

Study of atomic excitations in sputtering with the use of Be, B, and C targets

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Solid targets of Be, B, and C have been bombarded with 80-keV Ar^+ ions, and photon emission from sputtered particles has been studied. For beryllium, several strong Be I and Be II emission lines have been observed, and the photon intensities have been converted to relative level population data. Essentially no radiation could be detected with a boron target, and only weak molecular emission was observed for carbon. The results are discussed. They are in accordance with the ideas behind a newly proposed electron-pickup model for atomic excitation in sputtering, but seem not to support a statistical (or binary-collision) model.

I. INTRODUCTION

This work is a continuation of our attempts to systematically study atomic excitation in sputtering processes. There are at present essentially two models for the formation of excited atoms in sputtering processes. These are the electron-pickup model¹ and the statistical (or binary-collision) model.² Other models have been discussed and ruled out in Refs. 1 and 2.

The electron-pickup model¹ has been proposed for solid metal targets, and it draws a parallel between beam-foil events and sputtering. The initial condition in the electron-pickup model is, that in an undisturbed metal, the atoms are in a crude picture sitting as ion cores immersed in an electron gas consisting of the valence electrons of the individual atoms. The motion of a valence electron is delocalized in the metal. The sputtered atoms are initially set in motion from the surface in the same charge state as they exist in the solid, i.e., as positive ions. The majority of them will become neutralized when they leave the solid, because they pick up electrons. Such an electron pickup can lead to sputtering of excited species, simply because some of the electrons may be picked up into some excited state and not the ground state. The electron-pickup model is based on the electronic structure of solid metals, as explicitly specified above in the initial condition.

The statistical model² focuses attention to the last collision involved in the sputtering of an atom. That collision is almost binary, and the atom will initially be located at or very close to the surface. The initial condition in the statistical model is that the atoms are sitting almost as free atoms in their ground state, and excitation in sputtering results from atom-atom binary collisions. According to such a model, ideally, the excitation would be

described in terms of molecular potential-energy curve-crossing processes,³ as in real binary, low-energy atomic collisions. However, since this was regarded² as being prohibitively complicated to carry out for outer-shell excitations in any but the lightest atoms, a random, inelastic energy transfer was introduced.² In passing we mention that all disturbances are so strong during the collision cascade that application of any perturbation treatment like the Born approximation clearly will be inadequate.

We have bombarded solid targets of elemental beryllium, boron, and carbon in an attempt to clear up the diversity concerning the excitation mechanism in sputtering events. These three elements have similar surface atomic binding energies. Therefore, the total sputtering yields will be similar,⁴ and so will the kinetic energy distributions of the sputtered particles.⁴ Furthermore, since these three elements are adjacent in the Periodic Table, the evolutions of the collision cascades leading to sputtering will be similar.⁴ It turns out for these three elements that the atomic excitation energies of relevance are close to each other,⁵ and furthermore, since these atoms are light, the molecular potential-energy curves can be estimated well enough for a qualitative discussion of possible curve crossings of relevance for excitation phenomena.

II. EXPERIMENTAL

The accelerator,⁶ the experimental equipment,¹ as well as the data treatment,¹ have been described previously. Therefore, only a very brief description will be given here.

Solid targets of elemental beryllium, boron, or graphite of high-grade purity (99.99%) were bombarded with 80-keV Ar^+ ions at a residual gas pressure of 10^{-9} Torr, which equals 1.3×10^{-7} Pa.

Photons emitted from sputtered particles were observed with a quantum-efficiency calibrated, one-meter scanning monochromator, working in the wavelength region 200–1000 nm.

The relative population N'_j of level j (uncorrected for cascade contributions) is given by¹

$$N'_j = S(\lambda_{jk}) / [K(\lambda_{jk})b_{jk}],$$

where $S(\lambda_{jk})$ is the signal of the transition from an upper level j to a lower level k (at wavelength λ_{jk}), $K(\lambda_{jk})$ is the quantum efficiency of the detecting device, and b_{jk} is the branching ratio for the transition. Only relative level populations uncorrected for cascades have been determined in this work.

III. RESULTS

The relative level population results, uncorrected for cascades, are given in Table I. They are all on the same scale.

