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CHARGE-DENSITY WAVES OBSERVED WITH A TUNNELING
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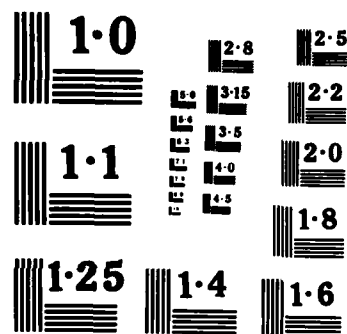
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by

and Paul K. Hansma

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Charge-density waves observed with a
tunneling microscope

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Charge-density waves on cleaved surfaces of 1T-TaS_2 appeared at

77K as hexagonal arrays of mounds with spacings of $3.5 \pm 0.3a_0$ where

$a_0 = 3.346\text{\AA}$ is the lattice spacing of the 1T-TaS_2 . In contrast, cleaved

surfaces of 2H-TaSe_2 at 77K showed only atoms. The tunneling microscope

was operated under liquid nitrogen with a $\text{Pt}_{0.8}\text{Ir}_{0.2}$ tip for both types

of samples.

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Tunneling microscopy is evolving into an important tool for surface analysis. Milestones in this evolution have included profiling grating surfaces^{1,2}, observing steps one atom high^{3,4,5}, detailing the atomic positions in semiconductor reconstructions^{6,7}, demonstrating small scale variations in the superconducting energy gap at the surface of a thin film⁸, observing single atoms in a close-packed layer⁹, and spectroscopic imaging¹⁰. The above results were obtained with tunneling microscopes operating in vacuum.

Here we report the first results obtained with a tunneling microscope operating submerged in liquid nitrogen and show that charge-density waves CDM's can be observed directly. The liquid nitrogen was used to cool the sample below the charge-density wave transitions in layer structure compounds and provided damping for mechanical vibrations.

The tunneling microscope was a hybrid between IBM Zurich designs³⁻⁶ and squeezable electron tunneling junctions.¹¹⁻¹³ The x-y translator was cut from a 3 x 3 x 0.635cm. block of C5400 lead titanate lead zirconate piezoelectric material.¹⁴ The z translator was a half circular bimorph made from two 1mm thick, 1.5cm radius half disks of C5800 lead titanate lead zirconate piezoelectric material¹⁴ glued together with epoxy. The z translator was supported about the x-y translator with three tungsten spacers near the edges and warped down in the center at $\approx 36\text{A/V}$ to bring the sample near the $\text{Pt}_{0.8}\text{Ir}_{0.2}$ tip.

The microscope was submerged in a dewar of liquid nitrogen and supported by a spring. The dewar was in turn supported by three rubber tubes from the ceiling. Details of the construction and operation of the microscope will be presented elsewhere.

Figure 1(a) shows individual atoms on a cleaved 2H-TaSe_2 surface. It is a photograph of a storage oscilloscope screen. The horizontal deflection is 6.6A/division times the x motion across the sample. The vertical deflection is 6.6A/division times the y motion across the sample plus 18A/division times the

z motion giving a pseudo three dimensional image. Crude calibrations were obtained by calculation based on the manufacturer's values for d_{31} , d_{32} and ϵ_{33} followed by extrapolation to 77K using another manufacturer's data¹⁵ for similar materials¹⁶. A refined calibration for x and y motion, ~20% higher, was obtained by assuming that these were indeed atoms with the spacing given by Wilson and Yoffe:¹⁷ 3.434Å. This refined calibration was used for measuring the wavelength of the charge-density waves. A refined calibration for the z motion is not yet available.

Figure 1(b) shows charge-density waves on a cleaved surface of 1T-TaS₂. A hexagonal array of mounds is clearly visible with a lattice spacing, $\lambda_{CDW} = 3.5 \pm 0.3a_0$, where $a_0 = 3.366\text{Å}$.¹⁷ The apparent height of the mounds is of order 4Å, in contrast to of order 0.5Å for the atoms in 2H-TaSe₂, (although, as mentioned above, the calibration of the z-axis is only approximate).

