

CDW phase of TiSe_2

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Structural phase transition and the soft phonon mode[1, 2] Disalvo and his collaborators[1] carried out a neutron scattering experiment on TiSe_2 and showed that TiSe_2 undergoes a continuous structural phase transition around 202K. Below the transition temperature, it forms a $(2 \times 2 \times 2)$ commensurate superlattice.

Figure 1 shows the normalized intensity of the $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ superlattice peak at different temperature. The intensity around the transition temperature is approximately proportional to the reduced temperature $t = \frac{T-T_c}{T_c}$. And the intensity is proportional to the order parameter (the displacement of atomic positions). We can say that the intensity $I(3/2, 1/2, 1/2)$ is proportional to $t^{1/2}$. With this result, they argue that the mean-field theoretic behaviour is observed. (I get that $\frac{1}{2}$ is the only exponent that the mean-field theory can give. But, I'm not sure whether it is because all of thermal fluctuations have been integrated out or not.)

Also, they did measure the intensities of several superlattice peaks on different zones. They found that well below the transition temperature, no superlattice occurs in the plane containing $(h, 0, l)$. (Without this knowledge, I had tried to find a superlattice peak at $(\frac{1}{2}, 0, \frac{3}{2})$ for a quite long time.) It tells that the atomic displacements are perpendicular to this plane. Using the symmetry constraints, they got the displacement eigen vectors of the Ti and Se atoms.

Along with other materials exhibiting the structural phase transition, TiSe_2 has a soft phonon mode at the zone boundary. Due to the small scattering cross-section of the neutron scattering, it's difficult to observe the soft mode by the neutron scattering. But, the thermal diffuse X-ray scattering has been done and shows the frequency of phonon mode at the zone boundary tends to zero as the temperature approaches down to the critical temperature. In the adiabatic limit, the thermal diffuse intensity is given by

$$I(q) = \sum_{j=1}^9 \frac{|F_j(q)|^2}{\omega_j(q)} \coth\left(\frac{\hbar\omega_j(q)}{2k_B T}\right)$$

Upon cooling, the diffuse scatterings are generally decreased because of a reduction of the thermal phonon. But, figure 3 shows the opposite trend. It can be explained by the reduction of the phonon frequency. Such mode softening leads to the increase in the phonon population in spite of the reduction of the Boltzmann factor.

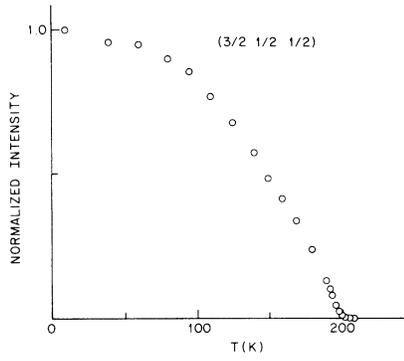


Figure 1: Temperature dependence of the intensities of $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ superlattice peak

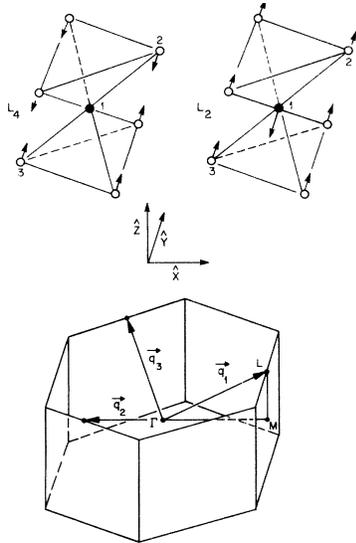


Figure 2: L_4 and L_2 representations of the space group D_{3d}^3 and the equivalent L point in the first Brillouin zone

