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SYNCHROTRON RADIATION STUDY OF V(100)

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The electronic structure of V(100) has been studied by means of synchrotron radiation. Normal emission (n.e.) spectra, taken in the energy range between 15 and 100 eV, were analysed in terms of existing band structure calculations. The obtained data support our previous reports suggesting that the peak at the Fermi level has a bulk and surface component. The variation of the intensity at the Fermi level was measured in the constant initial state (CIS) mode. In the photon energy range between 40 and 100 eV the variation of the intensity at the Fermi level is generally following the energy dependence of the resonant spectrum of vanadium films. However, the resonant spectrum obtained from V(100) appears to be significantly narrower than the spectra reported for films.

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1. Introduction

A specific interest in V(100) arises ever since theoretical calculations have indicated the possibility of magnetic ordering on this surface making the V(100) surface one of the popular examples of the quest for surface magnetism. Allen [1] was first to suggest that paramagnetic vanadium may exhibit surface magnetism on V(100). Motivated by the magnetic susceptibility measurements [2], which indicated the existence of the surface magnetism of small vanadium particles, Grampel and Ying [3] have studied electronic and magnetic properties of the V(100) surface. Their calculations predicted for this surface a large peak in the density of states near the Fermi level. As the authors themselves pointed out, this feature, which appears to be characteristic of the transition metal bcc-(100) surfaces [4], leads to the drastically different magnetic properties of the V(100) surface compared to the bulk ones.

However, up to date, the only experimental support for the existence of the magnetic ordering on V(100) comes from the electron capture spectroscopy experiment by Rau et al. [5] who reported a ferromagnetic ordering. It appears that the inhibiting factor in more productive research of this interesting system is the difficulty in preparing the atomically clean surface [6]. Electronic structure of the V(100) surface has been experimentally investigated by several authors [7–12]. A knowledge of the electronic structure (e.g., the density of states (DOS), the existence of surface states or resonances etc.) is very essential for a better understanding of possible magnetic ordering. However, it is only recently that the first results on the experimental study of the surface and bulk electronic states on V(100) were reported [9–12]. The occupied electronic states were studied by means of angular resolved photoemission (ARUPS) [9,10,12] and empty states by means of K-resolved inverse photoemission (KRIPES) [11,12]. The He-I photoemission spectroscopy [12] suggests that the part of the spectral intensity at the Fermi level could be associated with the transition from the surface resonance, as predicted by Grempel and Ying [3].

In this paper we present the first synchrotron radiation study of the V(100) surface. Normal emission spectra taken for different photon energies gave us the possibility to explore the electronic states of the vanadium valence band along the $\Gamma - \Delta - \mathrm{H}$ high symmetry line. The intensity of the peak at the Fermi level has been measured in the wide range of excitation energies (15-100 eV), whereas a strong resonant photoemission was evident at photon energies exceeding 40 eV.

2. *Experimental*

The experiments were performed on beamline 6.2 of the Daresbury Synchrotron Radiation Source (SRS). The apparatus was equipped with an ARUPS facility based on a 50 mm hemispherical analyser (VG ADES 400). The mounting of the analyser supported its free rotation in and out of the horizontal plane. The light was incident on the V(100) surface at an angle of 40°, while the analyser was kept at the position of normal emission (n.e.) The typical angular acceptance of the analyser was $\pm 1.5^\circ$ and the constant energy resolution of 200 meV for 10 eV pass energy was maintained throughout the experiment. The measured intensities were normalised with respect to the measured beam intensity.

The cleaning procedure of the vanadium sample is described in details elsewhere [6]. Basically, long sputtering at 650 K, followed by occasional annealing to 1500 K would remove the most troublesome contaminants; carbon and oxygen. The vanadium surface was considered clean when the photoemission spectra taken at $h\nu = 21$ eV showed no intensity maxima at energies around 6 eV (corresponding to oxygen contamination) and 3.7 eV below the Fermi level (corresponding to carbon contamination) [12].

