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# Thermal expansion and effect of pressure on superconductivity in $\text{Cu}_x\text{TiSe}_2$

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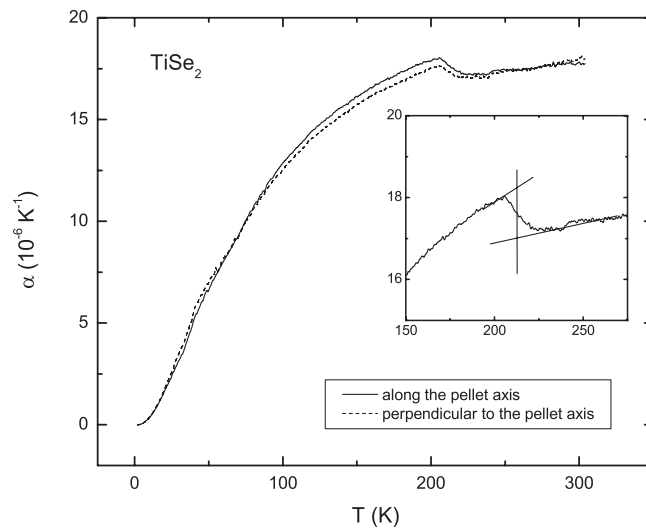
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## Abstract

We report measurements of thermal expansion on a number of polycrystalline  $\text{Cu}_x\text{TiSe}_2$  samples corresponding to the parts of  $x$ - $T$  phase diagram with different ground states, as well as the pressure dependence of the superconducting transition temperature,  $T_c$ , for samples with three different values of Cu doping. Thermal expansion data suggest that the  $x$ - $T$  phase diagram may be more complex than initially reported.  $T_c$  data at elevated pressure can be scaled to the ambient pressure  $\text{Cu}_x\text{TiSe}_2$  phase diagram; however, significantly different scaling factors are needed to accommodate the literature data on the charge density wave transition suppression under pressure.

## 1. Introduction

The transition metal dichalcogenides and their intercalate complexes have received a lot of attention in the past several decades [1–3] due to their low dimensionality, the tunability of their properties, and an abundance of curious physical phenomena associated with this class of materials. Of those,  $\text{TiSe}_2$  was one of the first compounds where a charge-density-wave (CDW) transition was observed; however, the physical mechanism governing this transition is abstruse and the number of studies related to this material continues to grow. Recently, a new development in transition metal dichalcogenides was reported: Cu intercalation in  $\text{Cu}_x\text{TiSe}_2$  caused continuous suppression of the CDW transition followed by (or, initially, coexistent with) a superconducting state near  $x = 0.04$ , with a maximum superconducting temperature  $T_c \approx 4.15$  K for  $\text{Cu}_{0.08}\text{TiSe}_2$  [4]. The physics behind the intriguing phase diagram for  $\text{Cu}_x\text{TiSe}_2$  presented in [4] is still not fully understood. In search of clues, in this work we report measurements of thermal expansion for number of Cu concentrations corresponding to different parts of the phase diagram, as well as the pressure dependence of the superconducting transition temperature for three different values of Cu doping.



**Figure 1.** Temperature-dependent thermal expansion of a pure  $\text{TiSe}_2$  sample measured along and perpendicular to the pellet axis. Inset: enlarged region near  $T_{\text{CDW}}$  with definitions of  $T_{\text{CDW}}$  and  $\Delta\alpha$  used throughout this paper.

