Point spectroscopy and dI/dV line maps

For the investigation of the electronic structure extensive sets of dI/dV spectroscopy measurements have been taken. The result of the point spectroscopy (*Fig.23*) depends drastically on the position on the surface where they were recorded.

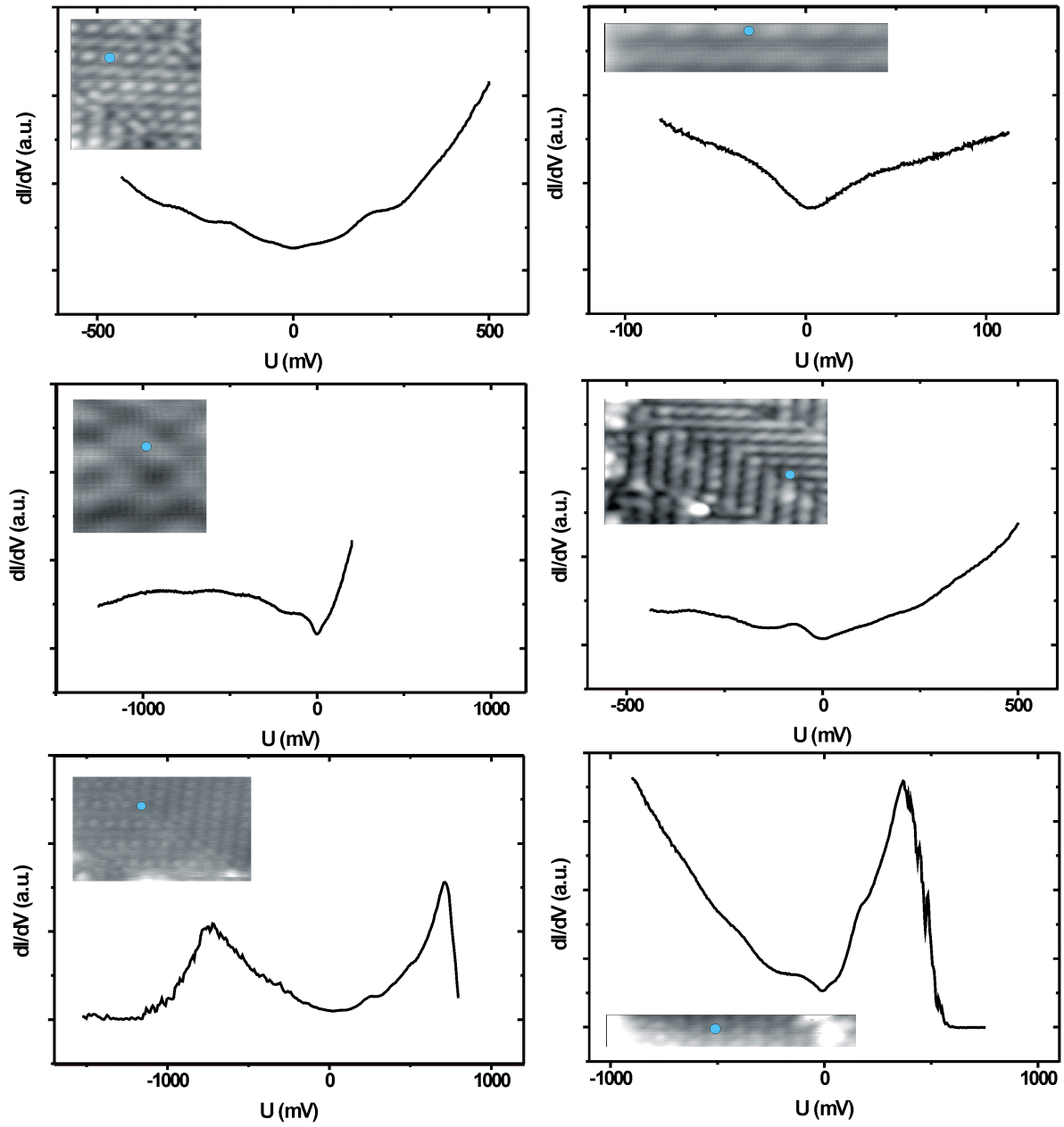

Fig.23

Point spectra taken at different locations.

