YU ISSN 0015-3206
FZKAAA 13 (1) 23 (1981)

SURFACE AND BULK OPTICAL PHONONS AND PLASMONS IN BILAYER FILMS I. DISPERSION RELATIONS AND THE HAMILTONIAN FORMALISM

Z. LENAC*

»Ruđer Bošković« Institute, P. O. B. 1016 Zagreb, Croatia, Yugoslavia

and

M. ŠUNJIĆ

Department of Physics, Faculty of Science, P. O. B. 162, Zagreb, Croatia, Yugoslavia

and

Institute of Physics of the University, P. O. B. 304,
Zagreb, Croatia, Yugoslavia

Received 10 November 1980

UDC 538.975

Original scientific paper

A quantum-mecanical approach to collective oscillations in bilayer films is presented in the nonretarded approximation. The dispersion relations for surface and bulk modes are found for an arbitrary dielectric function $\varepsilon(\omega)$. The Hamiltonian formalism is developed for optical phonons in ionic crystals and plasmons in metals, and for inert dielectrics in contact with an ionic crystal or metal. The interaction of collective oscillations with charges is studied and the coupling functions are calculated for various thin film combinations.

---

[*] Present address: Pedagogical Faculty, Rijeka, Yugoslavia.

1. *Introduction*

Collective oscillations, as a description of longwavelength correlations between electrons and ions in a medium, are a suitable method for studying many of the bulk$^{1)}$ and surface$^{2)}$ properties of materials. Kliewer and Fuchs$^{3)}$ were the first to investigate the coupling of a (retarded) electromagnetic field and a restoring force in thin ionic crystal films, in terms of collective oscillations — bulk and surface polaritons. The quantization of the polariton field was then performed by Hopfield$^{4)}$ for the bulk case and by Lucas et al.$^{5)}$ for a single thin film in the nonretarded approximation.

Many experiments have been performed with two or more thin films, or with a thin film placed on a substrate, and they have stimulated the theoretical study of such coupled systems. Economou$^{6)}$ described the dispersion properties of multilayer metallic films using a plasmon dielectric function. Later on many other investigations were performed on multilayer films$^{2)}$.

In the present paper we want not only to find the eigenfrequencies of collective oscillations, but also to quantize (in the long-wavelength approximation) the Hamiltonian of the bilayer system. We adopt this approach because it enables us to solve many interesting physical problems in a closed form and especially to give a theoretical description of many experiments performed on bilayer systems.

Some of these problems, such as electron energy loss spectroscopy (EELS) for electrons reflected on a thin film placed on an optically active substrate$^{16)}$ EELS for the electron transmitted through two thin films$^{16)}$, X-ray photoemission spectra (XPS) from an inert dielectric film placed on a metallic substrate$^{17)}$ and the image potential of a point charge$^{17)}$, are successfully treated in the present formalism.

Let us note that some problems, e. g., EELS applied to multilayer films$^{7,8)}$, can be solved essentially in the framework of classical electrodynamics. Hovewer, typical quantum-mechanical features, such as multiple-excitation processes in EELS$^{9,10)}$ are naturally incorporated only in the quantum-mechanical approach.

In section 2 we study the general properties of a model consisting of two dielectric plates. In section 3 we find surface and bulk polarization eigenmodes together with their dispersion relations, and discuss the asymptotic behaviour of surface modes. In both sections we generalize the approach developed in Refs. 3,5,6 to an arbitrary dielectric function $\varepsilon(\omega)$. This generalization enables us, for example, to handle an inert dielectric in the same formalism.

In section 4 we specify the dielectric function to describe an ionic crystal or a metal, and find general properties of polarization eigenmodes. We quantize the Hamiltonian of a free system and discuss the limitations (cutoff wave vectors) of our long-wavelength approximation. In section 5 we find the coupling functions for a point charge interacting with a bilayer system. In both sections (4 and 5) we generalize the method of Ref. 5 to a bilayer system. Such a generalization is nontrivial because in bilayer films, for example, the surface polarization eigenmodes are no longer orthogonal

In section 6 we extend our model to an inert dielectric and an ionic crystal with finite electron polarizability$^{12,13)}$. We discuss the dispersion relations and the coupling functions of surface modes and show them explicitly for some interesting cases. In section 7 we summarize the results.

2. *Formulation of the problem*

We study a system consisting of two adjacent parallel plates infinite in the $\vec{\varrho} = (x, y)$ plane. The z axis is perpendicular to the plates, and we take the plane $z = 0$ be the interface. The plates are denoted by $n = 1$ and $n = 2$, and their thicknesses by a and b, respectively, so the surfaces of the system are at $z = -b$, 0, a (Figs. 1b, 2b).

We assume no free charges in the system and neglect the retardation effects. The latter approximation is satisfactory$^{6)}$ for the interaction of the system with nonrelativistic particles. The equations of electrostatics are

$$\vec{E}(\vec{r}) = - \nabla \Phi(\vec{r}), \tag{1}$$

$$\Delta \Phi(\vec{r}) = 4\pi \nabla \cdot \vec{P}(\vec{r}), \tag{2}$$

where $\vec{E}$, Φ and $\vec{P}$ are the electric field, the (scalar) potential and the polarization, respectively.

Equation (2), together with the boundary condition $\Phi(\vec{\varrho}, \quad z = \pm \infty) = 0$, has a solution in $\vec{k}$-space ($\vec{k}$ is a twodimensional wave vector parallel to the surfaces of the plates):

$$\Phi(\vec{k}, z) = - \int \mathrm{d}z' \, \mathrm{e}^{-k|z-z'|} 2\pi \vec{\varkappa}(z - z') \cdot \vec{P}(\vec{k}, z'), \tag{3}$$

where $\vec{\varkappa}(z) = \mathrm{i}\hat{k} - \operatorname{sgn}(z)\, \hat{z}$.

