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PHOTO FIELD EMISSION SPECTROSCOPY OF THE TANTALUM BAND STRUCTURE BY HeNe LASER RADIATION

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Photo field-emission current versus the voltage characteristics of clean and barium covered tantalum were investigated under UHV conditions using 1.96 eV HeNe laser radiation. The field strength and average work function were determined from Fowler–Nordheim plots of the field emission currents and take into account the emission from planes with a low work function. According to a two-step photo field emission model, shoulders in the characteristics are ascribed to transitions in the band structure of tantalum as calculated by Mattheiss. Mostly nondirect transitions from and to the marked features of the band structure in the vicinity of the Fermi edge were found. The density of states and the density of the states "product" of the initial and final states are also considered as an explanation of the transitions observed.

1. *Introduction*

Photo field emission (PFE) proved to be a valuable tool for studies of band structure features of transition metals [1, 2]. As it is already obvious from theoretical considerations [3] and the first experimental results [4], a simple free electron Sommerfeld model cannot provide a definite explanation for the experiments [4]. According to one concept [5] which was applied with apparent success to tungsten [1] and tantalum [2], the photo field-emission current-voltage characteristics can be used to detect transitions with a high probability in the band structure. The predominant contribution of ordinary field emission can be suppressed in favour of the very small part of the photoexcited electrons ($10^{-5}-10^{-7}$) by phase sensitive detection techniques. However, there are problems with light intensity due to the very small field emission tip ares and, consequently, the low PFE current. Laser radiation appears to be a powerful light source and has been used by different groups to determine in particular the energy distribution of photo field emission which has been

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interpreted in terms of a free electron model [6, 7]. The present experiments with HeNe laser radiation reveal the influence of the band structure features also in the laser-induced field emission.

2. *Experimental*

The measurements were made with a glass UHV system with several Hg diffusion pumps arranged in a series. The pressure was lower than 2×10^{-10} Torr as estimated by a Bayard–Alpert gauge and the time-dependent change in field emission current. The all-glass field emission tube has two windows of optical quality for the illumination of the tip by a lens system and adjustment of the focus. Using an external magnetic field the emitted electrons can be deflected either onto the anode with a screen or onto the collector [8]. Using the first mode one can observe the field emission pattern to check the emitter cleanness or adsorbate coverage and to take Fowler–Nordheim characteristics. During the photo current measurements in the other mode with the collector, the phosphorous screen is not bombarded by electrons. The emitter consisting of a 0.1 mm diameter tantalum wire was spot-welded to a 0.2 mm diameter tungsten loop. The tube is equipped with a barium source carefully shielded and directed onto the tip, this allows only very small amounts of barium to be evaporated from a SAES getter. The emitter assembly is formed in the shape of a cooling finger permitting measurements at approximately liquid nitrogen temperature.

The tip has been illuminated in the axial direction by radiation from a 3 mW HeNe laser (HNA 50, VEB Carl Zeiss, Jena). A lens and a screen behind the second window on the opposite side of the tube served to adjust the focus onto the tip (for details see Ref. [8]). The determination of the very small PFE currents was done using the modulation technique as introduced earlier [4]. There the light beam was chopped by a toothed wheel at a frequency of 1000 Hz. After preamplification the alternating photo field emission current is fed to a narrow-band amplifier (Nanovoltmeter Unipan 208), rectified and indicated by a phase-sensitive detector (Homodyne Rectifier Unipan 202 B) and recorded simultaneously.

3. *Results*

Figure 1 shows PFE characterics obtained with the clean tantalum tip by HeNe laser illumination together with the Fowler–Nordheim field emission current versus voltage curve. It is obvious that the photo current characteristics have breaks in their slope as already observed with mercury arc radiation, and several shoulders can be determined. L II and L IV differ slightly in their appearance which seems to originate from a somewhat varied adjustment of the laser beam onto the tip. Between these measurements which were performed on different days the field emission tube was baked and the tip cleaned. According to the literature, the average work function of the clean tip is assumed to be 4.22 eV and using this value and the Fowler-Nordheim characteristic, the field factor, β, is calculated (compare [2]).

