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# Photoemission and inverse photoemission spectroscopy of V(100)

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**Abstract.** The electronic structure of the V(100) surface has been studied by means of angularly resolved photoelectron spectroscopy (ARUPS) and momentum- ( $k$ -) resolved inverse photoemission spectroscopy (KRIPES). A narrow peak in the photoemission spectrum which is seen at the Fermi level is attributed to a transition from a surface resonance. The existence of this surface resonance at the Fermi level of the V(100) surface is potentially very important for the occurrence of the expected magnetic ordering of this surface. The energy of the critical point  $H_{25}^*$ , which defines the top of the unoccupied part of the 3d band, has been determined to be within 3.0–3.2 eV above  $E_F$  from the normal incidence KRIPES spectra.

## 1. Introduction

An important motive for much of the research during the last two decades into the electronic structure of vanadium and, in particular, of the V(100) surface, is the possibility of observing a magnetic ordering (ferromagnetic or antiferromagnetic) at the surface or in ultra-thin films of this otherwise paramagnetic crystal. Theoretical studies [1–4] do suggest the possibility of magnetic ordering at the (100) surface of vanadium but as yet to our knowledge there has been only one experimental attempt to observe this fascinating phenomenon [5]. This is probably due to the fact that the experimental activity has been mainly focused on a search for magnetic ordering in the more promising vanadium ultra-thin films [6–10] or clusters [11, 12].

A detailed knowledge of the band structure, the possible surface induced band narrowing and the density of states of the itinerant electrons is essential for understanding of phenomena such as surface magnetism. A peak in the density of states at the Fermi level is favourable for the occurrence of ferromagnetic ordering [13], and theoretical calculations [1–4] predict an increased density of states at the Fermi level on the V(100) surface with respect to the bulk. This high density of states at the Fermi level has been associated with a surface resonance [2] which appears to be characteristic for the (100) surfaces of the bcc transition metals [14]. A recent experimental study of the V(100) valence band structure [15, 16], however, shows no conclusive evidence for the existence of such a resonance. This same study indicates that the width of the occupied part of the vanadium 3d band may be somewhat narrower than had been generally believed. In particular, ARUPS measurements showed that, within a free electron final state model, the critical points  $H_{12}$  and  $N_1$  occur at an energy of around 2.6 eV below the Fermi level. No measurements of the energy of any of critical points above the Fermi level have been reported for vanadium to date. However, an estimate of

the width of the empty part of the vanadium valence band has been reported by Speier *et al* [17]. Based on the comparison of x-ray bremsstrahlung isochromat spectroscopy (BIS) data and density of states (DOS) calculations they came to the conclusion that the width of the empty part of the band is between 3.4 and 3.8 eV.

In this paper we address two issues. The first one is the existence of the surface resonance at the Fermi level and a second one is the width of the unoccupied part of the 4d band. We report on He I normal emission ARUPS measurements from the V(100) surface which strongly suggest the existence of a state at the Fermi level which can be associated with the theoretically predicted surface resonance. We also present the first *k*-resolved inverse photoemission spectroscopy (KRIPES) results for the V(100) surface. The energy of the critical point  $H_{2.5}$  has been estimated from the normal incidence isochromats. The KRIPES isochromats taken along the  $\Gamma$ - $\Delta$ - $M$  symmetry line have been found to be in general agreement with published band structure calculations [18–20].