The dielectric properties of the model we consider are described by the constitutive equation

$$\vec{P}(\vec{k}, z) = \chi_n(\omega) \vec{E}(\vec{k}, z), \quad -b < z < a, \tag{4}$$

where the susceptibility χ_n is taken to be a real function which depends only upon the frequency ω. This approximation is correct in the long-range limit where only the geometrical dispersion of collective oscillations is important$^{2)}$. Eq. (4) also implies perfectly smooth surfaces and a sharp charge density step at the surfaces. Eqs. (1) — (4) give the standard integral equation for $\vec{P}^{5)}$ but generalized to an arbitrary dielectric function $\varepsilon_n(\omega) = 1 + 4\pi\chi_n(\omega)$ of the plate n:

$$\frac{1}{\chi_n(\omega)} \begin{pmatrix} 1 & 0 \\ 0 & \varepsilon_n(\omega) \end{pmatrix} \vec{P}(\vec{k}, z) = \int \mathrm{d}z' \, \overset{\leftrightarrow}{M}(z - z') \vec{P}(\vec{k}, z'). \tag{5}$$

Here:

$$\vec{P}(\vec{k}, z) = \hat{k} P_k(k, z) + \hat{z} P_z(k, z),$$

$$\overset{\leftrightarrow}{M}(z - z') = 2\pi k \, \mathrm{e}^{-k|z-z'|} \begin{pmatrix} -1 & -\mathrm{i}\operatorname{sgn}(z - z') \\ -\mathrm{i}\operatorname{sgn}(z - z') & +1 \end{pmatrix}. \tag{6}$$

Eqs. (5) and (6) define the eigenvalues $\omega_i(\varkappa)$ corresponding to the polarization eigenmodes $\vec{P}^i(\vec{k}, z)$. The index i denotes all possible (linearly independent) solutions of Eq. (5). Noting that $\overleftrightarrow{M}^\dagger(z - z') = \overleftrightarrow{M}(z - z')$, we can express the orthogonality relation for the polarization eigenmodes in a rather general form:

$$\int \mathrm{d}z\, [\chi_n^{-1}(\omega_i) - \chi_n^{-1}(\omega_{i'})] \vec{P}^{i*}(\vec{k}, z) \cdot \vec{P}^{i'}(\vec{k}, z) = 0. \tag{7}$$

For each $\vec{P}^i$ we find $\vec{E}^i$ and Φ^i from relations (1) and (3) or (4):

$$\vec{E}^i(\vec{k}, z) = \left(\mathrm{i}\vec{k} + \frac{\partial}{\partial z}\hat{z}\right) \Phi^i(k, z) = \chi_n^{-1}(\omega_i)\, \vec{P}^i(\vec{k}, z), \tag{8}$$

$$\Phi^i(\vec{k}, z) = -2\pi \int \mathrm{d}z'\, \mathrm{e}^{-k|z-z'|}\, \vec{\varkappa}(z - z') \cdot \vec{P}^i(\vec{k}, z') \tag{9a}$$

$$= (\mathrm{i}/k)\, E_k^i(k, z) = (\mathrm{i}/k)\, \chi_n^{-1}(\omega_i)\, P_k^i(k, z). \tag{9b}$$

The right-hand sides of relations (8) and (9b) containing χ_n are valid only for $-b < z < a$. The integral equation (5) can be transformed into two differential equations:

$$\chi_n^{-1}(\omega_i) \frac{\mathrm{d}}{\mathrm{d}z} P_k^i(k, z) = \chi_n^{-1}(\omega_i)\, \mathrm{i}k\, P_z^i(k, z), \tag{10}$$

$$\varepsilon_n(\omega_i)\, \chi_n{}^{1}(\omega_i) \frac{\mathrm{d}}{\mathrm{d}z} P_z^i(k, z) = -\, \varepsilon_n(\omega_i)\, \chi_n^{-1}(\omega_i)\, \mathrm{i}k\, P_k^i(k, z). \tag{11}$$

By introducing the displacement $\vec{D} = \vec{E} + 4\pi\, \vec{P}$, it follows that

$$E_k^i(k, z) \quad \text{and}\; D_z^i(k, z) = \varepsilon_n(\omega_i)\, E_z^i(k, z) \tag{12}$$

must be continuous functions of z in the whole space. Relations (10—12) are equivalent to the integral equation (5), but are much simpler to solve.

3. *Polarization eigenmodes*

The solution of Eqs. (10—12) can divided into two groups[2]:

3.1. Surface modes: $\chi_n^{-1}(\omega_i) \neq 0$, $\varepsilon_n(\omega_i) \neq 0$

From Eqs. (10) and (11) we find

$$\vec{P}_S^s(\vec{k}, z) = C_S^s(k)\, [F_n^s(k)\, \mathrm{e}^{kz}(\mathrm{i}\hat{k} + \hat{z}) - G_n^s(k)\, \mathrm{e}^{-kz}(\mathrm{i}\hat{k} - \hat{z})], \tag{13}$$

where S denotes surface modes, and $s = 1, 2, 3$...

The electric field inside the plates is defined by Eqs. (8), (12) and (13), while the electric field outside the plates is, according to Eqs. (1), (3) and (13), given by

$$\vec{E}_S^s(\vec{k}, z) = C_S^s(k) \begin{cases} D_2^s(k) \exp\,[-k\,(z-a)]\,(\mathrm{i}\hat{k} - \hat{z}), & z \geq a, \\ D_2^s(k) \exp\,[+k\,(z+b)]\,(\mathrm{i}\hat{k} + \hat{z}), & z \leq -b. \end{cases} \tag{14}$$

Let us apply the continuity conditions (12) to the boundaries $z = -b, 0, a$. Using the definitions

$$F_n^s(k) = \chi_n(\omega_S)\, A_n^s(k), \quad G_n^s(k) = \chi_n(\omega_s)\, B_n^s(k), \tag{15}$$

where A_n^s and B_n^s are the coefficients determining the electric field in the plates, we find

$$\begin{aligned} D_1^s(k) &= -1, \\ A_1^s(k) &= (1-\varepsilon_1)\exp(-ka)/(2\varepsilon_1), \\ B_1^s(k) &= (1+\varepsilon_1)\exp(+ka)/(2\varepsilon_1), \\ A_2^s(k) &= [(\varepsilon_1+\varepsilon_2)\,A_1^s + (\varepsilon_1-\varepsilon_2)\,B_1^s]/(2\varepsilon_2) \\ B_2^s(k) &= [(\varepsilon_1-\varepsilon_2)\,A_1^s + (\varepsilon_1+\varepsilon_2)\,B_1^s]/(2\varepsilon_2), \\ D_2^s(k) &= [\exp(-kb)\,A_2^s - \exp(+kb)\,B_2^s]. \end{aligned} \tag{16}$$

Here $\varepsilon_n = \varepsilon_n(\omega_s)$. According to Eqs. (13—16), the requirement for the nontrival solution for $C_S^s(k)$ leads to the dispersion relation $\omega_s(k)$ for surface modes. The corresponding dispersion equation and the limiting cases $k \to 0$ and $k \to \infty$ are given in Table 1.