The left upper point spectrum is a typical spectrum most commonly observed. It shows a pronounced minimum at the Fermi energy, surrounded by a number of shoulders. The right

upper spectrum has been measured in a smaller energy interval with a higher energy resolution. Usually a modulation amplitude of 10mV was used in the lock-in amplifier, this spectrum was taken with a modulation amplitude of 4mV. A further reduction of the modulation amplitude did not influence the spectrum. Although Ga becomes superconductive in the bulk at 1.8 K, by comparing this spectrum with the superconductive gaps on layered materials or metals, surface superconductivity is not likely to be present. The point spectra depend on the location, e.g. taken from the `bumps` in the `bump` rows, or between the `bumps`, or from the `zigzag` row, or from the domain boundary. The two lowest spectra show some noise at higher voltages. Here the tip becomes instable and the measurement is not reliable. But despite of this all taken spectra contain similar features. They show the minimum at the Fermi energy and flat plateaus (or shoulders) symmetric to the Fermi level. The spectra show a continuously growing background symmetric to the Fermi energy originating from the pseudogap. The pseudogap displays the covalent character of the crystal. It has a width of about 2 eV, which is the distance between the molecular levels of the Ga dimers (see Photoemission results section).

More information can be obtained from the line dI/dV maps. On these maps for positive voltages (*Fig.24, left*) and for negative voltages (*Fig.24, middle and right*) the intensity of each line has been rescaled individually to fit from black to white.