## 2. Experimental methods

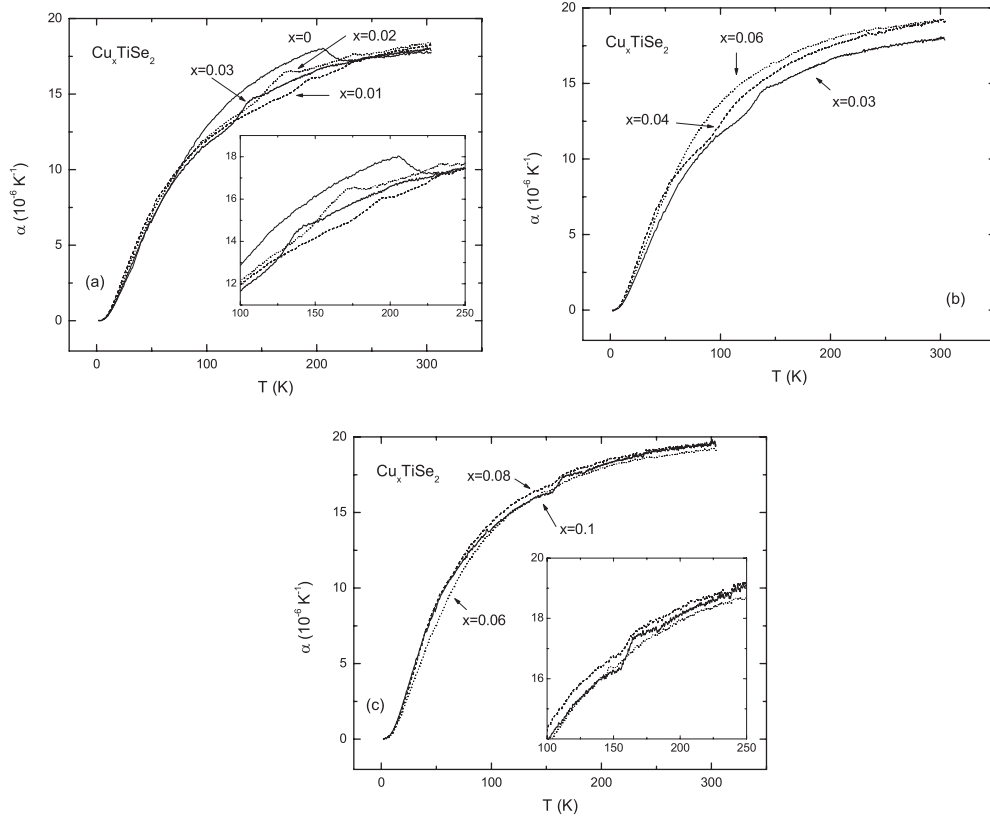
Polycrystalline  $\text{Cu}_x\text{TiSe}_2$  samples were synthesized by two-step solid-state reaction (see [4] for more details) and were in the form of homogenous purple-grey pellets which were  $75\% \pm 10\%$  of theoretical density. Thermal expansion (TE) was measured approximately along the axis of the pellet; the samples were shaped using a dry diamond-impregnated wire saw followed by a light, dry, sandpaper polishing. For pure  $\text{TiSe}_2$ , thermal expansion was measured both along the axis of the pellet and perpendicular to the axis to address the possible preferential orientation of the grains forming the pellet. Thermal expansion was measured using a capacitive dilatometer constructed of oxygen free high conductivity copper; a detailed description of the dilatometer is presented elsewhere [5]. The dilatometer was mounted in a Quantum Design PPMS-14 instrument and was operated over a temperature range of 1.8–300 K. The same set-up was used in our recent work on  $\text{YNi}_2\text{B}_2\text{C}$  and  $\text{ErNi}_2\text{B}_2\text{C}$  [6, 7].

The piston-cylinder clamp-type pressure cell made out of non-magnetic Ni–Co alloy *MP35N* used in this work was designed to fit a commercial Quantum Design MPMS-5 SQUID magnetometer (see [8] for a detailed description of the cell). Pressure was generated in a Teflon capsule filled with approximately 50:50 mixture of n-pentane and mineral oil. The shift in the superconducting transition temperature of 6 N purity Pb, placed in the capsule together with the sample, was used to determine pressure at low temperatures [9]. DC magnetization measurements were performed in an applied field of 25 Oe in a zero-field-cooled warming protocol.