Practically, the asymptotic value $\omega_s(k \to \infty)$ is reached for $(ka, kb) > 2$, so the density of states $g(\omega_s) \sim (\partial\omega_s/\partial k)^{-1}$ becomes very large when $\omega_s(k)$ is close to $\omega_s(k \to \infty)$. This has a significant influence, e. g. in electron energy loss spectroscopy, where the sharp maxima in the spectrum appear close to $\omega_s(k \to \infty)$[9]. Therefore, we classify surface modes according to their asymptotic behaviour. The modes for which $(1+\varepsilon_1) \to 0$ (or $(1+\varepsilon_2) \to 0$) for $k \to \infty$, have an appreciable electric field close to the surface $z = a$ $(z = -b)$, while those for which $(\varepsilon_1 + \varepsilon_2) \to 0$ for $k \to \infty$, are important close to the surface $z = 0$. We may deduce that each surface mode is »connected« with one surface $(z = -b, 0, a)$.

The results obtained for two thin films can be easily applied to some specific cases, such as a thin film on a semi-infinite substrate, a thin film and a semi-infinite medium. The dispersion equations for all these cases are also shown in Table 1.

Table 1

(i) Two thin films (a, b finite).

$$\frac{(1-\varepsilon_1)(\varepsilon_1+\varepsilon_2)+(1+\varepsilon_1)(\varepsilon_1-\varepsilon_2)\,e^{2ka}}{(1-\varepsilon_1)(\varepsilon_1-\varepsilon_2)+(1+\varepsilon_1)(\varepsilon_1+\varepsilon_2)\,e^{2ka}}=\frac{(1+\varepsilon_2)}{(1-\varepsilon_2)}\,e^{2kb}$$

$k \to 0$: $|\varepsilon_1 \text{ or } \varepsilon_2| \to \infty, (\varepsilon_1 \text{ or } \varepsilon_2) \to 0$

$k \to \infty\ (1+\varepsilon_1) \to 0, (\varepsilon_1+\varepsilon_2) \to 0, (1+\varepsilon_2) \to 0.$

ii) Thin film on a substrate ($b = \infty$).

$$(1-\varepsilon_1)(\varepsilon_1-\varepsilon_2)\,e^{-2ka}+(1+\varepsilon_1)(\varepsilon_1+\varepsilon_2)=0$$

$k \to 0: \varepsilon_1 \to 0, (1+\varepsilon_2) \to 0, |\varepsilon_1| \to \infty$

$k \to \infty: (1+\varepsilon_1) \to 0, (\varepsilon_1+\varepsilon_2) \to 0$

(iii) Thin film of thickness a ($b = 0$).

$\varepsilon = -\mathrm{cth}\,(ka/2), \ \varepsilon = -\mathrm{th}\,(ka/2)$

$k \to 0: |\varepsilon| \to \infty, \ \varepsilon \to 0$

$k \to \infty: (1+\varepsilon) \to 0$

(iv) Semi-infinite medium ($a = 0$, $b = \infty$).

$(1+\varepsilon) = 0$

Dispersion equations of surface modes.

3.2. *Bulk modes*: $\chi_n^{-1}(\omega_l) = 0$ *or* $\varepsilon_n(\omega_l) = 0$

Bulk modes in a dielectric n are dispersionless in our model and are determined only by the properties of this dielectric, as a consequence of the assumption (4).

For example, let us take $n = 1$, i. e. $0 < z < a$. Then the requirement $\chi_n^{-1}(\omega_l) = 0$ or $\varepsilon_1(\omega_l) = 0$ defines the electric field which vanishes in the whole space except (possibly) in the region $0 < z < a$.

3.2.1. *Transverse bulk modes*: $\chi_1^{-1}(\omega_l) = 0$.

We must have $\vec{E}(\vec{r}) = 0$ in the whole space, i. e. $\vec{D}(\vec{r}) = 4\pi\vec{P}(\vec{r})$. This gives $\chi_1^{-1}(\omega_l)\,\varepsilon_1(\omega_l) = 4\pi$, and $\vec{P}_l(\vec{k}, z)$ is determined by Eqs. (11) and (12). Thus we obtain

$$\vec{P}_T^q(\vec{k}, z) = C_T^q\,[\mathrm{i}\cos(qz)\,\hat{k} + (k/q)\sin(qz)\,\hat{z}],\ 0 < z < a, \qquad (17)$$

where T denotes the transverse bulk modes, and $q = (\pi/a) \cdot m$, $m = 1, 2, 3, \ldots$.

3.2.2. *Longitudinal bulk modes*: $\varepsilon_1(\omega_l) = 0$

Here $\vec{D}(\vec{r}) = 0$, i. e. $\vec{E}(\vec{r}) = -4\pi\,\vec{P}(\vec{r})$. We find $\chi_1^{-1}(\omega_l) = -4\pi$, so $\vec{P}^l(\vec{k}, z)$ follows from (10) and (12):

$$\vec{P}_L^q(\vec{k}, z) = C_L^q(k)\,[\mathrm{i}\,(k/q)\sin(qz)\,\hat{k} + \cos(qz)\,\hat{z}],\quad 0 < z < a. \tag{18}$$

The index L denotes the longitudinal bulk modes.

For $n = 2$, i e. for the bulk modes in the region $-b < z < 0$, we can apply the same discussion. Particularly, expressions (17) and (18) for $\vec{P}^q$ are correct if we replace a by b in q, C_T^q and C_L^q. The parameter q may be interpreted as a z component of a three-dimensional wave vector $\vec{K} = \vec{k} + q\hat{z}$. For surface modes we have $q = 0$. In the limit $b \to \infty$, the discrete parameter $q = (\pi/b)\cdot m$ becomes a continuous parameter, $0 < q < \infty$. In order to help the convergence of P^q at $z \to -\infty$, we define $\eta = 0^+$ and simply make the replacement[15]:

$$[\sin(qz), \cos(qz)] \to \exp(\eta z)\,[\sin(qz), \cos(qz)],\ -\infty < z < 0.$$

4. *The Hamiltonian of free collective oscillations*

In the preceding sections we have described the dielectric properties of a bilayer system without specifying the dielectric function $\varepsilon(\omega)$. In order to determine $\varepsilon(\omega)$, we have to find the equation of motion for dielectric media.