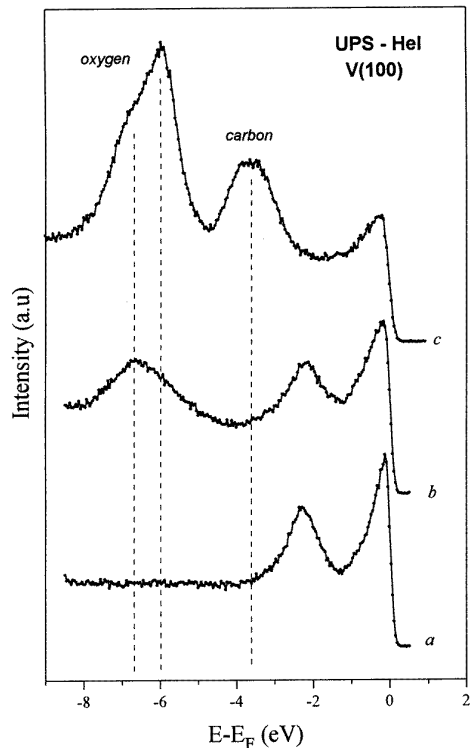
## 2. Experimental

The experiments were carried out in two separate experimental chambers. The first one, in which photoemission spectroscopy was performed, was equipped with a 180° hemispherical electron energy analyser (VSW HA 100). The acceptance angle of the analyser is  $\pm 3.5^\circ$  which corresponds to a momentum resolution parallel to the surface of  $\approx 0.12 \text{ \AA}^{-1}$  ( $\Gamma$ - $M$  in the vanadium surface Brillouin zone is  $1.47 \text{ \AA}^{-1}$ ). The energy resolution is 150 meV. The position of the analyser as well as of the discharge lamp was fixed and changes of emission angle were achieved by rotation of the sample [15]. The KRIPES experiments were carried out in the second UHV system where the data were obtained in the isochromat mode using an LiF lens as a dispersing element and taking two different isochromats (10.0 and 11.5 eV) simultaneously [21]. The electron gun typically delivered beam currents of 10–15  $\mu\text{A}$  to the sample at 10 eV electron energy. The spectral resolution at the photon energies of 10.0 and 11.5 eV is 0.6 and 0.4 eV respectively. Both experimental systems were additionally equipped with Auger electron spectrometers and LEED optics.

The sample was mounted on the sample holder such that the band mapping was performed in the  $\Gamma$ NPH plane in *k*-space and accordingly the normal emission ARUPS and normal incidence KRIPES experiments ( $k_{\parallel} = 0 \text{ \AA}^{-1}$ ) were probing the states along the  $\Gamma$ - $\Delta$ - $H$  high-symmetry line of the bulk Brillouin zone.

It is the experience of many experimentalists that it is rather difficult to prepare an atomically clean vanadium surface, even on *in situ* deposited films [22, 23]. In this work extensive argon sputtering and annealing cycles were performed to obtain an atomically clean and well ordered vanadium surface (the detailed procedures used are described in [24]). For a proper ordering of the surface it appeared to be of great importance to occasionally perform annealing at temperatures as high as 1500 K. Segregated oxygen or carbon was removed from the surface by room-temperature sputtering followed by annealing at around 900 K.

The most commonly observed contaminants were carbon and oxygen which appeared as a result of adsorption from the residual gas atmosphere or segregation from the bulk during the annealing procedure [24]. In this context we would like to comment on the findings of Binns *et al* [9] who observed in the valence band spectrum of a vanadium film an increase of the intensity at binding energy of 6 eV as a result of residual atmosphere gas adsorption. They attributed this peak to the  $5\sigma$  and  $1\pi$  states of adsorbed CO because CO was dominant in the residual atmosphere of their chamber. By contrast, annealing experiments of Valla *et al* [24] and the oxygen adsorption experiment of Perić *et al* [16] indicate that the peak at 6.5 eV should correspond to the emission from O 2p level of atomic oxygen. On the basis



