1. Introduction

2D transition metal (M) trichalcogenides MX₃ (X = S, Se, Te) have become an interesting platform to study the interplay between charge density wave (CDW) and superconductivity (SC). CDW are known to present in NbS₃ [1] and TaS₃ [2] whereas NbSe₃ exhibits SC on cooling below 2.1 K [3]. The competing interaction between the CDW state and SC in MX₃ is known to be sensitive with the application of pressure, such as in the case of NbSe₃, where SC can be induced as the CDW state is suppressed by pressure [4]. Among MX₃ system, ZrTe₃ has emerged as an intriguing compound to investigate, as it provides a rare example where the CDW and SC can coexist without any chemical or structural modifications. ZrTe₃ exhibits metallic behavior at room temperature, and shows both the presence of CDW at \( T_{\text{CDW}} \approx 63 \text{ K} \) and SC below \( T_C = 2 \text{ K} \) [5–7]. The SC was attributed to be a filamentary in nature with no diamagnetic signal in a small applied magnetic field [7].

Several attempts have been made to tune the interplay between CDW and SC in ZrTe₃, for example by intercalation, substitution and disorder. Upon intercalation of Cu, Ni and Ag, the filamentary SC of undoped ZrTe₃ turns into a bulk SC, with \( T_C \) of 3.8 K, 3.1 K and 5.1 K, respectively [8–10]. The CDW coexists with SC in CuₓZrTe₃ [8] while it is suppressed as the bulk SC appears in NiₓZrTe₃ [9]. Substitution of Te with Se in ZrTe₃−ₓSeₓ revealed the emergence of SC as the CDW is suppressed upon Se doping [11]. Disorder also can tune ZrTe₃ into bulk SC which is accompanied by the suppression of CDW [12].

Pressure is known to be a powerful way to tune the interaction between CDW and SC in ZrTe₃. Initial pressure study show the enhancement of \( T_{\text{CDW}} \) reaching a maximum of ~105 K at 1.1 GPa, while at the same time the filamentary SC disappears [13]. A dome-like behavior in \( T_{\text{CDW}} \) is observed at higher pressures up to 5 GPa, above which the CDW suddenly disappear and a bulk SC emerges, providing evidence for a pressure-induced re-entrant SC [14]. Raman spectroscopy studies suggest the occurrence of a structural phase transition accompanying the pressure-induced CDW to SC transition [15]. However, no such indication of a structural
phase transition was observed from x-ray diffraction (XRD) measurements up to 6 GPa [16]. Despite these high pressure investigations, previous studies were limited to pressures below 12 GPa. This aspect renders our understanding on what happens to the superconducting state of ZrTe3 at higher pressures, in particular whether the SC state will be suppressed or enhanced in the higher pressure regime remains unknown.

Here, we report the results of our study to investigate the evolution of SC in ZrTe3 up to ~33.3 GPa. We found that the superconducting temperature is increased on compression, and no sign of suppression of SC is observed up to the highest pressure of measurement of ~33 GPa. On compression around 21 GPa, we found an enhancement of SC reaching a maximum \( T_C \sim 7 \) K at \( \sim 28 \) GPa which remains relatively constant up to \( \sim 33 \) GPa.

2. Methods

The ZrTe3 single crystals were purchased from the 2D Semiconductors Company. The sample was crystallized to a bulk form with 1 mm in thickness and 5 \times 5 mm in size. Energy dispersive spectrum was employed to detect the composition of the sample. The obtained atomic ratio is Zr:Te = 1.298, which is close to the expected stoichiometric ratio. In order to determine one surface normal to the sample, single crystal XRD was measured with Cu Kα radiation using a PANalytical X-Pert Pro diffractometer, following a method by Jesche et al [17].