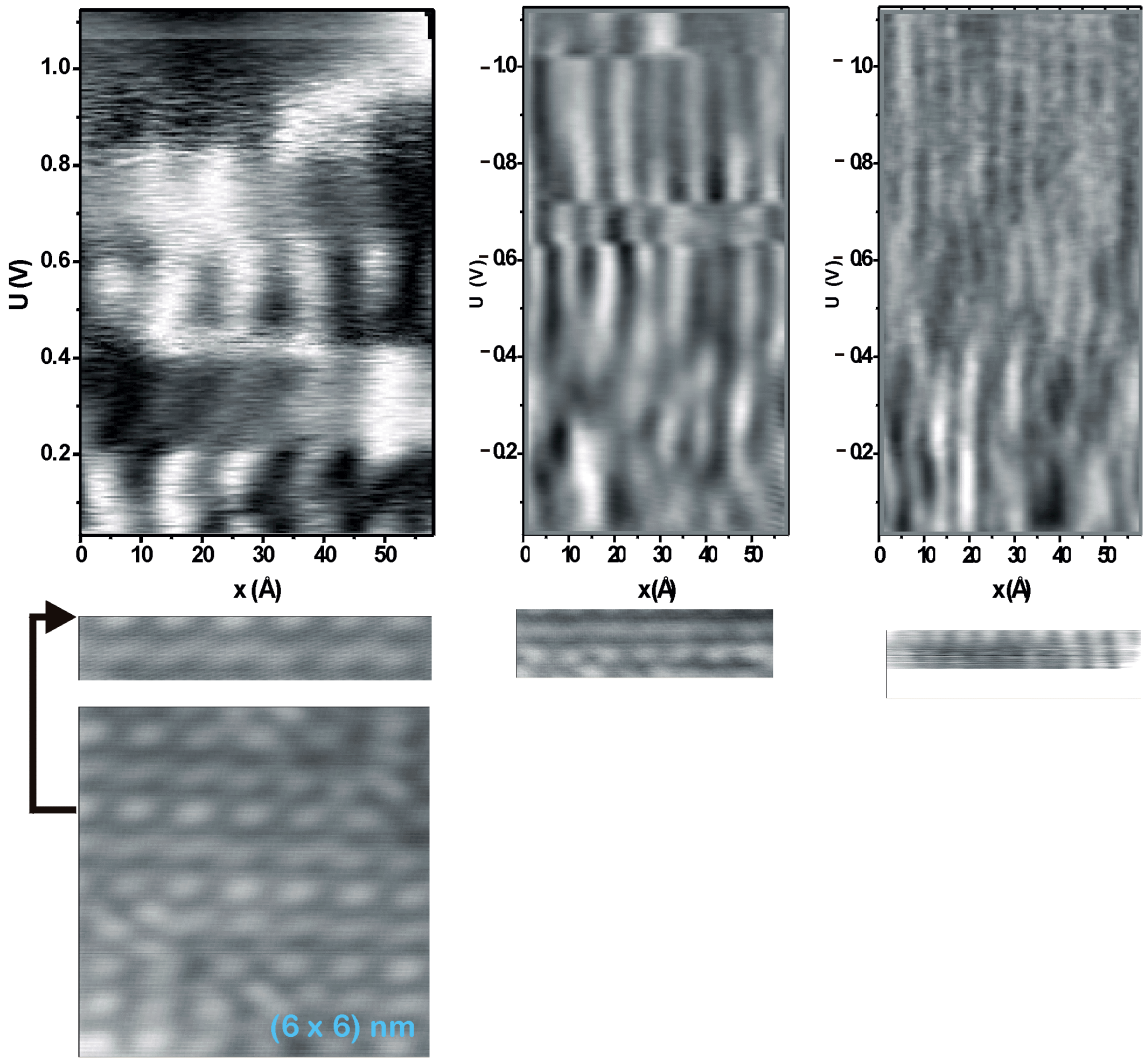

Fig.24

Left: dI/dV line map for positive voltages displayed together with the area where it is taken from. Middle and Right: dI/dV line maps for the negative voltages together with the area where it is taken from.

By taking a look on the dI/dV map for positive voltages (*Fig.24, left*) one can see at certain voltages (each 200 mV) an intensity change and a phase shift in the dI/dV map. This phase shift occurs at the same voltage (200 mV) as observed as a shoulder in the point spectroscopy. For negative voltages (*Fig.24, middle and right*) the data is less clear but again one can observe phase shifts. The data has been taken with closed feed-back loop. This means that the tip height is not constant and the height dependence of the current can cause an additional modulation of the intensity. The results of the spectroscopy shall be discussed in terms of a charge density wave.

Charge density wave introduction

When metals are cooled, some of them undergo a phase transition (in the 1D case this is called a Peierls transition) to a state exhibiting a charge density wave (CDW). A CDW is a periodic modulation of conduction electron density and an associated modulation of lattice atom positions. Materials which undergo such a transition could show strikingly nonlinear and anisotropic electrical properties, gigantic dielectric constants, unusual elastic properties, and rich dynamic behavior.

In *Fig.25 (left and right)* a single particle energy band is shown. The left image corresponds to the case when electron and phonon systems are not coupled. In that case the ions are equally spaced and the charge density – represented by the red line – is uniform. When electron and phonon systems are allowed to interact (*Fig.25, right image*), the competition between the elastic and the electronic energies leads to a static lattice deformation and a periodically modulated charge density. Due to the periodicity of the lattice deformation, the electron density becomes periodically modulated. As a result of the modulation a gap opens up in the single particle excitation spectrum at the Fermi level, and a spatially periodic charge density modulation is formed with wave-vector $2k_F$. The deformation is limited by the corresponding increase in the elastic energy.

