Electron-Lattice Interaction on α-Ga(010)

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We have investigated the (010) surface of α-Ga by angle-resolved photoemission and low energy electron diffraction. We find a surface state around the $\bar{C}$ point of the surface Brillouin zone. The electron-phonon coupling at this surface is very strong with an electron-phonon mass enhancement parameter of $\lambda = 1.4 \pm 0.10$. Our spectra show high background intensity in a projected bulk band gap which cannot be accounted for by defect scattering and is therefore interpreted as indicating a nonquasiparticle behavior. Upon cooling the sample below 220 K we observe a phase transition accompanied by spectral changes near the Fermi level. [S0031-9007(98)06909-9]

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Semimetals such as beryllium or α-gallium have a low density of states at the Fermi level but their surfaces can support electronic states which cross E_F and render the surface much more metallic than the bulk [1–3]. Hence, these surfaces form simple test cases for probing the properties of quasi-two-dimensional metals. The motivation for the work presented here is to study the effect of the electron-phonon coupling on the electronic structure of a two-dimensional metal. Although this effect is restricted to a small energy window around E_F, it can be quite dramatic: In three dimensions it is predicted to lead to a nonquasiparticle behavior in the spectral function [4], an effect which has, to our knowledge, never been observed directly.

The (010) surface of α-gallium is a very promising candidate for establishing an influence of the electron-phonon coupling on the dispersion of the electronic states. The size of the effect is given mainly by two factors: The phonon bandwidth $E_{\max}$ sets the energy scale and the so-called electron-phonon mass enhancement parameter λ describes the change in curvature of the dispersion at E_F. Both are relatively high in bulk α-Ga ($E_{\max} = 40$ meV [5] and $\lambda = 0.98$ [6]). A very important practical requirement for an investigation with angle-resolved photoemission is a geometrically flat surface because the small effect would otherwise be smeared out in momentum space. This seems to be fulfilled in the case of α-Ga(010) as shown by the scanning tunneling microscopy (STM) results obtained by Züger and Dürig [7,8]. Finally, the surface has to support a surface state which crosses E_F. Such a state was actually predicted for α-Ga(010) in a recent first-principles calculation by Bernasconi, Chiarotti, and Tosatti (BCT) [3]. The state was found to form an electron pocket centered around the corner (the $\bar{C}$ point) of the surface Brillouin zone (SBZ) and to have a bandwidth of about 1.5 eV.

Our α-gallium sample was cut mechanically from a bulk single crystal. The natural (010) surface was subsequently polished. Experiments were carried out in a UHV chamber on a toroidal grating monochromator beam line (TGM-4) at the Berlin synchrotron radiation source (BESSY). The chamber was equipped with a VG Instruments ADES400 spectrometer for angle-resolved photoemission measurements, an Omicron LEED optics, and an electron gun for Auger electron spectroscopy (AES). The energy resolution was around 80–100 meV for all the photoemission measurements reported here. The angular resolution was $\pm 1°$. The base pressure after bakeout was lower than 5×10^{-11} mbar. For the temperature-dependent measurements the sample was cooled with liquid nitrogen and heated indirectly by a tungsten filament. Sample heating and measurements were alternated to avoid any influence of the electromagnetic field on the photoemission results.

The surface was cleaned by short sputtering cycles with 0.5–1.0 keV Ne^+ ions at about 273 K. The cleanliness was monitored by AES as well as by the quality of the surface state and Ga $3d$ core level peaks. At 273 K a sharp (1×1) LEED pattern was observed. Every odd-integer spot in the [100] direction is missing, consistent with the glide-plane symmetry in bulk α-gallium. There are at least three different possible terminations for this surface, all of which are consistent with a glide-plane symmetry [3].

When the sample is cooled below about 220 K the LEED pattern changes reversibly from (1×1) to $c(2 \times 2)$. The superstructure spots are weaker and less sharp than the (1×1) spots; spots can be observed at

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all integer positions which is compatible with the loss of the glide plane symmetry. A very recent reinvestigation of the LEED pattern with a better LEED optics showed additional spots at low temperature in the $c(2 \times 4)$ positions. These are, however, much weaker than the $c(2 \times 2)$ spots such that the structure might be regarded as a slight distortion of $c(2 \times 2)$ [9].