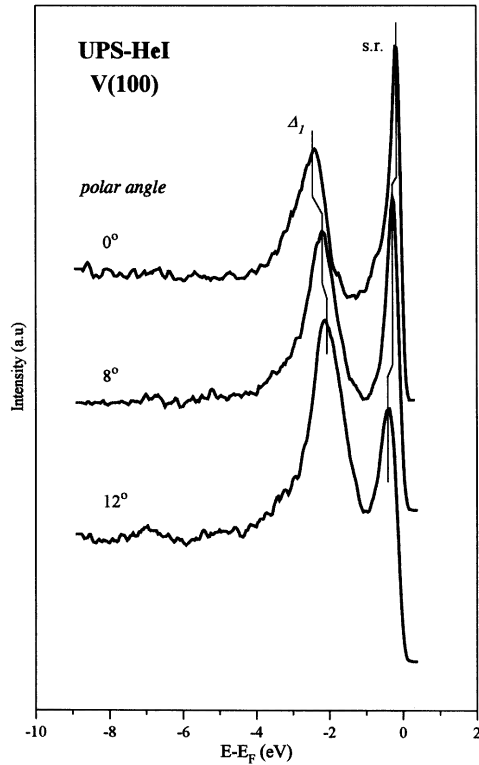
**Figure 1.** He I UP spectra (normal emission) of a clean V(100) surface (*a*) and of the same surface contaminated by adsorbed oxygen (*b*) and by segregated carbon and oxygen (*c*).

of the simple ‘work function rule’ [25], it is very unlikely that CO would adsorb molecularly on any vanadium surface; rather one would expect that CO would adsorb dissociatively on vanadium. Figure 1 shows the normal emission photoemission spectra of the clean V(100) surface (spectrum *a*) and of the same surface contaminated by adsorbed oxygen (spectrum *b*) and by segregated carbon and oxygen (spectrum *c*). In each case the presence of oxygen, or of oxygen and carbon, was checked independently by AES. For small oxygen coverages photoemission from the O 2p level produces a peak at 6.5 eV and for higher coverages a second peak appears at 6 eV. On the other hand a peak associated with carbon appears at 3.7 eV below the Fermi level.

### 3. Results and discussion

#### 3.1. Angularly resolved photoemission

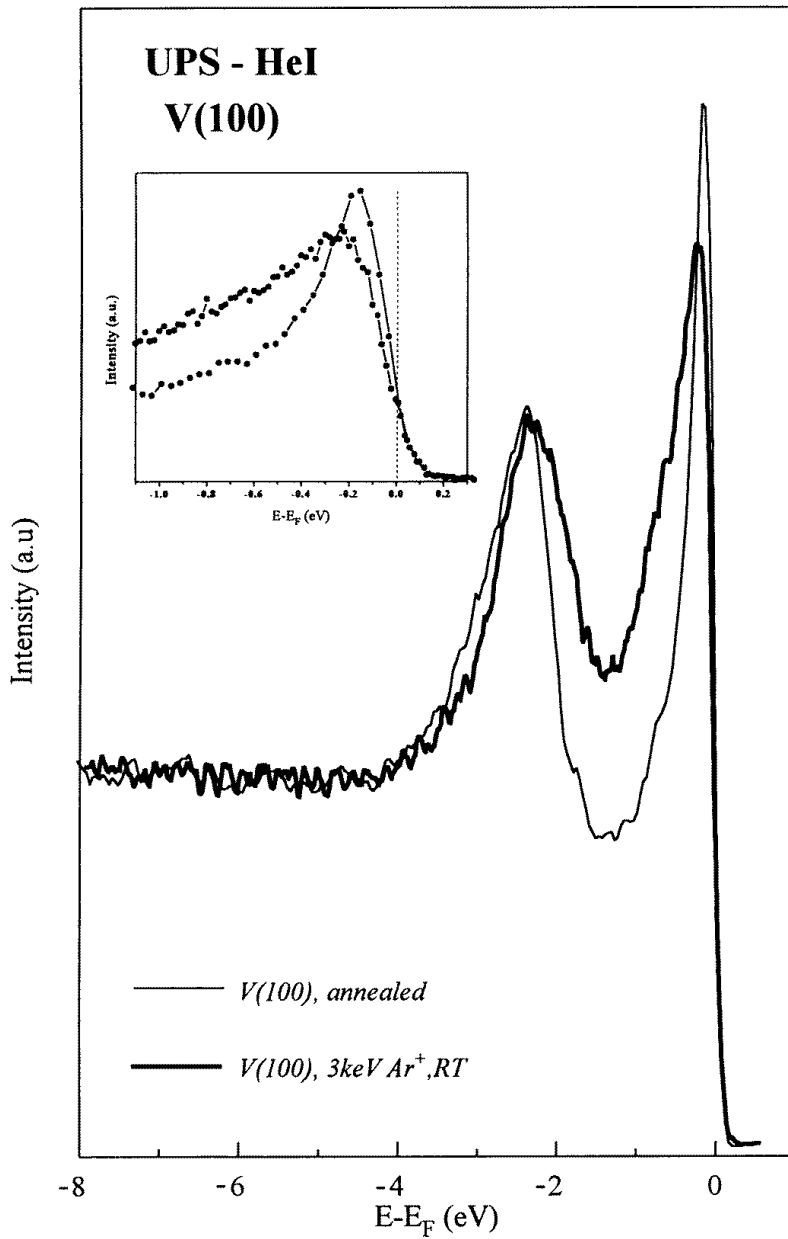
Figure 2 shows angularly resolved photoemission spectra of the clean V(100) surface in the very narrow range of the surface Brillouin zone around its centre ( $\Gamma$ ). It is clear that the peak at the Fermi level shifts from the Fermi level and decreases in intensity as the emission angle is increased away from the surface normal, while the second peak at around 2.3 eV disperses towards the Fermi level with increasing polar angle. The behaviour of this second peak has already been well documented [15, 16] and in the case of normal emission it has been attributed to a direct transition from the  $\Delta_1$  band [15, 16]. The nature of the peak at the Fermi level is much less clear. Based on the band structure calculations for bulk vanadium [18–20], no direct optical transition which would contribute to the intensity at the