With a beryllium target, a number of lines was observed, some of them being very bright. With boron, only one weak line, namely the $2s\ 2p\ ^1P-2p^2\ ^1D$ transition at 345.1 nm in singly ionized boron (B II) was observed with certainty. The signals at wavelengths of 249.7 and 209.0–209.9 nm, corresponding to the transitions $2s^2\ 2p\ ^2P-2s^2\ 3s\ ^2S$ and $2s^2\ 2p\ ^2P-2s\ 2p^2\ ^2D$ in neutral boron (B I) were essentially at background level, so that even for these resonance transitions in neutral boron, the corresponding level populations could not be measured.

We observed very little radiation with a carbon target. The C I transition at 247.8 nm was hardly seen. No traces of impurities occurred, except of hydrogen, from which the two first Balmer lines were observed, with very low intensity. Also, the CH band at 431 nm occurred, indicating that a com-

plete cleaning of graphite is questionable.

A broad spectral feature occurred with graphite in the interval 450–470 nm. It could be identified as the so-called high-pressure bands of the C₂ Swan system.⁷ These are bands with $\nu'=6$ (ν' being the vibrational quantum number of the upper term; we use the same notation as Ref. 7). However, the bands with other values of ν' in the Swan system did not occur.

It is worth noting that with a carbon target, we observed radiation from the C₂ molecule, whereas with a boron target, no radiation was observed from molecules.

The very low excitation probabilities for boron and carbon are remarkable, especially for boron, because the resonance lines of this element are at wavelengths where the overall detection efficiency is high. Also, we have work in progress, in which aluminum and other metals like gold (copper, silver, cadmium), which are easy both to manufacture with high purity and to keep clean of oxygen, are bombarded under the same vacuum conditions as those of this work. We find that the spectral line intensities of Be, Al, and other metals like gold are of similar strengths. Therefore, we believe that the strong Be signals are appropriate to Be metal itself and are not caused by an oxygen contamination of the Be target. Rather, we believe that the weakness of the boron signals is the peculiar case, being at variance with many metals. As an example, for aluminum strong excitations are seen for many levels of this element which is homologous to boron. This is in clear contrast to the weak excitation of boron, because the level schemes, the excitation energies, and the ionization potentials for aluminum are very similar to those for boron. With an aluminum target, the level excitation probabilities measured for sputtered Al are comparable to those for Be, and excitation of Al II and Al III is observed besides Al I.

The very faint signals with a boron target was a great surprise, and we believe it to be an important finding, since we, in an earlier study⁸ with similar detecting efficiency, saw strong signals for the above-mentioned resonance lines in neutral boron as well as for other transitions. Also, Kelly *et al.*⁹ observed strong signals when bombarding boron-containing targets. The only significant difference between the present study and those reported in Refs. 8 and 9 is that the present measurements have been carried out under ultrahigh vacuum conditions, ensuring a clean surface, contrary to the previous works.^{8,9} To test whether the reduction in signal is caused by the surface cleaning, the valves between the target chamber and the pumps were closed, so that the pressure in the target chamber increased to the ordinary diffusion pump pressure of 10^{-4} Pa in

TABLE I. Relative level population results, uncorrected for cascades.

Target	Level	Relative level population
Be	Be I $2s\ 3s\ ^3S$	0.13
	$2s\ 3d\ ^3D$	0.25
	$2s\ 3d\ ^1D$	0.017
	$2s\ 4d\ ^1D$	0.0010
	$2p\ 3s\ ^3P$	0.0008
	Be II $2p\ ^2P$	1
B	$4d\ ^2D$	0.012
	$4f\ ^2F$	0.0020
	B I $2s^2\ 3s\ ^2S$	<0.001
B II $2p^2\ ^1D$	0.011	

the accelerator. By doing so, the signals of various B I, B II, and B III lines increased immediately some orders of magnitude, indicating the role of surface impurities in the excitation process. This, at the same time, implies that the signal observed under ultrahigh vacuum conditions for the 345.1-nm transition in B II, and thus the boron level population result given in Table I, may partly be caused by remnants of surface impurities and need not be representative of an entirely clean surface. A clean surface may lead to an even lower excitation efficiency than that observed here.

The increase in signals observed with a boron target and closed pump valves are consistent with results published by Tsong.¹⁰ He measured absolute photon yields for a number of elements bombarded with 20-keV Ar⁺ ions, and with oxygen present at the target surface. From his results he deduced detection limits for various elements, and found the detection limit for boron to be only a factor of 2 higher than that for beryllium. With clean surfaces we find the detection limit to be at least 2 orders of magnitude in difference, using the same transitions as Tsong¹⁰ (Be I, 234.8 nm, and B I, 249.7 nm).

