Coexistence of superconductivity and charge-density wave in the quasi-one-dimensional material HfTe$_3$

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We present the first experimental evidence for metallicity, superconductivity (SC) and the co-existence of charge density waves (CDW) in the quasi-one-dimensional material HfTe$_3$. The existence of such phenomena is a typical characteristic of the transition metal chalcogenides however, without the application of hydrostatic pressure/chemical doping, it is rare for a material to exhibit the co-existence of both states. Materials such as HfTe$_3$, can therefore provide us with a unique insight into the relationship between these multiple ordered states. By improving on the original synthesis conditions, we have successfully synthesised single phase HfTe$_3$ and confirmed the resultant structure by performing Rietveld refinement. Using low temperature resistivity measurements, we provide the first experimental evidence of SC at ~1.4 K as well as a resistive anomaly indicative of a CDW formation at ~82 K. By the application of hydrostatic-pressure, the resistivity anomaly shifts to higher temperature. The results show that HfTe$_3$ is a promising new material to help study the relationship between SC and CDW.

The coexistence of superconductivity (SC) and charge- and/or spin-density waves (CDW and/or SDW) is fundamental to our understanding behind the mechanism of high-$T_c$ SC and is one of the most significant challenges in condensed matter physics. CDWs favor low dimensionality and materials such as the layered/chain-like transition metal di/trichalcogenides (MQ$_2$/Q$_3$) (where M = groups IV–VI transition metals and Q = sulfur, selenium and tellurium) have been collectively studied for such phenomena. Examples include TaS$_2$ and NbS$_3$, which exhibit CDWs and TaSe$_2$, which becomes a SC below 2.1 K. Studies of SC in the MQ$_2$/Q$_3$ family often support a competitive relationship between the SC and CDW states; SC can be induced/enhanced by the suppression of the CDW. This is typically achieved by the application of hydrostatic pressure such as in the case of NbSe$_2$ and NbSe$_4$ or by chemical doping for Na$_x$TaS$_2$ and Cu$_x$TiSe$_2$. However, it is rare that the materials without chemical/physical modification exhibit the co-existence of both states. ZrTe$_3$ is a material which shows the coexistence of a CDW at ~63 K and filamentary SC at 2 K as does NbSe$_2$. In the case of ZrTe$_3$, by the application of pressure, intercalation of Cu$^{2+}$ and Ni$^{2+}$ or the substitution of Se at the Te site, the CDW can be suppressed and bulk SC induced at ~5 K. The electronic structure of ZrTe$_3$ is unique amongst the MQ$_3$ family owing to the strong contribution of the Te–Te p$_{\sigma}$ band at the vicinity of the Fermi level, therefore the inter-chain interactions affects the electronic structure as well as the physical properties. Similar cross-chain interactions are absent in other members of the MQ$_3$ family (when M = group IV transition metal and Q = S/Se). Of the MTe$_3$ materials, HfTe$_3$ is the only other material expected theoretically. There are no known reports for TiTe$_3$ or Nb/TaTe$_3$. However, by using the reaction conditions outlined by Brattås et al., we found that the successful synthesis of HfTe$_3$ was reproducible. Therefore, although theoretical band structure calculations have predicted HfTe$_3$ to be metallic there is currently no experimental confirmation. As far as the authors are aware, the available experimental data for HfTe$_3$ include the original structural characterization and the determination of its basic magnetic properties (temperature-independent diamagnetism). In addition, it has been recently reported by scanning tunneling...
spectroscopy that Hf/HfTe5/HfTe3 films exhibited a superconducting gap-like spectra22. HfTe3 and ZrTe3 are iso-structural materials whose features raise the possibility that HfTe3 may also exhibit the coexistence of SC and CDW state. Therefore, it would be an important task to synthesize the high quality bulk compound, and to explore the aforementioned electrical phenomena.

By modifying the original synthesis conditions18,19, polycrystalline HfTe3 samples have been successfully synthesized. The crystal structure has been analyzed using Rietveld refinement and the first experimental evidence of metallicity in this material is reported. The resistivity data exhibits an anomaly suggestive of a CDW formation at ~82 K and subsequently zero resistivity below 2 K. By the application of hydrostatic pressure, the resistivity anomaly shifts to higher temperature. In addition, we note that HfTe3 is highly air-sensitive, where the behaviour of ρ-T characteristics changes from metallic to insulating upon exposure in air (See Supplementary information).