3. Results and discussion

Figures 1a and b show normal-emission photoemission spectra of V(100) in the wide photon energy range, between 16 and 71 eV. Due to the symmetry conditions, in the n.e. geometry only the electronic states which lie on the $\Gamma - \Delta - \mathrm{H}$ high symmetry line of the bulk Brillouin zone are excited from the bcc-(100) surface [13]. The spectra taken in the photon energy range between 15 and 36 eV are characterized by the two pronounced intensity maxima: at the Fermi level (labelled as 1) and 2.3 eV bellow the Fermi level (labelled as 2). In the energy interval between 16 and 32 eV, there is hardly any change in the energy position of both peaks. Only a slight variation in the relative intensity ratio of peaks 1 and 2 is present (an energy dependence of the intensity of the peak 1 will be discussed in details later in the text). For the excitation energies above 32 eV, a slight drift of the peak 2 away from the Fermi level is visible. Above the 3p threshold energy ($\approx$ 37 eV), a contribution of the MVV Auger transitions (denoted by A) start to dominate the valence band spectrum.

The two-peak structure in the n.e. spectra of V(100) surface has already been observed and discussed [9,10,12]. Two possible contributions to the intensity of the peak 1 at the Fermi level have been suggested: (a) the emission from the surface resonance and (b) the density of states contribution associated with the emission from the $\Gamma_{25'}$ symmetry point. The experiments with the fixed photon energy showed [12] that the intensity of the n.e. photoemission spectrum at the Fermi level is rather sensitive to the surface contamination which is one of the indications for the surface nature of an electronic state. Our present measurements, which clearly show that the peak 1 does not disperse in the large photon energy range, are certainly another argument for assuming its surface character. However, one should bear in mind that the density of states contributions do not disperse with photon energy as well. In the case that the final electron states of our photoemission process were in the band gap, a relaxation of the k-conservation takes place, and the intensity peaks in the photoemission spectrum would originate dominantly from critical points giving rise to the one-dimensional density of states (ODDOS) contributions [14]. The ODDOS features do not disperse with photon energy ($\mathbf{k}_\perp$) but do disperse with $\mathbf{k}_\parallel$. In addition, as these final states are localised very close to the surface these features show certain sensitivity to the surface contamination as well. The analysis of the peak intensity, as it will be demonstrated later, also supports the existence of both, bulk and surface contributions to the peak 1.

Regarding the nature of the peak 2, the experiments with fixed photon energy (21.2, 16.8 and 11.8 eV) [9,10,12] gave some evidence that the peak 2 might be the result of a direct transition from the Δ_1 bulk band. This assumption was based on the fact that (a) due to the symmetry conditions, the Δ_1 is the only band available for the photoemission from the (100) surface under the normal emission