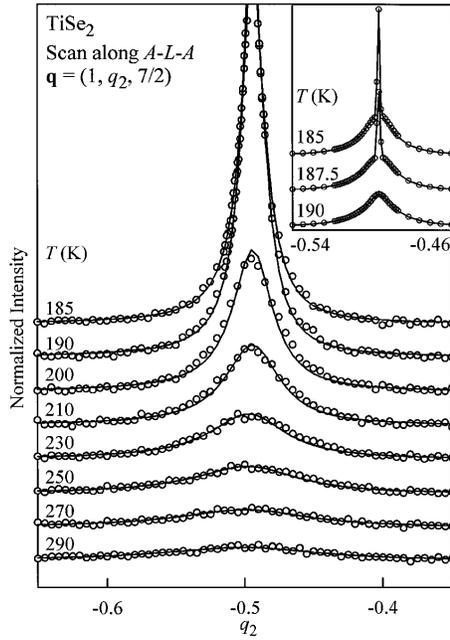


Figure 3: Linear scan along A-L-A in reciprocal space. At the temperature close to the transition, finer k resolution scans were carried. And these show the bragg peak (superlattice peak) at the L point. In this figure, the transition temperature is between 187.5 and 190. This discrepancy is due to the high intensity of the incident X-ray beam. Temperature readings in this figure are from the thermal diode contacted to the cold finger. Thus, the actual temperatures are about 10K higher than the diode readings.

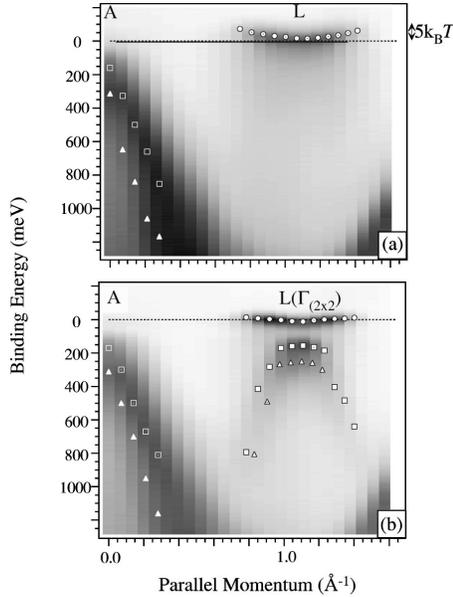


Figure 4: ARPES data for Γ ALM plane at room temperature (a) and at 120K (b) Two valence bands derived mainly from the Se 3p bands and the open triangle and rectangle represent the two Se 4p band split by the spin-orbit coupling.

ARPES experiments and the mechanisms of CDW [3, 5, 6] The electronic structure of TiSe_2 has been extensively studied experimentally and theoretically. Band theory calculation predicts that TiSe_2 is a semimetal with small negative band gap. But the experimentally, it has not been completely resolved due to the small gap between 4p type valence band and the 3d type conduction. Several experiments show inconsistent results. Also, several explanation of the CDW mechanism of TiSe_2 have been proposed to explain the CDW phase formation. Those include the excitonic insulator mechanism, a band-type Jahn-Teller mechanism, and indirect Jahn-Teller mechanism and excitonic interaction. Followings are some of works corroborating each of the proposed explanation. At first, Pillo and collaborators claimed that the excitonic insulator mechanism is mostly like to explain the CDW transition in TiSe_2 . They investigate the band structure of TiSe_2 in the Γ ALM plane in the reciprocal space (Actually, their experimental setup could not access to the Γ and A points, thus they took the data from the Anderson's work[4]). Usually, ARPES can only measure the valence bands. But in this case the conduction 3d type band are very close to the Fermi level and its effective mass is very large, these facts allow ARPES observe the energy dispersion of bands above the Fermi level.

In the low temperature plot, $L(\Gamma_{(2 \times 2)})$ represent the reconstructed zone center. After the $(2 \times 2 \times 2)$ superlattice formation. L points are back-folded

