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THEORY OF SURFACE PLASMARONS

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Elementary excitations on the surfaces of ionic solids in the presence of an accumulation layer of electrons are studied. The surface phonons and the two-dimensional plasmon couple together to form hybrid excitations termed surface plasmarons. Formulas for the energy–momentum relations of these excitations are derived. The coupling constants for the interaction of these excitations with external charges are computed. In one limit this represents a generalization of the Frohlich interaction to the case of surface phonon–electron coupling. Application is made to the case of zinc oxide crystal. The stability of the plasmarons is studied.

1. Introduction

The understanding of the interaction between electrons and phonons has played a fundamental role in the development of theories of the bulk transport properties of solids [1]. In recent years attention has turned to the surface properties of solids. There again it is essential to know how electrons interact with phonons in order to interpret the surface transport properties. In addition high resolution inelastic electron loss spectroscopy experiments are now being performed which require a knowledge of how "probe" electrons interact with the surface phonons.

The purpose of this paper is twofold. First we wish to study the basic excitations that exist on the surface of an ionic solid and in particular to derive the energy–momentum relations for these excitations. Second we wish to describe how these excitations couple to electrons. In the second section the basic theory is developed. Contact is made with the limiting cases. This is followed in the third section by an application to zinc oxide. In the fourth section the decay of the elementary excitations is analyzed.

2. Theory

Consider a diatomic crystal which is polar (or at least partially so) and assume that an accumulation layer of electrons exists on its surface. The crystal will be

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treated as a semi-infinite medium. We are interested here in two physical questions: (1) What is the nature of the elementary excitations that exist on the solid's surface? (2) How do these excitations couple to external probes, such as charged particles?

In answering the first question we begin with a knowledge of the limiting cases. In the absence of an accumulation layer the crystal exhibits a surface phonon spectrum that has been extensively studied [2]. On the other hand a surface layer of electrons is expected to exhibit a two-dimensional plasmon [3]. In the problem of interest here both phonons and plasmons are present and, as we shall see, couple together. The resulting excitations will be called surface plasmarons. In answering the second question we are again guided by the limiting cases, although these have not been studied in detail. One knows, for example, how charges interact with bulk optical phonons [4]. The analogous problem here is to generalize the Frohlich interaction to the case of surface optical phonons. Similarly the coupling of charges to both bulk and surface plasmons as well as to two-dimensional plasmons [5] has been studied in the literature.

We shall start with a classical description of the system and quantize the theory at a suitable point. Let N be the instantaneous number of surface electrons per unit area and N_0 be the mean of this quantity. In those cases where overall charge neutrality is preserved, N_0 will also correspond to the surface density of positive (ionic) charge. Since the thickness of the accumulation layer is much smaller than other significant lengths (e.g. the phonon wavelength), the layer will be treated as a sheet of charge. In addition let us place a distributed test charge on the surface, which will be taken to be a wave of amplitude Q and wave-vector $\boldsymbol{k}_{/\!/}$. The free charge density is

$$\rho = [-e(N - N_0) + Q \exp(\mathrm{i}\boldsymbol{k}_{/\!/} \cdot \boldsymbol{r}) + Q \exp(-\mathrm{i}\boldsymbol{k}_{/\!/} \cdot \boldsymbol{r})]\, \delta(z) \,, \tag{1}$$

where e is the magnitude of the electron charge and $\boldsymbol{k}_{/\!/}$ is parallel to the surface (the x–y plane). We have written eq. (1) for the case where there is compensating positive charge of density N_0. If there is no such charge then N_0 is to be omitted in eq. (1). This term drops out in subsequent equations. Gauss' law relates ρ to the divergence of the electric displacement vector, $\boldsymbol{D}$

$$\nabla \cdot \boldsymbol{D} = 4\pi\rho \,. \tag{2}$$

Let $\boldsymbol{J}_{/\!/}$ be the current density vector. It obeys the continuity equation

$$\nabla_{/\!/} \cdot \boldsymbol{J}_{/\!/} + \partial\rho/\partial t = 0 \,, \tag{3}$$

