Chapter 4

The α-Ga (010) surface investigated by room and low temperature scanning tunneling microscopy and spectroscopy

Introduction

Ga is a trivalent metal with an unusual crystal structure in the stable low-pressure phase called $\alpha - Ga$. Ga has a phase diagram with several stable and metastable crystalline phases. *Fig.1* shows stability regions for the solid $\alpha - Ga$, GaII and GaIII phases. Many other metastable phases are also experimentally observed, but not all of their structures are known. $\alpha - Ga$ is a stable phase at ambient pressure, while two other phases (GaII and GaIII) are stable at high pressure and/or high temperature.

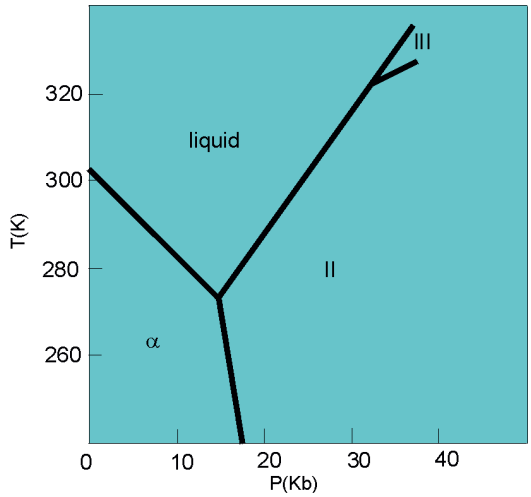

Fig.1
Stability region for solid $\alpha - Ga$, GaII, and Ga III phases [1].

$\alpha - Ga$ itself is an unusual elemental solid. On the one hand, it is a metal with a low density of states at the Fermi energy, on the other hand most of its properties are strikingly different than those of other metals. The crystal structure of $\alpha - Ga$ is not a close-packed configuration

but is rather complicated. It is commonly described in the terms of a face-centered orthorhombic unit cell with 8 atoms per unit cell (*Fig.2*). The primitive unit cell has 4 atoms.

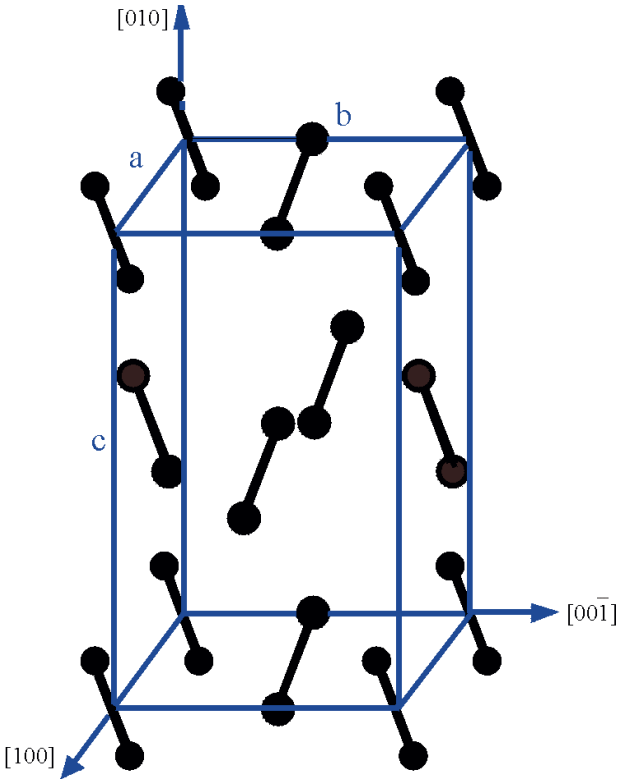

Fig.2

Crystal structure of $\alpha - Ga$

Each Ga atom has only one nearest neighbour at a bonding distance of 2.44 $\mathring{A}$. The second, third, and fourth shells each contains two atoms, and are 0.27, 0.30, and 0.39 $\mathring{A}$ further apart. The charge is highly localized in the short bond (*Fig.3*).

