CDW Transition in Fe Intercalated $TiSe_2$

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Abstract. Polycrystalline $TiSe_2$ and its Iron intercalated samples have been successfully grown by solid state synthesis method. The electrical transport property of pure sample is semiconducting in the entire temperature range with a clear anomaly depicting the onset of charge density wave (CDW) at 200K. Temperature that corresponds to CDW peak and CDW transition onset ($T_{CDW-onset}$ & $T_{CDW-peak}$) decreases linearly with concentration of Iron (Fe). The 7.5% Fe intercalated sample shows a crossover from semiconductor to metallic nature at 145 K with linear contribution at high temperature side. Below 145K the resistance was fitted with -lnT contribution, which may be associated with Kondo like interactions due to the guest Fe moments with the conduction electrons of the host. However, the robustness of the resistance variation in magnetic fields point towards other mechanisms as well.

INTRODUCTION

During the past several decades Metal-Insulator Transition (MIT) is one of the considered topics among researchers in condensed matter physics, due to its variety of unusual and exotic ground states including that of metallic side. Doping on gapped system such as semiconductor gives interesting ground states which will be very useful to improve efficiency of semiconducting electronics. This is especially true for magnetic element doping provided no segregation is there. Such DMS systems have high potential on spintronics applications. Various ground states can be achieved through doping or employing magnetic field, pressure, etc. Substituting phosphorus on silica is one of classic example that has been well studied on both insulating as well as metallic side of the ground states. Substitutional impurities have variety of effects on host atomic lattice. Impurities may give electron or hole. This may lead to impurity states around Fermi level. Upon higher side of doping, it may evolve in to an impurity band that will dominate the entire temperature range above critical concentrations.

Impurities make Fermi level to move either towards conduction band (in case of electron doping) or valance band (in case of hole doping) that eventually leads to conduction. On the other way, impurities shall make chemical pressure effect so that that band gap start to overlap and disappears at large concentration of external impurities. Physical properties may be entirely different on electron doping as compare to hole doping on gapped systems. For example, doping cobalt on FeSi makes itinerant ferromagnetic ground state while doping Al on Si site makes it a heavy Fermion metal ground state. Metal insulator transition is a very broad and interesting field and there are numerous investigations on the electronic transition for their potential application in industry.

Charge Density Wave (CDW) is a phase transition that arises especially in low dimensional materials due to periodic lattice distortion. $TiSe_2$ is a quasi-2D material which undergoes CDW transition at ~ 200K (1). This material is very sensitive to doping and intercalation by a small amount, where the CDW state gets suppressed. Inducement may be possible due to reconfiguration in lattice instability. In general, CDW peak is suppressed upon intercalation of transition metal like Co, Fe, Ni, Cu etc. in $TiSe_2$ as reported by M. Sasaki et al (2). However recently N V Selezneva et al (3) has reported on Cr intercalated samples where there is suppression and inducement depending on the concentration of guest atom. In addition to this many investigations on the band structure and interaction involved in $TiSe_2$ such as exciton-phonon driven charge density wave state (4), electron-hole coupling using ARPES study (5), pseudo gapconfirmation with STM technique (6) have been reported. Here we have reported the transport properties of Iron (Fe) intercalated polycrystalline $TiSe_2$. There is drastic decrement in CDW peaks and the corresponding transition temperature with Fe intercalation is reported by Heon-Jung Kim[7].

Preparation and Experimental Details

All the samples were prepared by solid state reaction route from the stoichiometric amount of elemental powders. They were mixed properly, pressed into pallets and then vacuum sealed in quartz tube (~10-5 mbar) and put into the furnace. First the temperature has been set to 350C, held for 1 hour and then increased to 650 C at the rate of 50 C/hour and held for 22 hr. Synthesized powders are again pressed into pellets and then annealed at 625C for 40 hr. X-ray diffraction measurement was done with advanced Bruker D8 diffractometer using Cu Kα radiation to find the crystal structure. Resistivity measurement was carried out in QD PPMS (14T,2K) system.