Photographs were taken with different scan rates and at different magnifications. At higher scan rates, > 15Hz, the amplitude of the bumps was reduced. At lower scan rates, < 5 Hz, its overall shape was the same but random noise and drift were more troublesome. Thus we obtained the best results at the fastest scan rates at which the tip could track the surface, ~10Hz. Photographs at different magnifications were taken; the ones selected for this paper were a compromise to allow seeing the atoms and the charge density waves at the same magnification. In all, approximately 30 photographs of atoms on three different samples of 2H-TaSe₂ and 20 photographs of charge-density waves on three different samples of 1T-TaS₂ have been obtained. No clear photographs of atoms on 1T-TaS₂ or charge-density waves on 2H-TaSe₂ have been obtained.

1T-TaS₂ and 2H-TaSe₂ both show superlattices due to charge-density wave formation and at 77K the CDW's are commensurate in both crystals. In 1T-TaS₂ the CDW forms at high temperatures (600K) oriented along three equivalent a-axis directions with $\lambda_{CDW} = 3.6a_0$,^{18,19}. This gives a triple CDW lattice

which is incommensurate with the crystal lattice. At 350K there is a first order transition where the triple CDW rotates to approximately 11° away from the a-axis in an attempt to become commensurate. Finally near 200K another first order transition occurs in which the triple CDW becomes commensurate with a rotation of 13.9° from the a-axis and $\lambda_{CDW} = \sqrt{13}a_0$. In the low temperature commensurate phase, the unit cell is triclinic and contains 13 formula units, so that the full superlattice is $\sqrt{13}a_0 \times \sqrt{13}a_0 \times 13c_0$.

In 2H-TaSe₂ an incommensurate triple CDW forms in a second-order (or nearly second-order) transition at 122.3K followed by a first order transition near 90K below which the CDW superlattice is commensurate with $\lambda_{CDW} = 3a_0$. The superlattice is then $3a_0 \times 3a_0 \times c_0$ resulting from the superposition of 3 CDW's.

The formation of the CDW's is accompanied by a periodic structural distortion in which the atomic displacements are on the order of 0.1 to 0.25Å. The CDW transitions are driven by Fermi surface instabilities²¹ with wave vectors near $2k_F$ and result in substantial gapping of the high temperature Fermi surface. This can result in almost complete annihilation of the Fermi surface area or in a substantial rearrangement of the Fermi surface geometry.

In the case of 1T-TaS₂ the gapping of the Fermi surface results in an extremely low carrier concentration in the commensurate state and at the lowest temperatures the resistivity rises indicating either semiconducting²² behavior or some type of metal-insulator transition²³. (See Fig. 2). The band calculations of Myron and Freeman²⁴ showed that in the commensurate phase nesting occurred over substantial regions of the Fermi surface consistent with a large reduction of Fermi surface area in the CDW phase. If an activated conductivity is assumed the activation energy derived from Arrhenius plots of $\rho(T)$ versus T between 50 and 150K is Δ=5meV although a single energy gap does not suffice at all temperatures. X-ray photoelectron spectroscopy²⁵ of the Ta 4f core levels also showed that the CDW amplitude in 1T-TaS₂ was extremely large at low temperatures, on the order of one electron per atom. The CDW transitions in 1T-TaS₂ produce large changes in

the resistivity parallel to the layers as shown in Fig. 2. All of these observations suggest that a large fraction of the conduction electrons have condensed into the CDW phase at 77K.