In the point-ion approximation the equation of motion takes the form[1,5]

$$\frac{\partial^2}{\partial t^2}\vec{P}(\vec{r}, t) + \omega_{Tn}^2\,\vec{P}(\vec{r}, t) = \frac{\omega_{Pn}^2}{4\pi}\,\vec{E}(\vec{r}, t), \tag{19}$$

which leads to

$$\varepsilon_n(\omega) = \frac{\omega_{Ln}^2 - \omega^2}{\omega_{Tn}^2 - \omega^2},\quad \chi_n(\omega) = \frac{1}{4\pi}\,\frac{\omega_{Pn}^2}{\omega_{Tn}^2 - \omega^2}. \tag{20}$$

Obviously, $\omega = \omega_{Tn}$ defines the transverse bulk modes and $\omega = \omega_{Ln}$ defines the longitudinal bulk modes, while

$\omega_{Pn}^2 = \omega_{Ln}^2 - \omega_{Tn}^2$ is the ion-plasma frequency in the dielectric n.

Eqs. (7) and (20) give the orthogonality relation

$$\int_{-b}^{a} \mathrm{d}z\,\vec{P}^{l*}(\vec{k}, z)\cdot\vec{P}^{l'}(\vec{k}, z)\,\omega_{Pn}^{-2} = \delta_{l,l'}. \tag{21}$$

Eq. (21) differs from the standard orthogonality relation by a weighting factor ω_{Pn}^{-2} [5].

The condition (21) determines the constants $C_l(k)$:

$$C_S^s(k) = \sqrt{k}\,\omega_{P1}\,\omega_{P2}\cdot\{\omega_{P_1}^2\,[F_2^{s^2}(1-\mathrm{e}^{-2kb})+$$

$$+G_2^{s^2}(\mathrm{e}^{2kb}-1)]+\omega_{P_2}^2\,[F_1^{s^2}(\mathrm{e}^{2ka}-1)+G_1^{s^2}(1-\mathrm{e}^{-2ka})]\}^{-1/2}, \tag{22}$$

$$C_B^q(k) \equiv C_T^q(k) = C_L^q(k) = \omega_{Pn}\left(\frac{2}{z_0}\right)^{1/2}\frac{q}{(q^2+k^2)^{1/2}}, \tag{23}$$

where $z_0 = a, b, \pi$ if $n = 1$, $n = 2$, or $b \to \infty$, respectively.

According to Eqs. (5) and (21), any physical quantity f related to $\vec{P}$ can be expanded in terms of $\vec{P}_l$ in each dielectric plate. This statement is expressed by the closure relation

$$\sum_l \vec{P}^{l*}(\vec{k}, z)\,\vec{P}^l(\vec{k}, z') = \omega_{P_n}^2\,\delta(z-z')\,\overleftrightarrow{E}. \tag{24}$$

In the limit $b \to \infty$ we assume $\delta_{q,q'} \to \delta(q-q')$ and $\sum_q \to \int \mathrm{d}q$ in the region $z < 0$.

The dielectric properties of a metallic plate n are described by[2)]

$$\varepsilon_n(\omega) = 1 - \frac{\omega_{Pn}^2}{\omega^2}, \quad \chi_n(\omega) = -\frac{1}{4\pi}\frac{\omega_{Pn}^2}{\omega^2}, \tag{25}$$

where ω_{P_n} now denotes the electron plasma frequency. Eq. (25) is formally obtained from Eq. (20) by making the substitutions $\omega_{Tn} \to 0$ and $\omega_{Ln} \to \omega_{Pn}$.

Following (24), we expand $\vec{P}$ in terms of $\vec{P}^l$:

$$\vec{P}(\vec{k}, z) = \sum_l h_l(\vec{k})\,[a_l(\vec{k}) + a_l^\dagger(-\vec{k})]\,\vec{P}^l(\vec{k}, z), \tag{26}$$

where $a_l^\dagger(\vec{k})$ and $a_l(\vec{k})$ are the standard creation and annihilation operators for bosons. The total hamiltonian H_0 of the bilayer system can be diagonalized in a similar way as described in Ref. 5. Here we choose

$$h_l(k) = \frac{1}{2\pi}\left[\frac{\hbar}{8\pi A\,\omega_l(\vec{k})}\right]^{1/2}, \tag{27}$$

where A is the normalization area. This choice differs from the usual one by a factor ω_P^2[5)], which explicitly enters the orthogonality relation (21). Then we obtain:

$$H_0 = \int H_0(\vec{r})\,\mathrm{d}\vec{r} = A\int \mathrm{d}\vec{k}\sum_l \hbar\omega_l(\vec{k})\left[a_l^\dagger(\vec{k})\,a_l(\vec{k}) + \frac{1}{2}\right]. \tag{28}$$

H_0 is the Hamiltonian of the long-wavelength collective oscillations in the bilayer system. These oscillations (optical phonons in an ionic crystal and plasmons in a metal) are well defined for $K < K_c$, where $\vec{K}_c$ is the cutoff wave vector as a limit of our continuum approximation. For surface modes ($q = 0$) we define the cutoff wave vector $\vec{k}_c$ parallel to the surfaces of the system, while for bulk modes ($q > 0$) we also have to define a cutoff wave vector $\vec{q}_c$ in a direction perpendicular to the surface. The summation over q and the integration over $\vec{k}$ should be performed up to the limit determined by the sphere $\varkappa^2 + q^2 = K_c^2$[15]. We can roughly estimate K_c to be of the order of 10^6 cm^{-1} for all cases involved.

Let us note that the closure relation (24) is a purely mathematical statement which implies $0 \leq q < \infty$. If this relation is used to avoid the summation over volume modes[5,9], $q_c = \infty$ is implicitly assumed, which may not always be a good approximation[10,15,16].

The Hamiltonian (28), together with the polarization (26) and the polarization eigenmodes and eigenfrequencies defined in section 3, gives a complete description of the bilayer system in the long-wavelength approximation. In order to solve the problems we have mentioned in the Introduction we have to take into account the appropriate interaction.

