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Dispersion of plasmons at the surface of a metal and at the interface between two metals

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The dispersion of plasmons at the surface of a metal and at the interface between two metals is derived by a proper combination of electrodynamics with the hydrodynamic approximation. With a two-step model we discuss the effect of a transition region at the surface of a metal and we so explain recent measurements by Krane and Raether for aluminum.

I. INTRODUCTION

A surface of a metal of an interface between two metals has an effect on collective excitations which propagate near that interface. Since the amplitude of the excitation has to satisfy certain boundary conditions the dispersion is modified resulting in special interfacial excitations. We treat here surface plasmons and interfacial plasmons in metals. In this context we take up the question of the appropriate boundary conditions which are necessary to investigate the reflection and transmission of propagating waves at such interfaces. The surface plasmons are the eigensolutions of this optical problem. In this way the boundary conditions determine the dispersion of the surface plasmons.

In standard optics the amplitude of the outgoing transverse wave on either side is calculated from the continuity of the tangential component of the electric field and the normal component of the displacement vector. This treatment neglects the excitation of a plasma wave in the metal which also is a homogeneous solution of Maxwell's equations and therefore should be included in the general solution. Sauter[1] has specified the three boundary conditions which make it possible to calculate the three amplitudes at a vacuum-metal interface: (i) continuity of the tangential component of the electric field; (ii) continuity of the normal component of the electric field; and (iii) continuity of the normal component of the electric current. These conditions follow from Maxwell's equations assuming the finiteness of charge and current densities and of all fields at the surface. In this way the optics of a metal film[2] and the dispersion of surface plasmons[3] has been studied.

Considering metal-metal interfaces one has to determine one additional amplitude, namely, the amplitude of the plasma waves in the other metal. Therefore, a fourth boundary condition must be added to the three conditions of Sauter. This fourth condition has been recently derived by the authors[4] from the continuity of the normal component of the energy current density. In this paper we apply these boundary conditions to explore the eigensolutions of two simple systems involving metal-metal interfaces.

In Sec. II we discuss the new boundary condition. The dispersion relation of the interfacial plasmon at the boundary of two different metals is calculated in Sec. III. Our result is different from that of Stern and Ferrell[5] because they do not include longitudinal waves. In Sec. IV we simulate the gradual decrease of the charge density at a metal surface by a two-step model. Such a model has already been investigated by various authors[6-8]. In particular, our treatment is similar to that of Ref. 7b. However, we use a well-justified boundary condition at the inner interface. In addition, we consider as a more consistent local density approximation to vary not only the plasmon frequency but also its dispersion as function of density. These differences have important consequences when the model is applied to explain recent measurements of the dispersion of surface plasmons of aluminum.[9] Section V consists of a discussion of the model and the results.

II. FOURTH BOUNDARY CONDITION

A macroscopic treatment of plasma waves is most often done via the so-called hydrodynamic approximation[6-8,10,11] of the equation of motion of the electron gas such that

$$\frac{\partial \vec{j}}{\partial t} = \omega_p^2/4\pi \vec{E} - \gamma \vec{j} - D\,\mathrm{grad}\rho\,, \tag{1}$$

with $\vec{j}$ and ρ current and charge densities, $\omega_p^2 = 4\pi ne^2/m$, and $\gamma = \tau^{-1}$ an inverse lifetime. From Eq. (1) follows the correct bulk plasmon-dispersion relation if $D = \frac{3}{5} v_F^2$. Combining Maxwell's equation with Eq. (1) the energy theorem can be written in the following form[4]:

$$-\frac{\partial}{\partial t}\left(\frac{1}{8\pi}\vec{E}\cdot\vec{D}+\frac{1}{8\pi}\vec{B}\cdot\vec{H}+\frac{2\pi}{\omega_p^2}j^2+\frac{2\pi}{\omega_p^2}D\rho^2\right)$$
$$=\operatorname{div}\left(\frac{c}{4\pi}(\vec{E}\times\vec{H})+\frac{4\pi}{\omega_p^2}D\vec{j}\rho\right)+\frac{4\pi\gamma}{\omega_p^2}j^2. \quad (2)$$

On the left-hand side stands the change of the energy density which contains, in addition to the field energy, the kinetic energy associated with the drift velocity of the electrons and a potential energy due to the inhomogeneity of the electron gas introduced by a longitudinal plasma wave. The energy current density consists of the Poynting vector and the energy current of the plasma wave. One can show that for a pure longitudinal wave the latter term is the product of energy density and phase velocity. This is the same relation as for the Poynting vector of a pure transverse wave. The last term on the right-hand side is the energy dissipation.

