Effect of Fe-doping on charge density wave in
1T-TaS$_2$: Instability and induced superconductivity

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Abstract. We report the induced superconductivity by Fe-doping in charge-density-wave (CDW) system 1T-TaS$_2$ and discuss the interplay between CDW and superconductivity. The grown 1T-phase Fe$_x$Ta$_{1-x}$S$_2$ (0 $\leq$ x $\leq$ 0.05) single crystals are experimentally measured and the electronic structures are calculated by density functional theory (DFT). Our results shows that the CDW is suppressed gradually accompanied by the disappearance of pseudogap/Mott-gap. The induced new superconducting state appears at low temperatures for samples with moderate doping levels (x = 0.02 and 0.03). The induced superconductivity and CDW phases may be separated in real space. For high Fe-doping concentration (x $\geq$ 0.04), the Anderson localization (AL) state is observed due to the occupation disorder, which results in an insulating behavior.

Transition-metal dichalcogenide (TMD) compounds have been of widespread interest for a long time because of their unique structural and electronic properties. 1T-TaS$_2$ is a typical layered TMD that exhibits charge density wave (CDW) which, depending on temperature, is incommensurate, nearly commensurate, or commensurate[1]. The commensurate CDW (CCDW) phase at low temperatures (T $<$ 180 K) accompanies periodic lattice distortions that form a ($\sqrt{13}$ $\times$ $\sqrt{13}$)-13.9$^\circ$ supercell with star-of-David clusters[2]. Recent studies have shown the CDW insulating phase can be inhibited by the external pressure[3], disorder[4], and photoexcitation[5]. One can expect the doping could also effectively suppress the CDW state and in some cases the metallic state (or potential superconducting state) might arise and develop within the CDW state.

Electronic band structure calculations for the 1T-TaS$_2$ without CDW structure predicate a good metallic character[6]. The CDW splits the Ta-$d_{z^2}$ band into subbands and brings the pseudogap near the Fermi level caused by the lattice distortions[7], resulting in a semimetal behavior. Actually, an insulating state at low temperatures is experimentally observed, which is believed to arise from Mott-Hubbard transition[8]. It is important to obtain the electronic structure in the CCDW phase to understand the Mott-Hubbard localization.

In the present work, we investigate the 1T-TaS$_2$ single crystals by Fe-doping, since the doping can effectively modify the electronic band structure by altering the crystal structure and carriers concentration. We present the combined experimental and theoretical study, and discuss the effect of Fe-doping on CDW and the interplay between the induced superconductivity and CDW order.

Single crystals of Fe$_x$Ta$_{1-x}$S$_2$ (0 $\leq$ x $\leq$ 0.05) were grown via the chemical vapor transport (CVT) method with iodine as a transport agent. The sample structure and quality were verified.
by x-ray diffraction (XRD). The composition of Fe<sub>x</sub>Ta<sub>1−x</sub>S<sub>2</sub> was checked by inductively coupled plasma atomic emission spectrometry (ICP-AES). The resistivity was measured in a Quantum Design physical property measurement system (PPMS), and the magnetization measurements were performed on a superconducting quantum interference device (SQUID) system. The band structure calculations were performed in the framework of density functional theory (DFT) within the local-density approximation (LDA), using the ab initio program ABINIT [9]. Norm-conserving pseudopotentials and a plane-wave basis set with a kinetic energy cutoff of 1600 eV were used. For the undistorted 1T-phase a 14×14×8 Monkhorst k-point sampling was used, while for the CCDW phase (√13×√13×1 supercell with 13 Ta and 26 S atoms), a 6×6×8 mesh of k points was used. The self-consistent-field calculations are performed on the optimized/relaxed structure. In order to describe the strong correlation of electrons in Mott-Hubbard physics, we adopted a LDA+U method where U is the onsite Coulomb repulsion.