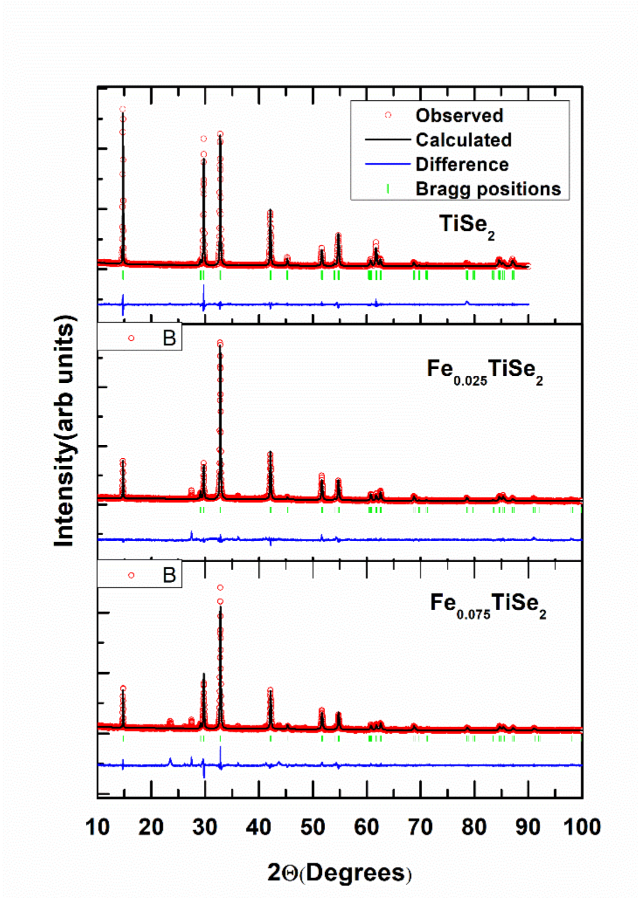
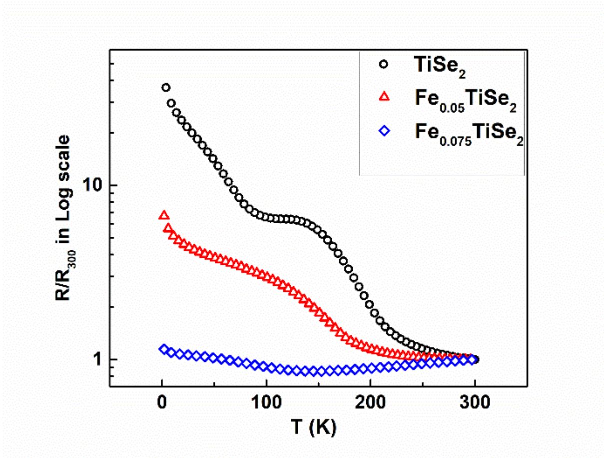


FIGURE 1. Rietveld refinement of XRD pattern of $TiSe_2$ and its Fe intercalated samples