The finiteness of all fields as well as current and charge densities implies the finiteness of the divergence of the energy current. Then the usual pill-box argument leads to the continuity of the normal component of the energy current at any interface. The first three boundary conditions make the normal component of the Poynting vector continuous. Therefore, the normal component of $(D/\omega_p^2)\vec{j}\rho$ must be continuous. At a vacuum-metal surface the continuity of the normal component of $\vec{j}$ makes it vanish and therefore the new condition is automatically satisfied. For a metal-metal interface we obtain as the fourth boundary condition: (iv) continuity of $(D/\omega_p^2)\rho$. One might think that $\vec{j}\cdot\vec{n}=0$ would again be an alternative condition for a continuous energy current. But the equation of motion, Eq. (1), shows that also in this case condition (iv) must not be violated. The three boundary conditions of Sauter supplemented by this fourth condition make a macroscopic treatment of metal optics possible.

III. DISPERSION OF PLASMONS AT THE INTERFACE OF TWO METALS

As a surface plasmon exists at a metal-vacuum boundary, a corresponding mode is found at the interface between two metals.[12] Stern and Ferrell[5] give as condition for the eigen mode

$$\epsilon_1(\omega)+\epsilon_2(\omega)=0, \quad (3)$$

which yields

$$\omega_i=[\tfrac{1}{2}(\omega_{p1}^2+\omega_{p2}^2)]^{1/2}. \quad (4)$$

This is the limit for large $k_\parallel$ (wave vector parallel to the interface) in a treatment according to standard optics. In this approximation the dispersion relation for the full $k_\parallel$ range including the small $k_\parallel$ values where retardation is important follows from

$$[(\omega^2/c^2)\epsilon_2-k_\parallel^2]^{1/2}\epsilon_1+[(\omega^2/c^2)\epsilon_1-k_\parallel^2]^{1/2}\epsilon_2=0, \quad (5)$$

which is a generalization of an expression given by Sommerfeld[13] for the dispersion of the so-called Zenneck waves.

We derive the dispersion relation of the interfacial mode accounting explicitly for the existence of plasma waves on both sides.

The method is to treat reflection and transmission of a transverse or longitudinal wave at the interface. The four boundary conditions lead to four linear equations for the four unknown amplitudes. The dispersion of the transverse wave is given by

$$k_\parallel^2+k_\perp^2=(\omega^2/c^2)[1-\omega_p^2/\omega(\omega+i\gamma)]. \quad (6)$$

The dispersion of the longitudinal wave reads

$$\omega(\omega+i\gamma)=\omega_p^2+\tfrac{3}{5}v_F^2(k_\parallel^2+k_\perp^2). \quad (7)$$

The values of the plasma frequency ω_p, the damping constant γ, and the Fermi velocity v_F characterize the two different metals. The eigen mode at the interface is obtained as the self-sustaining solution without incoming waves. Therefore, the determinant of the system of four linear equations must vanish. This condition yields the dispersion of the interfactial plasmon at the interface of two metals. The coefficient matrix is

$$M=\begin{bmatrix}1 & 1 & -1 & -1\\ k_1 & -1/l_1 & k_2 & -1/l_2\\ \sigma_{\perp 1} & \sigma_{\parallel 1} & -\sigma_{\perp 2} & -\sigma_{\parallel 2}\\ 0 & -\eta_1/l_1 & 0 & -\eta_2/l_2\end{bmatrix},$$

with the normal components of the wave vector in units of $k_\parallel$,

$$k_b=\{(\omega^2/c^2k_\parallel^2)[1-\omega_{pb}^2/\omega(\omega+i\gamma_b)]-1\}^{1/2},$$
$$l_b=\{[\omega(\omega+i\gamma_b)-\omega_{pb}^2]/D_bk_\parallel^2-1\}^{1/2},$$

the conductivities

$$\sigma_{\perp b}=i\omega_{pb}^2/4\pi(\omega+i\gamma_b), \quad \sigma_{\parallel b}=i\omega/4\pi,$$

and

$$\eta_b=\omega(\omega+i\gamma_b)/\omega_{pb}^2-1,$$

where b is 1 or 2 on the respective side. For an evaluation we take the parameters for magnesium on aluminum and obtain the result in Fig. 1. Also shown is the dispersion according to Eq. (5). The dispersion in the small $k_\parallel$ region is obviously determined by the transverse waves while at larger $k_\parallel$ the gradient in the charge density increases the frequency. The limit at very small $k_\parallel$ is