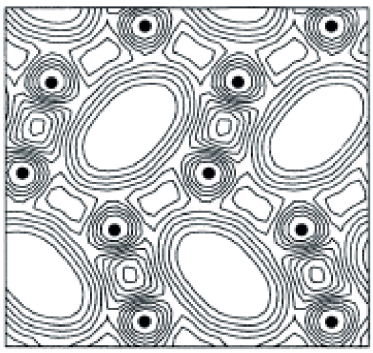

Fig.3

Electron (pseudo)charge density map of $\alpha - Ga$ *[100] plane computed at the equilibrium volume of this phase [1].*

Therefore the crystal may be viewed as having been constructed of Ga_2 dimers as elemental building blocks. So it is possible to say that apart from being a metal $\alpha - Ga$ is still to some degree a covalently bonded solid. For example the thermal and electric conductivity are much higher in the (010) plane, which is almost perpendicular to the dimers[1]. So it is possible to view $\alpha - Ga$ as a solid which is molecular and metallic at the same time. The molecular properties are related to the presence of Ga_2 dimers, while the metallic properties are attributed to the (010) buckled plains. The electronic density of states of $\alpha - Ga$ is rather structured and shows a pronounced pseudogap at the Fermi level [2]. The residual states in the pseudogap are mainly related to the overlap of the electronic wave functions along the buckled planes perpendicular to the molecular bond. Such kind of states lead to the metallic behavior, which thus coexists with the molecular states. s-like states are localized in the buckled planes and are the main contribution to the density of states. The coexistence of two kind of bondings, covalent and metallic, apparently contributes to the stability of this structure.

$\alpha - Ga$ has a low melting temperature of about 302 K. This fact requires special experimental conditions: One needs a constant cooling of the sample to avoid melting of the crystal and a contamination of the UHV chamber.

LEED and SPA-LEED.

$\alpha - Ga$ undergoes a phase transition at around 235 K. Therefore in the following the terms room temperature and low temperature phases refer to the phases above and below this temperature. The first investigations of the surface structure above and below the phase transition were done by LEED and SPA-LEED measurements [3,4]. For this experiment the Ga surface was cleaned by sputtering with Ne^+ between –20°C and 0°C and was kept at 0°C for the measurements. LEED measurements were taken at an energy of 90 eV. The LEED measurements show (1x1) pattern, every second spot in one direction is missing (*Fig.4*). The missing spots can be explained by the glide-plane symmetry of the bulk in the [100] direction. This symmetry does not seem to be broken at the surface.

[1] The dimers are tilted by 14°.

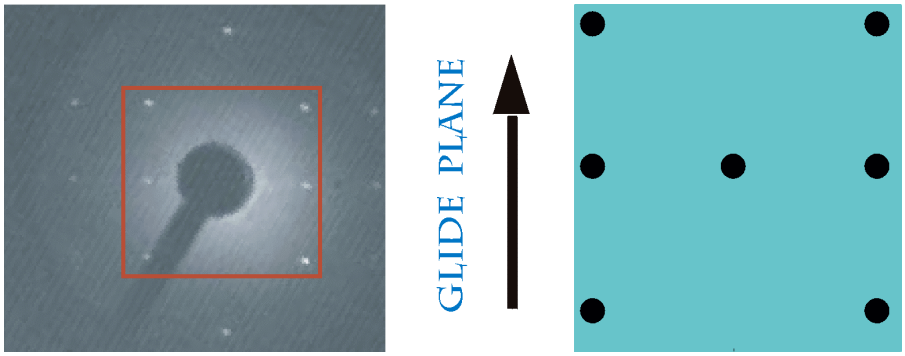

Fig.4

LEED 90 eV pattern and an intensity scheme of the room temperature phase of $\alpha - Ga\,(010)$ *[3].*

While cooling down below 235 K a c(2x2) pattern is observed in the LEED measurements. The missing spots from the room temperature measurements are now visible (*Fig.5, left image*).