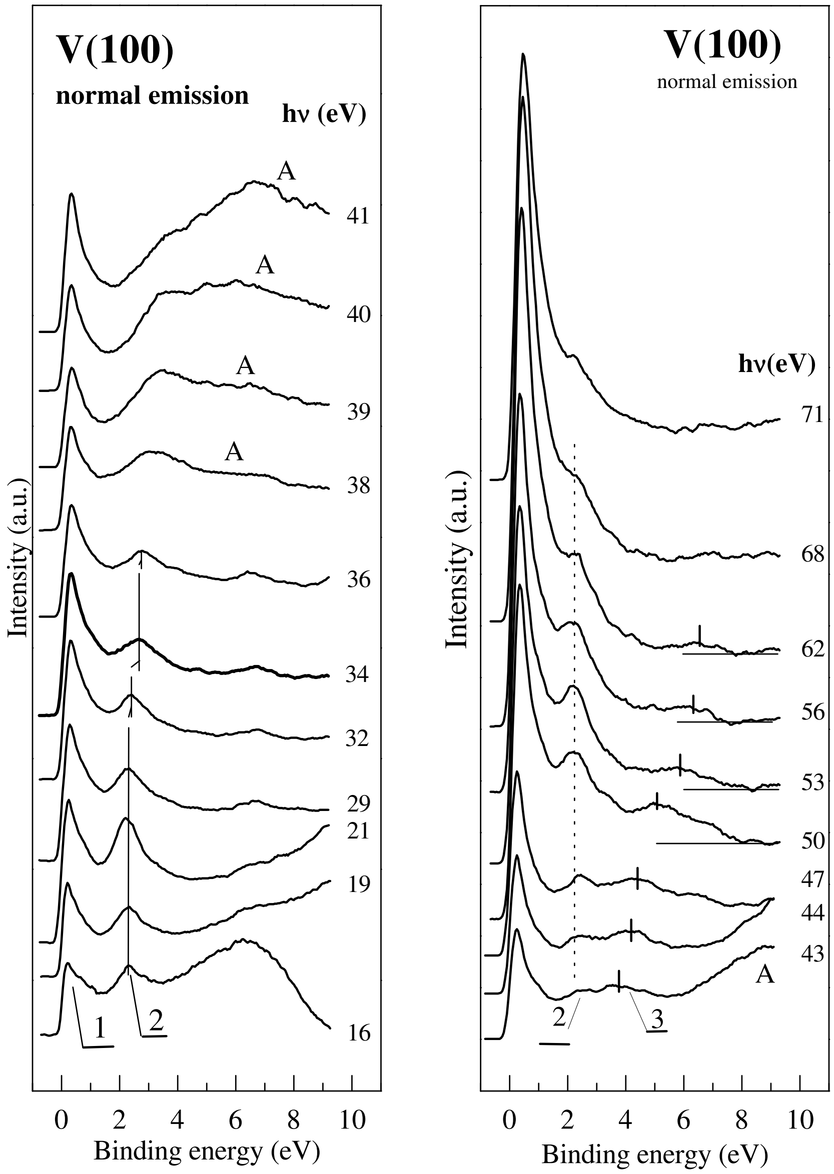

Fig. 1 a, b. Normal emission spectra of V(100) at different photon energies. The valence band states are labelled by 1,2 and 3 and the structure which is associated with the MVV Auger transition is marked by A. Solid lines and tick marks indicate the shift of the peaks 2 and 3.

conditions at this binding energy and (b) that a small shift, towards the Fermi level, was observed as the excitation energy was changed from 11.8 to 21.2 eV. The n.e.

spectra shown in Fig. 1a clearly do not support this assumption; for photon energies between 16 and 32 eV, the peak is found to correspond to the same binding energy - 2.3 eV. The band structure calculation show, however, that Δ_1 band disperses from 2.5 eV (at the H zone boundary) to 6 eV below the Fermi level (at the Γ_1 critical point) [15–17]. If the peak 2 were to be associated with the direct transition from the Δ_1 band, it should show a significant dispersion with the excitation energy. The fact that the state persists at the fixed binding energy for different photon energies is usually taken as a clear indication for associating it with a surface state or resonance. However, as we have pointed above, one-dimensional density-of-states contributions to the photoemission intensity do not disperse with photon energy as well. For several reasons (see further), we are inclined to attribute the state 2 to be ODDOS feature rather than a surface state. The Δ_1 band goes through the maximum close to the boundary edge H, and according to our model calculation, it produces a peak in the ODDOS at around 2.5 eV. The ODDOS along the $\Gamma - \Delta - \mathrm{H}$ high symmetry line appears to be also a significant contribution the total DOS [18] as the calculated total DOS exhibits a local maximum at around 2.5 eV as well. An experimental corroboration for this was found in XPS measurements of a vanadium film where the valence band spectrum showed also a peak at 2.4 eV below the Fermi level [19]. One possible reason why the ODDOS contributions appear to be dominant in the n.e. spectra shown in Fig. 1a can be found in the fact that the final state band, Δ_1, encounters the zone boundary at H around 10 eV above the Fermi level where the large gap opens [17]. Based on the band structure calculations, it is expected that the Δ_1 band back-folds towards Γ at $25 - 30$ eV above the Fermi level. From our spectra, it is difficult to estimate when the Δ_1 band is again available as a final state band in the photoemission process. A small shift of the peak 2 to higher binding energies can be observed at 32 eV. This trend continues with the increase of the excitation energy and for 37 eV photon energy, the binding energy of the state 2 increases to 2.7 eV. The shift of the peak 2 might be an indication for the direct optical transition. If this is correct, then the back folding of the Δ_1 band takes place around 30 eV above the Fermi level. Unfortunately, we were not able to follow the dispersion of the peak above the 3p excitation threshold (36.5 eV) as the valence band region in the photoemission spectrum above this energy is strongly affected by the appearance of the $M_3M_{45}M_{45}$ Auger transition (labelled as A). One may wonder if it is possible that the shift of the peak 2 has been affected by the Auger transition at energies below 36.5 eV. Kaurila at al. [20] investigated the possibility of the occurrence of the $M_3M_{45}M_{45}$ Auger transition below the 3p threshold, but have found no evidence for this effect in vanadium.