In contrast to IT-TaS_2 , the 2H-TaSe_2 resistivity parallel to the layers as also shown in Fig. 2 shows only a small anomaly at the CDW transition (120K) and the resistivity remains metallic down to the lowest temperatures. The Fermi surface is gapped by the CDW, but this results in substantial rearrangement of the Fermi surface due to band folding rather than annihilation. A large number of normal electrons remain below the CDW transition. Wilson²⁶ in a band folding model attempted to identify the parts of the 2H-TaSe_2 Fermi surface affected by the CDW. Details of the CDW structure and phasing in 2H-TaSe_2 have also been given by Wilson²⁷ and Wilson and Vincent.²⁸

DeHaas van Alphen²⁹ and Shubnikov de Haas³⁰ experiments on 2H-TaSe_2 show up to 11 frequencies in the range 1 to 45MG. The angular dependence of these frequencies can be fit to undulating cylinders running parallel to the c-axis consistent with the two dimensional character of these layer compound Fermi surfaces. Doran and Woolley³¹ have presented detailed calculations of the band structure density of states and total band structure energy of the 2H phase in the 3×3 CDW state. They find six doubly degenerate electron cylinders and their calculated density of states is similar to that calculated for the normal high temperature phase.³² In both cases the Fermi energy lies just above the main peak suggesting that the peak is an important feature in the CDW stabilizing.

Although the details of this peak vary with CDW amplitude the magnitude of the DOS at the Fermi level does not seem to vary substantially from that of the high temperature phase.

The tunneling microscopy results reported here clearly reflect the large differences in the CDW condensate that exist between IT-TaS_2 and 2H-TaSe_2 . The local tunneling density of states in the case of IT-TaS_2 appears to be dominated

by the CDW condensate structure while in 2H-TaSe_2 the presence of a large number of normal electrons below the CDW transition causes the local tunneling density of states to be predominately modulated at the lattice period of 3.43Å.

A detailed microscopic model of how the CDW condensate contributes to the local tunneling density of states needs to be developed. The tunneling directions in these experiments are predominately perpendicular to the layers while the group velocities of the electrons are predominately parallel to the layers. This may introduce some directional anisotropy into the problem as well as the need to consider anisotropy in the CDW gap structure in any detailed analysis. Nevertheless the results have shown that the tunneling microscope is highly sensitive to the details of the charge-density wave transition in representative layer compounds. In addition the ability to produce highly perfect surfaces by cleaving makes the transition metal dichalcogenides ideal specimens for tunneling microscopy. The characteristic of layer structures has also been used to advantage in molecular beam diffraction by Bosto, et al.³³ They used helium beam diffraction to observe satellite peaks corresponding to the surface corrugation effects due to charge-density waves in 1T-TaS_2 . Experiments are under way on a number of other phases and compounds which exhibit CDW transitions in order to further characterize the ability of tunneling microscopy to detect charge-density wave structure.

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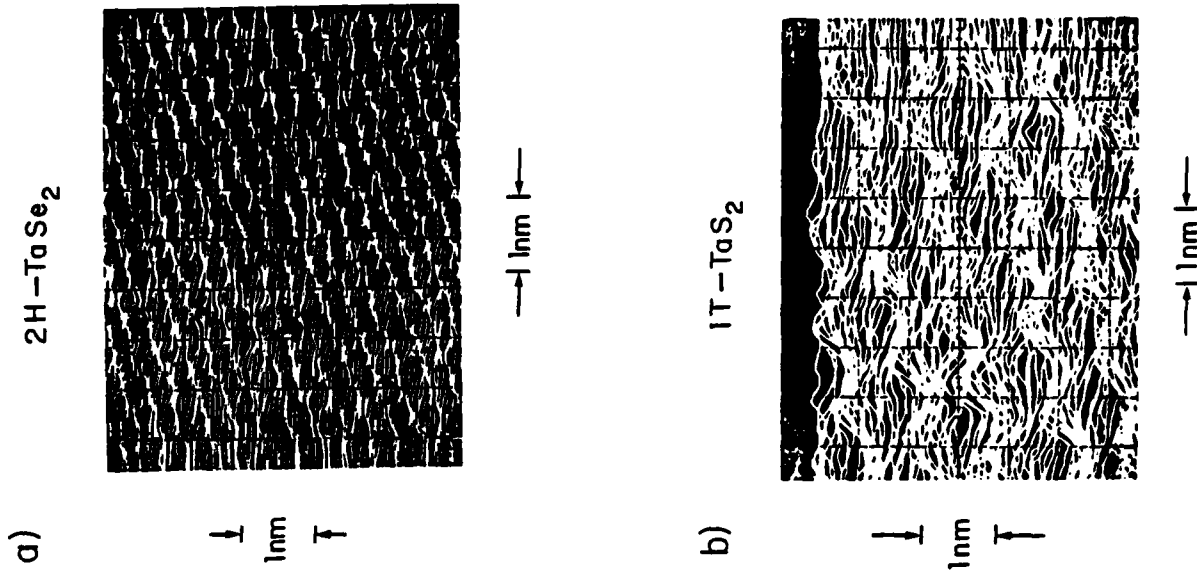
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Figure Captions