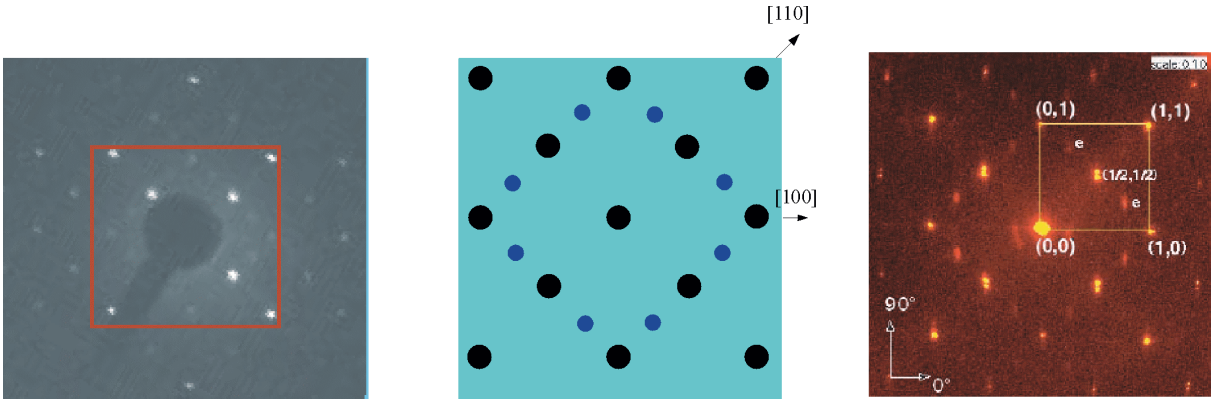

Fig.5

LEED 90 eV pattern, schematic representation, and SPA-LEED 85 eV pattern of the low temperature phase of $\alpha - Ga$*. In the intensity scheme the black circles correspond to the LEED observations, the smaller blue circles are additional spots found by SPA-LEED [3,4].*

With the SPA-LEED additional spots in the low temperature phase are observed (*Fig.5, right image*). These spots are only visible in a narrow energy range. With a standard LEED technique they are not resolvable. The SPA-LEED instrument is a high resolution LEED and permits to make two-dimensional or one-dimensional scans along certain directions. The big advantage of this instrument is the possibility to study with high resolution the spot profile

which yields information e.g. about the order and the kind of domains which can be present on the surface.

SPA-LEED measurements in the low temperature phase show that the fractional order spots (½, ½) are split along the direction of the glide plane, which denotes a long range periodicity with a period of 18 unit cells. Our LT STM measurements (see Topography Section) show that this splitting can be explained by the existence of two stripe-like domains in the low temperature phase of Ga. The two split spots are rather close to each other. The `*e*` spots are visible in the first zone and in the higher zones. This confirms that the structure is $\left(2\sqrt{2}x\sqrt{2}\right)R45°$. The intensity of the ` *e* ` spots is small and shows up in the LEED measurements only at energies of 80-90eV. So the (½ , ½) spots show a clear splitting while the *e* spots are elongated in the same direction. Because of the low intensity of these spots it cannot be determined whether these spots also split or not. The only spot which does not show any elongation or splitting is the (0,1) spot which symmetry vanishes in the room temperature phase due to the presence of the glide plane symmetry of the (1x1) structure.

The intensity of the (0,1) spot during the phase transition shows that the intensity drops rapidly during the phase transition. This means that the phase transition is step-like (*Fig.6*), a signature of a first order phase transition [4]. Theory predicts that the transition is a second-order transition. This is also shown by the helium atom scattering experimental results. HAS is exclusively surface sensitive, therefore this applies only to the topmost atomic surface layer.

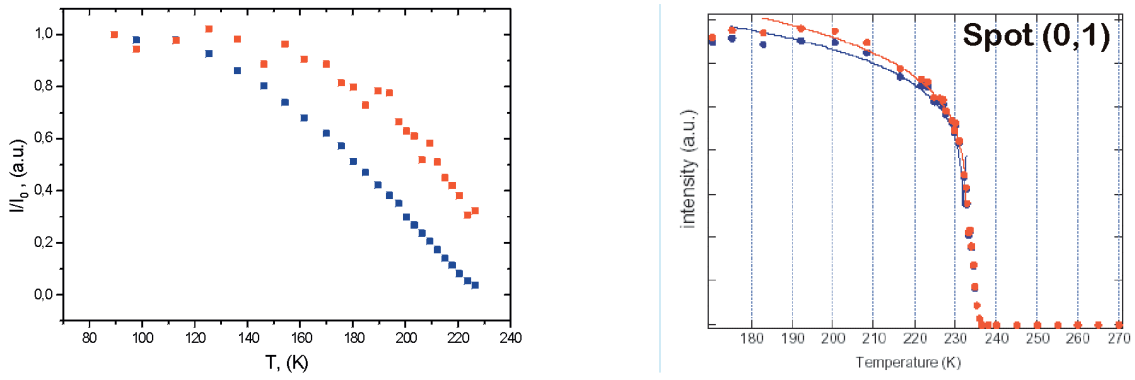

Fig.6

The intensity of the (0,1) spot during the phase transition measured by HAS (left) and SPA-LEED (right) [4].