**Figure 2.** Angularly resolved UP spectra of a V(100) surface along the  $\Gamma$ -M symmetry line of the surface Brillouin zone.

Fermi level is expected for (100) surface at a photon energy of 21.2 eV [26]. Therefore, this photoemission maximum could be associated either with indirect transitions, probably from the  $\Delta_5$  band, or with emission from a surface state. It appears there is evidence to support the idea that the peak contains contributions from both of these processes. A common test for a contribution from a surface state is that it is very sensitive to surface contamination and critically dependent on the concentration of surface defects. As the preparation of virtually any atomically clean surface requires prolonged sputtering (this is certainly true for vanadium [24]), which necessarily introduces a certain level of defects, thorough annealing at an elevated temperature is very important in order to heal induced defects. Annealing, on the other hand, very often induces segregation of impurities from the bulk to the surface. It is thus important to find the optimum between the requirement for a long annealing to improve surface long-range order and the need to avoid segregating surface impurity atoms (usually O and C) of a sufficient concentration to affect the electronic structure of the surface layer.

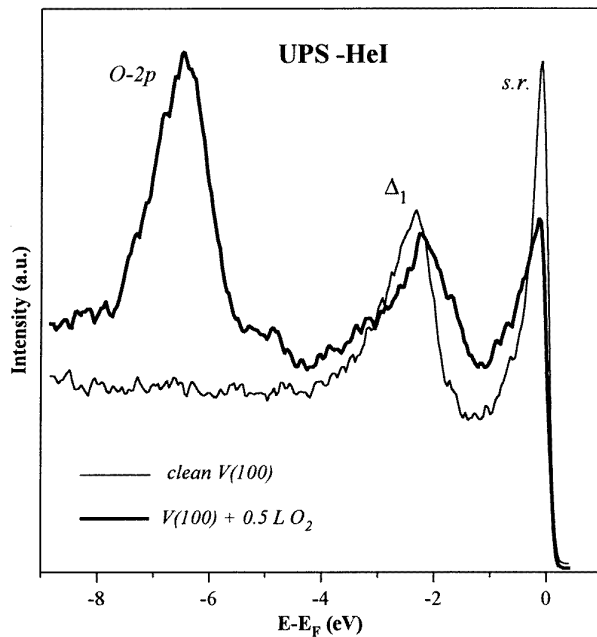
We have found that the photoemission peak seen at the Fermi level is very sensitive to pure surface order or contamination leading us to the conclusion that the intensity just at the Fermi level is due to emission from a surface resonance. Figure 3 shows normal emission spectra from a clean and well annealed V(100) surface (spectrum a) and from the same surface sputtered by 3 keV  $\text{Ar}^+$  at room temperature for 3 min. In the very narrow energy range just below the Fermi level the intensity has been substantially reduced (see the inset). At the same time the  $\Delta_1$  state is virtually unaffected due to its bulk nature. The substantial intensity increase which is centred around 0.8 eV below the Fermi level