IV. DISCUSSION

As mentioned in the Introduction, there are presently two models for atomic excitation in sputtering: the electron-pickup model¹ and the statistical (or binary-collision) model.²

The most significant result of this experimental investigation is the low excitation efficiencies for boron and carbon, in contrast to those observed for beryllium. There are no excitation cross-section data available for binary atomic collisions for these elements. However, normally, excitation cross sections for atomic collision processes do not change very abruptly when the collision system is changed. Therefore, remembering that all of the kinematics of the sputtering processes as well as the sputtering yields are very similar for these elements (cf. Sec. I), the absence of excitation for boron and carbon compared with beryllium is at variance with what one should expect from the statistical model.² The absence of excitation for boron, compared with that for beryllium, can be interpreted as absence of binary-collision induced excitations in sputtering processes, because of all of the similarities between the overall situations for beryllium and boron.

According to the statistical model,² the excitation observed should be describable in terms of molecular curve crossings, as in real, binary atomic collisions. Since beryllium, boron, and carbon are few-electron systems, the molecular-orbital diagrams of relevance for a qualitative discussion of curve-crossing phe-

nomena are easy to construct. A starting point for a discussion of excitation in slow, binary atomic collisions is the so-called molecular-orbital (MO) correlation diagram,³ which gives a schematic representation of how the atomic configurations in the separated collision partners correlate to the configurations in the united atoms limit, when the internuclear distance is reduced during the collision. The correlation diagrams of relevance for the Be-Be and B-B atomic collisions are readily constructed from the rules outlined by Barat and Lichten,³ namely that the number of nodes in the radial part of the wave functions (equal to $n - l - 1$, where n is the principal quantum number and l is the orbital angular momentum quantum number) is conserved, at the same time as the Pauli principle is obeyed.

The correlation diagram for the Be-Be collision is shown in Fig. 1. Molecular orbitals which carry electrons in the incoming channel have been drawn with full lines, whereas initially empty orbitals are shown with dashed lines. We observe from the

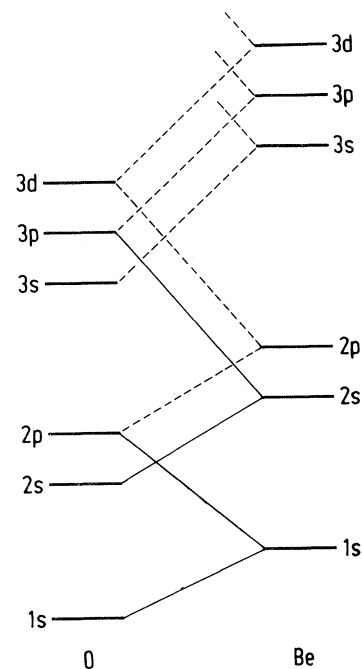


FIG. 1. Diabatic molecular-orbital diagram for the beryllium-beryllium collision shown schematically. To the right of the figure is shown some terms of the separated beryllium atoms (not to scale), and the corresponding united atoms terms (oxygen) are given to the left (not to scale). The terms of the separated and the united atoms have been connected by straight lines to indicate how the levels correlate during a binary collision. Correlations for terms carrying electrons in the incoming channel are shown with solid lines, whereas originally empty orbitals are given by dashed lines. See also the text.

correlation diagram that only the $2p$, $3s$, and $3p$ configurations in beryllium can become excited through electron promotion processes³ at MO curve crossings. Also, the MO correlations do not lead to ionization. However, from Table I we learn that (i) the $3s$ level in BeI is populated less than the $3d$ level is, (ii) both of these level populations are surpassed by excitation of the $2p$ level in ionized beryllium, which involves ionization combined with excitation. Both of these findings disagree with the expectations from the MO correlation diagram.

The correlation diagram for the boron-boron collision is shown in Fig. 2. Naturally it is very similar to that for the Be-Be case (Fig. 1), and thus gives no explanation for the absence of excitation for boron.