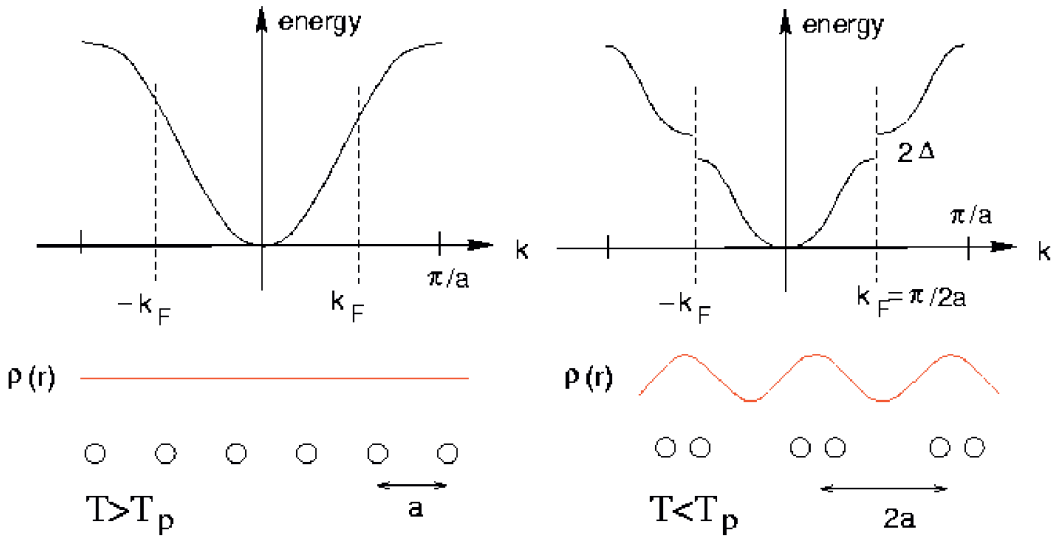

Fig.25

Single particle energy band in the case when electron and phonon systems are not coupled (left) and when these systems are allowed to interact (right).

The formation of a CDW is energetically favoured. In the left image of *Fig.25* a situation is described when allowed conduction electron states form a band. States inside the Fermi surface with energies less than E_F and wave-vectors less than k_F will be occupied, and states outside the Fermi surface will be empty. If a energy gap is opened at $k = \pm k_F$ (*Fig.25, right image*), then the energy of the occupied states below E_F will be lowered, reducing the total electronic energy.

For metals at low temperatures the elastic energy cost to modulate the atomic positions is less than the gain in the conduction electron energy, so the CDW state is the preferred ground state. At high temperatures the electronic energy gain is reduced by thermal excitation of electrons across the gap, so the metallic state is stable. The transition between the metallic and CDW state is of second order and is called the CDW or Peierls transition. Hence a metal can reduce its energy by developing a charge density wave. A CDW itself consists of coupled modulations of the conduction electron density and atomic positions, and produces an energy gap at the Fermi surface $k = k_F$. The modulation of atomic displacements and conduction electron density are usually quite small: The atomic displacements are only about 1% of the interatomic spacings, the conduction electron density varies only about 10%.

The same process considered from the point of view of the dispersion of the phonons is called a Kohn anomaly and is shown in *Fig.26* for the cases of 1D, 2D, and 3D.

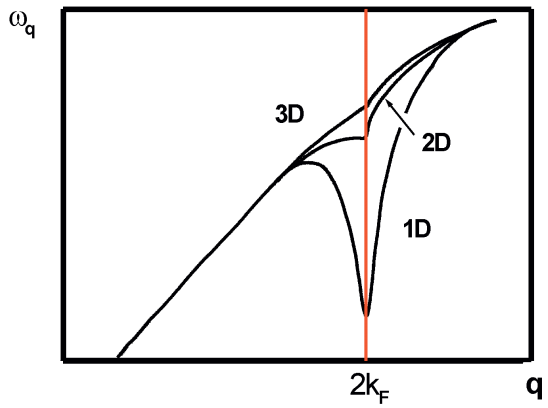

Fig.26

Modification of the phonon dispersion. Kohn anomaly or phonon softening at $2k_F$.

A number of examples from literature is shown explaining how the charge density wave shows up in the STM topography images (*Fig.27*) and in the spectroscopy (*Fig.28*) for different layered materials.