5. *Interaction of a point charge with collective oscillations*

The interaction of a point charge e at $\vec{r}_e = (\vec{\varrho}_e, z_e)$ with collective oscillations of the bilayer system is described by the Hamiltonian

$$H_I = e\,\Phi\,(\vec{r}_e). \tag{29}$$

Using Eqs. (3) and (26), we can write (29) in the form

$$H_I = A \int \mathrm{d}\vec{k}\, \mathrm{e}^{i\vec{k}\vec{\varrho}_e} \sum_l \Gamma_l\,(k, z_e)\,[a_l\,(\vec{k}) + a_l^\dagger\,(-\vec{k})], \tag{30}$$

where the coupling functions (interaction matrix elements) are

$$\Gamma_l\,(k, z_e) = e\,h_l\,(k)\,\Phi^l\,(k, z_e) = \Gamma_l^*\,(k, z_e). \tag{31}$$

In similar problems[5,9], Eq. (9a) for $\Phi^l\,(k, z)$ is used to express $\Gamma_l\,(k, z_e)$. In this case the integration has to be performed over z and the results obtained are rather complicated. In fact, the coupling functions, which are defined for the whole space, are expressed in terms of polarization eigenmodes, which are nonvanishing only inside the plates. Therefore, to express $\Gamma_l\,(k, z_e)$, e. g. at $0 < z_e < a$, one has to involve the expressions for $\vec{P}^l\,(\vec{k}, z)$ in both regions, $0 < z_e < a$ and $-b < z_e < 0$. A much simpler result follows if we use Eq. (9b), i. e. $\Phi^l\,(k, z) = (i/k) E_\varkappa^l\,(k, z)$. Then $\Gamma_l\,(k, z_e)$ is expressed by $E_k^l\,(k, z_e)$ that corresponds to the same region. An explicit proof of the identity between these two results is rather tedious, though straightforward.

Starting with Eq. (9b), we find $\Gamma_S(k, z)$ for surface modes:

$$\Gamma_S^s(k, z) = -e\, C_S^s(k)\, h_S^s(k)\, \gamma_S^s(k, z_e)/k, \tag{32}$$

$$\gamma_S^s(k, z) = \begin{cases} -\exp[-k(z-a)], & z > a, \\ A_1^s \exp(kz) - B_1^s \exp(-kz), & 0 > z > a, \\ A_2^s \exp(kz) - B_2^s \exp(-k, z), & -b < z < 0, \\ D_2^s \exp[k(z+b)], & z < -b, \end{cases}$$

and for bulk modes:

$$\Gamma_L^q(k, z_e) = 4\pi e\, C_B^q(k)\, h_L^q \sin(qz_e)/q, \quad -b > z_e > a, \tag{33}$$

$$\Gamma_T^q(k, z_e) = 0. \tag{34}$$

The total Hamiltonian for a point charge interacting with collective oscillations of the bilayer system is

$$H = H_0 + H_I + H_e, \tag{35}$$

where $H_e = p_e^2/2m_e$ is the electron kinetic-energy operator.

Let us note that H can be diagonalized only in a semiclassical approximation, which is exact in two opposite limits$^{5)}$: for a charge at rest$^{1\,5)}$ (large potential energy, $V_e \gg \hbar\omega_l$) and for a very fast point charge$^{9)}$ (large kinetic energy, $E_e \gg \hbar\omega_l$).

6. *Comments on some special cases*

In the preceding sections we have developed a full description in the long-wavelength approximation of collective oscillations in two adjacent plates. The theory is satisfactory for systems where the dielectric properties can be approximated by the dielectric functions (20) or (25). Here we extend the model to some other interesting cases.

6.1. *An inert dielectric*

There are many materials for which the dielectric functions (20) or (25) are not appropriate. In some materials (inert dielectrics), the dielectric function is roughly independent of ω for all frequencies of interest.

Still, we can apply our formalism to an inert dielectric plate n by taking formally $(\omega_{Tn}, \omega_{Ln}) \gg \omega$ and defining

$$\varepsilon_n = \frac{\omega_{Ln}^2}{\omega_{Tn}^2}, \quad \chi_n = \frac{1}{4\pi}\frac{\omega_{Pn}^2}{\omega_{Tn}^2}, \tag{36}$$

where $\omega_{Pn}^2 = (\omega_{Ln}^2 - \omega_{Tn}^2) \gg \omega^2$.

This is consistent with the equation of motion (19) which reduces to $\vec{P}(\vec{r}, t) = \chi_n \vec{E}(\vec{r}, t)$ in the inert dielectric n. No bulk modes exist in the inert dielectric. Surface modes extend also into the inert dielectric owing to the presence of the optically active medium. It is very important to note that $H_0(\vec{r}) = 0$ in the inert dielectric. This result is obtained because no charge oscillations appear in that region. However, we must be careful when calculating the total Hamiltonian (35) of the bilayer system interacting with the external charge. It can be shown that (35) is a correct expression for H if we define H_e as

$$H_e = \frac{p_e^2}{2m_e} + U(\vec{r}_e), \tag{37}$$

where $U(\vec{r}_e)$ is the potential energy of a point charge interacting with the inert dielectric only[17]. Therefore, the coupling functions (31—34) describe the interaction of an electron with collective oscillations in an optically active medium in the presence of an inert dielectric. Expressions (31—34) are correct and the requirement $\omega_{P1} \gg \omega_{P2}$ leads to a rather simple relation for $C_S^s(k)$:

$$C_S^s(k) = \sqrt{k}\, \omega_{P2} \left[F_2^{s^2}(1 - e^{-2kb}) + G_2^{s^2}(e^{2kb} - 1)\right]^{-1/2}. \tag{38}$$

Here we suppose the inert dielectric to be in the region $n = 1$, i. e. at $0 < z < a$. According to (5) and (7), the orthogonality (21) and closure (24) relations are still valid, but they are restricted to $-b < z < 0$.

6.2. *A dielectric with electronic polarizability*

In the equation of motion (19) we considered only the ionic contribution and neglected the electronic contribution to the polarization. If we take into account the electronic polarizability in the dielectric n, we have to replace (20) by[1]:

$$\varepsilon_n(\omega) = \varepsilon_{\infty n} \frac{\omega_{Ln}^2 - \omega^2}{\omega_{Tn}^2 - \omega^2}, \quad \chi_n(\omega) = \frac{1}{4\pi}\left[\varepsilon_n(\omega) - 1\right], \tag{39}$$

where $\varepsilon_{\infty n}$ describes the dielectric function at high frequencies ($\omega \ll \omega_{Ln}, \omega_{Tn}$). The conclusions of sections 2 and 3 remain valid. However, the equation of motion (19) in section 4 and the relations that follow are no longer correct. Nevertheless, it can be shown[12,13] that the polarization can be expanded in the form (29). Then, the interaction of a point charge with dielectric plates described by (39) has the form (30).

The theory developed in sections 2 and 3, combined with the approach of Ref. 13, allows a consistent inclusion of electronic polarizability.