Excitation of triplet levels in neutral beryllium is of interest due to the Wigner spin-conservation rule,¹¹ which says that if during an atomic collision the spin-orbit coupling is weak, the total electronic spin will be conserved. If it is believed² that atomic excitation in sputtering results from binary collisions between atoms which initially are in their

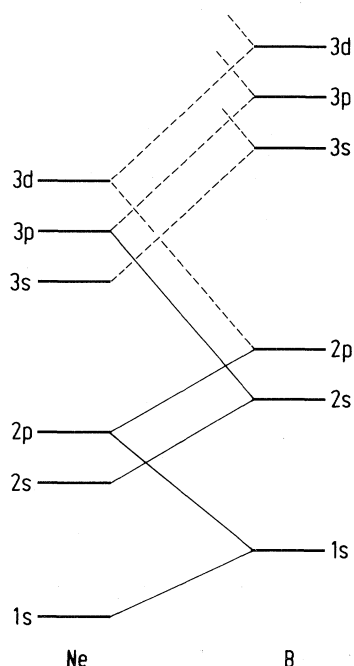


FIG. 2. Diabatic molecular-orbital diagram for the boron-boron collision shown schematically. To the right of the figure is shown some terms of the separated boron atoms (not to scale), and the corresponding united-atoms terms (neon) are given to the left (not to scale). The terms of the separated and the united atoms have been connected by straight lines to indicate how the levels correlate during a binary collision. Correlations for terms carrying electrons in the incoming channel are shown with full lines, whereas originally empty orbitals are given by dashed lines. See also the text.

ground states, then, excitation of a triplet term in one of the colliding beryllium atoms can only take place if the collision partner also becomes excited to a triplet level (or is ionized). This is because of the Wigner spin-conservation rule,¹¹ and because beryllium is well described in the LS -coupling limit, so that spin-orbit couplings are known to be weak for Be. However, since excitation of both collision partners will be less probable than excitation of only one of them, due to their low kinetic energies, one would, in a binary-collision picture,² expect the triplets to be less excited than the corresponding singlet levels, as has been observed in some gas collisions. However, this is not the case for beryllium. The $3d^3D$ level is excited with a probability of more than ten times as large as that for the $3d^1D$ level, cf. Table I. Also this finding speaks against the binary collision picture.² Indeed the factor of more than 10 in population between these two levels is remarkable, since one would from a statistical weight ratio viewpoint expect a factor of 3. The preferential population of triplets is, on the other hand, understandable from the electron-pickup model taken together with the electronic properties of metallic beryllium. The divalent metal beryllium would be an insulator, were it not for the overlap of the $2p$ band with the $2s$ band.¹² The conductivity arises from holes at the top of the $2s$ band, the holes being created by the electron overspill into the $2p$ band.¹² The electrons picked up by an ion core in a sputtering event will preferentially come from the top of the valence band, because such electrons are closest in binding energy to the atomic states in question. Such electrons in the solid will locally tend to have their spins aligned parallel¹² (i.e., to form triplet structures) because this is energetically favorable. This is a common feature and is known as Hund's rule. Thus triplet levels will be favored in two-electron-pickup processes.

The electronic structures of solid beryllium and boron are very different, and the reduction in excitation probabilities observed by going from Be to B undoubtedly finds its explanation in the different electronic structures of the solids. Beryllium is a metal with a reasonable electrical conductivity, whereas boron is a semiconductor. In other words, solid beryllium can in a crude picture be regarded as being built of ion cores (Be^{2+}) immersed in a gas of free electrons,¹³ whereas the atomic bonds in solid boron are of covalent nature, i.e., an electron from each free atom is transferred to the region between the atoms joined by the bond in the solid.¹² In a covalent bond, the atoms tend, in a sense, to fill up their originally empty valence shell orbitals by sharing electrons with neighbor atoms. Thus when a boron atom during a collision cascade is set into

motion leading to its sputtering, the electrons are already—loosely speaking—in orbits which in shape are very similar to those of the ground state of the free atom. During the sputtering event they will be able continuously to adjust their motions adiabatically, so that they end up in the atomic ground state. The same picture can be applied to carbon, but the situation is very different for beryllium. For that element, the valence electrons are initially in the valence band of the solid. Thus their initial orbits are very different from atomic orbitals. They have to change their orbits drastically during the sputtering event. Since the geometric overlap between initial and final state is better for larger orbitals (i.e., excited states), excitation can well occur for Be. The lack of excitation for B compared with Be can thus be regarded as a predictive test of the electron-pickup model.¹

It is remarkable that the only excitation seen with a boron target is the $2p^2$ configuration in B II rather than the $2p$ configuration in B I, because excitation of the $2p^2$ configuration in B II from the $2s^2 2p$ ground configuration in B I involves ionization of one of the two $2s$ electrons and excitation of the other $2s$ electron, whereas excitation of the $2p$ level in B I only involves excitation and not ionization. Therefore, this observation also speaks against the statistical model,² whereas it can be understood from the electron-pickup model.¹ In solid boron, most of the bonds will be of covalent nature, as discussed above, but in few cases, a boron atom will be bound differently, either because of presence of an impurity like oxygen, or due to imperfections of the solid structure. In some cases, the sputtered atom may initially be sitting as an ionic core, and then the electron-pickup model¹ is applicable.