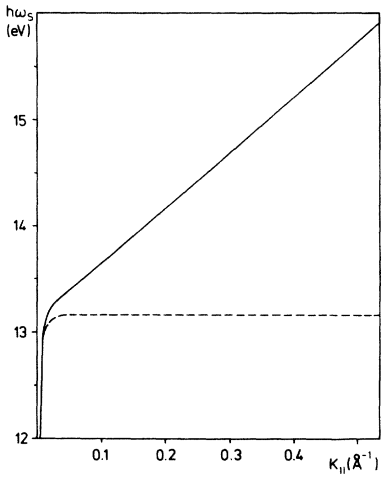

FIG. 1. Dispersion of plasmons at the interface of aluminum and magnesium (full curve). The broken curve is the dispersion according to Eq. (5).

$$\omega^2 = \omega_{p1}^2 + c^2 k_{\parallel}^2 ,$$

with ω_{p1} the smaller of the two plasma frequencies.

IV. DISPERSION OF THE SURFACE PLASMON OF ALUMINUM

Recently, Krane and Raether[9] published measurements of the dispersion of surface plasmons over a very extended range of wave vectors for the free surface of aluminum. These measurements, reproduced in Fig. 4, show as function of $k_{\parallel}$ three regimes: (a) flat plateau near $\omega_p/\sqrt{2}$ for $0.05 \lesssim k_{\parallel} \lesssim 0.3$ Å^{-1}, (b) a decrease of the plasmon frequency for small wave vectors,[14] and (c) a strong increase at large $k_{\parallel}$ values. The dispersion of surface plasmons has been studied theoretically in several papers essentially by two different approaches: (i) a treatment within standard optics which neglects charge density waves inside the metal.[13,15,16] One assumes $\mathrm{div}\vec{E} = 0$, except at the surface where the charge density is infinite; (ii) a proper treatment of charge densities either by many body theory or its hydrodynamic approximation[10,11,17-21] but reducing electrodynamics to the use of $\mathrm{div}\vec{E} = 4\pi\rho$; that is neglecting retardation. Electrodynamics gives the correct dispersion at small $k_{\parallel}$ values, starting with the lightline $\omega_s = ck_{\parallel}$, but at large $k_{\parallel}$ the limit is $\omega_s = \omega_p/\sqrt{2}$ without any dispersion corresponding to the interface results, Eqs. 4 and 5. The decrease of the frequency for long wavelengths reflects the noninstantaneous coupling of the charges at large distances. The hydrodynamic approximation, originally used by Ritchie[10] in the discovery of the surface plasmon, leads to the dispersion $\omega_s = \omega_p/\sqrt{2} + \frac{1}{2}\sqrt{\frac{3}{5}}\, v_F k_{\parallel}$, where v_F is the Fermi velocity. The origin for this dispersion is, as for bulk plasmons, the internal pressure of the electron gas, the resistance against compression, which, in the hydrodynamic approximation, produces a force proportional to $\mathrm{grad}\rho$. This dispersion has been confirmed by microscopic calculations[11,17] sometimes with slight changes in the coefficient of the linear term. It does not go to zero at small $k_{\parallel}$ and is too strong for intermediate wave vectors. A third ingredient is the observation that the gradual decrease of the charge density at the metal surface has the effect of lowering the plasmon frequency with growing $k_{\parallel}$; because the fields of the surface plasmon penetrate less into the bulk of the metal with increasing $k_{\parallel}$ the average charge density involved decreases and so does the effective $\omega_p/\sqrt{2}$. This has been shown by several calculations which account for the charge profile of the metal surface.[6,7,19,20] The three concepts lead to the dispersion curves shown in Fig. 2. The increase due to the electron gas pressure and the decrease due to a soft charge profile are competing. A flat region for intermediate wave vectors is the result.

