Drastic Suppression of CDW (Charge Density Wave) by Pd Addition in TiSe₂

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Abstract
TiSe₂ is a known topological semi-metal (TSM) having both the semi-metallic and topological characters simultaneously along with the charge density wave (CDW) at below 200 K. In the current short article, we study the impact of Pd addition on CDW character of TiSe₂ and the possible induction of superconductivity at low temperatures. Bulk samples of TiSe₂ and Pd₀.₁TiSe₂ are synthesized by solid-state reaction route, which are further characterized by powder X-ray diffraction (PXRD) and field emission scanning electron microscopy (FESEM), respectively, for their structural and micro-structural details. The vibrational modes of both samples are being analyzed by Raman spectroscopy, showing the occurrence of both A₁g and E₉ modes. CDW of pure TiSe₂ seen at around 200 K in electrical transport measurements in terms of sharp semi-metallic to metallic transition peak with hysteresis in cooling/warming cycles is not seen in Pd₀.₁TiSe₂ and rather a near metallic transport is seen down to 2 K. Although superconductivity is not seen down to 2 K, the CDW transition is seemingly completely suppressed in Pd₀.₁TiSe₂. It is clear that Pd addition in TiSe₂ suppresses CDW drastically. Trials are underway to induce superconductivity in Pd-added TiSe₂. Density functional theory (DFT) calculations show primary evidence of suppression of CDW by addition of Pd in TiSe₂ due to an increase in the density of states.

Keywords: Charge density wave · Structural details · Raman spectroscopy · Electrical transport · Density of states

1 Introduction

The charge density wave (CDW) is an exotic phase of the quantum matter and is considered to be a symmetry-broken state of the same. This interesting electronic phase contains the spatially periodic variation in the density of conduction electrons, which frequently results in a dramatic renormalization of the electronic spectrum, including the appearance of energy gaps [1–3]. TiSe₂ is one of the extensively studied CDW materials, which is a member of the family of Group IV transition metal dichalcogenides (TMDCs). TMDCs contain covalently bonded trilayers in which the transition metal layer is in the middle of two chalcogen layers [4–6]. These trilayers are stacked and held together by weak Van der Waals forces [7–9].

Doped TiSe₂ shows a variety of properties as the same shows the Kondo effect on doping of 3d transition elements due to the presence of spin-flip centers in the TiSe₂ unit cell [10]. The electronic state of TiSe₂ is debatable as it is reported to have one of two typical states: either a semi-metal [11] or a semi-conductor [12] with a modest indirect gap. TiSe₂ shows CDW transition below 200 K, with no intermediate incommensurate phase [13, 14]. More interestingly, TiSe₂ is found to show superconductivity with doping of Cu or Pd atoms, which is accompanied by suppression of CDW [15, 16]. Intercalation and chemical substitution are the most suited routes to alter the electron counts, which further adjust the CDW transition in TiSe₂ [15, 16]. Here, we present the drastic suppression of CDW in 1 T-TiSe₂ caused by doping with electrons through intercalation of Pd in TiSe₂. Density functional theory (DFT) is a very promising tool in predicting and confirming material properties by computational simulations [17]. We have calculated the band structure and density of states for pure and Pd-added
In this short letter, we report the synthesis of polycrystalline Pd$_{0.1}$TiSe$_2$. The synthesized sample is examined in the context of phase purity and elemental composition through XRD and energy-dispersive X-ray analysis (EDAX) techniques, respectively. Raman modes are also observed for TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ through Raman spectroscopy. The signature feature of TiSe$_2$, i.e., CDW, is found to be marginal or nearly non-existent in Pd$_{0.1}$TiSe$_2$. The characteristic hysteresis in the cooling and warming cycle observed earlier [18] in $\rho$-$T$ measurements is suppressed in Pd$_{0.1}$TiSe$_2$. Furthermore, we present primary evidence of suppression of CDW by the addition of Pd in TiSe$_2$ due to an increase in the density of states.