The surface state at the $\bar{C}$ point predicted by BCT was indeed found experimentally. We can use the temperature dependence of its linewidth to determine the magnitude of the electron-phonon mass enhancement parameter λ at the surface following a procedure carefully outlined and illustrated by McDougall, Balasubramanian, and Jensen using the example of the Cu(111) surface state [10]. Assuming that the impurity scattering and Auger decay contributions to the hole lifetime are negligible, the temperature dependence of the linewidth can be calculated from the Eliashberg coupling function [6]. Figure 1 shows the energy distribution curves (EDCs) of the surface state at $\bar{C}$ for temperatures between 127 and 270 K. Apart from the obvious broadening, the peak shifts slightly towards lower binding energies with increasing temperatures. The upper part of Fig. 2 displays the Lorentzian width of the peak as a function of temperature. It was determined by fitting the peak with a Voigt line and a linear background. The curve through the points is the result of a fit to the theoretical linewidth within the Debye model. The only fit parameter in this calculation is λ. The best fit is obtained with a value of $\lambda = 1.4 \pm 0.10$ using $\omega_D = 28$ meV and $E_B = 1.1$ eV. The surprisingly high quality of this fit in Fig. 2 suggests that the width of the peak is almost exclusively given by the phonon contribution to the lifetime, i.e., that the impurity scattering and Auger decay contributions are very small. This is indicating that the surface has very few defects, consistent with the STM results [7,8]. The electron-phonon coupling on this surface is very strong, even stronger than for bulk α-gallium. This is consistent with our expectation that the surface physical properties should be very different from those of the bulk.

As a comparison the bottom of Fig. 2 shows the data for Cu(111) from Ref. [10] together with the theoretical prediction for the phonon contribution to the linewidth. In this case just by varying λ no satisfactory fit to the data can be achieved due to the contributions of Auger decay and defect scattering. The authors have circumvented this problem by assuming that the two latter contributions give a temperature-independent offset to the linewidth. Then, in the high-temperature limit, λ can be extracted from the slope of a straight-line fit to the data. On Cu(111) λ is 10

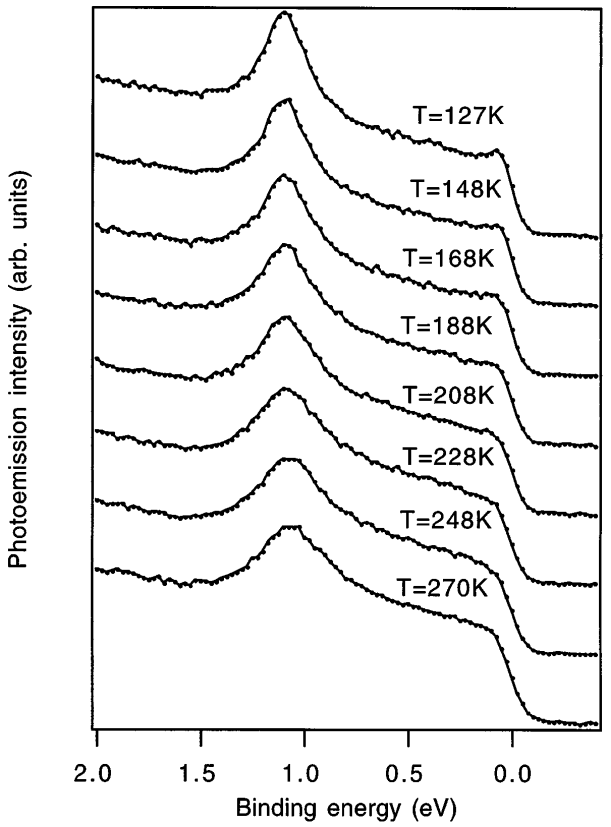

FIG. 1. Temperature dependence of the surface state linewidth near $\bar{C}$: energy distribution curves recorded at different temperatures and a photon energy of $h\nu = 16$ eV. Note the appearance of a feature right below the Fermi level for the lowest temperatures.

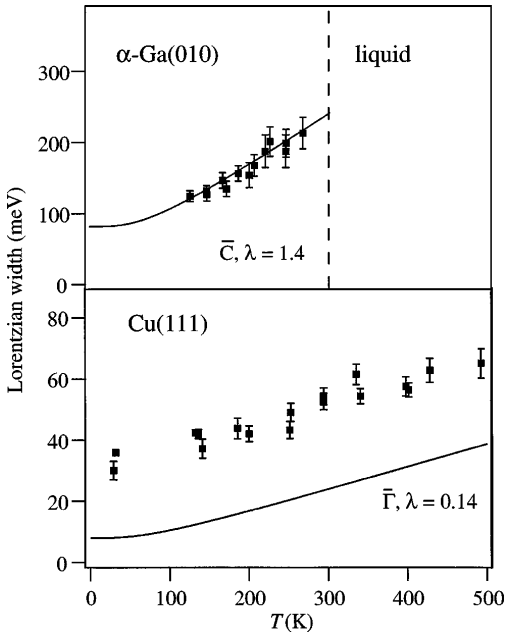

FIG. 2. Top: Lorentzian contribution to the linewidth as a function of temperature obtained from the data in Fig. 1. The error bars represent the uncertainties resulting from the fitting. The curve is a fit to the theoretical phonon contribution to the linewidth within the Debye model which yields $\lambda = 1.4 \pm 0.1$. Bottom: corresponding data for Cu(111) taken from Ref. [10]. For this surface the authors have determined $\lambda = 0.14 \pm 0.02$. It is clearly visible that the phonon contribution does not account for the full linewidth.