The concepts of electrodynamics and of the hydrodynamic treatment are combined calculating the fields from Sauter's boundary conditions. This has been done by Sturm.[3] His dispersion (broken line in Fig. 4, for parameters appropriate for aluminum) combines the retardation region at small $k_{\parallel}$ and the electron gas dispersion at large $k_{\parallel}$. It behaves essentially like the result for the interface shown in Fig. 1.

In order to include effects of the transition re-

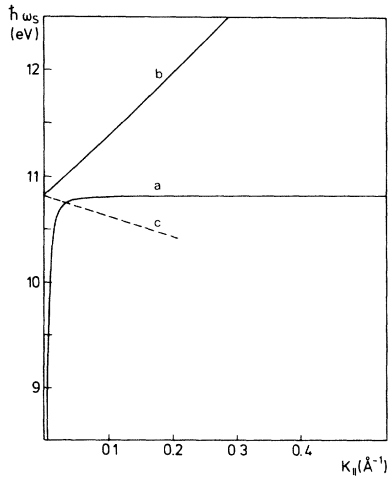

FIG. 2. Surface-plasmon dispersion calculated by standard electrodynamics (a) and by hydrodynamics without retardation (b) for parameters of aluminum. Curve (c) indicates schematically the decrease of the plasmon frequency caused by the gradual fall off of the charge density at the surface.

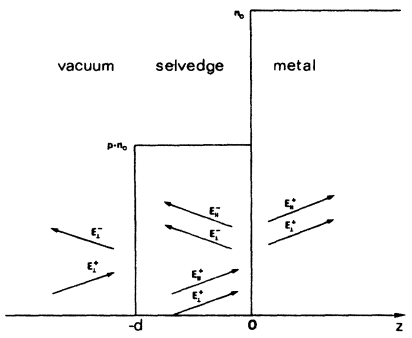

FIG. 3. For the two-step model the electric fields are indicated at the vacuum-metal transition region. $E_\perp$ is the transverse wave, $E_\parallel$ is the longitudinal plasma wave. The plus and minus signs refer to the direction of propagation.

gion we approximate the decreasing charge density at the surface by a two-step model (Fig. 3) with a precursor step of thickness d and of density pn_0 with $p<1$ and n_0 being the bulk charge density. Our boundary condition (iv) enables us to calculate the amplitudes at the inner metal-metal interface and therefore we can find the eigen mode of this layer system. From the three boundary conditions at the vacuum side and four conditions at the inner boundary we obtain a system of seven linear equations for the amplitudes of the electric field. Again, the determinant must vanish for the eigensolutions. The coefficient matrix is

$$M=\begin{bmatrix} A_v & \frac{-1}{A_s} & \frac{-1}{B_s} & -A_s & -B_s & 0 & 0 \\ k_vA_v & \frac{k_s}{A_s} & \frac{-1}{l_sB_s} & -k_sA_s & \frac{B_s}{l_s} & 0 & 0 \\ 0 & \frac{\sigma_{\perp s}}{A_s} & \frac{\sigma_{\parallel s}}{B_s} & \sigma_{\perp s}A_s & \sigma_{\parallel s}B_s & 0 & 0 \\ 0 & 1 & 1 & 1 & 1 & -1 & -1 \\ 0 & -k_s & \frac{1}{l_s} & k_s & \frac{-1}{l_s} & k_m & \frac{-1}{l_m} \\ 0 & \sigma_{\perp s} & \sigma_{\parallel s} & \sigma_{\perp s} & \sigma_{\parallel s} & -\sigma_{\parallel m} & -\sigma_{\parallel m} \\ 0 & 0 & \frac{\eta_s}{l_s} & 0 & \frac{-\eta_s}{l_s} & 0 & \frac{-\eta_m}{l_m} \end{bmatrix},$$

with the same notation as in the previous section. The index b here indicates the regions, vacuum, selvedge, metal, $b=v,s,m$:

$$A_b=\exp(i\vec{k}_b\cdot\vec{d}),\quad B_b=\exp(i\vec{l}_b\cdot\vec{d}).$$

The plasmon dispersion relation, given by $\det M=0$, was evaluated for values of $\omega_p=15.3$ eV, $v_F=2.12\times10^8$ cm sec^{-1}, and $\gamma=\frac{1}{50}\omega_p$, appropriate for aluminum. Only the thickness d the fraction p of the bulk density in the selvedge are disposible parameters. The result for $d=4$ Å and $p=0.7$ is shown in Fig. 4 (full curve). It turns out that only a very narrow range of parameters leads to the kind of agreements shown. Dispersion curves for parameters outside the range of $p=0.75$, $d=5.5$ Å and $p=0.65$, $d=3$ Å cannot be considered good fits to the experiments (see Fig. 5). An increase of d as well as a decrease of p shifts the plateau to lower values of ω_s and deepens the minimum.