**Figure 3.** He I UP spectra of a V(100) surface showing the influence of ion bombardment disordering.

we attribute to a bulk density of states contribution which appears in the spectrum as a result of surface umklapp processes. Disordering of the surface relaxes the requirement of parallel momentum conservation introducing into the spectrum contributions from other parts of the bulk Brillouin zone [27]. A DOS contribution to the photoemission spectrum of a vanadium surface is indeed expected to be significant at around 1 eV below the Fermi

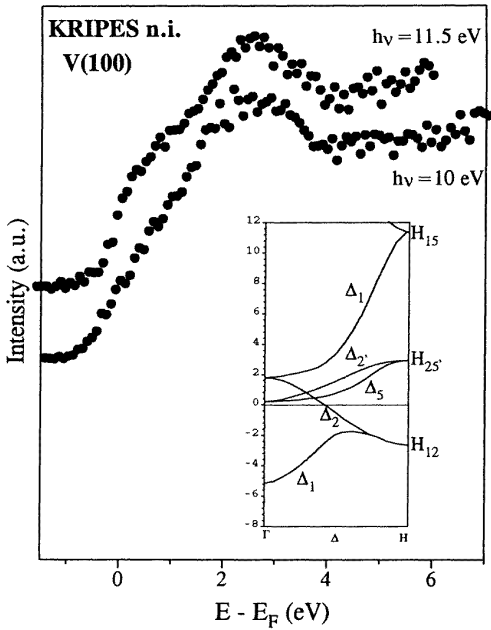
level where a high density of states at critical points— $N_2$  and  $P_4$ —appears in the bulk band structure [18]. This trend of increasing intensity in the energy range between 0.5 and 1.5 eV continues as the long-range order of the vanadium surface decreases [28]. The influence of contamination (in this case produced by oxygen exposure) on the intensity at the Fermi level is shown in figure 4. There is a substantial reduction of the peak intensity due to an oxygen exposure of around 0.5 L. The  $\Delta_1$  state, as expected, proves to be much less affected by adsorbed oxygen. We have also found that surfaces with higher concentrations of surface defects show no intensity reduction at the Fermi level when exposed to oxygen but rather a small increase (see figure 3 in [16]). The intensity increase between 0.5 and 1.5 eV is probably of the same origin as for the sputtered surface, i.e. transitions induced by surface umklapp processes.