The 43 eV spectrum, in which the Auger peak is far away from the valence band region, reveals a significant increase of width of the peak 2. The increase of the peak width is actually a dispersion onset of the state 3 which, we believe, can be attributed to the direct transition from the bulk Δ_1 band. We can follow the dispersion of the Δ_1 peak up to 6 eV (62 eV photon energy) which is the calculated bottom of the vanadium sp-band [15,17]. In contrast to the 30 to 40 eV energy region, where there is a shift of the 2, here we see it at a fixed energy (2.3 eV), while peak 3 disperses away from the Fermi level. A similar behaviour was observed in n.e.

spectra of Nb(100) [21]. However, the onset of the Δ_1 band dispersion occurred at much lower photon energies (17 – 18 eV) suggesting apparently somewhat different final band structure compared to vanadium.

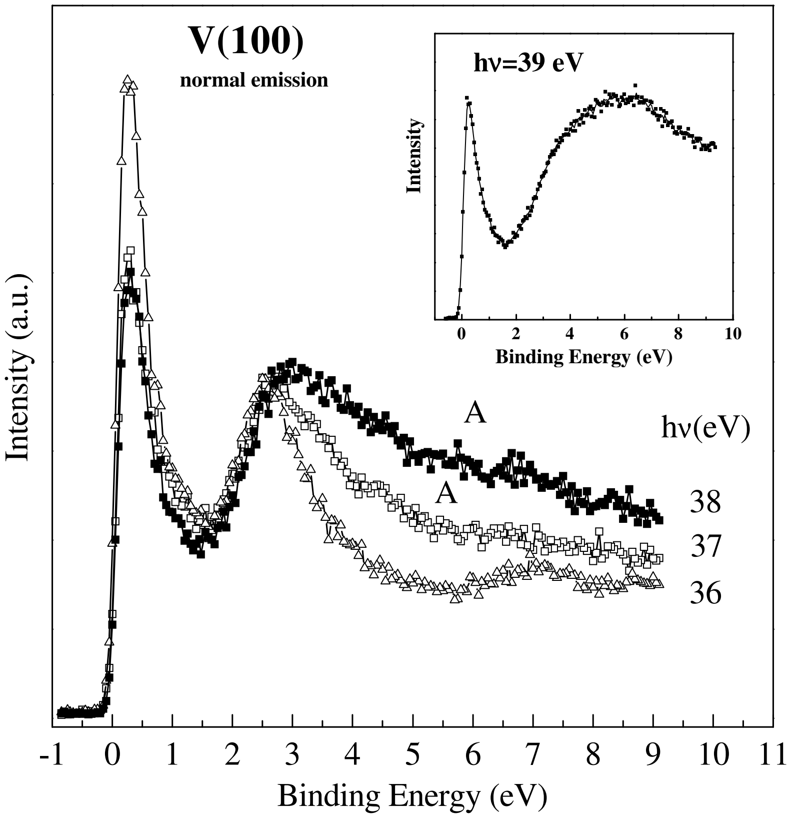

Fig. 2. Normal emission spectra of V(100) for the photon energies around the V 3p *threshold energy. The increase of the intensity between 3 and 8* eV *below the Fermi level indicates the presence of the MVV Auger process. The inset shows a fully developed Auger peak.*