Figure 2 shows the PFE current from a barium covered tip where the average work function is reduced to 3.76 eV as evaluated from Fowler-Nordheim characteristics and the

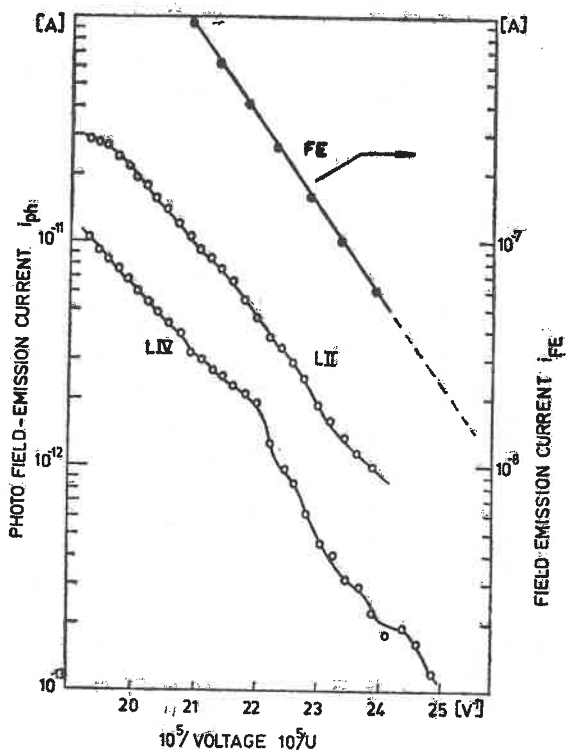

Fig. 1

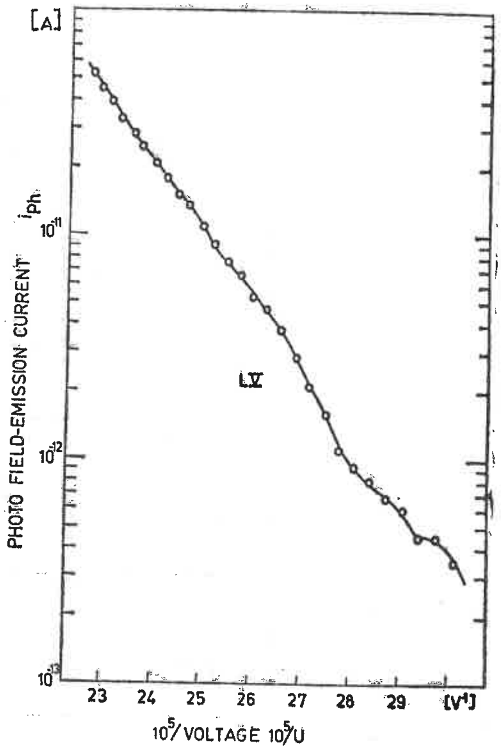

Fig. 2

Fig. 1. Photo field-emission current, L II, and, L IV, of clean tantalum obtained with HeNe laser radiation and total field emission current, FE, versus reciprocal voltage

Fig. 2. Photo field-emission current, L V, of barium covered tantalum obtained with HeNe laser radiation versus reciprocal voltage. The average work function of 3.76 eV is from Fowler–Nordheim characteristics

field factor, β, determined for the clean tip. This curve also has breaks or shoulders like those in Fig. 1. Table I gives their $10^5/U$ values, the average work function of the tip and the field factor. From

$$10^{-7}F\,[\mathrm{V/cm}] = 10^{-2}\beta\,[\mathrm{cm}^{-1}]/(10^5/U\,[\mathrm{V}]) \tag{1}$$

the field at the tip can be calculated. Weak shoulders are given in parantheses.

