume that coherence lengths are isotropic in the  $\hat{a} - \hat{b}$  plane ( $\xi_a \sim \xi_b = \xi_{ab}$ ) and we estimate [35] coherence lengths using  $H_{c2}^c(0) = \Phi_0 / (2\pi\xi_{ab}^2)$  and  $H_{c2}^{ab}(0) = \Phi_0 / (2\pi\xi_{ab}\xi_c)$  where  $\Phi_0$  is the flux quantum. The Ginzburg - Landau (GL) parameters  $\kappa_i$  and penetration depths are estimated from  $H_{c2}^i(0)/H_{c1}^i(0) = 2\kappa_i^2 / \ln \kappa_i$  ( $i = ab, c$ ) and  $\kappa_{ab}(0) = \lambda_{ab}(0)/\xi_c(0)$ , respectively. Finally, from  $H_c(0) = H_{c1}^{ab}(0)/\sqrt{2}\kappa_{ab}(0)$ , we es-

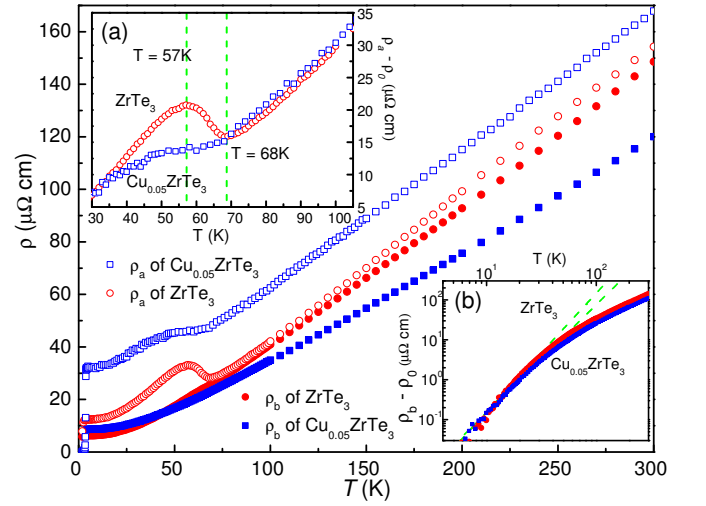


FIG. 4. Temperature dependence of resistivity along Zr - Zr chains ( $\rho_b$ ) and orthogonal to the chains ( $\rho_a$ ) for  $\text{ZrTe}_3$  and  $\text{Cu}_{0.05}\text{ZrTe}_3$ . (a) Temperature dependence of  $\rho_a - \rho_0$  for  $\text{ZrTe}_3$  and  $\text{Cu}_{0.05}\text{ZrTe}_3$ ; the peak ( $T = 57$  K) and the valley ( $T = 68$  K) of CDW anomaly in  $\text{ZrTe}_3$  are marked with two dashed green lines. (b) Logarithmic plots of temperature dependence for  $\rho_b - \rho_0$  with fitting results (dashed green lines) for the Umklapp scattering process (see text).

estimate the thermodynamic critical field. The anisotropy in obtained superconducting parameters can be approximately estimated from the anisotropic GL relation:

$$\gamma_{anis} = \sqrt{\Gamma} = \frac{H_{c2}^{ab}}{H_{c2}^c} = \frac{\xi_{ab}}{\xi_c} = \frac{\lambda_c}{\lambda_{ab}} = \frac{\kappa_{ab}}{\kappa_c} \sim \frac{H_{c1}^c}{H_{c1}^{ab}} \quad (2)$$

where  $\Gamma = \frac{m_c^*}{m_{ab}^*} = \frac{\rho_c}{\rho_{ab}}$  with the effective electron mass  $m_i^*$  along the  $i$  direction. The obtained mass tensor anisotropy  $\Gamma \sim 7$  is comparable with the experimental resistivity ratio  $\sim 10$  of  $\text{ZrTe}_3$  [16]. This points to small anisotropy in the gap function  $\Delta(k_F)$  [36]. We list the obtained superconducting parameters in Table 1.