where $\nabla_{/\!/}$ represents the gradient with respect to coordinates parallel to the surface. The current density is given by

$$\boldsymbol{J}_{/\!/} = -eN\boldsymbol{v}\, \delta(z) \,, \tag{4a}$$

where $\boldsymbol{v}$ is the velocity field of the electrons. Since v will vanish in the absence of any excitation, we shall linearlize this expression and replace N by its mean value

$$J_{\parallel} \doteq -eN_0 \mathbf{v}\, \delta(z) . \tag{4b}$$

The Newtonian equations of motion may be written as

$$\delta(z)[m^* \, \partial \mathbf{v}/\partial t + \nabla_{\parallel}\varphi] = 0 , \tag{5}$$

where m^* is the effective mass of an electron moving parallel to the surface. We are assuming, for simplicity's sake, that the mass-tensor is isotropic in this plane. In eq. (5) we have introduced the electrochemical potential φ. In the Thomas–Fermi approximation we have

$$\varphi = \hbar^2 k_{\mathrm{F}}^2/2m^* - e\phi , \tag{6}$$

where ϕ is the electrostatic potential and k_{F} is the magnitude of the two-dimensional Fermi wave vector,

$$k_{\mathrm{F}} = (2\pi N)^{1/2} . \tag{7}$$

For the sake of simplicity we do not go beyond the Thomas–Fermi approximation here. The electric field is realted to the electrostatic potential through the relation

$$\boldsymbol{E} = -\nabla\phi . \tag{8}$$

The electric displacement is related to the electric field through the relation

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{P} , \tag{9}$$

where $\boldsymbol{P}$ is the electric polarization vector.

Following Frohlich [4] we assume $\boldsymbol{P}$ to consist of the sum of an electronic contribution, $\boldsymbol{P}_{\mathrm{e}}$, and an ionic contribution, $\boldsymbol{P}_{\mathrm{i}}$

$$\boldsymbol{P} = [\boldsymbol{P}_{\mathrm{e}} + \boldsymbol{P}_{\mathrm{i}}]\, \Theta(-z) , \tag{10}$$

where the unit step function, Θ, guarantees that the polarization vector vanishes outside the crystal. The ions are acted upon by two forces – a harmonic restoring force and the force due to the local electric field at the ion site. Thus the equation of motion for $\boldsymbol{P}_{\mathrm{i}}$ is

$$\partial^2 \boldsymbol{P}_{\mathrm{i}}/\partial t^2 + \omega_{\mathrm{i}}^2 \boldsymbol{P}_{\mathrm{i}} = (nq^2/\mu)\, \boldsymbol{E}_{\mathrm{loc}} , \tag{11}$$

where ω_{i} is the restoring frequency, n is the number of ion pairs per unit volume, q is the charge of one member of an ion pair, μ is the reduced mass of an ion pair, and the local electric field is

$$E_{\mathrm{loc}} = \boldsymbol{E} + \tfrac{4}{3}\pi \boldsymbol{P} . \tag{12}$$

The electronic part of the susceptibility is assumed to respond instantaneously to the local field

$$\boldsymbol{P}_{\mathrm{e}} = \chi_{\mathrm{e}} \boldsymbol{E}_{\mathrm{loc}} , \tag{13}$$

where χ_e is the electronic part of the susceptibility of the ion pair. In eq. (1) there is no contribution to the polarization field due to the mobile electrons. The electron response is already taken into account in eqs. (3) to (7).

After some algebra one may reduce the above set of equations to a set of five coupled equations

$$\delta(z)\left[-\frac{em^*}{N_0}\frac{\partial^2(N-N_0)}{\partial t^2}+\nabla_{/\!/}^2\left(\frac{\pi e\hbar^2 N}{m^*}-e^2\phi\right)\right]=0\,, \tag{14}$$

$$-\nabla^2\phi+4\pi\nabla\cdot\boldsymbol{P}$$
$$=4\pi\delta(z)[-e(N-N_0)+Q\exp(\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})+Q\exp(-\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})]\,, \tag{15}$$