TABLE I

Observed shoulders of the field emission currents

No. of experiment	Fig.	Average work function [eV]	Field factor $10^{-2}\beta$ [cm^{-1}]	Reciprocal voltage ($10^5/U$) [V^{-1}] of the observed shoulders
L I		4.22	74.3	24.6; 22.3
L II	1	4.22	74.3	24.2; 24.4; 19.6
L III		4.22	74.3	25.1; (23.9); 20.8; 19.4
L IV	1	4.22	73.36	24.4; (23.7); (22.6); 22.0; (20.8)
L V	2	3.76	61.8	(29.75); 26.6; 24.75; (23.2)
L VI		3.76	61.8	29.4; 28.4; 27.2

4. *Discussion*

4.1. Determination of observed transitions

According to the concept mentioned in the introduction, the shoulders of the PFE characteristics should be correlated to transitions in the band structure. The first step in finding the possible transitions is the determination of the electric field corresponding to these shoulders (Eq. (1)) by using the calculated field factor, β, from Fowler–Nordheim characteristics for clean tantalum. A shoulder should appear when the final energy of a strong transition starts to look over the surface potential barrier with an increasing field. Therefore, the energy of the top of the barrier, $E_{\max}$, for the shoulders observed is calculated by:

$$E_{\max} = E_F + \phi - 1.2\sqrt{10F}\,. \tag{2}$$

E energies are in eV and the field in V/Å, ϕ is the work function and E_F is the Fermi energy. $E_{\max}$ corresponds to the final energy level and initial energy is obtained by subtracting the excitation energy of 1.96 eV. Because of the small energy of the HeNe laser radiation the observed transitions should occur in the vicinity of the Fermi edge. Taking the average work function for the clean tantalum tip, leads, however, to the location of the initial energy of some transitions into an energy region above the Fermi energy, E_F, where not enough occupied levels are available. The postulation of multiphoton transitions might eventually explain this fact and indeed some support for such a model could be found from a few preliminary measurements of the PFE current versus light intensity dependence

[9]. Yet these results must await further confirmation and this hypothesis is omitted in the present discussion.

Another more probable explanation is the preferred emission of photoelectrons from regions with work function smaller than the average work function of the tip. According to Eq. (2) and the model used, a lower barrier maximum consequently leads to a shift of the transition arrows ([1], Fig. 8) to smaller energies. Drandarov [10] found the {111} and {100} planes of the clean tantalum tip to have the smallest work functions of 3.95 eV and 4.10 eV, respectively. With these values the corresponding barrier height is evaluated and plotted versus the electric field in Fig. 3. The same procedure is applied to the average work function of the barrium covered tip. Fig. 3 and Table II show that the use of the reduced work functions instead of the average values is favourable for two reasons. First, the initial states for all transitions are now occupied states, at least within experimental errors. Second, the number of different transitions is considerably reduced as is obvious from Table II where the brackets include various shoulders from different experiments or assumed planes which give the same transition within the experimental errors. Four of the five transitions thus obtained are therefore reproduced by several shoulders. They partly belong to experiments with different coverages. The possibilities to "reproduce" a transition in various ways are discussed in Ref. [2]. It is not possible to explain the observed shoulders by the periodic current deviations of photo field emission as observed earlier [11]. Such deviations were also observed with barium on tantalum [12] but they appear especially at higher voltages and can easily be recognized by their large amplitudes. In the present experiments such periodic deviations were not observed.