## 3. Results and discussion

### 3.1. Thermal expansion

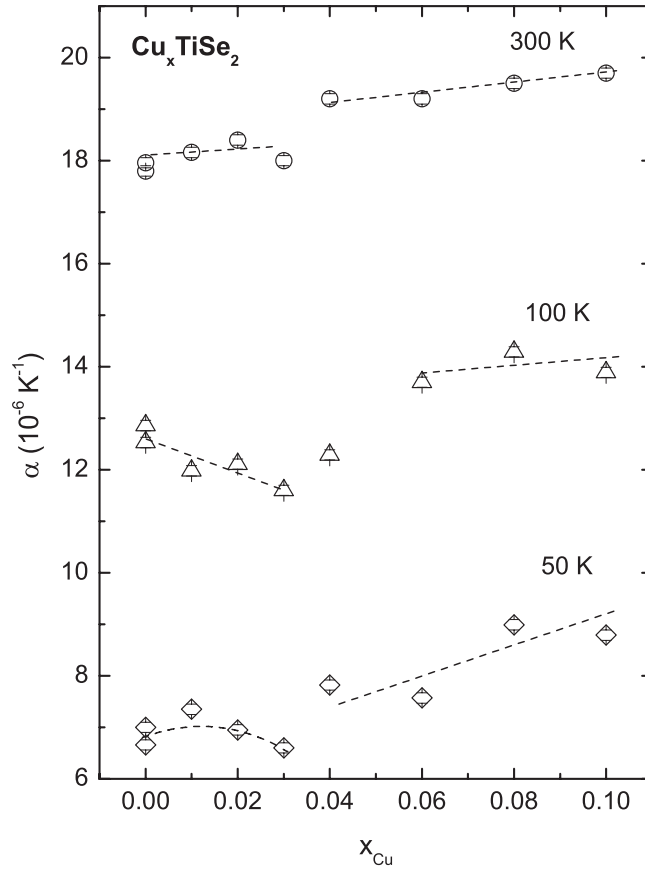
Figure 1 shows the temperature-dependent thermal expansion coefficient of pure, polycrystalline  $\text{TiSe}_2$  measured along the pellet axis as well as perpendicular to it. The two curves are very similar, suggesting that the distribution of the grains within the sample is rather



**Figure 2.** Temperature-dependent thermal expansion of  $\text{Cu}_x\text{TiSe}_2$  polycrystalline samples. Note that the data for  $\text{Cu}_{0.03}\text{TiSe}_2$  and  $\text{Cu}_{0.06}\text{TiSe}_2$  are plotted twice, on different panels, for comparison. Insets to (a) and (c): enlarged region near the features in  $\alpha(T)$ .

uniform. A sharp, distinct, feature in the temperature dependence of the thermal expansion coefficient,  $\alpha(T)$ , at  $\approx 213$  K marks the CDW transition. The change of  $\alpha$  at the transition, defined as sketched in the inset to figure 1, is, as averaged from the two measurements,  $\Delta\alpha \approx -1.2 \times 10^{-6} \text{ K}^{-1}$  (here we will use the following sign convention:  $\Delta\alpha > 0$  if  $\alpha(T)$  increases at  $T_{\text{CDW}}$  on warming and vice versa). Literature data on thermal expansion of  $\text{TiSe}_2$  at  $T_{\text{CDW}}$  are somewhat inconsistent and make comparison with our data ambiguous: Weigers [10] reported  $\Delta\alpha_c \approx 7.5 \times 10^{-6} \text{ K}^{-1}$ , and no measurable change in  $\Delta\alpha_a$ , whereas Caillé *et al* [11] claimed a clear change in the  $a$ -axis thermal expansion coefficient at  $T_{\text{CDW}}$ ,  $\Delta\alpha_a \approx -2.5 \times 10^{-6} \text{ K}^{-1}$ . From the data of Weigers [10]  $\Delta\alpha_{\text{poly}} = (2 \times \Delta\alpha_a + \Delta\alpha_c)/3 \approx \Delta\alpha_c/3 = 2.5 \times 10^{-6} \text{ K}^{-1}$ , whereas using  $\Delta\alpha_c$  and  $\Delta\alpha_a$  from [10] and [11] respectively,  $\Delta\alpha_{\text{poly}} \approx 0.8 \times 10^{-6} \text{ K}^{-1}$ . Both these estimates of  $\Delta\alpha_{\text{poly}}$  differ in sign and value from our measurements. The reason for this discrepancy is not understood; however, if we take the difference in the literature values of  $\Delta\alpha_a$  [10, 11] as a measure of the error bars in the literature data, this discrepancy will be removed; additionally, the estimate of the thermal expansion of a polycrystal as a simple average over all directions may be an oversimplification for an anisotropic material like  $\text{TiSe}_2$  (see the brief discussion in chapter 7 of [12] and references therein).