2 Experimental

TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline samples were synthesized utilizing a simple self-flux technique as reported in ref. 18. Ti (99.99%), Se (99.99%), and Pd (99.99%) powders were taken in stoichiometric proportions and were completely ground in an argon-filled MBRAUN glove box. The acquired mixed powders were compressed into a rectangular pellet using a hydraulic press, and it was then vacuum-encapsulated in a quartz tube at around 5 x 10$^{-5}$ Torr vacuum. The vacuum-encapsulated samples were put into PID controlled muffle furnace and were heat-treated as per the detailed protocol given in ref. 18. For clarity, the schematics for both stages of the polycrystalline TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ synthesis process are shown in Fig. 1(a, b).

Rigaku Miniflex II X-ray diffractometer fitted with Cu-Kα radiation of wavelength 1.5418 Å is used to record XRD pattern for the structural analysis and phase purity determination. Rietveld refinement of PXRD patterns is performed using Fullprof software, and unit cells are extracted using VESTA software, which utilizes refined parameters from Rietveld analysis. Zeiss EVO-50 FESEM is used to determine surface morphology and EDAX measurement. Raman spectra of bulk TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ are taken at room temperature using the Jobin Yvon Horiba T64000 Raman Spectrometer for a wave number range of 100–350 cm$^{-1}$. The magneto-transport measurements of the produced TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline sample were performed utilizing the Quantum Design Physical Property Measurement System (QD-PPMS), with a conventional four-probe approach.

3 Results and Discussion

The PXRD pattern of synthesized TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline samples is shown in Fig. 2(a). The PXRD patterns of synthesized TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline samples are well-fitted with the parameters of a trigonal crystal structure with P-3m1(164) space group. All of the peaks can be indexed with their respective planes in the applied unit cell parameters, suggesting that the synthesized sample is phase pure and visibly no impurity is present in the samples. The parameter of the goodness of fit, i.e., $\chi^2$, is found to be 5.63 and 4.34 for TiSe$_2$ and Pd$_{0.1}$TiSe$_2$; these values are in the acceptable range indicating the quality of Rietveld refinement of PXRD data. The Rietveld-refined unit cell parameters are $a=b=3.549(2)$Å, $c=6.011(4)$Å and $a=b=3.581(2)$Å, $c=5.972(4)$Å respectively for TiSe$_2$ and Pd$_{0.1}$TiSe$_2$. The lattice parameters of Pd$_2$TiSe$_2$ differ from pure TiSe$_2$ as both the $a$ and $b$ parameters are increased with a slight decrement in the $c$ parameter. This shows that the Pd intercalation in the TiSe$_2$ unit cell results in contraction along the $c$ axis, with a slight expansion along the $ab$ plane. These results are in agreement with ref. 16 on Pd-added TiSe$_2$. Crystallographic information files (CIF) obtained from Rietveld refinement are processed in VESTA software to draw unit cells of synthesized samples and the same is shown in Fig. 2(b). It is obvious from unit cells that the investigated TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline sample displays a layered structure separated by the
The presence of the Van der Waals gap provides ample opportunity to intercalate foreign atoms in the TiSe$_2$ unit cell. In Fig. 2(b), Pd atoms in Pd$_{0.1}$TiSe$_2$ are shown to reside in the Van der Waals gap of TiSe$_2$ as Pd does not substitute Ti in the same.

Figure 3(a) exhibits the FESEM image of the synthesized Pd$_{0.1}$TiSe$_2$ polycrystalline sample. The FESEM image shows the presence of grains, which are separated by grain boundaries confirming the polycrystalline nature of the synthesized sample. Figure 3(b) shows the bar chart of the elemental composition of the synthesized polycrystalline sample Pd$_{0.1}$TiSe$_2$. EDAX measurements confirm the presence of Pd atoms, which shows that the same is successfully intercalated in the TiSe$_2$ unit cell. All the constituent elements viz. Pd, Ti, and Se are found to be in close proximity to stoichiometric ratios. The FESEM details of pristine TiSe$_2$ are reported earlier in ref. [18].