The resistivity data of single crystal sample at high pressure was measured in a diamond anvil cell made of Be–Cu non-magnetic alloy. The size of the diamond culet was 300 \( \mu m \) in diameter. Be–Cu gasket was initially pre-indented to a thickness of 35 \( \mu m \), then a hole of 280 \( \mu m \) was drilled using laser drilling system. A mixture of epoxy and cubic boron nitride (cBN) powder was pressed into the hole to form an insulating layer between the electrodes and the Be–Cu gasket. A hole of 120 \( \mu m \) in diameter was re-drilled in the cBN + epoxy gasket as a sample chamber. ZrTe3 single crystal was cut into a square of 50 \( \mu m \) in width with 10 \( \mu m \) in thickness. We used the van der Pauw four probe method to measure electrical resistance using platinum (Pt) foil as electrodes. In order to ensure a quasi-hydrostatic condition, we used silicon oil as a pressure-transmitting medium. Several ruby balls were loaded into the sample chamber as pressure calibrants [18].

High-pressure synchrotron powder XRD (\( \lambda = 0.6199 \) Å) was performed at room temperature at Beamline 12.2.2 in the Advanced Light Source at Lawrence Berkeley National Laboratory. The patterns were collected using a MAR 3450 type detector. Neon was used as a pressure transmitting medium and ruby balls as pressure calibrants for synchrotron XRD experiments. The DIOPTAS [19] program was used for image integrations and the Le Bail method was employed to fit the XRD data using the Fullprof program [20, 21]. First-principles calculations were performed using a Material Studio CASTEP module. The generalized gradient approximation was utilized for the exchange correlation potential [22].

3. Results and discussions

The XRD pattern of single crystal ZrTe3 is shown in figure 1. All the diffraction peaks match the (0 0 l) peaks belonging to the monoclinic ZrTe3 phase (PDF Card No. 802224) which indicates that the surface of the crystal is perpendicular to the \( c \)-axis with the plate-shaped surface parallel to the ab-plane. In figure 2(a), we show resistivity \( R(T) \) data obtained at various pressure points between 4 GPa and 33 GPa with the electric current applied on the crystal ab-plane. The resistivity data at 4.1 GPa shows a typical metallic behavior with a linear decrease in resistivity as the temperature is lowered. We observed an appearance of a broad peak at \( \sim 40 \) K which can be related to \( T_{\text{CDW}} \) as reported previously [13, 14]. Upon increasing pressure, this CDW state disappears and we observed a drop in resistance at \( 8.2 \) GPa, signaling a pressure-induced re-entrant SC [14]. The onset of SC still exists to the highest pressure of \( \sim 33 \) GPa.

Low temperature resistivity (2 K–10 K) of ZrTe3 collected at various pressures between 8 GPa to 33 GPa is shown in figure 2(b). The onset of SC at 8.2 GPa is 4.3 K which then increases to \( \sim 6 \) K at 15 GPa, above which it is relatively constant as the pressure is increased to 23 GPa. A slight difference in \( T_C \) compared with previous report [14] might be due to the difference in hydrostatic condition. On compression above 23 GPa, we observe a sudden increase of \( T_C \) from 6 K to 7 K at 27.7 GPa. Further compression until 33 GPa does not change \( T_C \). In figure 8(a), we show the evolution of the onset temperature of SC (\( T_C \), onset) as a function of pressure. Anomalous enhancement of \( T_C \) is observed on compression above \( \sim 21 \) GPa. It also can be seen that the maximum of \( T_C \) occurs at around 27.7 GPa.

The appearance of SC in ZrTe3 at high pressures (above 15 GPa) is further confirmed by our resistivity measurements under different applied magnetic fields, as shown in figure 3(a). Zero-resistance at 20.7 GPa, observed at zero magnetic field, is gradually lifted with increasing magnetic field, resulting in a decrease of \( T_C \). Superconducting state is almost fully suppressed by an application of magnetic field of 3.15 T (figure 3(a)). The upper critical field, \( H_{c2} \), determined