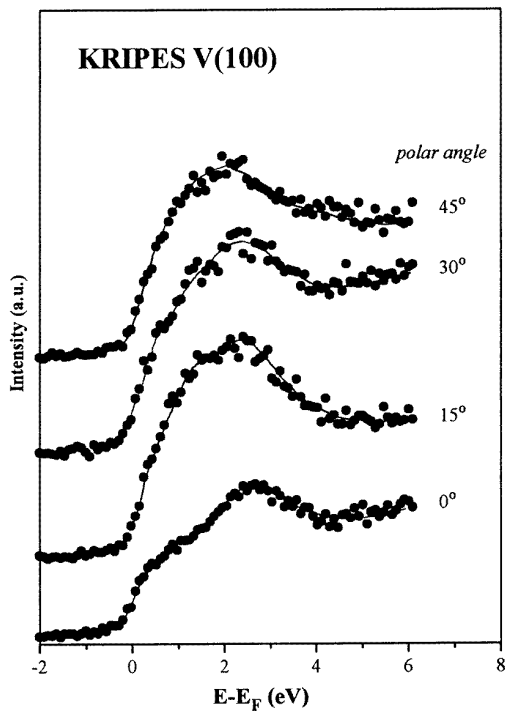
**Figure 4.** Normal emission UP spectra of clean and oxygen exposed V(100) surfaces.

In addition, we have also found that the intensity of the state at the Fermi level is temperature dependent. The spectral intensity at the Fermi level is reduced as the temperature of the sample is increased [29]. It is believed that in the case of surface states there is an enhanced coupling to the phonons which accordingly makes them more temperature dependent [30].

We believe that all of this evidence strongly indicates the existence of a state at the Fermi level which can be associated with a surface resonance. Further information could, of course, be obtained by varying the photon energy to show that the state at the Fermi level does not disperse with  $k_{\perp}$  but this was not possible with the existing equipment. On the basis of the available data it is also not possible to determine the symmetry of this state. It is known that, in the case of normal emission spectroscopy from the (100) surface of BCC crystals, only photoemission from bands with  $\Delta_1$  and  $\Delta_5$  symmetry is allowed. To distinguish between these two symmetries it would be necessary to probe the states with polarized light, which was not available in this experiment.



**Figure 5.** Normal incidence KRIPES spectra of a V(100) surface at 10 and 11.5 eV photon energies.



**Figure 6.** KRIPES spectra recorded at 11.5 eV isochromat energy from a clean V(100) surface at various electron incidence polar angles as indicated in the figure.

### 3.2. *k*-resolved inverse photoemission

Figure 5 shows the normal incidence KRIPES spectra of the clean V(100) surface at 10.0 and 11.5 eV photon energies. Inspection of the calculated vanadium band structure along