Briefly, our theory remains valid if one redefines ω_{Pn} [which enters the coefficient $C_l(k)$] for surface modes[12]:

$$\omega_{Pn} \to 2\omega_{Sn}\left[(\varepsilon_{\infty n} + 1)^{-1} - (\varepsilon_{on} + 1)^{-1}\right]^{1/2}, \tag{40}$$

and for bulk modes[13]:

$$\omega_{Pn} \to \omega_{Ln} (\varepsilon_{\infty n}^{-1} - \varepsilon_{on}^{-1})^{1/2}. \tag{41}$$

Here $\varepsilon_{on} \equiv \varepsilon_n (\omega \to 0) = \varepsilon_{\infty n} (\omega_{Ln}/\omega_{Tn})^2$, while ω_{Sn} is the asymptotic frequency of the surface modes of the dielectric n alone, i. e. $\omega_{S1} = \omega_{a1}$, $\omega_{S2} = \omega_{a4}$, and ω_{a1}, ω_{a4} are given in Table 2. The statement (40) is only approximative, while the statement (41) is exact. In the limit $\varepsilon_{\infty n} \to 1$, both Eqs. (40) and (41) reduce to $\omega_{Pn} \to \to (\omega_{Ln}^2 - \omega_{Tn}^2)^{1/2}$.

Table 2

$k \to \infty$	ω_{as}	ω_{as} (two metals)
$(1 + \varepsilon_1) \to 0$	ω_{a1}	$\omega_{P1}/\sqrt{2}$
$(\varepsilon_1 + \varepsilon_2) \to 0$	$\omega_{a2,3}$	$(\omega_{P_1}^2 + \omega_{P_2}^2)^{1/2}/\sqrt{2}$
$(1 + \varepsilon_2) \to 0$	ω_{a4}	$\omega_{P2}/\sqrt{2}$

$$\omega_{a1} = [(\varepsilon_{\infty 1} \omega_{L_1}^2 + \omega_{T_1}^2)/(\varepsilon_{\infty 1} + 1)]^{1/2}$$

$$\omega_{a4} = [(\varepsilon_{\infty 2} \omega_{L_2}^2 + \omega_{T_2}^2)/(\varepsilon_{\infty 2} + 1)]^{1/2}$$

$$\omega_{a2,3} = ([\omega_{LT}^2 \pm (\omega_{LT}^4 - 2\varepsilon_{\infty 12} \omega_{TL}^4)^{1/2}]/\varepsilon_{\infty 12})^{1/2}$$

$$\omega_{LT}^2 = \varepsilon_{\infty 1} (\omega_{L_1}^2 + \omega_{T_2}^2) + \varepsilon_{\infty 2} (\omega_{L_2}^2 + \omega_{T_1}^2)$$

$$\omega_{TL}^4 = \varepsilon_{\infty 1} \omega_{T_2}^2 \omega_{L_1}^2 + \varepsilon_{\infty 2} \omega_{T_1}^2 \omega_{L_2}^2$$

$$\varepsilon_{\infty 12} = 2 (\varepsilon_{\infty 1} + \varepsilon_{\infty 2})$$

Asymptotic frequencies of surface modes.

Up to this point we have described several models for the dielectric function, which in turn enable us to determine the dispersion of the collective oscillations (Table 1) in the corresponding system. These surface (or Fuchs-Kliewer[2]) modes exibit a strong dispersion which essentially depends on both the dielectric properties and the geometry of the medium. In our model the bulk modes are dispersionless, but each bulk mode is characterized by the discrete parameter q which plays an important role e. g. in the screening of the external charge[15] and in the electron-transmission experiment[16].

It is well known[2] that the collective modes are the dominant excitations in the small wave vector limit, so when essentially the same approach was applied to the thin film (or semiinfinite medium)[5,9], one was able to explain many interesting experiments (EELS, XPS, image potential, etc). The present theory enables one to describe the same experiments in the bilayer systems, which is obviously of great importance. Moreover, we have also outlined some important features of thin films such as the three dimensional cutoff wave vector and the discrete nature of the bulk excitations, which were usually neglected. Here, we have been able to connect them with real experimental situations[15,16].

This paper is mainly devoted to solving the general problem of charged particle interacting with the collective oscillations of bilayer systems, so it is appropriate to discuss the general behaviour of the dispersion relation $\omega_s(k)$ and the coupling functions $\Gamma_S^i(k, z)$. We stress again that our approach is a macroscopic one; if the experimental situation requires detailed knowledge of the microscopic properties of the system, our theory obviously could not give the complete answer.

6.3. Two dielectric or metallic plates

The dispersion relation for two *dieletric plates* with the dielectric functions (39) is shown in Fig. la. There are four surface modes for finite b and three surface modes in the case of semi-infinite substrate ($b = \infty$).

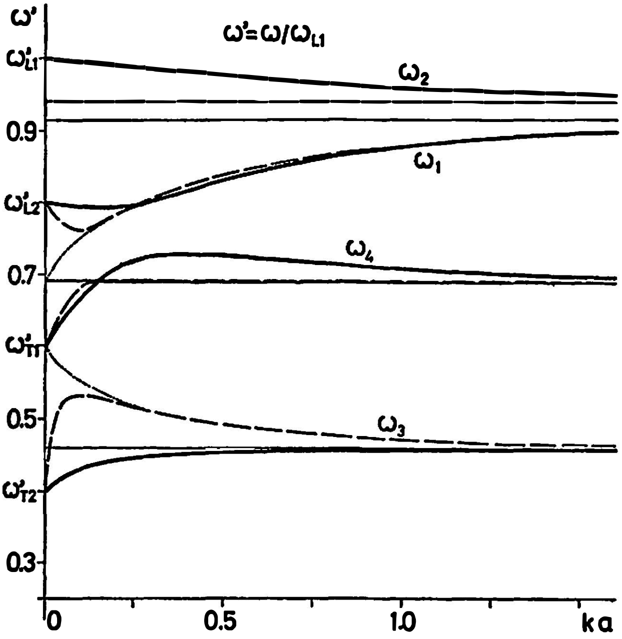

Fig. 1. Two dielectric plates in contact. The parameters are typical of ionic crystals: $\varepsilon_{\infty 1} = 3$, $\hbar\omega_{T1} = 0.06$ eV, $\hbar\omega_{L1} = 0.1$ eV and $\varepsilon_{\infty 2} = 2$, $\hbar\omega_{T2} = 0.04$ eV, $\hbar\omega_{L2} = 0.08$ eV. a) Dispersion relation. Full line: $b = a$, dashed line: $b = 10a$, dotted line: $b \leftarrow \infty$. b) Coupling functions (in arbitrary units), for $b = a$ and $ka = 2$. For larger ka, the coupling functions would have more pronounced maxima at the corresponding surfaces.

a) Dispersion relation. Full line: $b = a$, dashed line: $b = 10a$, dotted line: $b \rightarrow \infty$.