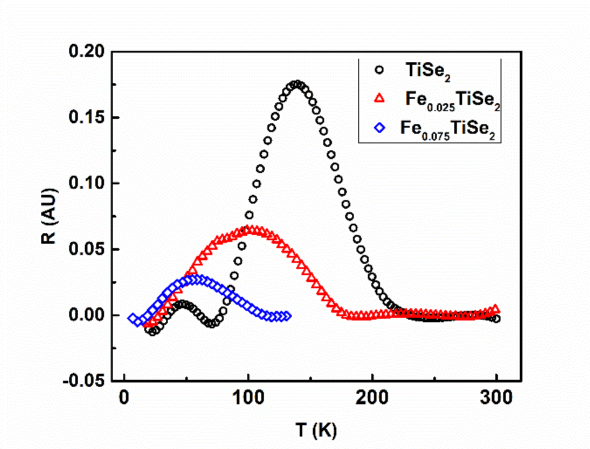
Results and Discussion

$TiSe_2$ crystallizes in hexagonal CdI_2 crystal structure with space group p$\bar{3}$m1. Figure 1 shows the Rietveld refinement of Fe_xTiSe_2 (x=0,0.025,0.075) done using FULL PROF software and The peaks were well matched with JCPDS database which confirms a single phase. There are negligible changes in lattice parameters upon Fe intercalation in pure sample as predicted from the refined data and is as expected. The lattice parameters are a=b=3.537 A and b= 6.007 A.

The electrical transport data of $TiSe_2$ shows a semiconductor behavior in 2-300 K temperature range except the CDW peak as shown in the R/R_{300} vs T plot of fig 2 (a). In our sample the residual resistance and effect of impurity is higher at low temperatures as compared to the literature which may be due to disorder and impurity in the sample. However, the data of pure sample resembles that of literature (8) indicating a similar nature of sample preparation. Figure 2(b) shows the extracted CDW peaks after background subtraction of resistance data which clearly indicates the decrease of temperature corresponding to the peak ($T_{CDW\text{-}peak}$) as Fe is intercalated in $TiSe_2$.Proper scaling (curve of $Fe_{0.025}TiSe_2$multiplied by 10 & curve of $Fe_{0.075}TiSe_2$ multiplied by 100) has been used to get the figures in 2(b) visible. The CDW transition temperature ($T_{CDW\text{-}onset}$) of the samples were found from the peak value of $\frac{d(lnR)}{d(1/T)}$ vs. 1/T curve. The systematic linear decrease in characteristic temperatures ($T_{CDW-onset}$& $T_{CDW-peak}$) is shown in Figure 3.The CDW peaks were fitted with Gaussian function (not shown in Fig) and the obtained values of area under the curve which is nothing but a measure of the intensity of the CDW transition decreases drastically with increase in Fe intercalation.



(a)



(b)

FIGURE 2. (a) Resistance vs temperature plot of resistance of TiSe2 and its Iron intercalated samples. **(b)**CDW peaks extracted after background subtraction with proper scaling (curve of $Fe_{0.025}TiSe_2$ multiplied by 10 & curve of $Fe_{0.075}TiSe_2$ multiplied by 100) showing decrease in peak intensity with increasing iron intercalation in TiSe2.