The temperature-dependent thermal expansion coefficient for different  $\text{Cu}_x\text{TiSe}_2$  samples is plotted in figure 2. These curves have several features of note.



**Figure 3.** Thermal expansion coefficient of polycrystalline  $\text{Cu}_x\text{TiSe}_2$  at 300, 100 and 50 K. Lines are guides for the eye. The two points for  $x = 0$  are from two measurements in figure 1. Error bars are roughly estimated from the noise in  $\alpha(T)$  data near 300 K.

- (i) For the samples in the range  $0 \leq x \leq 0.03$  the thermal expansion coefficient is quite similar near room temperature ( $240 \text{ K} \leq T \leq 300 \text{ K}$ ) and below approximately 70 K (figure 2(a)). On further increase of Cu intercalation, between  $x = 0.03$  and 0.06 (figure 2(b)),  $\alpha(T)$  increases in the whole temperature range, and then the general behaviour becomes very similar for  $0.06 \leq x \leq 0.1$  (figure 2(c)).  $\alpha(300 \text{ K})$  plotted as a function of  $x$ , the Cu concentration, (figure 3) shows an abrupt change between  $x = 0.03$  and 0.04.
- (ii) The temperature-dependent thermal expansion coefficient for  $\text{Cu}_x\text{TiSe}_2$  ( $0 \leq x \leq 0.04$ ) samples (figures 2(a), (b)) shows a clear feature at temperatures close to the  $T_{\text{CDW}}$  determined from resistivity or/and susceptibility measurements [4]. While for  $x = 0$  the value of  $\Delta\alpha$  at the CDW transition is negative, it is positive for  $x = 0.03, 0.04$ , and the feature has some intermediate shape for  $x = 0.01, 0.02$ .
- (iii) For  $x = 0.08, 0.1$  a step-like feature is seen at  $T \approx 160 \text{ K}$ . No feature in this temperature range was reported for  $\text{Cu}_{0.08}\text{TiSe}_2$  and  $\text{Cu}_{0.1}\text{TiSe}_2$  samples in the previous study [4].

It should be mentioned that we cannot detect superconducting transitions in our thermal expansion measurements (for  $x = 0.06, 0.08, 0.1$ ,  $T_c$  was reported [4] to be above our base

temperature); this is not surprising, bearing in mind the thermodynamic Ehrenfest relations and the small values of  $\Delta C_P$  at  $T_c$  [4] and pressure derivatives  $dT_c/dP$  (see below).