In Fig. 1(a) the room temperature XRD measurements for the single crystals and the crashed-single-crystal powder show a 1T-phase structure with space group P3m1. The orientations of the crystal surfaces are perpendicular to (00l) plane. Furthermore, the (003) peak position shifts to higher angle after Fe doping (see the right inset), implying the decrease of the lattice constant. This is different from the case of the intercalated systems. The observed reduction of lattice constant should be due to the substitution of Fe at Ta site, since the ion radius of Fe is smaller than that of Ta. Temperature dependent in-plane resistivity ρ<sub>ab</sub>(T) are shown in Fig. 1(b). For the undoped 1T-TaS<sub>2</sub>, the electrical conduction shows a semimetal behavior below 350 K due to the CDW distortion induced gap. Below 150 K, the resistivity abruptly increases due to the transition from nearly commensurate CDW (NCCDW) to CCDW Mott phase. The large thermal hysteresis behavior indicate that the transition is of first-order character. For the doped samples, the anomaly in resistivity near CCDW transition disappears, and instead a reduce in resistivity at low temperatures occurs as 0.01 < x < 0.04. Especially for x = 0.02, the resistivity reaches zero below 2 K, which evidently indicates an induced superconductivity. For the x ≥ 0.04 samples, the resistivity shows a large increase especially in the low-temperature range, which should be due to the Anderson localization (AL) of the conduction electrons by the occupation disorder of Ta/Fe atoms [10].

![Figure 1](image_url)

**Figure 1.** (a) XRD patterns of Fe<sub>x</sub>Ta<sub>1−x</sub>S<sub>2</sub> single crystals. The left inset shows the powder (crashed single crystal) XRD pattern. The right inset shows the magnification plot of the (003) peaks in XRD patterns. (b) Temperature dependent in-plane resistivity ρ<sub>ab</sub>(T). The top inset shows the details of low-temperature resistivity curves. (c) Temperature dependence of magnetic susceptibility for x = 0.02 sample. The top inset shows the magnetization hysteresis loops at 0.75 K when H || ab plane. The bottom inset shows the initial M(H) isotherm, and the black line is the linear fitting in the low-field range.
We measured the temperature dependence of dc magnetic susceptibility for the $x = 0.02$ sample with the maximum superconducting transition temperature $T_C$ and plot in Fig. 1(c). The magnetic field of 10 Oe was applied parallel to the $ab$ plane. The diamagnetism appears in the low-temperature region, which further confirms the existence of superconductivity. The insets in Fig. 1(c) show the magnetization hysteresis loops at 0.75 K. The $M$-$H$ results evidently show that Fe$_{0.02}$Ta$_{0.98}$S$_2$ is a type-II superconductor with the low superconducting critical field $H_{C1}$ of $\sim$13 Oe.

In order to understand the effect of Fe-doping on the CDW state and the induced new superconducting state, we calculated the electronic structure by DFT for the undistorted 1$T$-phase and CCDW phase. It is quite difficult to model the doped system with low Fe-doping level ($<0.05$), which needs a larger supercell and an unacceptable CPU-time consumption. Instead we model the $\sqrt{13} \times \sqrt{13} \times 1$ supercell which contains at least one-site substitution of Ta atom by Fe atom (1/13 doping level). Although the doping level in our calculation model is larger than the real one, we can still basically understand the Fe-substitution effect on the ground state from the band structure calculation. The calculated band structures of TaS$_2$ in the undistorted 1$T$-phase and CCDW phase are shown in Fig. 2(a). For the undistorted 1$T$ structure, the Ta-$d$ bands cross the Fermi level $E_F$ and strongly disperse along $\Gamma$-$M$-$K$-$\Gamma$ and $A$-$L$-$H$-$A$ with a width of about 2.5 eV, which leads to a good metallic character. Along the $k_z$ direction ($\Gamma$-$A$) only weak dispersion on the Fermi level is left, consistent with the quasi-2D character of the 1$T$-phase structure. The relaxed CCDW structure shows star-of-David clusters in which the first and second rings of Ta atoms averagely contract inwards by 5-6 %. The Ta star-of-David clusters cause the Ta-$d$ state to become localized in the in-plane directions, which results in a localized uppermost band along $\Gamma$-$M$-$K$-$\Gamma$ at about -0.3 eV. The band at the Fermi level disperses only along the $k_z$ direction, indicating the existence of quasi-one-dimensional Fermi surface (FS) that allows that electrons conduct only along the $c$-axis, and the $ab$-plane conductivity becomes worse in CCDW structure.

**Figure 2.** (a) Energy band structure near the Fermi level for the undistorted 1$T$-phase (blue point) and the reconstructed commensurate CDW superstructure (solid line). The band that crosses the Fermi level is plotted as a red line. (b) Density of states calculated for undistorted 1$T$-phase, CCDW phase, and Fe-doped CCDW superstructure (here we only plot the data for the Fe-doping level of 2/13). The Fermi level is set to zero.