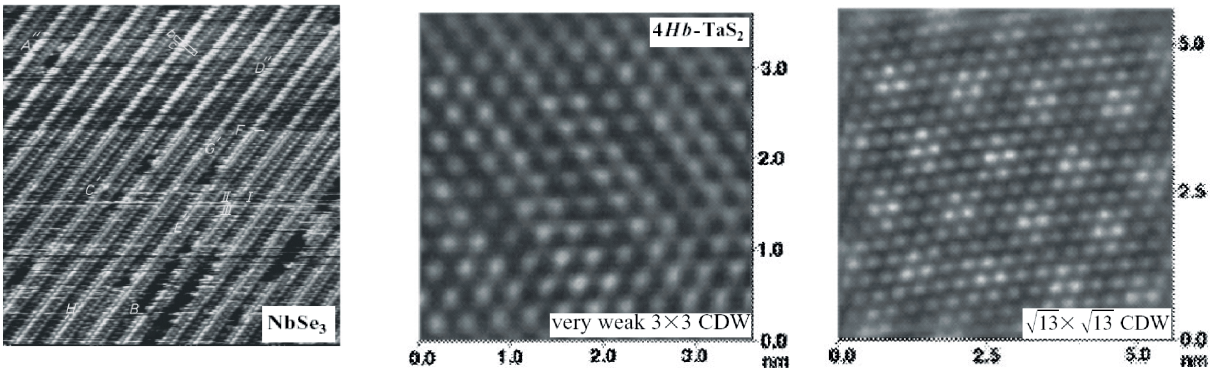

Fig.27

Left: Resolved Se atoms on the (100) van der Waals face of NbSe3 [10].

Middle and right: 4Hb-TaS2 displays very weak 3x3 CDW and Sqrt13xSqrt13 CDW [11].

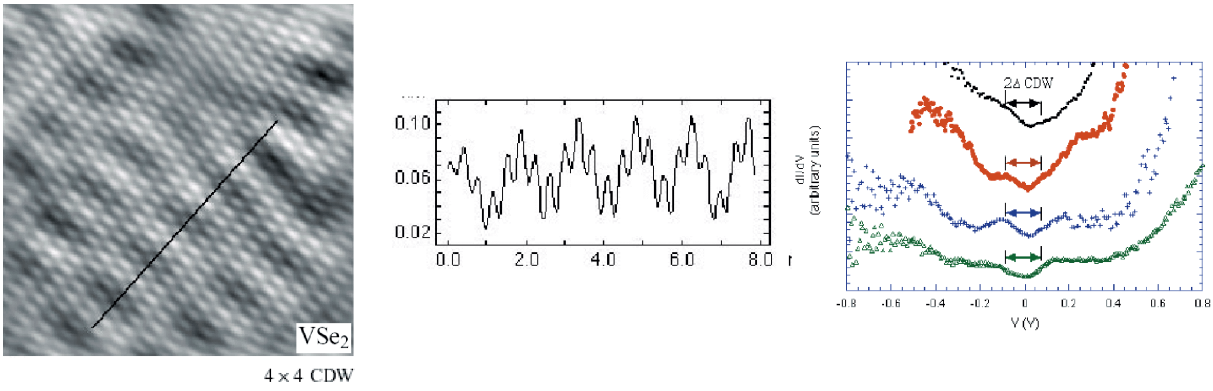

Fig.28

STM topography image, line scan and point spectroscopy showing the presence of a charge density wave on VSe_2 [12].

In all of the STM topography images one can see the modulation of the intensity, which is a sign of a commensurate 4x4 CDW, 3x3 CDW, and [redacted] CDW respectively. In the point spectroscopy data one can see a pronounced minimum at the Fermi energy and shoulders (plateaus) symmetric to the Fermi level as a result of the CDW gap.

The Charge Density Wave on $\alpha - Ga$ (010)

In this section the $\alpha - Ga$ (010) topography, point spectroscopy, dI/dV line and area map results will be discussed from the point of view of a charge density wave. In *Fig.29* one can see the topography image and a corresponding dI/dV area map taken at a voltage of –40 mV (for other energies see section CDW finestructure). In the dI/dV area map one can clearly see a wave-like modulation of the intensity of each second `bump` with wave fronts perpendicular to the row directions in both of the domains. In the right image of the *Fig.29* this modulation is marked by blue and violet lines for better visibility. This wave pattern is slightly visible also on the topography image for -40 mV, but does not show up in topographic images at higher voltages. Therefore one can conclude that this wave pattern is not a structural modulation. As this pattern is very regular, this wave-like modulation is not a standing wave resulting from scattering at adsorbates or defects. One can therefore conclude that the observed wave pattern is a CDW in the low temperature phase of $\alpha - Ga$ (010) in analogy to those shown in *Fig.27* and *Fig.28*.