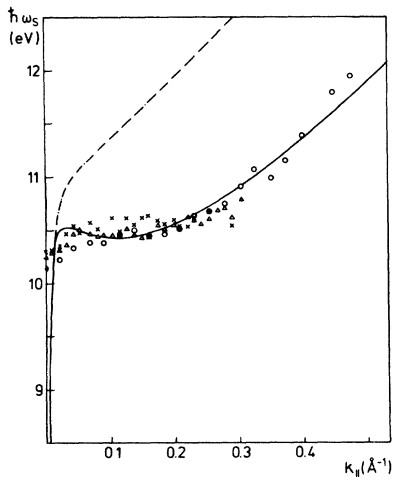

FIG. 4. Theoretical surface plasmon dispersion is compared to the experimental data from Ref. 1. The precursor step was chosen 4 Å thick with a density of $0.7\,n_{Al}$. The broken curve is the plasmon dispersion according to K. Sturm (Ref. 3).

The parameter values are plausible if one inter-

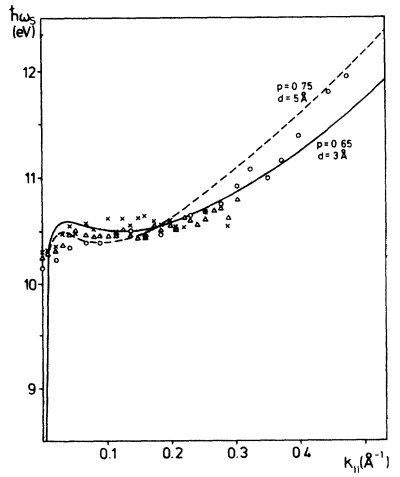

FIG. 5. Demonstration of the sensitivity of the dispersion curves to changes of the model parameters.

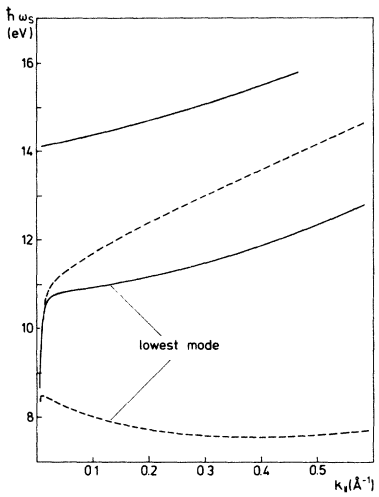

FIG. 6. Comparison of the surface plasmon dispersion and the dispersion of higher modes of Ref. 7 (solid line) with our theory (dashed line). The precursor step in this case is 1.36 Å thick with a density of $0.1\, n_{Al}$.

prets the transition region as caused not only by a Kohn-Lang type of charge density shape but also by some surface roughness. It should be checked by experiments if increasing surface roughness lowers the plateau. The systematically higher values of ω_s in the experiments shown by crosses in the paper by Krane and Raether and in Fig. 4 might be due to a flatter surface. This conjecture is supported by the fact, that in these experiments the lifetime of the surface plasmons is larger than on the other samples.[22]

Our results should be compared to those of a similar treatment of the surface-plasmon dispersion by Boardman, Paranjape, and Teshima, and Boardman, Paranjape, and Nakamura.[7] Their theory differs from ours in two respects: (a) They use the continuity of the fluctuating electron gas pressure as the fourth boundary condition at the inner boundary. This would make the normal component of the energy current discontinuous according to Eq. (2). (b) We also account for the dependence of the electron gas pressure, i.e., the plasmon dispersion on the local density. In Ref. 7 only the plasma frequency is affected by the inhomogeneity. Considering both dependences appears to be more consistent. The quantitative results do depend on these differences. In order to demonstrate this we compare curves according to Ref. 7 with our calculations for a set of parameters they have used (Fig. 6). In Ref. 7 the dispersion of their lower curve was claimed to be a reasonable fit to early experiments in a smaller k region.[23] Our results for this parameter set are completely off. Therefore, the difference between the two treatments is not only accademic. We obtain model parameters which give a more reasonable picture of the metal surface.