The appearance of the super-Coster-Kronig (sCK) $M_{2,3}M_{4,5}M_{4,5}$ Auger peak is shown in more detail in Fig. 2. The build-up of the intensity between 4 and 5 eV below the Fermi level is clearly visible in the 37 eV spectrum, which is just above the 3p threshold energy. There is also a significant decrease of the intensity of the peak at the Fermi level which is due to the negative interference of the photoemited and autoionization electron (a resonant photoemission effect). The energy of the $M_{2,3}M_{4,5}M_{4,5}$ transition is derived from the 39 eV spectrum (see the inset). The maximum of the peak is determined at a kinetic energy of 28.6 eV and it is within the range of values found by Kaurila et al. (29 eV) [22] and Cornaz et al. (28 eV) [8]. The full width at half maximum (FWHM) is estimated to be around 5 eV.

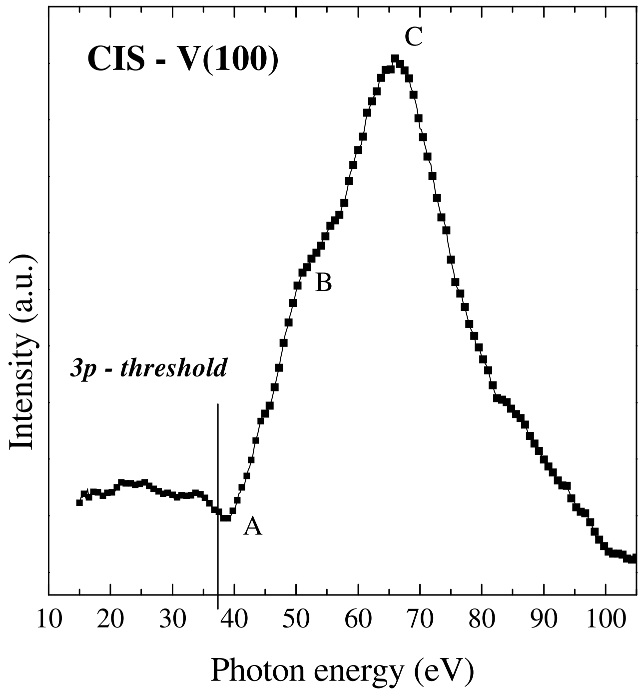

Fig. 3. Constant initial state spectrum of state 1 (measured at 0.3 eV *below the Fermi level under the normal emission geometry). The* V 3p *threshold energy is indicated in the figure. The structures associated with letters A, B and C are discussed in the text.*