![Figure 1. XRD pattern of single crystal ZrTe3 collected at ambient condition.](image-url)
Using the onset of the resistivity drop ($T_c$, onset) are plotted in figure 3(b). Using the conventional one band Werthamer–Helfand–Hohenberg (WHH) model, the upper critical field at $T = 0$ K is given by

$$\mu_0 H_{c2}(0) = -0.693 T_C \times \left(\frac{d\mu_0 H_{c2}}{dT}\right)_T$$

[23], where \(\left(\frac{d\mu_0 H_{c2}}{dT}\right)_T\) is the initial slope at $T_C$. The value of \(\left(\frac{d\mu_0 H_{c2}}{dT}\right)_T\) is determined to be $-0.81(2)$ T K$^{-1}$, which leads to the value of $\mu_0 H_{c2}(0) = 3.1(2)$ T. The $H_{c2}$ versus $T$ curve was then fitted with the empirical expression based on the Ginzburg–Landau (GL) theory (e.g. [24]) which takes the form

$$\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

It can be seen that the data in figure 3(b) can be fitted relatively well using equation (1). The fitted value of $\mu_0 H_{c2}(0)$ is $4.5(1)$ T at 20.7 GPa. It is interesting to mention that a positive curvature close to $T_c$ is observed in a compressed ZrTe$_3$, which suggests a possible multiband superconducting pairing, similar to those observed in 2H–NbSe$_2$ and 2H–NbS$_2$ [25, 26]. From the value of $\mu_0 H_{c2}(0)$, the coherence length $\xi(0)$ can be estimated with Ginzburg–Landau formula $\mu_0 H_{c2}(0) = \Phi_0/(2\pi\xi(0)^2)$ where $\Phi_0 = 2.07 \times 10^{-15}$ Wb is the flux quantum. The estimated GL coherence length at 20.7 GPa is 8.6 nm, which is comparable to those observed in the intercalated ZrTe$_3$ single crystals [8–10]. We note that our derived value of $\mu_0 H_{c2}(0)$ is well below the Pauli limiting field for a singlet pairing of $\mu_0 H_P(0) = 1.847 T_C$ [27], i.e. 10.3 T for $T_C = 5.6$ K.

In order to investigate the possible correlation between structural properties and SC, we performed synchrotron XRD experiments under pressure up to 36.3 GPa. The collected XRD patterns are shown in figure 4(a). Due to the strong preferred orientation of the compressed ZrTe$_3$ sample, all XRD patterns were refined using the Le Bail method. It can be seen that the ambient crystal structure of ZrTe$_3$ (monoclinic space group) is stable under compression until ~23 GPa. On compression above 23 GPa, we observed the splitting of two peaks at $2\theta \sim 13^\circ$ and $17^\circ$, respectively, hinting a possible phase transition (indicated by asterisks in figure 4(a)). However, the splitting of these two peaks resembles what is observed in the patterns taken at the lower pressure region ($P < 15$ GPa), which suggests that ZrTe$_3$ still retains its monoclinic structure even above 25 GPa. We have attempted to index these new diffraction patterns in order to search for a possible crystal structure using indexing softwares, however the attempts always led to the same monoclinic structure. Recent high pressure studies on the isomorphic TiS$_3$ revealed an isostructural phase transition without any change in the...
space group under compression [28] which suggests that similar isostructural transition could also occurs in ZrTe3. Hence, we fitted the XRD patterns above 23 GPa using the same monoclinic phase, and found that the patterns can be fitted with an identical space group. Selected fitting results using the Le Bail method to the patterns at 1.4 and 25.2 GPa are shown in figure 4(b).

The derived unit cell volume of ZrTe3 as a function of pressure \( V(P) \) is shown in figure 5(a). The unit cell volume was fitted using the third-order Birch–Murnaghan (B–M) equation of state which takes the form [29, 30]

\[
P = \frac{3}{2} B_0 \left[ \frac{V_0}{V} \right]^2 \left[ 1 - \left( 1 - \frac{3}{4} B'_0 \left( \frac{V_0}{V} \right)^{\frac{1}{3}} \right) \right] \]

where \( V_0 \), \( B_0 \), and \( B'_0 \) are the unit cell volume, bulk modulus, and first-order derivative of the bulk modulus at zero pressure, respectively. The fitting to the whole \( V(P) \) data using B–M equation as in equation (2) yields \( V_0 = 237(3) \text{ Å}^3 \) and \( B_0 = 41(2) \text{ GPa} \), whereas the value of \( B'_0 \) are fixed to 4. The experimentally derived lattice parameters are plotted in figure 5(b). All lattice parameters gradually decrease with the application of pressure. The lattice \( c \) parameter decreases faster than other lattice parameters due to the weak van der Walls bonding along the crystal \( c \)-direction.