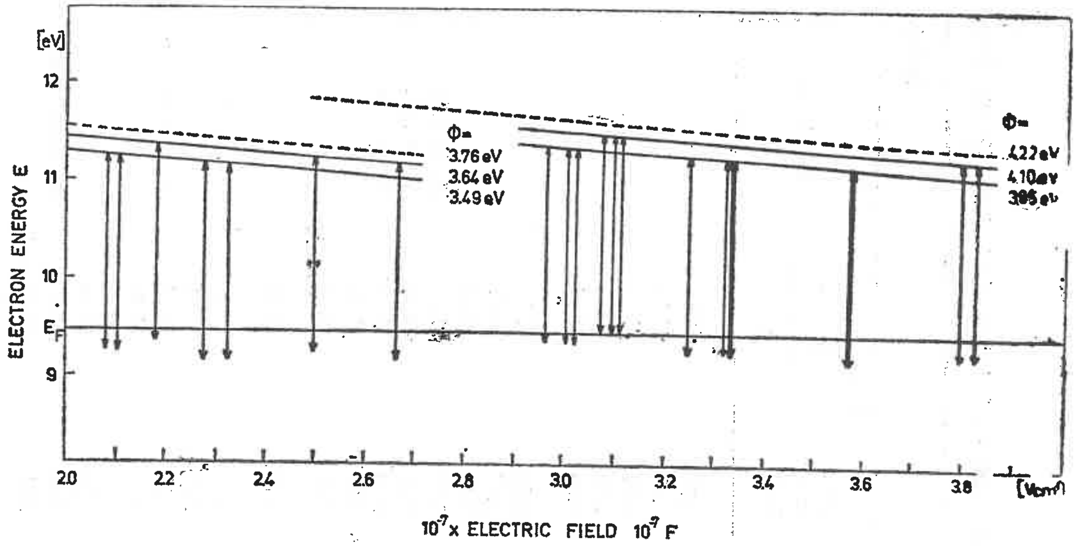

Fig. 3. Surface potential barrier maximum for clean and barium covered tantalum planes versus electric field at the tip. The work functions correspond to emission from the total tip and the (111) or (100) plane as explained in the text. The transition arrows correspond to the observed shoulders

TABLE II

Observed transitions compared with the tantalum band structure calculations of Mattheiss [13]. The Fermi level is $E_F(M) = 9.4757$ eV

Experiment					Relative band structure [13]		
No. of experiment	Field $10^{-7}F$ [V/cm]	Work function [eV]	Initial energy [eV]	Final energy (barrier maximum) [eV]	Initial state	Final state	Transition
L V	2.323	3.49	9.18	11.14			
L VI	2.272	3.49	9.20	11.16		G_1 (2, 6, 0)	
L III	3.572	3.95	9.20	11.16	—	G_1 minimum	Nondirect
L IV	(3.572)	3.95	9.20	11.16		G_1 (3, 5, 0)	
L V	(2.664)	3.64	9.20	11.16			
L V	2.497	3.64	9.26	11.22			
L VI	2.102	3.49	9.27	11.23			
L IV	3.335	3.95	9.27	11.23			
L III	3.824	4.10	9.27	11.23	Σ_1 (2, 2, 0)		
L V	2.077	3.49	9.28	11.24	Σ_1 minimum	—	Nondirect
L I	3.332	3.95	9.28	11.24	Σ_1 (3, 3, 0)		
L II	3.317	3.95	9.28	11.24			
L II	3.791	4.10	9.28	11.24			
L IV	(3.246)	3.95	9.30	11.26			?
L I	3.020	3.95	9.38	11.34	G_3 (2, 6, 0)	G_1 (2, 6, 0)	
L IV	3.000	3.95	9.39	11.35			Direct
L VI	2.176	3.64	9.39	11.35	G_3 (3, 5, 0)	G_1 (3, 5, 0)	
L III	2.960	3.95	9.40	11.36			
L III	(3.109)	4.10	9.50	11.46			
L IV	(3.095)	4.10	9.51	11.47	E_F Fermi edge	—	Nondirect
L II	3.070	4.10	9.51	11.47			

4.2. Comparison with the band structure features of tantalum

Because of the small excitation energy the main contribution to photo field emission with HeNe radiation stems from the vicinity of the Fermi edge. The band structure of tantalum has been calculated by Mattheiss using an APW method [13] and by Petrow and Viswanathan [14]. The interesting part for the present experiments in shown in Fig. 4.