Raman spectra of TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline samples are recorded at room temperature and the same is shown in Fig. 4. Raman modes are observed at 150 cm$^{-1}$, 255 cm$^{-1}$, and 155 cm$^{-1}$, 250 cm$^{-1}$, respectively for pure TiSe$_2$ and Pd$_{0.1}$TiSe$_2$. These vibrational modes are identified as the $A_{1g}$ and $E_g$ modes, and are in agreement with the prior study on the 1 T phase of TiSe$_2$ [19]. The schematic of the observed vibrational modes is given in the inset of Fig. 4. The $E_g$ mode indicates a doubly degenerate phonon mode in which the Se atoms move along the in-plane directions, and the $A_{1g}$ mode represents the phonon mode in which two Se atoms move along the out-of-plane directions of TiSe$_2$. Raman modes are observed to be slightly shifted for Pd$_{0.1}$TiSe$_2$ as compared to pure TiSe$_2$ due to the intercalation of Pd atoms, which results in a change in unit cell parameters. The shift in Raman modes also confirms the intercalation of Pd atoms in the TiSe$_2$ unit cell in Pd$_{0.1}$TiSe$_2$. 
Figure 5(a-c) show the resistivity versus temperature ($\rho$-$T$) measurement results of synthesized TiSe$_2$ and Pd$_{0.1}$TiSe$_2$ polycrystalline samples. TiSe$_2$ is found to show an intriguing anomaly in the temperature range of 150 to 200 K due to the ordering of charge carriers. This charge carrier ordering occurs due to the presence of the CDW phase in pure TiSe$_2$, and is a well-known phenomenon of the same [20–23]. Both warming and cooling data show a hysteresis in CDW, showing the same to be a first-order phase transition. TiSe$_2$ exhibits a dual electronic phase as seen in Fig. 5(a), as the temperature is lowered; the insulating phase begins to take precedence over the metallic phase. The metallic phase remains present despite the insulating phase being highest at CDW, and this presence of two electronic phases causes hysteresis in the warming and cooling cycle. Figure 5(b) shows $\rho$-$T$ measurement results of synthesized Pd$_{0.1}$TiSe$_2$ polycrystalline samples. Pd doping in TiSe$_2$ results in dramatic suppression in CDW transition, which is evident from Fig. 5(b). The $\rho$-$T$ plot of Pd$_{0.1}$TiSe$_2$ is found to be similar to normal metals. A small bump has been observed in the $\rho$-$T$ plot in the temperature range of 200–250 K, which can be regarded as a suppressed CDW transition; this is in agreement with the previous report [16]. The enhanced charge carrier concentration due to the intercalation of Pd atoms can be the reason for the suppression of the CDW phase in the same. The CDW transition occurs at higher temperatures as compared to pure TiSe$_2$. A small hysteresis is also observed around the resistivity anomaly signifying the presence of a
first-order phase transition. The smaller hysteresis in resistivity in the cooling and warming cycles in $Pd_{0.1}TiSe_2$ signifies the much reduced dual electronic conductivity nature the same as compared to pure $TiSe_2$, which is evident from the nearly metallic $\rho$-$T$ plot. Interestingly, $Pd_{0.1}TiSe_2$ is reported to show superconductivity below 2 K [16], found to be absent here as no sign of resistivity drop is observed down to 2 K (lowest temperature limit of our PPMS), though the possibility of occurrence of superconductivity at a temperature below 2 K cannot be neglected here. Furthermore, low-temperature measurements below 2 K are required to get more insight into the superconducting phase in $Pd_{0.1}TiSe_2$. Figure 5(c) shows the comparison of the normalized $\rho$-$T$ plot of both pure $TiSe_2$ and $Pd_{0.1}TiSe_2$. It is clear from Fig. 5(c) that the CDW phase in $Pd_{0.1}TiSe_2$ nearly disappeared in comparison to pure $TiSe_2$ and the same seems to be in the normal metallic phase. In pure $TiSe_2$, the resistivity value is found to increase 3 times the room temperature resistivity near CDW transition (170 K), while the same is not visible in $Pd_{0.1}TiSe_2$.