From figure 5(a), it can be seen that the fitting of the \( V(P) \) data using a single third-order B–M equation does not lead to a satisfactory result. The fitting results can be improved by considering two separate B–M equations, each of which is used to fit the data above and below 23 GPa (where the peak splitting occurs). However, the fitting parameters seem to be inconclusive given the lack of data points above 23 GPa. In order to better track the changes in the \( V(P) \) curve derived from the XRD data, we transformed the \( V(P) \) data into an Eulerian stress–strain \( F(f) \) diagram based on the following formula [31–33]

\[
F = P\left[ 3f(1 + 2f)^{\frac{5}{2}} \right]^{-1},
\]

Figure 4. (a) Synchrotron XRD patterns of ZrTe3 collected at various pressures up to 36.3 GPa. (b) Representative refinement of the patterns collected at 1.4 GPa and 25.2 GPa.

Figure 5. (a) Unit cell volume of ZrTe3 as a function of pressure. Solid lines are fits to the data based on third-order Birch–Murnaghan formula as in equation (2). Dashed line represents the calculated pressure-dependence of the unit cell volume based on geometry optimizations. (b) Pressure dependence of the experimental lattice parameters (a)–(c).
where \( f \) is the Eulerian strain, \( F \) is the corresponding normalized pressure, and \( V_0 \) is the volume at ambient pressure as determined from the B–M fitting. The values of \( B_0 \) and \( B_0' \) can be determined from the relationship between \( f \) and \( F \) as described

\[
F = B_0 + \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{-2/3} - 1 \right].
\] (4)

From equation (5), it can be seen that \( F(f) \) curve will be linear and the values of \( B_0 \) and \( B_0' \) can be determined from the intercept as \( F \to 0 \) and the slope, respectively. In the case of structural transformation, even a subtle one, the \( F(f) \) plot will show a change in slope [33].

The \( F(f) \) plot of \( ZrTe_3 \) is presented in figure 6. Different than the \( V(P) \) data, the \( F(f) \) plot shows a clear change in slope above Eulerian strain value of 0.08, which corresponds to \( P \sim 18 \text{ GPa} \). This change in slope indicates a change in mechanical properties which might be related to a subtle structural transformation. Linear fitting to the two set of data (\( f < 0.08 \) and \( f > 0.08 \)) yields \( B_0 = 30.9(9) \text{ GPa} \) and \( B_0' = 8.1(3) \) (for the phase below 18 GPa), and \( B_0 = 44(3) \text{ GPa} \) and \( B_0' = 3.6(4) \) (for the phase above 18 GPa). Comparing this result with the pressure-dependence of \( T_C \) (shown in figure 8(a)), it can be seen that there is a correlation between the anomalous enhancement of \( T_C \) at high pressures and the change in the structural properties. \( T_C \) of \( ZrTe_3 \) begins to enhance anomalously on compression above \( \sim 21 \text{ GPa} \) (indicated by arrow in figure 8(a)), and the mechanical properties, as observed from the \( F(f) \) plot, reveal a change in slope above \( \sim 18 \text{ GPa} \). This indicates that the anomalously enhancement of \( T_C \) in \( ZrTe_3 \) on compression above \( \sim 21 \text{ GPa} \) has a structural origin. We note that the difference in the transition pressure between these two experimental results are mostly due to the different hydrostatic conditions of the pressure mediums used (Neon for XRD experiments and silicon oil for high pressure electrical transport measurements).