As we have pointed out, surface modes can be classified according to their asymptotic behaviour for $k \rightarrow \infty$. The asymptotic frequencies $\omega_{as} = \omega_s(k \rightarrow \infty)$ are given in Table 2. The coupling functions (32) for the same system are shown in Fig. 1b. From Fig. 1b or by comparing Fig. 1a with Table 2 we find that one mode (ω_1) is connected with the surface $z = a$, two modes (ω_2, ω_3) with the surface $z = 0$ and one mode (ω_4) with the surface $z = -b$. In the limit $b \rightarrow \infty$, the frequency of the last mode (ω_4) becomes dispersionless and it is not a solution of the dis-

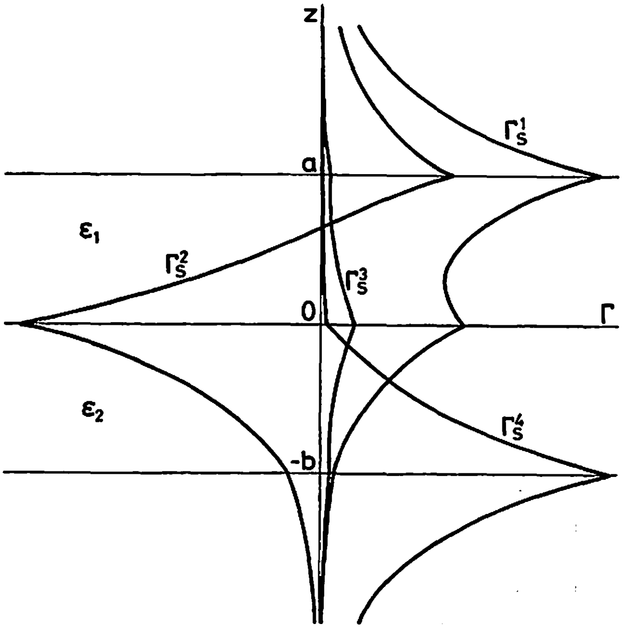

Fig. 1, b) Coupling functions (in arbitrary units), for $b = a$ and $ka = 2$. For larger ka, the coupling functions would have more pronounced maxima at the corresponding surfaces.

persion equation for a thin film on a substrate (Table 1). We point out that the upper (lower) interface mode ω_2 (ω_3) lies between ω_{L1}, ω_{L2} (ω_{T1}, ω_{T2}). Therefore, we call ω_2 the longitudinal interface mode and ω_3 the transverse interface mode. The first mode is strongly coupled, while the second mode is weakly coupled to the external charge.

For two *metallic plates* [Eq. (25)], the shape of the dispersion relation is essentially the same as in Fig. 1a provided we take $\omega_{T1} = \omega_{T2} = 0$. However, $\omega = 0$ ($|\varepsilon| \to \infty$) is not a solution for the transverse surface mode because $\omega = \omega_T = 0$ is a degenerate frequency of transverse (shear) bulk modes in metals. This means that (for finite b) we find three surface modes, i.e. one surface mode is connected with each metallic surface $z = a$, 0, $-b$. The asymptotic frequencies are given in Table 2. In the case $b = \infty$, we find two surface modes connected with the surface $z = a$, 0[11]. The coupling functions are of essentially the same shape as those for two ionic crystals. Obviously there is only one »interface« coupling function (Γ_S^2). The ratio of this function vs the »surface« coupling functions Γ_S^1 and Γ_S^4 is much smaller than the corresponding ratio in the case of ionic crystals. This is a consequence of a much stronger screening of the external field in the case of metallic plates.

6.4. A dielectric and a metallic plate in contact

The dispersion relation for the dielectric plate (39) ($n = 1$) and for the metallic plate (25) ($n = 2$) are shown in Fig. 2a. Again, we have four surface modes (or three, if one of the plates is infinitely thick). Fig. 2b shows the coupling functions (32).

The frequency of the surface mode (ω_1) connected with the dielectric surface ($z = a$) is much lower than that of the surface mode (ω_4) connected with the metallic surface ($z = -b$). There are two interface modes: The longitudinal interface mode starts from the phonon frequency $\omega_2 (k \to 0) = \omega_{L1}$, but approaches a typical plasmon frequency $\omega_2 (k \to \infty) \approx \omega_{P2}/(1 + \varepsilon_{\infty 1})^{1/2}$. The transverse interface mode is practically degenerate: $\omega_3 (k) \approx \omega_{T1}$, and its coupling function is negligible. The two »phonon« modes (ω_1, ω_3) exhibit much less dispersion than the »plasmon« modes (ω_2, ω_4). In fact, the »plasmon« modes behave as if the dielectric were approximated by $\varepsilon_1 (\omega) \approx \varepsilon_{\infty 1}$.

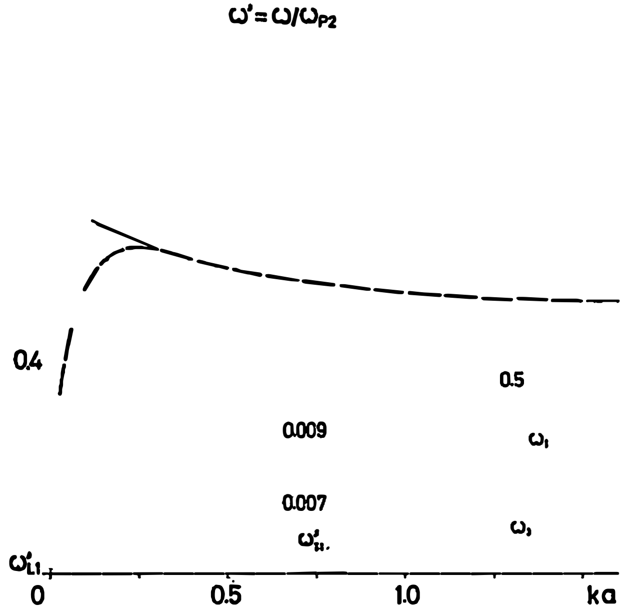

Fig. 2. Dielectric and metallic plate in contact. The dielectric plate ($\varepsilon_{\infty 1} = 3$, $\hbar \omega_{T1} = 0.1$ eV) is placed on a metallic plate ($\hbar \omega_{P2} = 10$ eV).

a) Dispersion relation. Full line: $b = a$, dashed line: $b = 10a$, dotted line: $b \to \infty$, dash-dotted line: $a = 10b$. The limit $a \to \infty$ has practically the same curve as $a = 10b$.