$$\boldsymbol{P}=(\boldsymbol{P}_e+\boldsymbol{P}_i)\,\Theta(-z)\,, \tag{10}$$

$$\frac{\partial^2\boldsymbol{P}_i}{\partial t^2}+\left(\omega_i^2-\frac{4\pi nq^2}{3\mu}\right)\boldsymbol{P}_i=-\frac{nq^2}{\mu}\nabla\phi+\frac{4\pi nq^2}{3\mu}\boldsymbol{P}_e\,, \tag{16}$$

$$\boldsymbol{P}_e=\frac{\chi_e}{1-4\pi\chi_e/3}\left[-\nabla\phi+\frac{4\pi\boldsymbol{P}_i}{3}\right]. \tag{17}$$

We now look for surface wave solutions to this set. Thus let

$$\phi=\varphi\exp(-k_{/\!/}|z|+\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})+\text{c.c.}\,, \tag{18}$$

$$\boldsymbol{P}=\boldsymbol{F}\exp(k_{/\!/}z+\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})\,\Theta(-z)+\text{c.c.}\,, \tag{19}$$

$$N-N_0=\eta\exp(\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})+\text{c.c.}\,, \tag{20}$$

$$\boldsymbol{P}_i=\boldsymbol{F}_i\exp(k_{/\!/}z+\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})+\text{c.c.}\,, \tag{21}$$

$$\boldsymbol{P}_e=\boldsymbol{F}_e\exp(k_{/\!/}z+\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r})+\text{c.c.}\,. \tag{22}$$

From our previous familiarity with surface phonons [2] we know that

$$\boldsymbol{F}_e=F_e(\hat{k}+\mathrm{i}\hat{k}_{/\!/})/\sqrt{2}\,, \tag{23}$$

$$\boldsymbol{F}_i=F_i(\hat{k}+\mathrm{i}\hat{k}_{/\!/})/\sqrt{2}\,, \tag{24}$$

$$\boldsymbol{F}=F(\hat{k}+\mathrm{i}\hat{k}_{/\!/})/\sqrt{2}\,. \tag{25}$$

where $\hat{k}$ is a unit vector normal to the surface.

Inserting eqs. (18)–(25) into eqs. (10), (14)–(17) leads to a set of three coupled equations:

$$Q=\frac{2\pi}{k_{/\!/}}\left(\frac{1-4\pi\chi_e/3}{1+2\pi\chi_e/3}\right)\left(Q-\eta e+\frac{F_i}{\sqrt{2}}\frac{1}{1-4\pi\chi_e/3}\right), \tag{26}$$

$$\frac{\partial^2\eta}{\partial t^2}+\eta\left[\frac{\pi N_0\hbar^2k_{/\!/}^2}{m^{*2}}+\frac{2\pi N_0e^2k_{/\!/}}{m^*}\left(\frac{1-4\pi\chi_e/3}{1+2\pi\chi_e/3}\right)\right]$$
$$-F_i\left(\frac{\pi\sqrt{2}N_0ek_{/\!/}}{m^*}\frac{1}{1+2\pi\chi_e/3}\right)=\frac{2\pi N_0ek_{/\!/}Q}{m^*}\left(\frac{1-4\pi\chi_e/3}{1+2\pi\chi_e/3}\right), \tag{27}$$

$$\frac{\partial^2 F_\mathrm{i}}{\partial t^2} - \eta\left(2\pi\sqrt{2}e\,\frac{nq}{\mu}\,\frac{1}{1+2\pi\chi_\mathrm{e}/3}\right)$$
$$+ F_\mathrm{i}\left(\omega_\mathrm{i} + \tfrac{2}{3}\pi\,\frac{nq}{\mu}\,\frac{1}{1+2\pi\chi_\mathrm{e}/3}\right) = -2\pi\sqrt{2}\,\frac{nq^2Q}{\mu}\,\frac{1}{1+2\pi\chi_\mathrm{e}/3}\,. \tag{28}$$