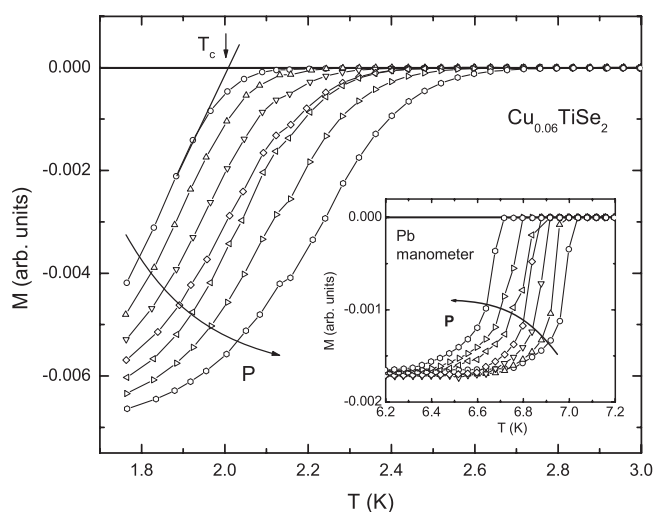
The features in TE for the samples with Cu concentration in the range  $0 \leq x \leq 0.04$  apparently correspond to the CDW transition, with slight differences in the characteristic temperatures probably being due to the width of the features observed in different measurements and adopted criteria for determining of  $T_{CDW}$  (see figure 6 below). The rather sharp change in  $\alpha_{300\text{ K}}(x)$  between  $x = 0.03$  and  $0.04$  (figure 3) hints at the possible existence of an additional phase line on the  $x$ - $T$  phase diagram and calls for additional studies of  $\text{Cu}_x\text{TiSe}_2$  by other techniques, including scattering. The evolution of  $\alpha_{100\text{ K}}(x)$  (figure 3) is consistent with crossing the composition of the CDW transition at this temperature, whereas  $\alpha_{50\text{ K}}(x)$  data suggest a gradual softening of the lattice on doping above  $x = 0.04$ . The fact that a clear feature near  $x \approx 0.03$  exists at all temperatures suggests that there may be a change in the nature of the compound as  $x$  increases through this value.

The origin of the step-like features in  $\alpha(T)$  of  $\text{Cu}_{0.08}\text{TiSe}_2$  and  $\text{Cu}_{0.1}\text{TiSe}_2$  samples (figure 2(c)) is not clear at this point. It should be mentioned that TE measurements on polycrystalline samples are potentially vulnerable to the morphology of the grains and grain boundaries and distribution of the grain orientation in anisotropic materials, but an extrinsic mechanism causing a step-like behaviour in  $\alpha(T)$  of single phase, polycrystalline, material is difficult to conceive. That said, TE measurements on *single crystals* would be instrumental for understanding of these complex materials.

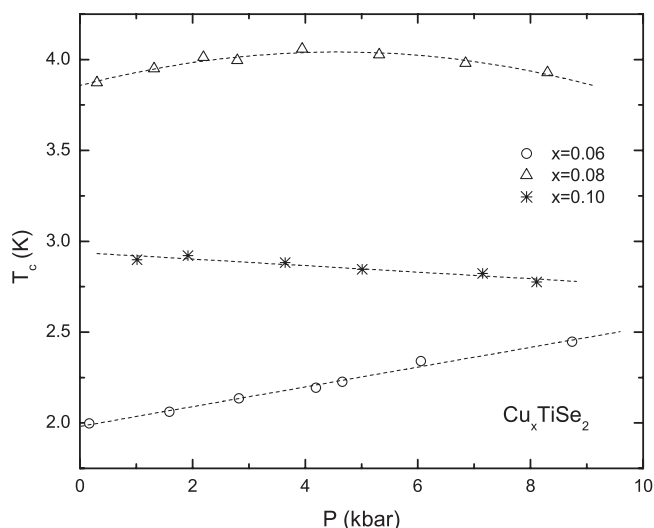
The observed features in the temperature-dependent thermal expansion for different Cu concentrations (step-like feature in  $\alpha_{300\text{ K}}$  versus  $x$  and change of sign of  $\Delta\alpha$  at  $T_{CDW}$ ) would be consistent with a change in the sample and nature of CDW transition as we cross from low doping ( $x \leq 0.03$ ) to intermediate doping ( $0.04 < x < 0.08$ ). For higher Cu intercalation ( $x \geq 0.08$ ) a new feature in  $\alpha(T)$  appears, that is not associated with any line in the initial phase diagram [4] and may point to possible structural distortion in highly Cu-intercalated samples at temperatures  $\sim 160$  K, or may even be related to the nearby Cu solubility limit ( $x = 0.11 \pm 0.01$ ) [4].