Figure 2(b) shows the density of states (DOS) in the undistorted 1$T$-phase and CCDW structure. For the undistorted 1$T$-phase, a large DOS locates at the Fermi level. In the CCDW structure, the DOS near the Fermi level decrease and shows a broad pseudogap structure, resulting in a semimetal conduction. Considering the correlation of Ta-$d$ electrons, we applied
LDA+$U$ method to the CCDW structure. The calculated results show that a deep Mott gap develops and the localized states form at the Fermi level, which accounts for the experimentally observed insulating behavior at low temperatures. By using $U = 0.55$ eV ($J = 0.05$ eV), the obtained Mott gap is about 0.22 eV close to the experimentally determined value[11]. With Fe-doping, the calculations indicate the CCDW distortions reduce. And hence the CCDW-distortion induced pseudogap is suppressed and the Mott correlation is weakened. The DOS increases at the Fermi level and leads to a metallic character. In addition, the calculated projected DOS show that the Fe-3$d$ band partially contributes to the DOS at the Fermi level (not shown here).

The dopant Fe can act as impurities on the Ta-plane and pinning centers for the CDW. It inhibits the long-range CDW order, and consequently the CCDW and Mott transitions are suppressed. The NCCDW phase consists of domains that are locally commensurate, separated by interdomain regions. The Fe-doping induced superconductivity can develops within the metallic interdomain regions in the NCCDW phase, which is similar to the case of the external-pressure induced superconductivity in 1T-TaS$_2$[3]. The induced superconductivity and the CDW compete with each other and are of intrinsic phase-separation character. On the other hand the electron-phonon interaction in CDW domains may plays an important role in the observed superconductivity[12]. In Fe$_x$Ta$_{1-x}$S$_2$, the superconductivity can only occur in a narrow doping range and the $T_c$ is very sensitive to $x$, which remains a puzzle. Further experimental and theoretical studies are needed to fully clarify the nature of the interplay between CDW and superconductivity.

In summary, we have shown the Fe-doping induced superconductivity in 1T-TaS$_2$ and discussed the interplay between CDW and superconductivity states. The signature of superconductivity appears for $x = 0.02$ and 0.03, and the maximum superconducting transition temperature is 2.1 K. The induced superconductivity and CDW phases may coexist in some extent. For high Fe-doping concentration ($x \geq 0.04$), the CDW order is fully suppressed and the Anderson localization state is induced by site-occupation disorder.

This work was supported by the National Key Basic Research under contract Nos. 2011CB00111 and 2007CB925002, and the National Natural Science Foundation of China under contract Nos. 51001094, 10804111, 10974205.

References

[1] Wilson J A, DiSalvo F J and Mahajan S 1975 Adv. Phys. 24 117
[2] Clerc F, Battaglia C, Cercellier H, Monney C, Berger H, Despont L, Garnier M G and Aebi P 2007 J. Phys.: Condens. Matter 19 355002
[3] Sipos B, Kusmartseva A F, Akrap A, Berger H, Forró L and Tutuš E 2008 Nature Mater. 7 960
[4] Xu P, Piatek J O, Lin P H, Sipos B, Berger H, Forró L, Ronnow H M and Grioni M 2010 Phys. Rev. B 81 172503
[5] Dean N, Petersen J C, Fausti D, Tobey R I, Kaiser S, Gasparov L V, Berger H and Cavalleri A 2011 Phys. Rev. Lett. 106 016401
[6] Matteiss L F 1973 Phys. Rev. B 8 3719
[7] Bovet M, Popović D, Clerc F, Koitzsch C, Probst U, Bucher E, Berger H, Naumović D and Aebi P 2004 Phys. Rev. B 69 125117
[8] Fazekas P and Tosatti E 1979 Philos. Mag. B 39 229
[9] Gonze X, Beuken J M and Caracas R et al. 2002 Comput. Mater. Sci. 25 478
[10] Di Salvo F J, Wilson J A and Waszczak J V 1976 Phys. Rev. Lett. 36 15
[11] Zwick F, Berger H, Vobornik I, Margaritondo G, Forró L, Beeli C, Onellion M and Panaccione G 1998 Phys. Rev. Lett. 81 1058
[12] Liu A Y 2009 Phys. Rev. B 79 220515(R)