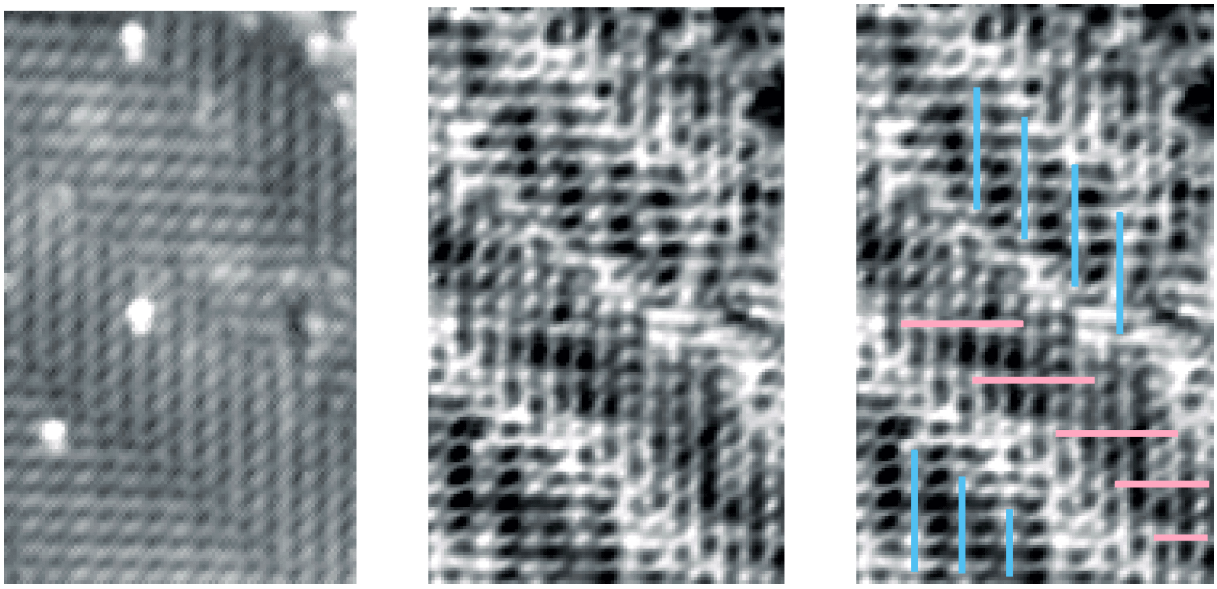

Fig.29

The topography image and corresponding dI/dV area map taken at -40 mV.

This interpretation of the image structures in terms of a CDW is further supported by the striking similarity of the measured point spectra with spectra of CDW systems published in the literature, e.g. (*Fig.28*, [12]).

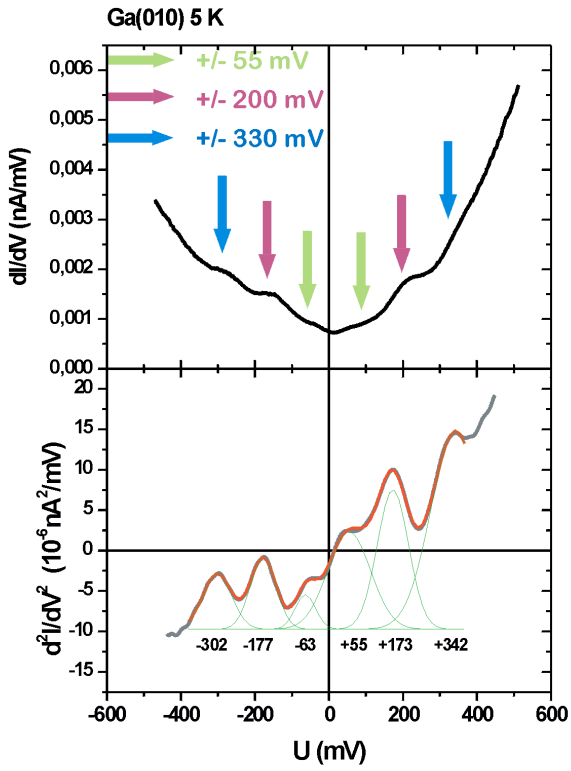

Fig.30

Point spectra of $\alpha - Ga\,(010)$ exhibiting CDW. The lower graph is the numerical derivative of the upper curve.