times smaller than on α-Ga which is reflected in the very different slope of the two curves. Furthermore, λ is very similar to the value for bulk Cu.

Figure 3 shows the surface state dispersion at 273 and at 120 K superimposed on the projected bulk band structure from BCT [3] as well as the SBZs for both phases. The surface states have been identified by the absence of dispersion with $k_\perp$, their sensitivity towards contamination and their position in gaps of the projected bulk band structure. The (E, k) data points for the dispersion of the surface state centered around $\bar{C}$ have been determined by fitting the spectra in the same way as for the temperature dependence. For the surface state close to E_F we have included a broadened Fermi edge in the fit function. The Gaussian width increases when we move away from $\bar{C}$ due to the steeper dispersion of the surface state. The precise values of the Gaussian and Lorentzian width as well as the peak shape itself (purely Gaussian or Voigt) do not have an appreciable influence on the resulting binding energy.

For both temperatures the peak clearly runs into the bulk bands in the $\bar{C}$-$\bar{W}$ direction. In the $\bar{C}$-$\bar{\Gamma}$ direction the situation is somewhat unclear: The peak can no longer be observed beyond a certain point due to the vicinity of the intense and broad transitions from the bulk bands.

The $\bar{C}$-$\bar{X}$ direction shows pronounced differences between the high- and the low-temperature measurements. While the surface state crosses E_F in the former it does not reach it in the latter and, again, runs into the bulk bands instead. Figure 4 shows the EDCs in the $\bar{C}$-$\bar{X}$ direction for both the high- and the low-temperature measurements. At 120 K the surface state peak moves towards E_F but never actually disappears before the bulk bands appear. The fitted peak position has a smallest binding energy of about 120 meV. Note, however, that this can only be an estimate since the line shape may not be described correctly by a Voigt line near E_F and our energy resolution does not permit a more detailed investigation of the line shape. For the high temperature phase, however, the surface state crosses E_F before the bulk bands move in.

Apart from this surface state band we find only one additional surface-related feature: Upon cooling a small peak can be observed very close to E_F in the immediate vicinity of $\bar{C}$. This feature is visible in Fig. 1 for the data taken at the lowest temperatures. When we try to fit the structure to determine its temperature dependence and dispersion it is not possible to decide whether it disperses upwards and disappears, or whether it just broadens out

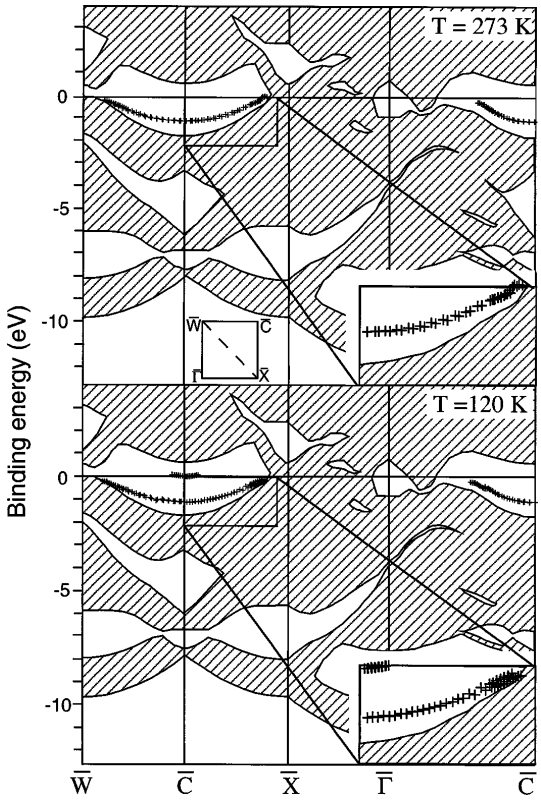

FIG. 3. Experimental surface state dispersion for $T = 273$ K and $T = 120$ K, i.e., above and below the (1×1) to $c(2 \times 2)$ phase transition. The energy positions are obtained by fitting the spectra as described in the text. The projected bulk band structure has been taken from Bernasconi, Chiarotti, and Tosatti (Ref. [3]). The inset in the top part of the figure shows the irreducible part of the surface Brillouin zones for the (1×1) (solid) and $c(2 \times 2)$ (dashed) phase.