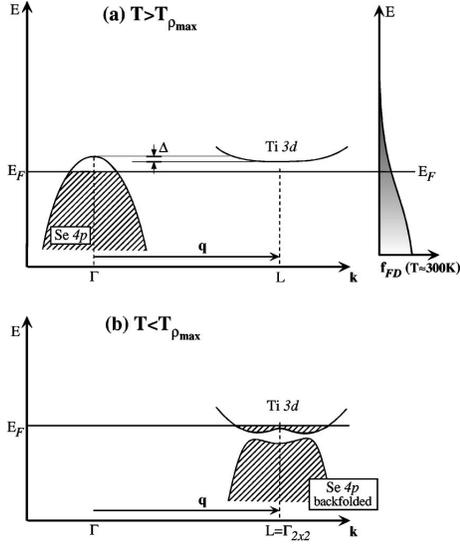
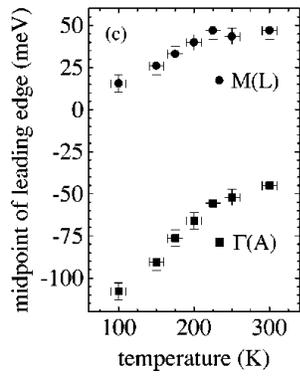
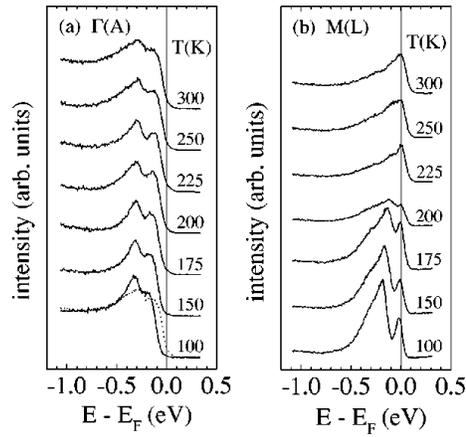
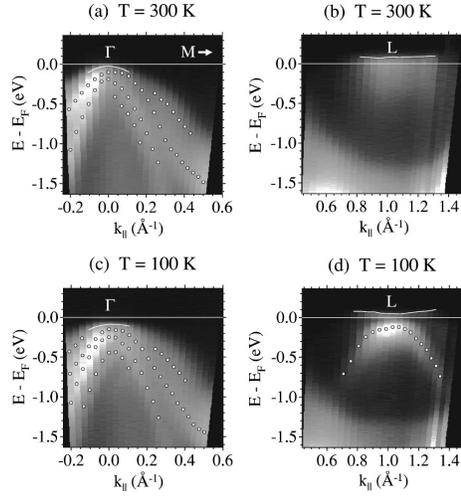


Figure 5: Band structure schematic above and below $T_{\rho_{max}}$. $T_{\rho_{max}}$ is the temperature where the resistivity has the maximum value.

into the zone center.

Second, Rossnagel and his collaborator have done ARPES for the ΓMAL . In contrast to the previous work. They found that the upper most Se 4p bands are located above the Fermi level and also this bands are lowered along with the Ti bands. In their result, the Ti 3d bands are also lowered. But, they do not cross the Fermi level. Also they found that the band gap between two bands continuously increases to about 80 meV. With these findings, they could explain the the increase of resistivity upon cooling by the removal of holes from the lowering Se p bands not the excitonic formation. Also. they argued that because of the increasing the band gap between two bands, the probability of the exciton formation steadily increases upon cooling. As the figure .. show, the bands lowerings become stronger below the CDW phase below T_c . This is the one of reason they favor the band-type Jahn-Teller mechanism to the excitonic insulator mechanism.

Lastly, Kidd and his collaborators carried out an ARPES experiment on several lines containing high symmetry points (Γ, L, H, A, K). These results show that TiSe_2 is a narrow gap semiconductor in the normal phase and the CDW phase. Contrary to the previous work, it shows a different behaviour of the minimal point of 3d conduction band at L points. Binding energy of the 3d bands is reduced in the CDW phase while the binding energy the back-folded Se 4p bands is enhanced in the CDW phase. Figure .. shows the band structure of TiSe_2 at the L and Γ points in the normal phase ($\approx 260\text{K}$) and the CDW



phase ($\approx 100\text{K}$). They proposed a reduced Hamiltonian like following

$$H = \begin{pmatrix} C & D & D & I & I' \\ D & C & D & I & I' \\ D & D & C & I & I' \\ I & I & I & V & 0 \\ I' & I' & I' & 0 & V' \end{pmatrix} + \Delta E_F$$