Eqs. (27) and (28) describe the coupled motion of the ionic polarization field, F_i, and the electron density field, η. They may be derived from the Lagrangian density

$$L = L_0\left[|\dot{F}_\mathrm{i}|^2 - \omega_\mathrm{s}^2|\dot{F}_\mathrm{i}|^2 + \frac{2m^*}{N_0 k_{/\!/}}\,\frac{nq^2}{\mu}\,|\dot{\eta}|^2\right.$$
$$- \left(\frac{2\pi nq^2\hbar^2 k_{/\!/}}{m^*\mu} + \frac{4\pi nq^2e^2}{\mu}\,\frac{1-4\pi\chi_\mathrm{e}/3}{1+2\pi\chi_\mathrm{e}/3}\right)|\eta|^2$$
$$+ \frac{2\pi\sqrt{2}}{1+2\pi\chi_\mathrm{e}/3}\,\frac{nq^2e}{\mu}\,(F_\mathrm{i}^*\eta + F_\mathrm{i}\eta^*) - \frac{2\pi\sqrt{2}}{1+2\pi\chi_\mathrm{e}/3}\,\frac{nq^2}{\mu}\,Q(F_\mathrm{i} + F_\mathrm{i}^*)$$
$$\left.+ \frac{4\pi nq^2eQ}{\mu}\,\frac{1-4\pi\chi_\mathrm{e}/3}{1+2\pi\chi_\mathrm{e}/3}\,(\eta+\eta^*)\right], \tag{29}$$

where L_0 is a constant. The value of L_0 may be fixed by recognizing that L must contain a term describing the interaction of the test charge Q with the electrostatic field, φ, i.e.

$$L_\mathrm{interaction} = -Q\varphi^* - Q\varphi\,. \tag{30}$$

Upon inserting eq. (26) into eq. (30) and comparing it to eq. (29) we deduce that

$$L_0 = \mu/2k_{/\!/}nq^2\,. \tag{31}$$

In eq. (29) we have let

$$\omega_\mathrm{s}^2 = \omega_\mathrm{i}^2 + \frac{nq^2}{\mu}\left(\chi_\mathrm{e} + \frac{3}{2\pi}\right)^{-1}\,. \tag{32}$$

As we shall see later, ω_s is the frequency of the surface optical phonon.

It is possible to relate the parameters χ_e and nq^2/μ to the high and low frequency dielectric constants [4]:

$$\chi_\mathrm{e} = \frac{3}{4\pi}\,\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\,, \tag{33}$$

$$\frac{nq^2}{\mu} = \frac{q}{4\pi}\,\omega_\mathrm{i}^2\,\frac{\epsilon_0 - \epsilon_\infty}{(\epsilon_0+2)(\epsilon_\infty+2)}\,. \tag{34}$$

Here ϵ_0 is the zero frequency dielectric constant and ϵ_∞ is the dielectric constant at a frequency high compared with the phonon frequencies but low compared with the electronic frequencies of the crystal.

Let us digress for a moment to discuss the two limiting cases. In the first case we consider a semi-infinite crystal without an accumulation layer. Thus we may disregard the variable η and the Lagrangian density reduces to

$$L = \frac{\mu}{2k_{/\!/}nq^2}\left[|\dot{F}_\mathrm{i}|^2 - \omega_\mathrm{s}^2|F_\mathrm{i}|^2 - \frac{2\pi\sqrt{2}}{1+2\pi\chi_\mathrm{e}/3}\,\frac{nq^2}{\mu}\,(F_\mathrm{i}+F_\mathrm{i}^*)\right]. \tag{35}$$

To quantize the theory we proceed in the following manner.

The free Hamiltonian density corresponding to eq. (35) is

$$H_\mathrm{free} = \frac{\mu}{2k_{/\!/}nq^2}\,(|\dot{F}_\mathrm{i}|^2 + \omega_\mathrm{s}^2|F_\mathrm{i}|^2)\,. \tag{36}$$

From eq. (35) one may then write the interaction part of the Hamiltonian as

$$H_\mathrm{int} = -Q\left[\frac{2\pi\hbar\omega_\mathrm{s}}{Ak_{/\!/}}\left(\frac{1}{\epsilon_\infty+1} - \frac{1}{\epsilon_0+1}\right)\right]^{1/2}. \tag{37}$$