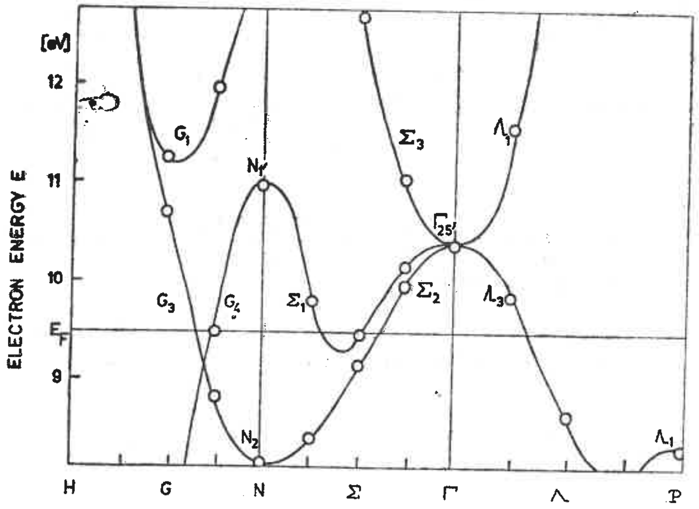

Fig. 4. Part of the band structure as calculated by Mattheiss [13] with relevant features for the present experiments

An attempt to locate the transition arrows of Fig. 3 on the band structure features of Fig. 4 leads to the transitions given on the right hand side of Table II. The three nondirect transitions have the Fermi edge or the Σ_1 minimum as initial states and the G_1 minimum as the final state, respectively. The notation, Σ_1 (2, 2, 0), Σ_1 minimum, Σ_1 (3, 3, 0) indicates that the initial state refers to the Σ_1 minimum located between the indicated points of the Brillouin zone where Σ_1 is the irreducible representation of the state and the integer, k, vector components are given in terms $4(a/\pi)k$ with the lattice constant a. Such marked features of the band structure are not involved with the direct transition given in Table II. Its transition arrow matches the bands G_3 and G_1 on the line connecting the points $(\pi/4a)(2, 6, 0)$ and $(\pi/4a)(3, 5, 0)$ in k space. Only one transition which is not observed more than once does not fit to the available structure which might be caused by an experimental error or by the fact that band structure features have been calculated only for directions of high symmetry. From Table II it is obvious that the transitions observed with barium coverage also "reproduce" transitions observed with clean tantalum. This can be interpreted again [1, 2] by assuming that the influence of the barium coverage only consists in reducing the work function. In photo emission investigations this effect very often is used to determine features in lower parts of the band structure [15]. Because of the high percentage of nondirect transitions it seems worthwhile to investigate the correlation of the experi-

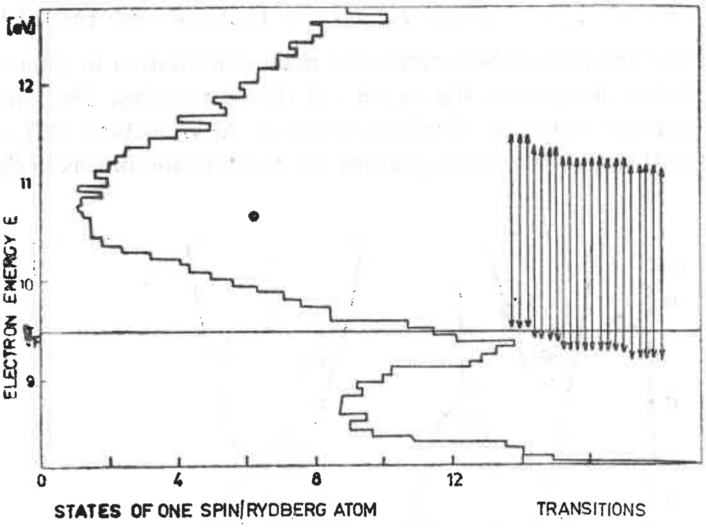

Fig. 5. Part of the density of states as calculated by Mattheiss [13] in the vicinity of the Fermi edge. The observed transitions are represented by the transition arrows of Fig. 3