, which describe the band structure near the gap. Where V and V' represent two spin-orbit-split $\text{Se}4p$ valence bands in normal phase. And C represents a triply degenerate $\text{Ti}3d$ conduction bands in the normal phase. Off-diagonal terms D is a interaction term for the crystal-field splitting. With only this off-diagonal terms, $3d$ orbital would be split into a non-degenerate A band and double degenerate E bands. But, the Hamiltonian has another diagonal term. This describes an interaction between $4p$ valence bands and $3d$ conduction bands. These two interaction terms I, I' , and D give rise to a CDW phase. As show in the figure ... this model closely matches to the experimental data. And their LDA calculation shows that the total energies of the normal phase and CDW phase do not have a significant lowering with respect to the lattice distortion. With these findings, they argue that the band-type Jahn-teller mechanism is not likely to explain the formation CDW phase, instead the excitonic interaction plays a major role. In some sense, this model is similar to the Jahn-Teller effect. But, the lattice distortion splits the unoccupied conduction bands not the occupied the valence bands. Thus, only with this effect, total energy cannot be lowered. However, the lowered conduction bands cannot cross the valence bands due to the excitonic interaction. Consequently, the lowered conduction bands push down the valence bands and lower the total energy.

Optical conductivity[7] Figure 7 shows the temperature dependence of the optical conductivities. At lower temperature, the spectral weight of low energy parts are substantially suppressed and transferred to the peak around 0.4 eV. This clearly indicates the formation of the gap between two bands. This figure has an indication of the value of the gap that can be defined by the linear extrapolation. With these data and the data from the previous ARPES works (I did not refer to the specific work), they proposed a semi-metal to semi-metal transition mechanism at T_c . But, these optical conductivity data also seem to be consistent with the semi-conductor to semi-conductor transition scheme[6].

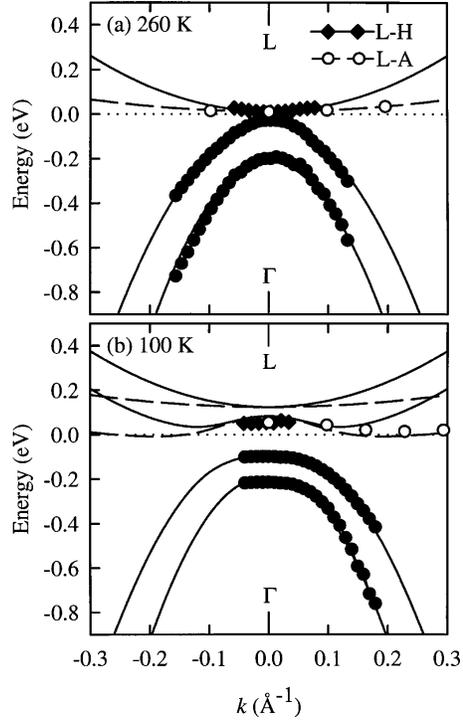


Figure 6: ARPES data taken along the $L - A$ and $L - H$ lines. Solid lines represents the best fit of the reduced Hamiltonian with the optimal choices of $I, I', D, \Delta E_F$

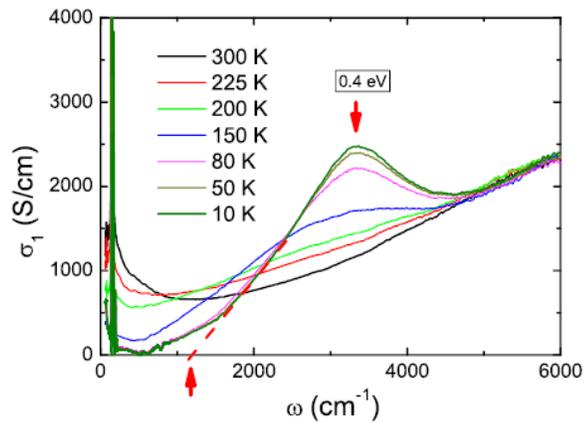


Figure 7: Temperature dependence of the optical conductivity

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