If we introduce creation and annihilation operators for the surface phonons the Hamiltonian may be written as

$$H = \sum_{\boldsymbol{k}_{/\!/}}\left\{(a^\dagger_{\boldsymbol{k}_{/\!/}}a_{\boldsymbol{k}_{/\!/}} + \tfrac{1}{2})\,\hbar\omega_\mathrm{s} + Q\left[\frac{2\pi\hbar\omega_\mathrm{s}}{Ak_{/\!/}}\left(\frac{1}{\epsilon_\infty+1} - \frac{1}{\epsilon_0+1}\right)\right]^{1/2}\right.$$

$$\left.[a_{\boldsymbol{k}_{/\!/}}\exp(-k_{/\!/}|z| + \mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{r}) + \mathrm{c.c.}]\right\}. \tag{38}$$

The second term is the surface analogue of the Frohlich interaction [4]. One may use a similar procedure to derive the standard bulk Frohlich interaction.

Let us return to the general expression for the Lagrangian density and simplify it by rescaling F_i. Let

$$F_\mathrm{i} \to \xi F_\mathrm{i}\,, \tag{39}$$

where

$$\xi = \left(\frac{qk_{/\!/}\omega_\mathrm{s}^2}{2\pi}\,\frac{(\epsilon_0-\epsilon_\infty)(\epsilon_\infty+1)}{(\epsilon_\infty+2)^2(\epsilon_0+1)}\right)^{1/2}, \tag{40}$$

so

$$L = |\dot{F}_\mathrm{i}|^2 - \omega_\mathrm{s}^2|\dot{F}_\mathrm{i}|^2 + \frac{m^*}{N_0k_{/\!/}^2}|\dot{\eta}|^2 - \frac{\pi}{k_{/\!/}}\left(\frac{\hbar k_{/\!/}}{m^*} + \frac{4e^2}{\epsilon_\infty+1}\right)|\eta|^2$$

$$+\,2e\left[\frac{\pi\omega_\mathrm{s}}{k_{/\!/}}\left(\frac{1}{\epsilon_\infty+1} - \frac{1}{\epsilon_0+1}\right)\right]^{1/2}(F_\mathrm{i}^*\eta + F_\mathrm{i}\eta^*)$$

$$-\,Q(F_\mathrm{i}+F_\mathrm{i}^*)\left[\frac{4\pi\omega_\mathrm{s}}{k_{/\!/}}\left(\frac{1}{\epsilon_\infty+1} - \frac{1}{\epsilon_0+1}\right)\right]^{1/2} + \frac{4\pi eQ}{k_{/\!/}}\,\frac{\eta+\eta^*}{\epsilon_\infty+1}\,. \tag{41}$$

Now we consider the other limiting case where we neglect the coupling to the surface phonons and consider only the two-dimensional electron gas. Then the Lagrangian density becomes

$$L = \frac{m^*}{N_0 k_{\parallel}^2} |\dot{\eta}|^2 - \frac{\pi}{k_{\parallel}} \left[\frac{\hbar^2 k_{\parallel}}{m^*} + \frac{4e^2}{\epsilon_\infty + 1}\right] |\eta|^2 + \frac{4\pi e Q}{k_{\parallel}} \frac{\eta + \eta^*}{\epsilon_\infty + 1} . \tag{42}$$

We quantize this in the same way as before. Let

$$\eta = \tilde{n} \exp(-i\omega_d t) , \tag{43}$$

where ω_d is the frequency of the two-dimensional plasmon, given by

$$\omega_d = \left\{\frac{4\pi N_0 e^2 k_{\parallel}}{m^*(\epsilon_\infty + 1)} \left[1 + \frac{\hbar^2 k_{\parallel}}{4m^* e^2} (\epsilon_\infty + 1)\right]\right\}^{1/2} . \tag{44}$$