Results and Discussion

Key requirements to synthesise single phase HfTe3. Suitable reaction conditions to produce single phase HfTe3 crucially depend on the maximum reaction temperature19. During this investigation it has been found that a slow cooling rate is also a key requirement. In brief, the favoured phase was HfTe2 at a higher temperature range (≥ 530 °C) and HfTe5 at lower temperature regions (≤ 470 °C). As reported by Brattås et al., we confirmed that the sintering condition of ca. 500 °C indeed favours the growth of the HfTe3 phase18. However, when rapid cooling from 500 °C (e.g. quenching in water) was applied19 the majority phase became HfTe2 together with unreacted tellurium. On the other hand, when slow cooling was performed (approx. −0.25 °C/h) until 470 °C after which the ampoules were cooled to room temperature at a rate of approx. −5 °C/h, then single phase HfTe3 could reproducibly be synthesised. The results suggest that HfTe3 primarily forms by reaction with the tellurium vapour upon cooling. If the reaction vessel is quenched, the solidification of the tellurium prevents its uptake and HfTe3 becomes the preferred phase. Namely, it is found that HfTe3 is the least thermodynamically stable phase within the Te-rich Hf alloys and as a result in order to inhibit the formation of trace amounts of HfTe5/HfTe2, it is necessary to control precisely both the sintering temperature and the cooling rate.

Crystallographic analysis. Figure 1(a) shows the powder X-ray diffraction (PXRD) result for HfTe3 together with the result of the Rietveld refinement using ZrSe3 as a reference model23, where the result was consistent with the monoclinic crystal symmetry (space group P21/m). Figure 1(b) represents the crystal structure
of HfTe₃ which is the pseudo-one-dimensional (1D) structure. As seen in Fig. 1(b), MQ₆ trigonal prismatic units propagate along the b-axis resulting in chain-like anisotropic crystal growth. By projection down the b-axis it can be clearly seen how the chains are bonded together by Van der Waals forces (see Fig. 1(c)). Reasonable values of $R_{wp} = 8.47\%$, $R_p = 6.60\%$ and $\chi^2 = 1.544$ were obtained. Refined lattice parameters of HfTe₃, $a = 5.8797(9) \text{ Å}$, $b = 3.8999(9) \text{ Å}$, $c = 10.0627(3) \text{ Å}$ agreed with the previously reported values. On the other hand, the angle $\beta = 98.38(8)°$ showed a slight expansion from the originally reported angle of $\beta = 97.98°$. The refinement results are summarized in Table 1. It was confirmed from X-ray fluorescence (XRF) results that the composition ratio of our HfTe₃ was Hf:Te = 26:74 (at%).

Table 1. Crystallographic data for HfTe₃. *Isotropic displacement factors were constrained during refinement. †Refer to Fig. 1(c).

Coexistence of SC and CDW. Resistivity of non-air-exposed HfTe₃ reproducibly exhibited metallic behaviour in the temperature range between 0.3 and 300 K as shown in Fig. 2(a). The residual resistivity ratio (RRR) defined as $\rho(275 \text{ K})/\rho(4 \text{ K})$ is ~2.4, which is lower than that of single crystal ZrTe₃ but is larger than that of polycrystalline-ZrTe₃ in which the lower RRR value is thought to arise from strong grain boundary effects. Therefore the influence of grain boundaries is likely to play a role in the reduction of RRR. The inset of Fig. 2(a) shows the temperature derivative of the resistivity $d\rho/dT$ and reveals a resistivity anomaly at 82 K assumed to be indicative of a CDW formation, where the CDW formation temperature $T_{\text{CDW}}$ is defined as the temperature at which $d\rho/dT$ exhibits a minimum. At $T_{\text{CDW}}$ the CDW gap is developed and the resistance anomaly appears owing to a reduction in the density of states at $E_F$ due to the CDW formation. Below 2 K, the resistivity showed a sharp drop exhibiting a SC transition at 1.8 K ($T_{\text{c onset}}$) and reached zero ($T_{\text{c zero}}$) at 1.45 K as can be clearly seen in Fig. 2(b). By increasing the applied current, a broadening of the SC transition was observed and it was accompanied by a downward shift in $T_{\text{c onset}}$ and $T_{\text{c zero}}$, whereas the normal state resistivity remains unchanged. The result suggests a weakening in the SC state as well as a decoupling of the Josephson junctions between individual SC grains of the polycrystalline material. I–V characteristics measured at $T > T_{\text{c}}$ revealed ohmic and non-ohmic behaviour, respectively. N.B. In the present study, we observe that HfTe₃ shows a rapid weakening of its metallic state within minutes of exposure in air (see Supplementary Fig. S1). This is likely the result of an insulating layer (such as tellurium oxides) forming around the individual grains of the polycrystalline material. The results emphasize that if one is to observe the intrinsic properties of HfTe₃ any measurements must be conducted in the absence of air.