6.5. *A dielectric or a metallic plate in contact with an inert dielectric*

The dispersion curves of an optically *active dielectric* (ionic crystal), described by (ε_∞, ω_L, ω_T) (30), in contact with an inert dielectric, described by $\varepsilon =$ const. (36), are essentially the same as the dispersion curves of the »plasmon« modes (ω_2, ω_4) in Fig. 2a, as it was pointed out in sec. 6. 4. For an optically active dielectric of finite thickness, two surface modes appear: one of them, $\omega_2 (k)$, connected with the interface, has the asymptotic frequency

$$\omega_2 (k \to \infty) = [(\varepsilon_\infty \omega_L^2 + \varepsilon \omega_T^2)/(\varepsilon + \varepsilon_\infty)]^{1/2} \tag{42}$$

and it corresponds to ω_2 in Fig. 2.a The other mode, ω_1 (k), is connected with the free surface of the optically active dielectric. It approaches the asymptotic frequency ω_1 ($k \to \infty$), given by Eq. (42) with $\varepsilon = 1$, and therefore corresponds to ω_4 in Fig. 2a.

For an infinitely thick optically active dielectric, only one surface mode appears with the asymptotic frequency (42). The number of surface modes is independent of the thickness of the inert dielectric.

The same conclusions are valid also for a *metallic plate* (25) in contact with an inert dielectric (36): there are two surface modes (ω_1, ω_2) in the case of finite, and only one surface mode in the case of infinite thickness of a metallic plate.

The coupling functions (32) for an inert dielectric placed on an ionic crystal or metal are obviously of the same shape as the »plasmon« coupling functions in Fig. 2b, i. e. Γ_S^1 looks like Γ_S^2 and Γ_S^2 looks like Γ_S^4 in Fig. 2b.

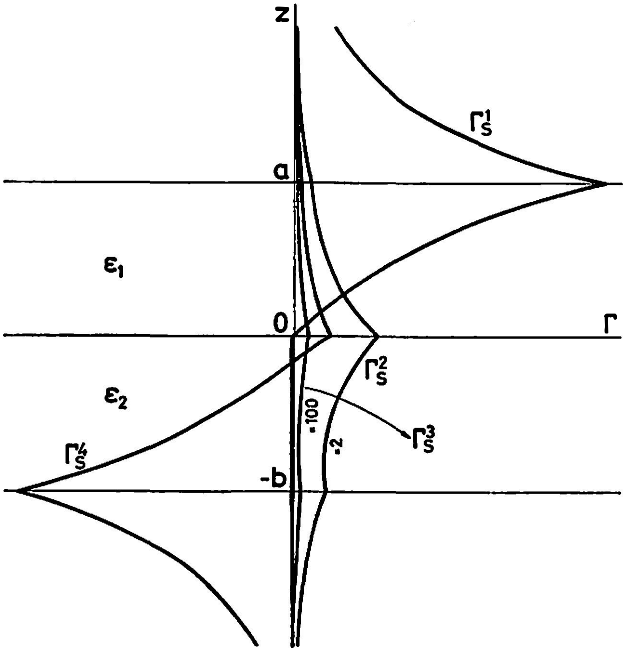

Fig. 2, b) Coupling functions (in arbitrary units), for $b = a$ and $ka = 2$. The coupling functions of the interface modes (particularly of ω_3) are rather weak owing to the influence of the metallic plate.

Finally, let us briefly note that one finds two surface modes for a thin film and only one surface mode for a semiinfinite metallic or an ionic-crystal plate[2]. In fact, the same conclusions (as in 6.5) are valid if we put $\varepsilon_1 = 1$ (vacuum) for an inert dielectric.

Similar systems, such as two semi-infinite plates separated by a thin vacuum[15] or an inert dielectric gap[14], can also be treated in terms of collective oscillations by using essentially the same formalism.

7. *Conclusions*

We have developed a theory which describes coupled colective oscillations in two different materials: ionic crystals with well-defined optical phonons or metals with plasmons or inert dielectrics.

We have diagonalized the Hamiltonian of a free system and found the Hamiltonian of a point charge interacting with collective oscillations of the system.

The Hamiltonian approach has a particular importance when the charged particle interacts strongly with the system. If the threshold energy for such a process is well below the particle kinetic energy, the multiple excitations play an important role in the EELS spectrum⁹⁾. As we can see from section 6, this is obviously the case when the bilayer system contains the metallic plate. In that case, the classical electrodynamics approach$^{9,10)}$, which gives only a single-excitation spectrum, is quite inappropriate. Moreover, the screening of the static charge distribution can be easily described in terms of collective oscillations of the system, i e. by the coherent states$^{5,15)}$ which involve all the excited states.

In conclusion, this paper provides a theoretical framework for further investigations of bilayer systems, such as the image potential of a point charge, or inelastic losses in EELS and XPS.

References

1) See, e. g. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954);

2) See, e. g. E. N. Economou and K. L. Ngai, Adv. Chem. Phys. **27** (1974) 265; K. L. Kliewer and R. Fuchs, Adv. Chem. Phys. **27** (1974) 355; R. C. Brown and N. H. March, Phys. Reports **24 C** (1976) 80;

3) K. L. Kliewer and R. Fuchs, Phys. Rev. **114** (1966) 495;

4) J. J. Hopfield, Phys. Rev. **112** (1958) 1555;

5) A. A. Lucas, E. Kartheuser and R. G. Badro, Phys. Rev. **B 2** (1970) 2488;

6) E. N. Economou, Phys. Rev. **182** (1969) 539;

7) A. Otto, Z. Physik **185** (1965) 232;

8) J. Heinrichs, Phys. Rev. **B 8** (1973) 1708;

9) M. Šunjić and A. A. Lucas, Phys. Rev. **B 3** (1971) 719;

10) J. J. Chang and D. C. Langreth, Phys. Rev. **B 5** (1972) 3512;

11) J. W. Gadzuk, Phys. Rev. **B 1** (1970) 1267;

12) S. Q. Wang and G. D. Mahan, Phys. Rev. **B 6** (1972) 4517;

13) J. J. Licari and R. Evrah, Phys. Rev. **B 15** (1977) 2254;

14) K. L. Ngai and E. N. Economou, Phys. Rev. **B 4** (1971) 2132;

15) Z. Lenac and M. Šunjić, Z. Physik **B 33** (1979) 145;

16) Z. Lenac, M. Šunjić and R. Brako, submitted to Fizika;

17) D. Šokčević, Z. Lenac, M. Šunjić and J. W. Gadzuk, to be published.