V. DISCUSSION

We use in our calculations the hydrodynamic approximation. The applicability to the surface problem has been tested by comparison of its results with those of calculations based on Boltzmann's equation.[11,24] Our results concern wavelengths larger than 12 Å which is more than twice the cutoff wavelength where the collective mode decays by single-particle excitations.

The other important approximation is the representation of the transition region at a metal surface, where the density gradually drops to zero, by a density step. This offers the advantage to analyze the essential physics within the transparent formalism of optics. This approximation is reasonable for solutions which smoothly vary in the direction normal to the surface. This is the case for the solution given in Fig. 4. Also, this dispersion continuously evolves from the dispersion of a metal surface without transition region as a selvedge with very small width and $p \lesssim 1$ is introduced. Our equations also contain higher modes corresponding to standing plasma waves in the selvedge. These are sensitive to the details of the model of the charge distribution because the fields vary strongly over the selvedge region while the lowest mode averages over the charge distribution. Moreover, the higher modes have such short wavelengths normal to the surface that they are not reasonable treated in the hydrodynamic approximation.

We understand the step of smaller density as an approximate representation of the combined effect of surface irregularities and the inherent charge density gradient of a perfect surface. At any rate, the parameters are confined to a narrow range, namely, to 1 Å in thickness and to 10% for the average charge density. It seems worthwhile to measure the dispersion for surfaces of different roughness.

Also, in the case of the plasmon at the interface between two metals, the effect of a transition region is to create a plateau which in its height and extension depends on the properties of the contact region.

[1]F. Sauter, Z. Phys. 203, 488 (1967).
[2]A. R. Melnyk and M. J. Harrison, Phys. Rev. Lett. 21, 85 (1970).
[3]K. Sturm, Z. Phys. 209, 329 (1968).
[4]F. Forstmann and H. Stenschke, Phys. Rev. Lett. 38, 1365 (1977).
[5]E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).
[6]A. J. Bennett, Phys. Rev. B 1, 203 (1970).
[7](a) A. D. Boardman, B. V. Paranjape, and R. Teshima, Surf. Sci. 49, 275 (1975); (b) A. D. Boardman, B. V. Paranjape, and Y. O. Nakamura, Phys. Status Solidi B 75, 347 (1976).
[8]A. Equiluz and J. J. Quinn, Phys. Lett. A 53, 151 (1975).
[9]K. J. Krane and H. Raether, Phys. Rev. Lett. 37, 1355 (1976).
[10]R. H. Ritchie, Prog. Theor. Phys. 29, 607 (1963).
[11]L. Kleinman, Phys. Rev. B 7, 2288 (1973).
[12]W. R. Miller, Jr. and N. N. Axelrod, Solid State Commun. 3, 133 (1965); C. Kunz, Z. Phys. 196, 311 (1966).
[13]A. Sommerfeld, Vorlesungen der Theoretischen Physik, VI, Leipzig, 1966 (unpublished); J. Zenneck, Ann. Phys. (Leipz.) 23, 846 (1907).
[14]With better resolution for small $k_{\parallel}$, one actually expects a decrease down to zero. This has been observed for Ag by Otto, Ref. 15.
[15]A. Otto, Z. Phys. 216, 398 (1968).
[16]E. Kretschmann and H. Raether, Z. Naturforsch. A 23, 2135 (1968).
[17]D. Wagner, Z. Naturforsch. A 21, 624 (1966).
[18]J. Harris, Phys. Rev. B 4, 1022 (1971).
[19]D. E. Beck and V. Celli, Phys. Rev. Lett. 28, 1124 (1972).
[20]P. J. Feibelman, Phys. Rev. Lett. 30, 975 (1973).
[21]B. B. Dasgupta, P. Kumar, and D. E. Beck, Surf. Sci. 48, 241 (1975).
[22]K. J. Krane (private communication).
[23]T. Kloss and H. Raether, Phys. Lett. A 44, 157 (1973).
[24]F. Forstmann, Z. Phys. 203, 495 (1967).