In order to better understand the evolution of SC, we performed first-principles calculations to study the effects of pressure to the electronic structure of \( ZrTe_3 \) under pressure. Here, we will only focus on the effects of pressure to the density of states at the Fermi level. Geometry optimizations of the lattice parameters and all the atomic coordinates are performed for each hydrostatic pressure point. The calculated unit cell volume at 1.4 GPa (224 Å\(^3\)) is only 2.1% smaller than the experimental value (228 Å\(^3\)). The theoretical bulk modulus is 52.1 GPa (shown as a dashed line in figure 5(a)), which is somewhat smaller than the experimentally derived bulk modulus using the B–M equation, i.e. 41 GPa. Such deviations are known to exist in generalized gradient approximation calculations.

The total and partial density of states of \( ZrTe_3 \) calculated at 8 and 21 GPa are shown in figure 7. It can be seen that the total density of states at the Fermi level \( (N(E_F)) \) is dominated by the Te 5p state mixed with the Zr 4d state, consistent with the previous report [34]. Increasing pressure from 8 GPa to 21 GPa, increases hybridization and bandwidth as seen by the reduction of the density of states above and below \( E_F \). Interestingly, \( N(E_F) \) increases gradually with increasing pressure due to the increases of Zr 4d and Te 5p states at \( E_F \). The change of the Zr 4d states at \( E_F \) is more pronounced than that of the Te 5d states, which suggests that the SC may be hosted by the Zr 4d states inside the \( ZrTe_3 \) prisms.

The calculated total density of states at the Fermi level \( (N(E_F)) \) as a function of pressure is shown in Figure 8(b). It can be seen that \( N(E_F) \) of \( ZrTe_3 \) shows a strong pressure dependence. It begins to increase at around 5 GPa, where the bulk SC initially appears under pressure [14]. \( N(E_F) \) keeps increasing under compression, reaching a maximum at about

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**Figure 6.** Normalized pressure \( F \) versus Eulerian strain \( f \) of \( ZrTe_3 \) derived with the volume at ambient pressure \( (V_0) \) derived from the fitting of the \( V(P) \) data using third-order B–M equation. Solid lines are fits to the data using equation (5).

**Figure 7.** (a) Calculated total density of states of \( ZrTe_3 \) at 8.2 GPa and 20.8 GPa, and the partial density of states for Zr (b) and Te (c) atoms at 8.2 GPa and 20.8 GPa. Vertical line indicates the Fermi energy.
27 GPa, above which it gradually decreases as the pressure is increased.

Based on the McMillan theory [35], the increase in the superconducting temperature is mostly contributed by the increase in the density of states at the Fermi level and the decrease in the characteristic phonon frequency. Previous Raman spectroscopy study up to 4 GPa revealed that the characteristic phonon frequency tends to increase under pressure [15], however no Raman spectroscopy studies on ZrTe3 at higher pressures have been reported to date. Under the assumption that the phonon frequency of ZrTe3 increases at higher pressure, the results shown in figures 8(a) and (b) suggest that the enhancement of $T_C$ in ZrTe3 under compression can be explained by the increase in $N(E_F)$. Therefore, it appears that the increase in $N(E_F)$ is the dominant contribution to the increase of $T_C$ in ZrTe3 under pressure. It would be of interest to investigate the Raman spectroscopy experiments on ZrTe3 at higher pressure to investigate the characteristic phonon frequency. It would also be beneficial to calculate the phonon density of states of ZrTe3 under pressure.

4. Conclusion

We have studied the evolution of SC in ZrTe3 at high pressures up to 33 GPa. With increasing pressure, $T_C$ raises from ~4 K reaching a maximum value of 7.1 K at ~28 GPa, above which $T_C$ remains constant up to 33 GPa. We found no sign of obvious structural phase transition up to 36 GPa, however a change in mechanical properties was observed on compression above ~18 GPa, which seems to correlate with the anomalous increase in $T_C$ above 21 GPa. Density of states at the Fermi level increases gradually with pressure which explain the enhancement of SC in ZrTe3 at high pressures.

Acknowledgments

We thank Dr Zhiqiang Chen (HPSTAR) for the helpful discussions. The authors acknowledge the use of beamline 12.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The authors would also like to thank the reviewers for their comments and suggestions which improved the quality of the paper.

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