Comparing the surface phonon spectra of the $\alpha - Ga\,(010)$ low temperature and room temperature phases one can see not just a Kohn anomaly (phonon spectra softening) but a complete change of the lattice periodicity (*Fig.31*). Since the atoms in the lattice shift from their initial positions not only by 1%, but undergo a drastic reconstruction, one is dealing here with a strong coupling CDW like discussed for semiconductor surfaces [18]. In such a case the atomic displacement is expected to change the phonon spectra, as is observed in the inelastic Helium Atom Scattering experiment.

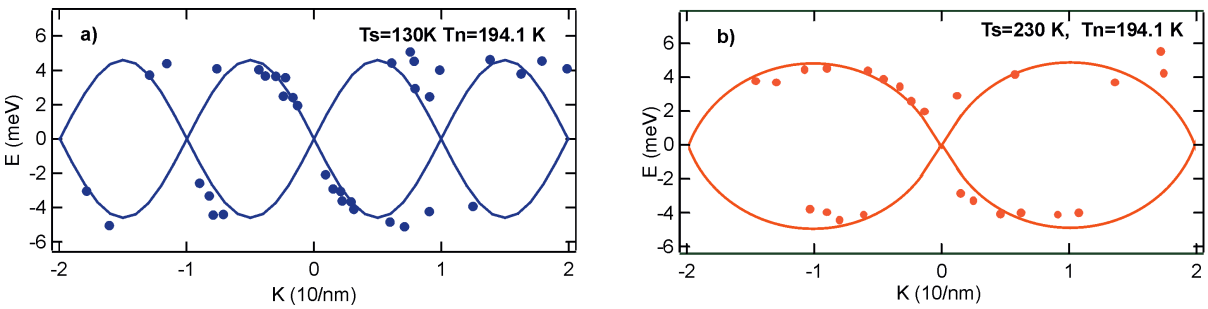

Fig.31

Complete change of the lattice periodicity observed in a phonon dispersion of Ga crystal a) below and b) above the phase transition by helium atom scattering (see HAS experimental chapter).

In [5], and [6] the surface state with a binding energy of about -1eV was investigated by photoemission spectroscopy. This surface state did not show up in the point spectra because of (1) tip instabilities at higher voltages and (2) short electron lifetimes [5]. Nevertheless the appearance of the CDW can be explained by the coupling of these surface electrons. Although the experimental STM results suggest a more complicated picture than given in [13], the line of argumentation is plausible and will be reviewed here. The CDW is explained with the nesting of the Fermi surface. In *Fig.32* one can see the bulk Fermi surface projection [13].

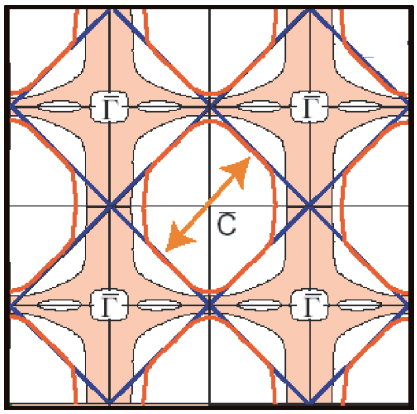

Fig.32

Bulk Fermi surface projection [13].

Here for simplicity the surface structure is assumed to be $\left(\sqrt{2}x\sqrt{2}\right)R45°$. The surface state contour is shown here with the red color. The dark blue colour is the BZ boundary. One can see that large parts of this contour run on the BZ boundary and can couple with each other. Therefore this periodicity favors nesting of parts of the Fermi contour to form a CDW. The observed periodicity is actually a $\left(2\sqrt{2}x\sqrt{2}\right)R45°$, but nevertheless the backfolding in one direction still remains.

The CDW finestructure

The point spectra show up to 6 plateaus, already indicating a more complex situation as proposed in the previous section, possibly caused by a multigap structure. In this section