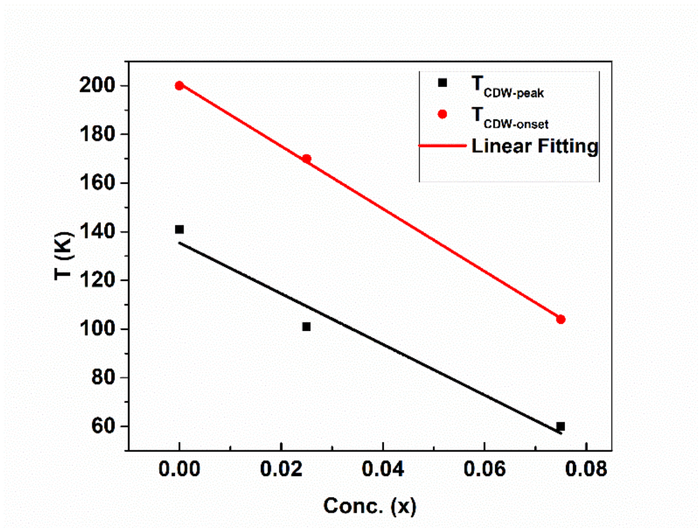
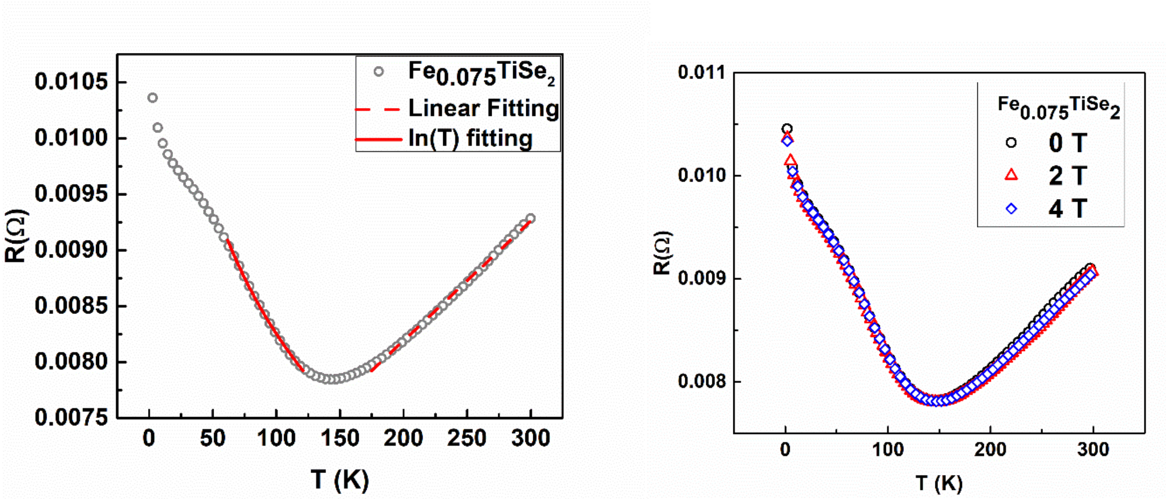


FIGURE 3. Liner fitting of Peak temperatures and CDW transition temperatures ($T_{CDW-onset}$& $T_{CDW-peak}$) that shows a decrease with increase in Fe concentration.



(a) (b)

FIGURE 4. (a) Semiconductor to metal transition as observed in -lnT fitting (solid line) at low temperatures while a linear fitting (dash line) is clear at high temperature. **(b)** Magnetoresistance transport data showing no effect in resistance.

We observed an anomalous transport characteristic of $Fe_{0.075}TiSe_2$sample as shown in fig 4. Heon-Jung Kim et al [7] have reported on the effect of disorder in $Fe_xTi(Se_{1-y}S_y)_2$ single crystals sample and found the similar feature for x=0.065. Our sample is polycrystalline and disordered as well. In-spite of this we could observe this feature for x=0. 075. Semiconductor to metal crossoveris found at ~ 145K. This is in agreement with the literature as semimetal to metal transition is in the intercalation concentration range$0.05<x<0.075$ and electronic band modification has also been predicted by X. Y. Cui et al [9].This crossover is due to localized carrier contribution because of high electron-electron interaction induced by the magnetic Fe impurity. We have fitted the resistance curve of $Fe_{0.075}TiSe_2$ sample with a logarithmic term(-lnT) below 145K (solid line) as shown in figure 4a while the high temperature side with linear fitting (dash line). There is no effect of magnetic field on the transport properties over the entire temperature range which predicts there may not be just a Kondo like scattering. However, the inference is that the CDW is more affected by disorder rather than impurity spins. More studies are needed to unravel this field independent feature.

CONCLUSION

A clear change in CDW state of $TiSe_2$ is seen upon Fe intercalation. There is a drastic but systematic decrease in characteristic temperatures ($T_{CDW-onset}$& $T_{CDW-peak}$). While the residual semiconducting behavior at low temperatures may be attributed to disorder in the sample, the decrement seen in CDW state upon Fe intercalation is attributed to the destruction of coherence due to magnetic scattering effects. A reverse MIT seen upon 7.5% Fe intercalation in $TiSe_2$ is quite anomalous and interesting feature that point towards the novel ground states. More efforts are needed to probe this.

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