### 3.2. Superconductivity under pressure

An example of magnetization measurements under pressure (for  $\text{Cu}_{0.06}\text{TiSe}_2$ ) is shown in figure 4. For this sample,  $T_c$  increases under pressure without a clearly detectable change in the superconducting transition width of the sample or in the Pb manometer. Evolutions of the superconducting transition temperatures for three samples,  $\text{Cu}_{0.06}\text{TiSe}_2$ ,  $\text{Cu}_{0.08}\text{TiSe}_2$ , and  $\text{Cu}_{0.1}\text{TiSe}_2$ , as a function of pressure are shown in figure 5. Each of the samples behaves differently under increasing pressure:  $T_c$  increases for  $x = 0.06$ , decreases for  $x = 0.1$ , and has non-monotonic behaviour with a broad maximum at around 4 kbar for  $x = 0.08$ . It is noteworthy that the effect of pressure on  $T_c$  of  $\text{Cu}_x\text{TiSe}_2$  is rather small,  $dT_c/dP \approx 0.054$  K kbar<sup>-1</sup> for  $\text{Cu}_{0.06}\text{TiSe}_2$  and  $dT_c/dP \approx -0.018$  K kbar<sup>-1</sup> for  $\text{Cu}_{0.1}\text{TiSe}_2$ . These differences are not surprising if compared with the  $T_c$  versus  $x$  behaviour at ambient pressure reported in [4]. The pressure data for the three samples can be approximately scaled with the same scaling factor ( $x/P \approx 5.6 \times 10^{-4}$  kbar<sup>-1</sup>) onto the superconducting ‘bubble’ of the ambient pressure  $x$ - $T$  phase diagram (figure 6). So, apparently, increases of pressure and Cu intercalation have a similar effect on the superconductivity of  $\text{Cu}_x\text{TiSe}_2$ . Although such a scaling is noteworthy as an empirical observation, it has to be pointed out that both lattice parameters of  $\text{Cu}_x\text{TiSe}_2$  increase with Cu intercalation [4]. This rules out the unit cell volume or any lattice parameter alone being a structural control parameter for the observed scaling of  $T_c$ .