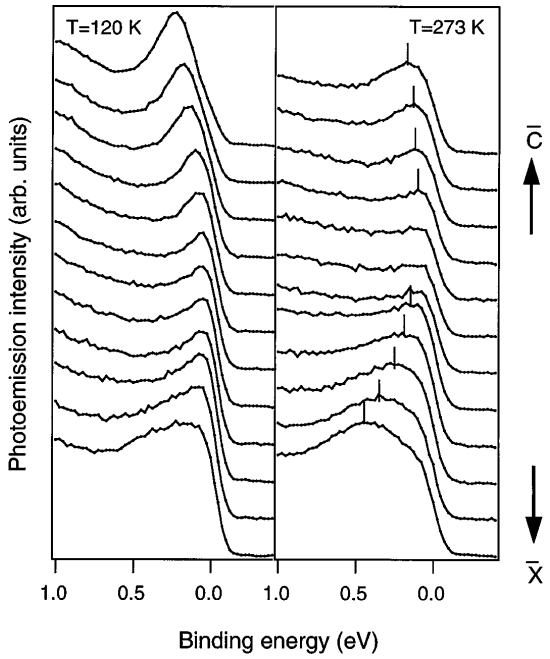

FIG. 4. EDCs in the $\bar{C}$-$\bar{X}$ direction for $T = 273$ K and $T = 120$ K ($h\nu = 16$ eV).The angular step between the EDCs is 1.0° which corresponds to a k step of $0.01 - 0.02$ Å^{-1}. Towards $\bar{X}$ the bulk bands can be observed to cross the Fermi energy. At $T = 273$ K the surface state crosses the Fermi level before the bulk band moves in. At $T = 120$ K the surface state peak is always visible.

as the separation from $\bar{C}$ increases or the temperature is raised. Hence, the weak dispersion indicated in Fig. 3 may be apparent: The points have been obtained by fitting the peak with a fixed width and a variable energy position.

While our fits to the surface state peak suggest that the phase transition causes the opening of a local band gap we have to be careful about such a statement. Note that there is still a significant spectral intensity measured at the Fermi edge after the quasiparticle peak has crossed E_F in Fig. 4. Indeed, all our data show a high background spectral intensity in the projected bulk band gap (see also Fig. 1), and our surface state to background ratio is significantly smaller than in other modern investigations of sp-derived surface states (see, e.g., Ref. [10]). For low-quality surfaces the occurrence of spectral intensity in bulk gaps is a common phenomenon due to defect-induced k smearing. This, however, seems very unlikely in view of the measured surface state linewidth (see above) and the STM results. It seems more likely that the spectral intensity is due to a breakdown of the quasiparticle picture for this system. A nonquasiparticle behavior would, in fact, be expected in the case of strongly coupled electron-phonon systems [4].

From our data alone it is not possible to clearly establish the mechanism of the phase transition. There are two possible pictures. Either the transition is a purely electronic long-range instability, i.e., a weak coupling charge density wave or it is caused by a short-range interaction [11,12]. Apart from the fact that the latter could explain a lower transition temperature [13] it would fit very well with the dangling bond character of the surface state at $\bar{C}$ suggested by BCT [3]. It seems likely that the surface gets rid of the dangling bonds by a dimerization of the surface atoms similar to the dimers in bulk α-Ga. A first step to the understanding of the phase transition would be the determination of the surface geometric structure at both temperatures.

In conclusion, we have studied the electronic structure and the electron-phonon interaction on α-Ga(010). We have determined the electron-phonon mass enhancement parameter at the surface to be $\lambda = 1.4 \pm 0.10$. This means that the electron-phonon interaction on the surface is very strong, even stronger than in bulk α-Ga. The lifetime broadening of the surface state line is almost exclusively caused by the electron-phonon interaction indicating that this surface has very few defects. Apart from the quasiparticle peak of the surface state the photoemission spectra show considerable intensity in the projected bulk gaps. In contrast to many other examples this can not be attributed to defect scattering caused by poor surface quality. Hence, we interpret the effect as a nonquasiparticle behavior of the coupled electron-phonon system. Furthermore we observe a phase transition below about 220 K which causes spectral changes close to the Fermi surface. While more investigations are necessary to determine the rearrangements of the geometric structure during the transition, we believe that it is likely to be associated with a dimerization between the surface atoms.

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