The change of the photoemission intensity contains also an important information on the electronic structure of the surface. Figure 3 shows the photoemission intensity of the state 1 as a function of the photon energy. This kind of spectrum is usually called "constant initial state -CIS" spectrum. The measured photoemission intensity has been normalised to the photon flux. In addition, in order to take into account the possible contribution to the intensity from the second-order light, the intensity is measured just above the Fermi level for all photon energies and subtracted from the spectrum. As Fig. 3 suggests, there is a very small intensity variation up to 40 eV photon energy. Above 40 eV up to 100 eV, there is a strong variation of the intensity which is governed by the resonant photoemission process. The spectrum clearly shows several features characteristic of resonant profiles of transition metals. A minimum, which normally appears just after the excitation threshold of the 3p level, is found at 38.7 eV. At 50 eV, a shoulder in the spectrum can be identified. This shoulder corresponds to the maximum of the atomic Fano profile and a local maximum in total-absorption spectrum [23]. The maximum of the CIS spectrum appears well above the 3p excitation threshold (66 eV). All energies of the characteristic features are in a rather good agreement with the values found in the 3d resonant profiles of vanadium films [20,23]. The only significant difference with respect to vanadium film is the width of the resonant profile. The Fano-like resonance of the thin vanadium films has a FWHM of 38 eV [20], while the FWHM of the resonance shown in Fig. 3 is only 29 eV. The total width of the resonant profile is probably determined by two effects. The excitation of the 3d band is non-adiabatic process and, accordingly, the final state spectrum should contain all possible multiplets of the $3d^{N+1}$ state in the presence of the 3p core hole [24]. In addition, it has been suggested that the increased width of the resonant spectrum of metals is due to the excitation of the shake-up satellites [23]. The continuum of empty states in metals allows that any difference between the energy of the excited 3p-electron and the resonance energy is transferred to the shake-up excitations which eventually lead to the shift of the maximum and broadening of the spectrum towards the higher photon energies. Taking this into account, the reduced width of the 3d-resonant spectrum of V(100) surface, compared to the vanadium thin films, can be an indication for the significant difference in the structure of their empty bands. The inverse photoemission spectra of V(100)[12] and bremsstrahlung isochromat spectra of vanadium film [25], which provide certain information about the DOS of the unoccupied part of the valence band of V(100) and vanadium films, respectively, do not indicate the difference in the empty band spectra which would account for the reduced width of the resonant spectrum of V(100).

However, there are several other effects which can also affect the energy of the maximum and the total width of the resonant profile. It is important to notice that the Fano-like resonant profile shown in Fig. 3 is obtained by measuring the photoemission intensity in the normal emission geometry. A different resonant profile can be expected in the case of angle-integrated and the angle-resolved measurement. Also, if the width and the position of the resonance is dependent on the unoccupied DOS, then an oxidation of the metal surface would have also certain effects. The interaction of oxygen with metal surfaces induces depopulation of the d-band (increases the unoccupied DOS) and consequently the enhancement of the resonant emission. Zajac et al. [23] clearly demonstrated this influence of the oxidation level on the resonant profile of Ti and Mn. Here, we would like to point out that early transition metal surfaces and films (Sc, Ti, V, Cr) are very difficult to produce oxygen free. To this end it is not clear to which extent the differences in the resonant spectrum width are due to the different electronic structure of the crystals, different experimental geometry or to the different level of surface contamination.

4. *Conclusions*

Vanadium (100) surface has been studied by synchrotron radiation in the range between 15 and 100 eV photon energy. The normal emission spectra of the valence band around Fermi level were interpreted in terms of the emission from a surface state and one-dimensional density-of-states contributions. The presented normal emission spectra, in contrast to previous reports [9,10], strongly indicate that the peak at 2.3 eV is a result of transitions to evanescent states (ODDOS contributions) rather than direct optical transitions. Only at energies above 40 eV, we have observed a strong shift of the spectral intensity to higher binding energies which can be associated with the dispersion of the Δ_1 band from to the point of the bulk Brillouin zone.

The resonant profile of the peak at the Fermi level shows the typical features of the resonant spectra already obtained for vanadium films. However, there is a significant difference in the width of the resonant profiles which we obtained for V(100) surface, compared the results reported for vanadium films.

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References

1) G. Allen, Phys. Rev. B **19** (1979) 4777;

2) H. Akoh and A. Tasak, J. Phys. Jpn. **42** (1977) 791;

3) D. R. Grempel and C. S. Ying, Phys. Rev. Lett. **4** (1980) 1018;

4) K. S. Shin, C. Y. Kim, J. W. Chung, S. C. Hong, S. K. Lee, C. Y. Park, T. Kinoshita, M. Watanabe, A. Kakizaki and T. Ishi, Phys. Rev., B **47** (1993) 13594; S. L. Weng. D. Singe and H. Krakauer, Phys. Rev. B **37** (1988) 3999; B. S. Fang, W. S. Lo, and H. H. Chen, Phys. Rev. B **47** (1993) 10671; G. Gewinner, J. C. Peruchetti, A. Jaéglé and R. Pinchaux, Phys. Rev. B **27** (1983) 3358; L. E. Klebanoff, R. H. Victoria, L. M. Falicov and D. A. Shirley, Phys. Rev. B **32** (1985) 1997;