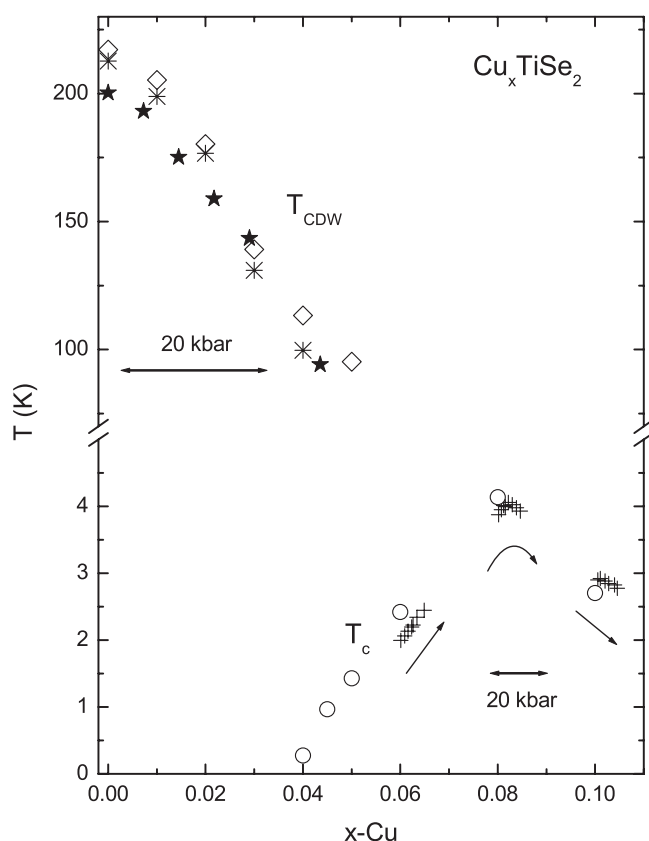


**Figure 4.** Temperature-dependent magnetization of  $\text{Cu}_{0.06}\text{TiSe}_2$  measured in 25 Oe applied magnetic field under pressures of 0.2, 1.6, 2.8, 4.2, 4.7, 6.1, and 8.7 kbar.  $T_c$  was defined as the onset of magnetization. The inset shows the Pb superconducting transition measured. The arrow shows the direction of the pressure increase.



**Figure 5.** Pressure-dependent  $T_c$  for  $\text{Cu}_{0.06}\text{TiSe}_2$ ,  $\text{Cu}_{0.08}\text{TiSe}_2$ , and  $\text{Cu}_{0.1}\text{TiSe}_2$  samples.

It seems enticing to check if the same scaling can be applied to the CDW transition. Figure 6 shows that change of  $T_{\text{CDW}}$  of the pure  $\text{TiSe}_2$  under pressure [13] can be scaled to the  $T_{\text{CDW}}(x)$  behaviour reported in [4] as well; however, the scaling factors for  $T_{\text{CDW}}$  and  $T_c$  differ by almost a factor of 3:  $1.5 \times 10^{-3}x \text{ kbar}^{-1}$  for  $T_{\text{CDW}}$  versus  $5.6 \times 10^{-4}x \text{ kbar}^{-1}$  for  $T_c$  (figure 6). If there were the same one-to-one correspondence between Cu intercalation and pressure in the  $0 \leq x \leq 0.1$  Cu concentration range, we would expect to observe a significantly (by almost a factor of 3) higher pressure response of  $T_c$ . This is consistent with pressure and Cu



**Figure 6.** Pressure-dependent  $T_c$  for  $\text{Cu}_{0.06}\text{TiSe}_2$ ,  $\text{Cu}_{0.08}\text{TiSe}_2$ , and  $\text{Cu}_{0.1}\text{TiSe}_2$  and  $T_{\text{CDW}}$  scaled on the  $x$ - $T$  phase diagram of  $\text{Cu}_x\text{TiSe}_2$  [4]. Open symbols are taken from in [4], asterisks ( $P = 0$ , thermal expansion) and crosses (magnetization under pressure) are from this work, and stars are data from [13]. Horizontal bars show the (different) scaling factors between  $x$  and pressure for  $T_{\text{CDW}}$  and  $T_c$ . Small differences in  $T_c(P = 0)$  between this work and published data are due to differences in  $T_c$  criteria used. Arrows indicate the direction of the pressure increase.

doping both affecting the density of states and degree of nesting in systematic and monotonic ways but by different mechanisms.

#### 4. Summary

Thermal expansion measurements on polycrystalline  $\text{Cu}_x\text{TiSe}_2$  samples confirmed the suppression of  $T_{\text{CDW}}$  by Cu intercalation and suggested that the  $x$ - $T$  phase diagram may be more complex than in the original publication [4]. These data raise the possibility that as Cu is added there is a change in the nature of the compound and perhaps of the CDW transition for  $x \geq 0.03$ . The pressure data for  $\text{Cu}_x\text{TiSe}_2$  samples ( $x = 0.06, 0.08, 0.1$ ) can be approximately scaled with the same scaling factor on the superconducting ‘bubble’ of the ambient pressure  $x$ - $T$  phase diagram; however, scaling of  $T_{\text{CDW}}(P)$  data for pure  $\text{TiSe}_2$  to the same phase diagram will require a significantly different scaling factor.

Both sets of measurements suggest that the mechanism of how the superconducting state emerges from the CDW state in  $\text{Cu}_x\text{TiSe}_2$  and the relevant control parameter for this evolution



of the ground state remain unclear, and additional experiments are required for a consistent physical picture.

### Acknowledgments

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