1. a) Atoms on a cleaved surface of $2H-TaSe_2$. The image was obtained in ~ 5 sec at a scan rate of 10Hz. The applied voltage was ~ 50 meV and the tunneling current was 2nA.
b) Charge-density waves on a cleaned surface of $1T-TaS_2$. The magnification and scan rate were the same as above. The applied voltage was ~ 50 meV and the tunneling current was 5.5nA.
2. The resistivity of $1T-TaS_2$ and $2H-TaSe_2$ measured parallel to the layers versus temperature. The resistivity of $1T-TaS_2$ shows much larger anomalies at the CDW phase changes than observed in $2H-TaSe_2$. $1T-TaS_2$ shows a two part incommensurate to commensurate transition with discontinuous resistance changes at 350 and 200K with an initial CDW onset at ~ 600 K. $2H-TaSe_2$ has an initial CDW onset at 120K with lock-in at 190K and a very weak resistance anomaly.



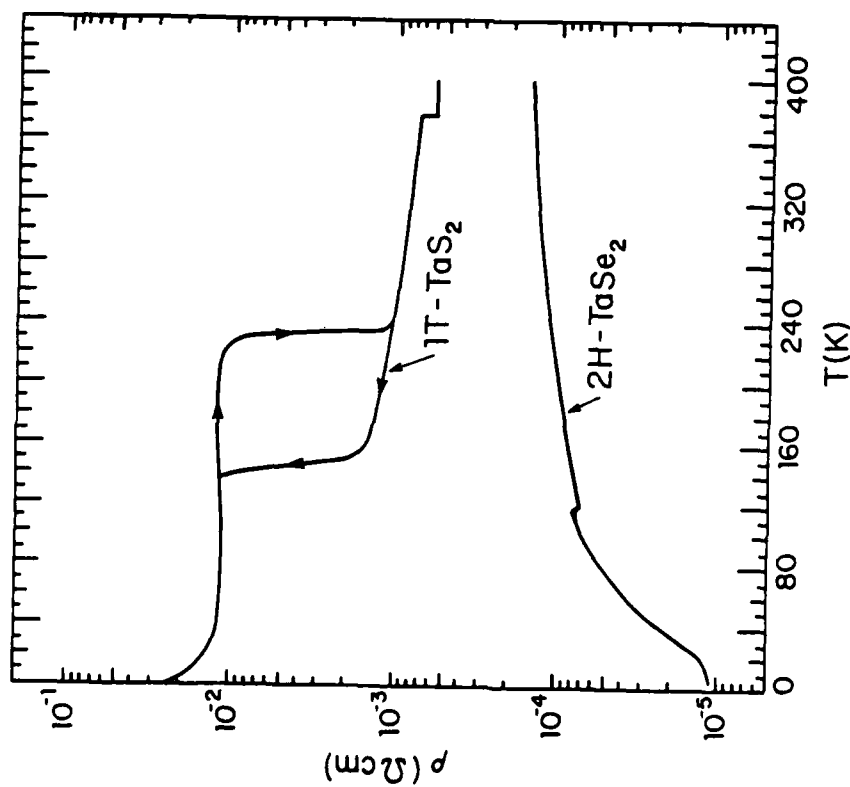


Fig. 2

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