Hence we may write the second quantized Hamiltonian for two-dimensional plasmons as

$$H = \sum_{\boldsymbol{k}_{\parallel}} \left\{(b_{\boldsymbol{k}_{\parallel}}^\dagger b_{\boldsymbol{k}_{\parallel}} + \tfrac{1}{2}) \hbar\omega_d + \frac{4\pi e Q}{\epsilon_\infty + 1} \left(\frac{\hbar N_0}{2m^* A \omega_d}\right)^{1/2} \right.$$
$$\left. \times \left[b_{\boldsymbol{k}_{\parallel}} \exp(i\boldsymbol{k}_{\parallel} \cdot \boldsymbol{r} - \boldsymbol{k}_{\parallel} |z|) + \text{c.c.}\right]\right\} , \tag{45}$$

where $b_{\boldsymbol{k}_{\parallel}}^\dagger$ is a creation operator for plasmons.

We now return to the general Lagrangian density eq. (41) and simplify it further. Let us rescale the variable η

$$\eta \to \eta (N_0 k_{\parallel}^2 / m^*)^{1/2} . \tag{46}$$

The Lagrangian density may then be written as

$$L = |\dot{F}_i|^2 - \omega_s^2 |F_i|^2 + |\dot{\eta}|^2 - \omega_d^2 |\eta|^2 + \Lambda(F_i^* \eta + F_i \eta^*)$$
$$+ g_F(F_i + F_i^*) + g_\eta(\eta + \eta^*) , \tag{47}$$

where Λ represents the intermode coupling

$$\Lambda = \left[\frac{4\pi N_0 e^2}{m^*} \omega_s^2 k_{\parallel} \left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\right]^{1/2} , \tag{48}$$

and g_F and g_η are the phonon and plasmon coupling coefficients

$$g_F = -2Q\left[\frac{\pi\omega_s^2}{k_{\parallel}} \left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\right]^{1/2} , \tag{49}$$

$$g_\eta = \frac{4\pi e Q}{\epsilon_\infty + 1} \left(\frac{N_0}{m^*}\right)^{1/2} . \tag{50}$$

By defining appropriate linear combinations of plasmons and phonons we may express the Lagrangian in terms of two independent modes (plasmarons). Thus

$$F_{\mathrm{i}} = X + \frac{\Lambda}{\omega_{\mathrm{s}}^2 - \omega_-^2}\, Y\,, \tag{51}$$

$$\eta = \frac{\Lambda}{\omega_{\mathrm{d}}^2 - \omega_+^2}\, X + Y\,, \tag{52}$$

where

$$\omega_\pm^2 = \tfrac{1}{2}(\omega_{\mathrm{s}}^2 + \omega_{\mathrm{d}}^2) \pm \left[\tfrac{1}{4}(\omega_{\mathrm{s}}^2 - \omega_{\mathrm{d}}^2)^2 + \Lambda^2\right]^{1/2}\,, \tag{53}$$

and

$$L = \left[1 + \left(\frac{\Lambda}{\omega_{\mathrm{d}}^2 - \omega_+^2}\right)^2\right](|\dot{X}|^2 - \omega_+^2|X|^2) + (X + X^*)\left(g_F + \frac{\Lambda g_\eta}{\omega_{\mathrm{d}}^2 - \omega_+^2}\right)$$
$$+ \left[1 + \left(\frac{\Lambda}{\omega_{\mathrm{s}}^2 - \omega_-^2}\right)^2\right](|\dot{Y}|^2 - \omega_-^2|Y|^2) + (Y + Y^*)\left(g_\eta + \frac{\Lambda g_F}{\omega_{\mathrm{s}}^2 - \omega_-^2}\right)\,. \tag{54}$$

Applying the previous quantization procedure we derive the magnitude of the normalization constants. Thus we finally obtain second quantized Hamiltonian describing the coupling of a charge to the plasmarons