| Crystal system | Monoclinic | No. Observations | 7500, |
|----------------|-----------|------------------|------|
| Space group    | P2₁/m (No. 11) | 31               |      |
| $a$ (Å)        | 5.8797 (9) | $R_{wp}$        | 0.0847 |
| $b$ (Å)        | 3.8999 (9) | $R_p$           | 0.066  |
| $c$ (Å)        | 10.0627 (3) | Goodness of fit, $\chi^2$ | 1.544 |
| $\beta$ (°)    | 98.38 (8)  | Temperature (K)  | 295 K |
| V (Å³)         | 228.28 (2) |                  |      |
| Z              | 2         |                  |      |
|               |            | Hf: 2e (x, 1/4, z) | Te(1): 2e (x, 1/4, z) |      |
| x              | 0.2590 (7) | x                | 0.7339 (7) |
| z              | 0.6881 (2) | z                | 0.5674 (3) |
| $100 \times U_{\text{iso}}$ (Å²) | 0.484 | $100 \times U_{\text{iso}}$ (Å²) | 0.484 |
| Occ            | 1         | Occ              | 1     |
|               |            | Te(2): 2e (x, 1/4, z) | Te(3): 2e (x, 1/4, z) |      |
| x              | 0.4173 (7) | x                | 0.9058 (6) |
| z              | 0.1625 (9) | z                | 0.1638 (3) |
| $100 \times U_{\text{iso}}$ (Å²) | 0.484 | $100 \times U_{\text{iso}}$ (Å²) | 0.484 |
| Occ            | 1         | Occ              | 1     |
| Selected bond lengths (Hf-Te) (Å) | Selected bond lengths (Te-Te) (Å) |      |
| Hf - Te(1) x₂ (b₁)† | 3.074 (6) | Te(2) - Te(3) x₁ (b₆)† | 2.870 (13) |
| Hf - Te(1) x₁ (b₂)† | 3.106 (8) | Te(2) - Te(3) x₁ (b₇)† | 3.010 (13) |
| Hf - Te(1) x₁ (b₃)† | 3.106 (6) |                    |      |
| Hf - Te(2) x₂ (b₄)† | 3.062 (7) |                    |      |
| Hf - Te(3) x₂ (b₅)† | 2.843 (6) |                    |      |