5) C. Rau, C. Liu, A. Schmalzbauer and G. Xing, Phys. Rev. Lett. **54** (1986) 2311;

6) T. Valla, P. Pervan and M. Milun, Surface Sci. **307/308** (1994) 843;

7) J. S. Foord, A. P. C. Reed and R. M. Lambert, Surface Sci. **129** (1983) 79;

8) A. Cornaz, M. Erbudak, P. Aebi, P. Stucki and F. Vannini, Phys. Rev. B **35** (1987) 3062;

9) P. Pervan, T. Valla and M. Milun, Solid State Commun. **89** (1994) 917;

10) B. Perić, T. Valla, M. Milun and P. Pervan, Vacuum **46** (1995) 1181;

11) T. E. Ollonquist, I. J. Vyrynen, O. G. Dmitrieva, O. M. Artamonov, Surface Sci. **352/354** (1996) 693;

12) P. Pervan, T. Valla, M. Milun, A. B. Hayden and D. P. Woodruff, J. Phys. C **8** (1996) 4195;

13) J. Hemanson, Solid State Comunn. **22** (1977) 9;

14) S. Hüfner, *Photoelectron Spectroscopy*, 2nd ed., Springer, Berlin (1996);

15) D. A. Papaconstantopoulos, J. R. Anderson and J. W. McCaffrey, Phys. Rev. B **5** (1972) 1214;

16) M. Yasui, E. Hayashi and M. Shimizu, J. Phys. Soc. Japan **29** (1970) 1446;

17) D. G. Laurent, C. S. Wang, and J. Callaway, Phys. Rev. B **15** (1978) 543;

18) L. L. Boyer, D. A. Papaconstantopoulos and B. M. Klein, Phys. Rev. B **15** (1977) 3685;

19) L. Lay, O. B. Dabouissi, S. P. Kowalczyk, F. R. McFreely and D. A. Shirley, Phys. Rev. B **16** (1977) 5372;

20) T. Kaurila, J. Väyrynen and M. Isokallio J. Phys. C **9** (1997) 6533;

21) B. S. Fang, C. A. Ballentine and J. L. Erskine, Phys. Rev. B **38** (1988) 4299;

22) L. Säisä, T. Kaurila and J. Väyrynen, Solid State Commun. **83** (1992) 407;

23) G. Zajac, S. D. Bader, A. J. Arko and J. Zak, Phys. Rev. B **29** (1984) 5491;

24) L. C. Davis and L. A. Feldkamp, Solid State Commun. **19** (1976) 413;

25) W. Speier, J. C. Fuggle, R. Zeller, B. Ackermann and K. Szot, Phys. Rev. B **30** (1984) 6921.

ISTRAŽIVANJE POVRŠINE V(100) UPOTREBOM SINKROTRONSKOG ZRAČENJA

U ovom se radu prikazuju rezultati istraživanja V(100) upotrebom sinkrotronskog zračenja. Spektri okomite fotoemisije u području fotonskih energija između 15 i 100 eV uspoređuju se s postojećim teorijskim proračunima za strukturu valentne vrpce vanadija. Dobiveni rezultati potvrđuju našu prije iznijetu tezu, da se maksimum fotoemisijskog intenziteta na Fermijevom nivou sastoji od dvije komponente, volumne i površinske. Promjena intenziteta na Fermijevom nivou mjerila se je u modu konstantnog početnog stanja. U području fotonskih energija između 40 i 100 eV, promjene fotoemisijske struje s Fermijevog nivoa vrlo su slične rezonantnom spektru vanadijevih tankih slojeva. Međutim, rezonantni spektar površine V(100) je značajno uži od rezonantnog spektra vanadijevih tankih filmova.