$\Gamma$ - $\Delta$ -H shows that the  $\Delta_1$  band disperses towards the vacuum level as  $k$  goes from  $\Gamma$  to H and at the boundary of the Brillouin zone reaches an energy of around 10.0 eV (critical point  $H_{15}$ )—see the inset in figure 5. A large gap of around 11 eV opens in the band of  $\Delta_1$  symmetry between the  $H_{15}$  and  $H_1$  points (this energy range is not shown in the inset). Therefore, no direct transitions can be expected for either of the isochromats at 10 and 11.5 eV and the only transitions which can occur are from the evanescent state in the  $H_{15}$ - $H_1$  band gap. Accordingly, the normal incidence spectra should be dominated by the density of states at the zone boundary H. Emission from the gap induces a substantial increase of the imaginary part of  $k_{\perp}$  [31] which smears  $k_{\perp}$  along the  $\Gamma$ - $\Delta$ -H symmetry line and introduces some contributions from the density of states along this symmetry line (one-dimensional density of states-ODDOS). The fact that no change in the peak position as well as no significant difference in the line shape of the spectra has been observed for two different isochromat energies (10 and 11.5 eV) supports this mechanism. The main characteristic of both isochromats is the relatively low spectral intensity at the Fermi level and the single maximum around 2.8 and 3.0 eV. The somewhat sharper appearance of the peak in the 11.5 eV isochromat may be largely attributed to the improved resolution of the instrument at this energy. The most probable origin of this peak is emission related to the transition into the band at critical point  $H'_{25}$ . One may, however, suspect that the intensity of the main peak can be accounted for by the contributions from the total DOS. The normal incidence 11.5 eV isochromat shown in figure 5 is, indeed, conspicuously similar to the BIS spectrum of vanadium film [17] which reflects the total DOS of vanadium. Its intensity maximum appears at 2.3 eV (this peak may be associated with the transitions at the critical points  $N_4$  and  $P_3$ ) i.e. closer to the Fermi level by more than 0.5 eV than the intensity maximum in our KRIPES spectra shown in figure 5. Therefore, we conclude these spectra are dominated by the ODDOS rather than DOS contributions and that the intensity maximum in both 10 and 11.5 eV isochromats should be attributed to the transition into the final state at the critical point  $H'_{25}$ . However, due to the finite momentum and energy resolution of our KRIPES spectrometer it is unfortunately not possible directly to attribute the energy of the spectral maximum to the position of the critical point. Based on model calculations [32] we came to the conclusion that the position of the critical point  $H'_{25}$  should be around 0.2 eV above the energy of the corresponding IPS maximum. This places the top of the empty part of the d band ( $H'_{25}$ ) at between 3.0 and 3.2 eV above the Fermi level which is about 0.5 eV closer to the Fermi level than has been suggested by Speier *et al* [17] (3.4–3.8 eV). Unfortunately, there is no full agreement in the calculated position of the  $H'_{25}$  point. Self-consistent calculations using a Gaspar-Kohn-Sham ( $\alpha = 2/3$ ) exchange potential place the critical point between 3.5 eV (SC APW) [20] and 4 eV (SC LCAO) [18] above the Fermi level while the energy of the  $H'_{25}$  point in the calculation using a full Slater exchange potential ( $\alpha = 1$ ) is smaller, i.e. 2.9 eV (SC APW) [18] and 3.1 eV (TB and APW) [19]. However, in associating the observed features in the experimental spectra with the calculated points in the band structure one should bear in mind that emission from evanescent initial states reduces the already very small depth which is probed by the inverse photoemission technique. Due to the reduced coordination number of atoms in the surface layer one can expect a band narrowing with respect to the bulk band width; this effect is the basis of the theory of magnetic ordering of the V(100) surface. In addition, one should not forget correlation effects either. In the case of the inverse photoemission final state there is an additional electron in the relatively localized d band which, according to the calculations of Bandyopadhyay and Sarma [33] will substantially increase the correlation energy; this in turn may have an effect on the observation of the band narrowing, related to its ground state value.

Figure 6 summarizes the KRIPES spectra at 11.5 eV photon energy of the clean V(100) surface at a range of incidence polar angles. A characteristic feature of the isochromats as the polar angle is increased ( $k_{\parallel}$  moves from  $\Gamma$  to M) is the build up of intensity in the energy interval between 0 and 1 eV and a slight shift of the total spectral intensity towards the Fermi level. This is broadly consistent with a dispersion towards the Fermi level of the  $G_1$  and  $G_3$  bands along the H–G–N and the  $F_1$  band along the H–F–P high-symmetry direction of the bulk Brillouin zone (see e.g. [19]). Also the band  $G_2$  shows little, if any, dispersion. This can also account for the fact that we see the spectral maximum in the energy range between 2.6 and 3.0 eV for all polar angles.

#### 4. Conclusions

We have performed angularly resolved photoemission spectroscopy of a V(100) surface. A normal emission photoemission spectrum of the well annealed V(100) surface shows an intense and narrow peak at the Fermi level. The peak was found to be temperature dependent and very sensitive to contamination (e.g. oxygen) and the defect concentration at the surface. This led us to attribute the peak at the Fermi level to the transition from a surface resonance as had been predicted by theoretical calculation [2].

Normal incidence momentum resolved inverse photoemission at isochromat energies of 10 and 11.5 eV enables us to probe the critical point  $H'_{25}$  of the bulk Brillouin zone. The energy of the critical point, which defines the top of the unoccupied part of the 3d band, was found to be between 3.0 and 3.2 eV. The spectra obtained at different polar angles were found to be in general agreement with the calculated dispersion of the bands in the  $\Gamma$ NPH plane of the bulk Brillouin zone.

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