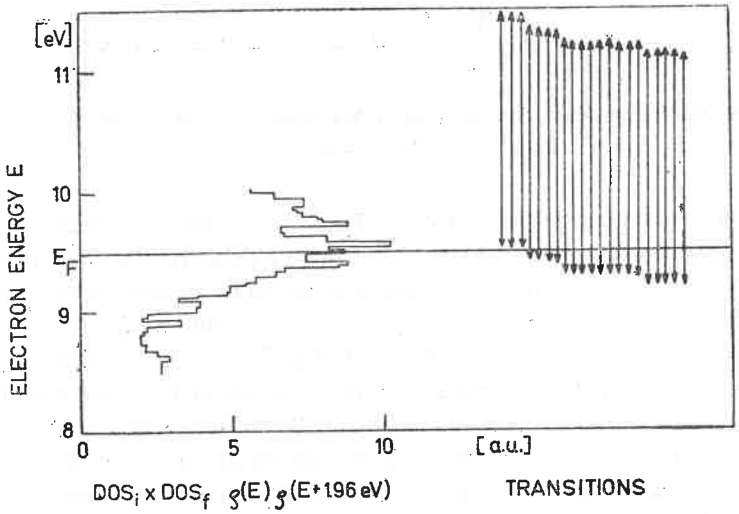

Fig. 6. Product of the density of states (arbitrary units) for initial and final energies separated by 1.96 eV (energy of HeNe laser light). The DOS product is plotted against the initial energy. The observed transitions are represented by the transition arrows of Fig. 3

mentally determined transition arrows with the density of states function (DOS) of tantalum available from the calculation of Mattheiss [13].

Figure 5 shows that the high density of states, $\varrho(E)$, in the vicinity of the Fermi edge and especially the DOS maximum immediately below E_F indeed supports the assumption that the initial states given in Table II are responsible for the observed shoulders. Another way to determine the importance of nondirect transitions is to look for the product of the density of states values for the initial and final energy,

$$\pi(h\nu) = \varrho(E_i)\varrho(E_f) = \varrho(E)\varrho(E+h\nu), \tag{3}$$

$h\nu$ is the excitation energy. The probability for indirect transitions increases with the magnitude of the DOS product, $\pi(h\nu)$. This idea has been used extensively by Spicer [15] and others to explain the photo emission energy distribution measurements and has been considered recently also by Teisseyre [16] for photo field emission.

Figure 6 shows the DOS product $\pi(h\nu)$ for an excitation energy of 1.96 eV as calculated from the values of Mattheiss and plotted against the initial energy. From the location of the arrows in the same diagram, indeed a certain correlation is obvious between the DOS products and the observed transitions especially for the maximum below the Fermi edge. It seems to be more appropriate, however, to compare the transition energies with the detailed band structure features as was done previously [1, 2] and in Table II of the present work.

5. *Conclusion*

The photo field emission experiments performed with a small power HeNe laser reveal changes in the slope or shoulders of the photo current versus voltage characteristics similar to those of former investigations with monochromatic mercury arc radiation. Adopting the same interpretation, the shoulders can certainly be ascribed to transitions in the band structure. The use of the work funtion values for the two planes with the strongest emission is supported by experimental evidence but should be checked by probe hole techniques independently. Its application which is well known from ordinary field emission investigations is favoured by the good focusing properties of laser radiation.

Several shoulders of the PFE characteristics are understood to represent marked transitions with a high probability in the band structure of tantalum as calculated by Mattheiss, thus supporting the applied hypotheses used here. Most of the transitions determined as described before are nondirect and their initial energies are in the immediate vicinity of the Fermi edge. The use of the 1.96 eV HeNe laser radiation is especially suitable for the investigation of band structure features in the occupied and unoccupied energy region near the Fermi level.

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