Photoemission results

The electronic structure of the $\alpha - Ga$ (010) has been studied in the room and low temperature phases with photoemission spectroscopy and will be reviewed here as far as relevant for the experimental results in this work. Semimetals such as $\alpha - Ga$ have a low density of states at the Fermi level but their surfaces can support surface states which cross E_F and render the surface much more metallic than the bulk (they can be considered as quasi-two-dimensional metals). The state which crosses E_F was predicted by calculations to exist in an electron pocket centered round the corner (the C point) of the surface BZ and to have a bandwidth of 1.5 eV [5]. It was indeed found experimentally. *Fig.7* shows the surface state dispersion at 273 K and 120 K superimposed on the projected bulk band structure [5]. The surface states have been identified by the absence of a dependence on $k_\perp$, their sensitivity towards contamination and their position in gaps of the projected bulk band structure.

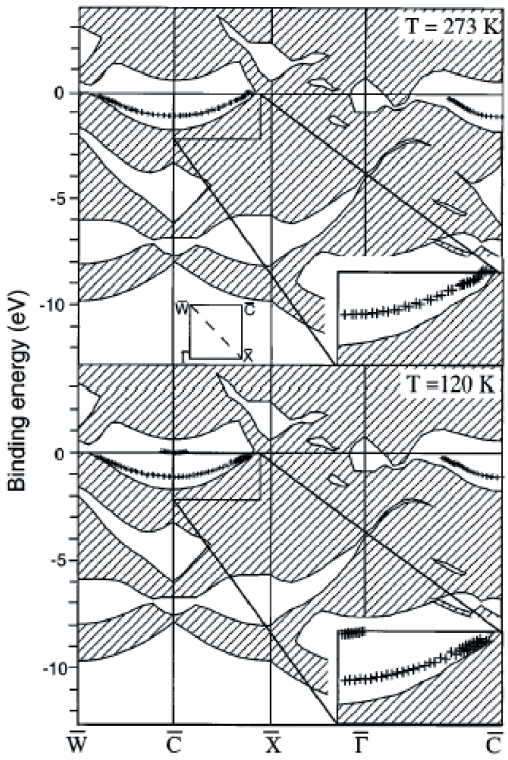

Fig.7

Surface states for room and low temperature Ga phases observed by photoemission.

For both temperatures the peak clearly runs into the bulk bands in the C-W direction. In the C-Γ direction the situation is unclear: The peak can no longer be observed beyond a certain point due to the vicinity of the intense and broad transition from the bulk bands. The C-X

direction shows pronounced differences between the high- and low-temperature measurements. While the surface state crosses E_F in the former, it does not reach it in the latter and runs into the bulk bands instead. Apart from this, only one surface-related feature was found: Upon cooling a small intensity peak can be observed very close to E_F in the immediate vicinity of C.

In an earlier work, angle resolved photoemission data was taken for the bulk [6]. The resulting dispersions are displayed with the calculated bands in *Fig.8*.