$$H = \sum_{\boldsymbol{k}_\parallel} \{\hbar\omega_+(c^\dagger_{\boldsymbol{k}_\parallel} c_{\boldsymbol{k}_\parallel} + \tfrac{1}{2}) + \hbar\omega_-(d^\dagger_{\boldsymbol{k}_\parallel} d_{\boldsymbol{k}_\parallel} + \tfrac{1}{2})$$
$$+ Q\gamma_+[c_{\boldsymbol{k}_\parallel} \exp(\mathrm{i}\boldsymbol{k}_\parallel \cdot \boldsymbol{r} - \boldsymbol{k}_\parallel |z|) + \text{c.c.}]$$
$$+ Q\gamma_-[d_{\boldsymbol{k}_\parallel} \exp(\mathrm{i}\boldsymbol{k}_\parallel \cdot \boldsymbol{r} - \boldsymbol{k}_\parallel |z|) + \text{c.c.}]\}\,, \tag{55}$$

where $c_{\boldsymbol{k}_\parallel}$ and $d_{\boldsymbol{k}_\parallel}$ are annihilation operators for the two plasmaron branches. The coupling parameters $\gamma_\pm$ are given by

$$\gamma_+ = \left[g'_F + g'_\eta \frac{\Lambda}{\omega_{\mathrm{d}}^2 - \omega_+^2}\right]\left[\frac{1}{2\omega_+}\frac{(\omega_{\mathrm{d}}^2 - \omega_+^2)^2}{(\omega_{\mathrm{d}}^2 - \omega_+^2)^2 + \Lambda^2}\right]^{1/2}\,, \tag{56}$$

$$\gamma_- = \left[g'_\eta + g'_F \frac{\Lambda}{\omega_{\mathrm{s}}^2 - \omega_-^2}\right]\left[\frac{1}{2\omega_-}\frac{(\omega_{\mathrm{s}}^2 - \omega_-^2)^2}{(\omega_{\mathrm{s}}^2 - \omega_-^2)^2 + \Lambda^2}\right]^{1/2}\,, \tag{57}$$

and $g'_F = g_F/Q$ and $g'_\eta = g_\eta/Q$. The terms involving $\gamma_\pm$ are the generalization of the Frohlich interaction to the case of surface plasmarons. In eq. (55), Q now represents the magnitude of the probe charge, which is located at the position $(\boldsymbol{r}, z)$.

3. Numerical results for ZnO

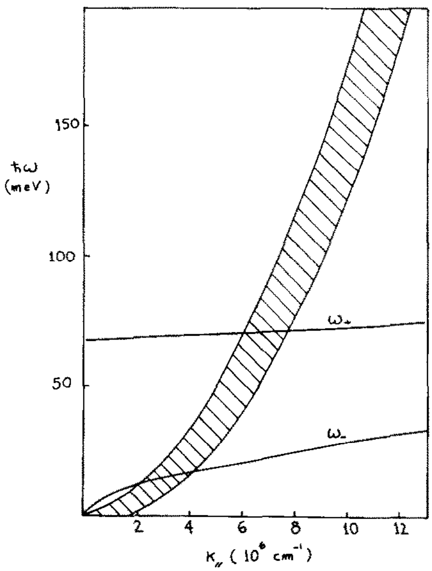
Let us now evaluate the plasmaron dispersion curves and coupling constants for the case of a typical II–VI semiconductor-ZnO. Numerical values [6] for the

Table 1
Numerical values of parameters for zinc oxide

Parameter	Value
$\hbar\omega_s$	0.068 eV
m^*	0.25 M_e
ϵ_0	8.0
ϵ_∞	4.0

parameters of our theory are tabulated in table 1. The value of the surface phonon frequency is taken from experiment [7].

In fig. 1 we plot the plasmaron dispersion curves for an accumulation layer density of 10^{11} cm^{-2}. The electron–hole decay region is shaded in, and the significance of it will be discussed in the next section. In fig. 2 the analogous dispersion curves for $N = 10^{13}$ cm^{-2} is shown. One sees that, quite generally, at small $k_{/\!/}$-values the lower branch is plasmon-like and the upper branch is phonon like. At large $k_{/\!/}$-values the roles are interchanged. The plasmarons are strong admixtures of the two excitations in the region where the bare plasmon and phonon cross.