Radiationless deexcitation of a sputtered, excited particle close to a metal surface has been discussed widely in the literature, see, for example, Refs. 8 and 14–18. The prerequisite for a one-electron nonradiative deexcitation process to occur is that the upper level of the excited, sputtered atom energetically coincides with an empty state in the conduction band of the solid. If that is the case, the excited electron may jump back from the atom to the solid. This is a resonance ionization process. If the surface of the metal is oxidized, such a resonance ionization process can become inhibited, because a band gap is introduced in the solid. The possibility of a resonance ionization process to occur at clean metal surfaces, combined with its disappearance when oxygen is admitted to the surface have been used repeatedly to explain the observation that atomic excitation probabilities increase rapidly with increasing concentration of oxygen at the target surface, see, for example Refs. 15–18.

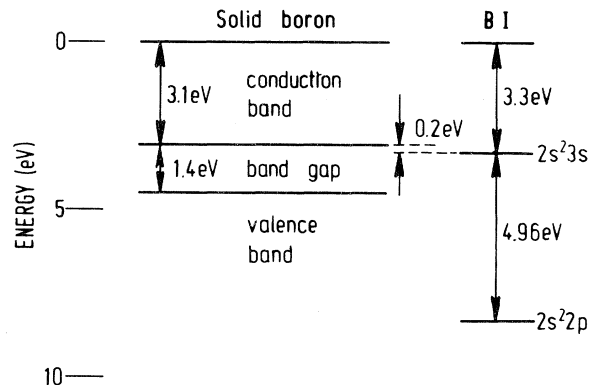


FIG. 3. The electronic energy structure of solid boron is shown together with the energy-level diagram for a free, neutral boron atom.

The electronic energy properties of solid boron seem to be somewhat uncertain. From the work-function values listed in Ref. 19, it seems most reasonable to use a value of 4.5 eV for this quantity. Of the bandgap values compiled by Strehlow and Cook,²⁰ a bandgap of 1.4 eV is most plausible to apply for amorphous boron. From these data, as well as from the ionization level and excitation energy diagram of the neutral boron atom,⁵ the energy diagram shown in Fig. 3 has been constructed. As seen from this figure, the lowest-lying excited level of B I is located 0.2 eV below the bottom of the conduction band in solid boron. Therefore, from the undisturbed energy diagrams shown in Fig. 3 one-electron radiationless deexcitation processes cannot occur for the lowest-lying excited level, and consequently, such processes cannot account for the low excitation efficiencies observed for a clean boron target. Rather, the prohibition of radiationless deexcitation should preserve atomic excitation with a boron target, contrary to the case of metals like Be and Al. However, energy-level shifts and broadenings have to be taken into account also. Such effects may or may not modify Fig. 3 so much that radiationless deexcitation becomes possible for the lowest-lying level in neutral boron. Anyway, if one-electron radiationless deexcitation does occur at a clean metal target surface, then the initial excitation with a clean metal target must be tremendously large, compared with that for boron.

In passing we mention that Loxton *et al.*¹⁷ have studied a possible influence of nonradiative transitions on bombardment-induced photon emission from titanium and titanium oxides. They concluded that they failed to observe any change in photon intensities corresponding to such a process, suggesting that it is not influencing the excited atoms leaving the surface. Also, they¹⁷ mention that there exists

no direct evidence for the occurrence of such a process from other works.

It is noteworthy to see how the excitation probabilities are increased for boron (cf. Sec. III) if oxygen is admitted to the target surface or bulk. This applies not only for weakly bound levels in B I, but also for B II levels bound 12 eV or more, and even B III lines are seen. These increases for B II and B III lines have clearly nothing to do with a prohibition of radiationless deexcitation as suggested for metals in oxygen, and must thus find another explanation. The following explanation has been suggested previously^{14,18} for metals and may also be applicable to boron. When the projectile penetrates the surface, electrons will become excited at the same time as the nuclear motions leading to sputtering are initiated. For clean metals, the relaxation times are much shorter than the total time evolution of the sputtering processes. Therefore, for clean metals, sputtered atoms will interact with a surface which mainly has relaxed. But for surfaces containing oxygen, the relaxation times will be comparable to or maybe even larger than the time scale of a sputtering event, so that the sputtered atoms will interact with a surface region more highly excited than is the case for atoms sputtered from clean surfaces. This can well lead to higher excitation probabilities^{14,18} at oxidized surfaces than at clean surfaces.