Previously, there are several rigorous first-principle studies on $TiSe_2$ [24–26]. To understand the suppression in CDW due to Pd addition in $TiSe_2$, we compute the electronic band structure and density of states for pure $TiSe_2$ and Pd-intercalated $TiSe_2$ within the DFT framework. From the previous report [15], the Pd atom is intercalated in between the 2D layers of $TiSe_2$. To simulate the intercalation, a supercell of size $3 \times 3 \times 1$ is created, and a Pd atom is inserted in between the TiSe layers, as shown in Fig. 6. Thus for simulation, we have Pd $\sim$ 11% in $TiSe_2$. All computational simulation was performed in Quantum Espresso software based on density functional theory (DFT) [27, 28]. First, self-consistent calculations were done using the experimental lattice parameters for pure and Pd-intercalated samples. After that, the bulk electronic band structure and density of states were calculated. For DFT calculation, GGA-incorporated Perdew-Burke-Ernzerhof (PBE)
type ultrasoft pseudopotentials are used to include the effect of electronic exchange and correlation corrections. For band structure calculation, first, the Brillouin zone (BZ) is discretized on a mesh of $11 \times 11 \times 5$ for pure and $4 \times 4 \times 6$ for doped systems given by Monkroft-Pack. For the convergence of self-consistent calculation, the cutoff is $1.2 \times 10^{-6}$ Ry, and the charge cutoff of 400 Ry and wave function cutoff of 48 Ry are used. The total energy convergence criteria are set to be $4 \times 10^{-4}$ eV/atom.

For the input of band structure calculations, unit cell parameters were taken from Rietveld-refined structures. The k-path followed for band calculations is determined from the SeeK-path: the k-pathfinder and visualizer [29]. The suggested optimized path is $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma \rightarrow A \rightarrow L \rightarrow H \rightarrow A$. Figure 7(a, b) show the electronic band structure for the pure and Pd-intercalated TiSe$_2$ respectively. Figure 7(c, d) show the DoS for the pure and Pd-intercalated TiSe$_2$ respectively. We observe a substantial change in the band structure as well as in DoS near the Fermi level. In Pd-intercalated TiSe$_2$, the near Fermi level bands are dense, indicating higher DoS. The same results were found by directly comparing the DoS of pure and Pd-intercalated TiSe$_2$. Increased DoS near the Fermi level implies a higher number of charge carriers, which is possibly the reason for the observed decrease in CDW. The substantial change in DoS also confirms the semi-metal-to-metal transition due to Pd addition.

### 4 Conclusion

In this study, we synthesized polycrystalline samples of TiSe$_2$ and Pd$_{0.1}$TiSe$_2$, which are well characterized using PXRD, FESEM, and Raman spectroscopy. Intercalation of Pd atoms in the TiSe$_2$ unit cell is confirmed by the change in lattice parameters and shift in Raman modes. Pd atoms are found to reside in the voids of the TiSe$_2$ unit cell. Intercalation of Pd atoms is shown to have a large impact on transport properties, as the CDW transition is completely suppressed in comparison to pure TiSe$_2$. We observed no superconducting transition down to 2 K. The theoretical simulations show that suppression in CDW is directly related to the increment in DoS due to Pd addition in TiSe$_2$.