The CDW and SC in  $\text{ZrTe}_3$  exhibit a rich interplay at high pressures[28]. The  $T_{CDW}$  initially increases below 2 GPa and then decreases up to the vanishing point  $T_{CDW} \sim 40$  K at 5 GPa. Coincidentally, a reentrant SC phase emerges at that  $P$  and its  $T_c$  rises above 4 K up to 11 GPa. In intercalated crystals  $\text{Cu}_{0.05}\text{ZrTe}_3$ , only a weak anomaly at  $T_{CDW}$  in  $\rho_a(T) - \rho_0$  (where  $\rho_0$  is the residual resistivity) can be observed (Fig. 4 (a)), whereas the Cu intercalation has no effect on  $\rho_b(T) - \rho_0$  (Fig. 4 (b)). This is in contrast to the observed shift of the resistivity hump anomaly for  $\text{ZrTe}_3$  ( $\rho_a(T)$ ) with  $0 < P < 5$  GPa [28] and 1T-TiSe<sub>2</sub> [3, 13]. The weaker resistivity anomaly around CDW transition in  $\text{Cu}_{0.05}\text{ZrTe}_3$  reflects a smaller reduction of density of states at the Fermi surface[28], but enhanced  $\rho_0$  for  $\rho_a(T)$  in  $\text{Cu}_{0.05}\text{ZrTe}_3$  implies more defect scattering. This suggests that the CDW energy gap of Fermi surface is partially filled. Anisotropic lattice

TABLE I. Parameters of superconducting state in  $Cu_{0.05}ZrTe_3$ .

$Cu_{0.05}ZrTe_3$		$H_{c2}^i(0)$ (kOe)	$H_{c1}^i(0)$ (Oe)	$H_c(0)$ (Oe)	$\kappa_i(0)$	$\xi_i(0)$ (nm)	$\lambda_i(0)$ (nm)
$i = ab$	<i>onset</i>	32(4)	8.3(1)	240(30)	93(14)	16(1.2)	605(210)
	<i>mid</i>	27(3)		225(27)	85(11)	18(1.8)	570(184)
$i = c$	<i>onset</i>	13(2)	27.7(4)	330(50)	28(5)	6.5(1.3)	1490(420)
	<i>mid</i>	10(2)		295(50)	24(5)	6.7(1.3)	1539(477)

expansion via Cu intercalation is rather different from the isotropic high pressures.

Even though the absolute values of resistivity are quasi two-dimensional [17], we show evidence for inherent in-plane anisotropy. The scattering along the  $\hat{b}$  - axis in the intercalated and the pure material are not related to the CDW. In quasi one-dimensional chains, electron - electron Umklapp process will result in a  $\rho(T) = \rho_0 + AT^n$  (where  $2 \leq n \leq 3$ ) for  $k_B T < (0.1 - 0.3)|\delta|$ , and in a linear relation at high temperature for  $k_B T > |\delta|$  [37]. The parameter A is a constant and the  $|\delta|$  is the typical inter-chain interaction energy. The  $\rho_b(T) - \rho_0$  along Zr-Zr metal in both intercalated and pure material follow this theory very well. The power law temperature dependence is observed for  $T < 25$  K with  $n = 2.98 \pm 0.03$  and  $n = 2.70 \pm 0.03$  for  $ZrTe_3$  and  $Cu_{0.05}ZrTe_3$ , respectively (Fig. 4 (inset,b)). The estimated  $|\delta|$  range is (100 – 250) K, which is consistent with the observed linear  $\rho_b(T)$  above 180 K (Fig.4).

In summary, we have shown that Cu intercalation in  $ZrTe_3$  results in the expansion of the lattice parameters in the  $\hat{a} - \hat{c}$  direction and partial filling of the CDW energy gap. Bulk SC with  $T_c = 3.8$  K is discovered in  $Cu_{0.05}ZrTe_3$ , and its superconducting parameters are given. The electron - electron Umklapp scattering is the dominant scattering mechanism along  $\hat{b}$  - axis. More measurements at higher  $P$  and different Cu intercalation  $x$  are needed in order to confirm the existence of  $T_c(P, x)$  dome in  $Cu_xZrTe_3$ . Further spectroscopic studies would be of interest in order to unfold the details of the phonon mode softening and CDW melting as a function of Cu intercalation.

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