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| Hf - Te(1) x₁ (b₃)† | 3.106 (6) |                    |      |
| Hf - Te(2) x₂ (b₄)† | 3.062 (7) |                    |      |
| Hf - Te(3) x₂ (b₅)† | 2.843 (6) |                    |      |
Behaviour under high-pressure. By the application of hydrostatic pressure ($P$), the resistivity anomaly gradually shifted to higher temperatures up to $\sim 99$ K for $P$ approaching 1 GPa as shown in Fig. 3. Similar behaviour has been reported for ZrTe$_3$ where in the case of an application of $P \leq 2$ GPa the $T_{\text{CDW}}$ was increased and the SC suppressed. At $P \geq 5$ GPa the CDW was fully quenched and gave way to reemergent SC, where $T_c$ increased to $\sim 4.5$ K when $P \sim 11$ GPa$^{15}$. In addition, in the case of HfTe$_5$, SC appeared by applying $P \sim 5$ GPa and a maximum $T_c$ of 4.8 K was attained by applying at $P \sim 20$ GPa$^{25}$. This suggests the possibility that HfTe$_3$ is likely to follow the same pattern as other members of the group IV-MTeX alloys. Namely by further application in pressure, it is expected that the $T_{\text{CDW}}$ will eventually be suppressed and $T_c$ will be enhanced.
Electronic structure. Studies regarding the electronic structure of HfTe₃ are limited, but the issue is briefly reported by Felser et al. who determined an electronic structure similar to that of ZrTe₃, i.e. a metallic state resulting from a large contribution of the Te p-bands at the Fermi level. These characteristics are supported by later density of states (DOS) calculations. ZrTe₃ exhibits a multi-component Fermi surface with contributions from the Te forming quasi 1D electronic sheets at the boundary of the Brillouin zone and from the Zr a 3D-hole character sheet around the Γ point. The resultant nesting characteristics at the Fermi surface have been determined to be responsible for the CDW formation in ZrTe₃. If one considers the iso-structural/electronic relationship between HfTe₃ and ZrTe₃, it is likely that similar interchain interactions between neighbouring Te(2) and Te(3) atoms (see Fig. 1(c)) play a dominant role in the metalllicity of HfTe₃ which in turn would give rise to the similar Fermi surface with nesting features reported for ZrTe₃. However, it cannot be categorically asserted that the observed resistivity anomaly is due to a CDW formation from our results only. As in the case of ZrTe₃, it would be necessary to confirm any coincidental low-temperature lattice distortions as well as to observe the features of the Fermi surface around the temperature of the anomaly. However the similarities between HfTe₃ and ZrTe₃ in the electronic structure as well as the results of the temperature/pressure dependence of ρ are strong indication that the observed resistivity anomaly for HfTe₃ is indeed the result of a CDW formation.

Conclusion

In summary, we have established a reproducible synthesis method for high-quality polycrystalline HfTe₃ and showed that it is an acutely air-sensitive material. By using high-quality HfTe₃ we found that the quasi-1D HfTe₃ is a novel SC with Tₘ = 1.4 K, and the SC state coexists with the CDW state which appears at T_{CDW} = 82 K. Furthermore, we provided the first accurate crystallographic data by Rietveld refinement of the PXRD of HfTe₃.

Methods

Single-phase polycrystalline HfTe₃ samples have been prepared using standard chemical vapour transport techniques: Ground mixtures of a 1:3 molar ratio of powdered Hf and Te were sealed in silica ampoules under a vacuum of c.a. 3 mTorr using a rotary pump. The ampoules were heated in a box furnace using the reaction procedure described in the results and discussion. To prevent exposure to air, all sample preparation was conducted in an argon filled glovebox.

PXRD was carried out using a Rigaku Smartlab diffractometer in flat plate geometry with a Cu Kα radiation (λ = 1.54056 Å). Diffraction data were typically collected for 5° ≤ 2θ ≤ 80° with a 0.01° step size with scan times of 3 hours. Rietveld refinement was performed using the GSAS software package via the EXPGUI interface. XRF analysis was performed using a JEOL JSX 1000 S ElementEye.

Resistivity measurements were performed on cold-pressed pellets using a standard four-terminal setup. Measurements for sample #A were performed between 0.3 and 300 K using an Oxford Instruments 3He cryostat, data were collected by an AC method using a low-noise amplifier and two lock-in amplifiers. Measurements for sample #B were performed by a DC method between 0.3 K and 15 K using a Quantum Design PPMS equipped with an adiabatic demagnetization refrigerator. The resistivity for Samples #C and #D were also measured by a DC method between 2 and 300 K using a closed cycle helium refrigerator. High-pressure resistivity measurements (up to 1 GPa) were performed using a BeCu/NiCrAl clamped piston-cylinder cell using Daphne 7373 as the fluid pressure transmitting medium with Pb employed as a manometer.

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**Author Contributions**
S.J.D. and N.M. designed, performed the experiments and analysed the experimental data and wrote the manuscript. A.Y. helped with the sample synthesis. K.T., M.N., S.W. I.T. and H.T. helped collect the low temperature resistivity data at $T < 2$ K. R.T. helped collect the XRF data.

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