As already mentioned, when a carbon target was bombarded, the so-called high-pressure bands of the C₂ Swan system⁷ were observed. These are bands with $\nu' = 6$. However, bands with other values of ν' of the Swan system did not occur. This, taken together with the work by Jeunehomme and Schwenker²¹ gives some insight into the formation of sputtered, excited molecules. They²¹ irradiated graphite under vacuum with a beam from a ruby laser, and photographed the photon spectrum. When the laser was focused exactly on the carbon surface, they ob-

served only C II lines. But when the focus was moved away from the target, the first bands detectable were the high-pressure bands of C₂. At larger distances between the focus and the surface, the intensity of the high-pressure bands were reduced, whereas the ordinary members of the Swan emission bands increased, passed through a maximum, and then finally disappeared. In other words, the high-pressure bands were produced in a relatively hot plasma (not necessarily at local thermodynamic equilibrium conditions), whereas the ordinary members of the Swan emission bands occurred when the plasma was colder. Thus our observation of only the high-pressure bands seems to indicate that excited C₂ molecules are formed only when two carbon atoms collide during the collision cascade at or very close to the surface. Fragmentation of the surface lattice does not lead to formation of stable, excited molecules.

V. CONCLUSION

The difference in excitation efficiency observed between beryllium and boron indicate that atomic excitation in sputtering for these systems is strongly influenced by the initial electronic structure of the solid. The net excitation induced through binary or near-binary atomic collisions or similar processes (boron) is much smaller than that resulting from electron-pickup for metals (beryllium).

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¹E. Veje, Surf. Sci. **110**, 533 (1981); N. Andersen, B. Andersen, and E. Veje, Radiat. Eff. **60**, 119 (1982).

²R. Kelly, Phys. Rev. B **25**, 700 (1982).

³See, for example, W. Lichten, Phys. Rev. **164**, 131 (1967); M. Barat and W. Lichten, Phys. Rev. A **6**, 211 (1972); J. S. Briggs, Rep. Prog. Phys. **39**, 217 (1976).

⁴See, for example, *Sputtering by Particle Bombardment I*, Vol. 47 of *Topics in Applied Physics*, edited by R. Behrisch (Springer, Berlin, 1981).

⁵S. Bashkin and J. Stoner, Jr., in *Atomic Energy Levels and Grotrian Diagrams* (North-Holland, Amsterdam, 1975), Vol. I.

⁶K. Jensen and E. Veje, Nucl. Instrum. Methods **122**, 511 (1974).

⁷R. W. B. Pearse and A. G. Gaydon, *The Identification of*

Molecular Spectra (Chapman and Hall, London, 1976).

⁸K. Jensen and E. Veje, Z. Phys. **269**, 293 (1974).

⁹R. Kelly, S. Dzioba, N. H. Tolk, and J. C. Tully, Surf. Sci. **102**, 486 (1981).

¹⁰I. S. T. Tsong, in *Inelastic Particle-Surface Collisions*, edited by E. Taglauer and W. Heiland (Springer, Berlin, 1981), p. 258.

¹¹E. Wigner, Nachr. Ges. Wiss. Goettingen, Math. Phys. Kl. **1927**, 375.

¹²C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971).

¹³A. Sommerfeld, Naturwissenschaften **41**, 825 (1927).

¹⁴E. Veje, Surf. Sci. **109**, L545 (1981).

¹⁵M. Braun, Phys. Scr. **19**, 33 (1979).

¹⁶I. S. T. Tsong and S. Tsuji, Surf. Sci. **94**, 269 (1980).

¹⁷C. M. Loxton, R. J. MacDonald, and P. J. Martin, *Surf. Sci.* 93, 84 (1980).

¹⁸P. Williams, *Surf. Sci.* 90, 588 (1979).

¹⁹*Handbook of Chemistry and Physics*, edited by R. C. Weast (Chemical Rubber, Cleveland, 1982).

²⁰W. H. Strehlow and E. L. Cook, *J. Phys. Chem. Ref. Data* 2, 163 (1973).

²¹M. Jeunehomme and R. P. Schwenker, *J. Chem. Phys.* 42, 2406 (1965).