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### References

1. Rossnagel, K., Phys. J.: Condens. Matter 23, 213001 (2011)
2. Hellmann, S., Rohwer, T., Kalliane, M., Hanff, K., Sohrt, C., Stange, A., Carr, A., Murnane, M.M., Kapteyn, H.C., Kipp, L., Bauer, M., Rossnagel, K.: Nat. Commun. 3, 1069 (2012)
3. Hu, Q., Liu, J.Y., Shi, Q., Zhang, F.J., Zhong, Y., Lei, L., Ang, R.: EPL 135, 57003 (2021)
4. Balandin, A.A., Zaitsev-Zotov, S.V., Gruner, G.: Appl. Phys. Lett. 119, 170401 (2021)
5. Lioi, D.B., Gosztola, D.J., Wiederrecht, G.P., Karapetrov, G.: Appl. Phys. Lett. 110, 081901 (2017)
6. Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O.V., Kis, A.: Nat Mater 2, 17033 (2017)
7. Titov, A.N., Yarmoshenko, Yu.M., Barrylews, P., Yablonskikh, M.V., et al.: Chem. Phys. Lett. 497, 187 (2010)
8. Dines, M.B.: Science 188, 1210 (1975)
9. Lee, C.H., et al.: Nat. Nanotechnol. 9, 676 (2014)
10. Sasaki, M., Ohnishi, A., Kikuchi, T., Kitaura, M., Kim, K.S., Kim, H.J.: Phys. Rev. B 82, 224416 (2010)
11. Lee, H.N.S., McKinzie, H., Tannhauser, D.S., Wold, A.: J. of App. Phys. 40, 602 (1969)
12. Friend, R.H., Frintd, R.F., Grant, A.J., Yoffe, A.D., Jerome, D.: J. Phys.: Solid State Phys. 10, 1013 (1977)
13. Kidd, T.E., Miller, T., Chou, M.Y., Chiang, T.C.: Phys. Rev. Lett. 88, 226402 (2002)
14. Woo, K.C., Brown, F.C., McMillan, W.L., Miller, R.J., Schaffrman, M.J., Sears, M.P.: Phys. Rev. B 14, 3242 (1976)
15. Morosan, E., Zandbergen, H.W., Dennis, B.S., Bos, J.W.G., Onose, Y., Klimeczuk, T., Ramirez, A.P., Ong, N.P., Cava, R.J.: Nat. Phys. 2, 544 (2006)
16. Morosan, E., Wagner, K.E., Zhao, L.L., Hor, Y., Williams, A.J., Tao, J., Zhu, Y., Cava, R.J.: Phys. Rev. B 81, 094524 (2010)
17. Tozer, D.J., Peach, M.J.: J. Phys. Chem. Chem. Phys. 16(28), 14333 (2014)
18. Saini, A., Kark, N.K., Kumar, K., Aloysius, R.P., Awana, V.P.S.: J. Supercond. Nov. Magn. 35, 1383 (2022)
19. Bhatt, R., Patel, M., Bhattacharyya, C., Basu, R., Ahmad, S., Bhatt, P., Chauhan, A.K., Navneethan, M., Hayakawa, Y., Singh, A., Gupta, S.K., J. Phys. Cond. Mat. 26, 445002 (2014)
20. Qian, D., Hsieh, D., Wray, L., Morosan, E., Wang, N.L., Xia, Y., Cava, R.J., Hasan, M.Z.: Phys. Rev. Lett. 98, 117007 (2007)
21. Behera, P., Bera, S., Patidar, M.M., Ganesan, V.: AIP Conf. Proc. 2100, 021113 (2019)
22. Sun, L., Chen, C., Zhang, Q., Sohrt, C., Zhao, T., Xu, G., Wang, J., Wang, D., Rossnagel, K., Gu, L., Tao, C., Jiao, L.: Angewandte Chemie 56, 8981 (2019)
23. May, M.M., Brabetz, C., Janowicz, C., Manzke, R.: J. Electron Spectrosc. Relat. Phenom. 184, 180 (2011)
24. Calandra, M., Mauri, F.: Phys. Rev. Lett. 106, 196406 (2011)
25. Hu, Q., Liu, J.Y., Shi, Q., Zhang, F.J., Zhong, Y., Lei, L., Ang, R.: EPL 135(5), 57003 (2021)
26. Liu, W., Luo, A., Zhong, G., Zou, J., Xu, G.: Phys. Rev. Research 4, 023127 (2022)
27. Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I., Dal Corso, A., De Giornico, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzini, N., Mauri, F., Mazzarello, R., Paolini, S., Passarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Schlaferher, G., Seitsonen, A.P., Smogunov, A., Umari, P., Wentzcovitch, R.M.: J. Phys. Condens. Matter 21, 395502 (2009)
28. Giannozzi, P., Andreussi, O., Brumme, T., Bnau, O., Buongiorno Nardelli, M., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Cococcioni, M., Colonna, N., Carneiro, I., Dal Corso, A., De Giornico, S., Delugas, P., Distasio, R.A., Ferretti, A., Floris, A., Fratesi, G., Frugalo, G., Gebauer, R., Gerstmann, U., Giustino, F., Gorni, T., Jia, J., Kawamura, M., Ko, H.Y., Kokalj, A., Kicukbeni, E., Lazzeri, M., Marsili, M., Marzini, N., Mauri, F., Nguyen, N.L.,
Nguyen, H.V., Otero-De-La-Roza, A., Paulatto, L., Poncé, S., Rocca, D., Sabatini, R., Santra, B., Schlipf, M., Seitsonen, A.P., Smogunov, A., Timrov, I., Thonhauser, T., Umari, P., Vast, N., Wu, X., Baroni, S.: J. Phys. Condens. Matter 29, 465901 (2017)

Hinuma, Y., Pizzi, G., Kumagai, Y., Oba, F., Tanaka, I.: Comput. Mater. Sci. 128, 140 (2017)

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