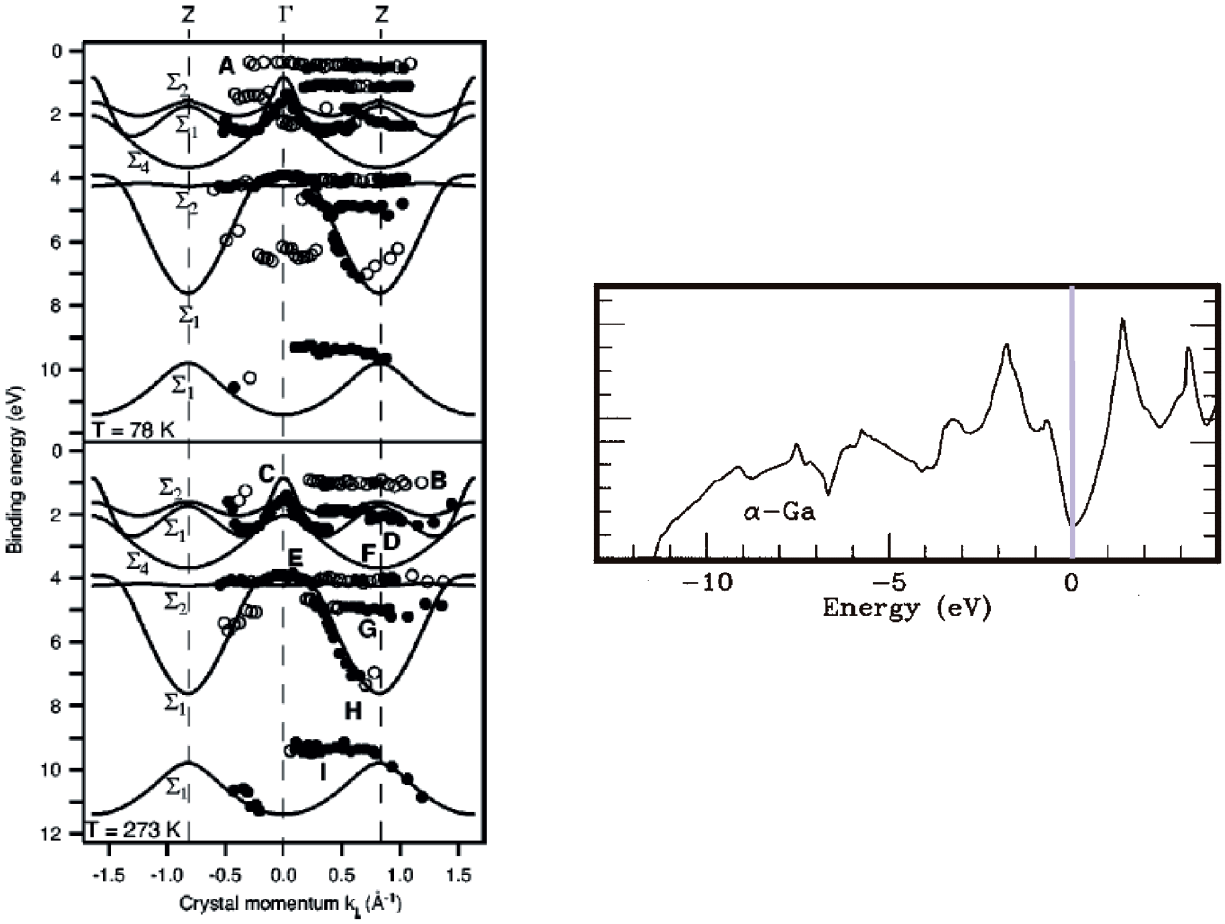

Fig.8

Left: Angle resolved photoemission data for low and room temperature Ga phases [6].

Right: Density of states calculated by [2] shows a pronounced pseudogap at the Fermi energy.

By comparing the detailed dispersion of the experimental bands and the calculation result, one can see a good agreement for the position of the high symmetry points in the dispersion of the C and E bands. The maximum of the dispersion of the H band is slightly shifted from the calculated position. The state A is assigned to an electronic surface state because its binding energy does not change as the photon energy is varied and because it falls in a projected bulk band gap as can be clearly seen by the calculated bands. The state A can be only observed in the low temperature data set. State B does not fall into the region of the calculated band gap. One can say that the state B is either another surface state, possibly only in a symmetry induced gap, or a surface resonance. The D and F states are interpreted as genuine bulk bands which agree very well with the calculation. The G state can be explained by the surface contamination: The G peak has the same binding energy as an oxygen induced peak. The main conclusion is that the presence of several rather flat bands in $\Gamma - Z$ direction allows to describe $\alpha - Ga$ as a metallic molecular solid.

Surface terminations

$\alpha - Ga$ is one of the elemental materials which do not crystallize in any of the simple crystal structures. The double nature – covalent and metallic – makes the surface of $\alpha - Ga$ especially interesting. The covalency of the dimer has its fingerprint in the electronic properties, in particular the presence of the pseudogap at the Fermi level in the electronic density of states has been confirmed by the first-principles calculations [7]. Ga has a very low melting temperature and a low vapor pressure of melting, which makes it a suitable system for the study of the surfaces very close to the melting temperature. Theoretical arguments suggest that the surface of $\alpha - Ga$ should display either nonmelting or incomplete (blocked) surface melting behavior. This comes from the presence of the attractive van der Waals forces between the liquid surface and the liquid-solid interface of solid Ga wetted by a thick liquid film.

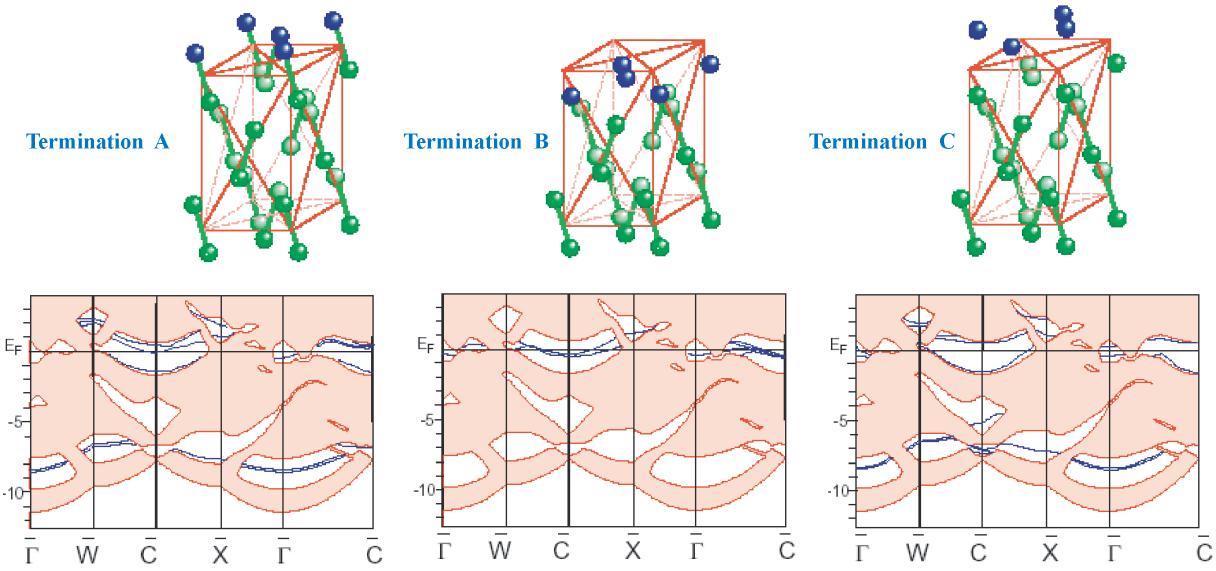

Fig. 9

Three possible terminations of $\alpha - Ga$ *together with results from DFT calculations [7].*

Two truncated bulk structures are possible for the $\alpha - Ga$ (010) surface, one with the dimers intact (Termination A) and one with the dimers broken or cut (Termination B), creating the surface with dangling bonds. In addition to these a third termination (Termination C) has been predicted by Bernasconi et al [7] described as a (1x1) reconstruction which can be thought of as two layers of GaIII, covering the (010) surface of $\alpha - Ga$. For all three terminations every odd-integer spot towards [100] direction is missing at the LEED pattern in normal incidence, because of the glide plane symmetry of bulk $\alpha - Ga$ which is preserved in the surface structure. Calculations show that the topmost layer appears identical in STM measurements for all three cases, therefore this method is not suited to distinguish between the terminations [6]. Recent x-ray [8] and quantitative LEED I-V investigations of the $\alpha - Ga$ surface show that the structure is the Termination B. In *Fig.9* the three possible terminations of the $\alpha - Ga$ (010) surface are shown together with results from DFT calculations [7].

Preparation of the sample

The preparation of the $\alpha - Ga$ (010) surface is not straight forward and depends critically on several factors. One needs to take into account the sputtering energy and current, chamber pressure from the sputter gas, sample temperature, speed of the cooling to liquid helium temperature in LT STM measurements and the residual background pressure during and after