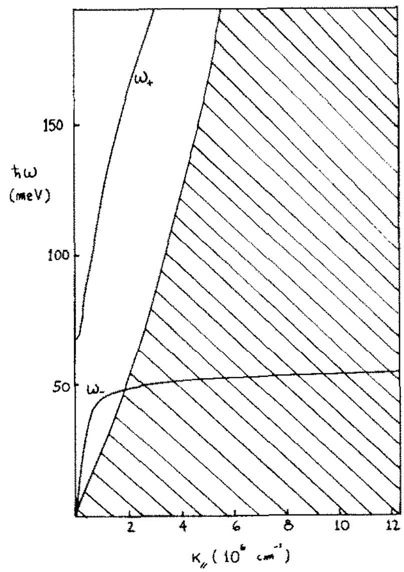
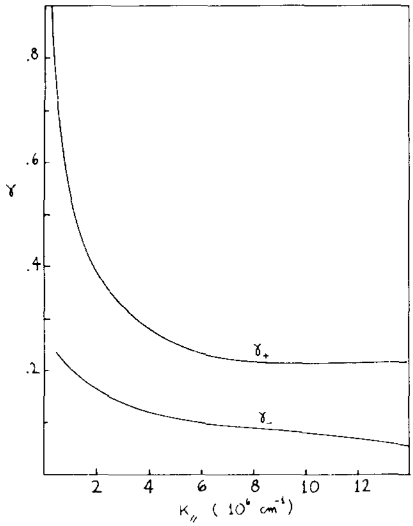


Fig. 1. The surface plasmaron energies, $\omega_\pm$, as a function of wave-vector $\boldsymbol{k}_{/\!/}$, corresponding to an electron density $N_0 = 10^{11}$ cm^{-2}. The shaded region depicts the region for two body decay of the plasmarons. The curve is for ZnO.

Fig. 2. Same as fig. 1, but for $N_0 = 10^{13}$ cm^{-2}.



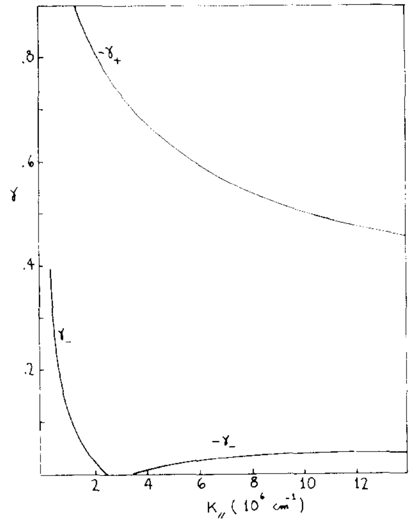


Fig. 3. The coupling constants for ZnO, $\gamma_{\pm}$, as a function of wave-vector, $k_{/\!/}$. Here $N_0 = 10^{11}$ cm^{-2}.

Fig. 4. Same as fig. 3, but for $N_0 = 10^{13}$ cm^{-2}.

In fig. 3 the coupling constants $\gamma_{\pm}$ are plotted as a function of $k_{/\!/}$ for $N = 10^{11}$ cm^{-2}. The coupling constants are observed to get very strong for small values. In fig. 4 the coupling constants for $N = 10^{13}$ cm^{-2} are given. We note that for low accumulation layer densities the coupling constants for the two plasmaron branches are of comparable magnitude. At high densities, however, the coupling to the lower branch is surpressed relative to that of the upper branch.

In our discussion we have assumed that the electron gas may be treated as two-dimensional plasma. This assumption is valid provided its thickness is less than the characteristic distance of fall off of the potential as one goes into the crystal. Since this latter distance is essentially the wavelength (viz. eq. (18)), this puts an upper bound on the value of the wave-vector for which these curves are valid.

4. Plasmaron decay

It is only under certain conditions that the plasmaron may be regarded as a long-lived excitation of the crystal surface. In this section we shall study two- and three-body decay mechanisms. In the case of two-body decay the plasmaron disappears and in its place an electron–hole pair is produced. As we shall see, it is only at sufficiently high values of the plasmaron wave-vector that this channel is open. This is a direct generalization of the familiar decay rule for plasmons. In the case of three-body decay, however, we shall see that a decay channel exists in which the upper branch of the plasmaron can decay to the lower branch plus an electron–hole pair. This is not a phase-space restricted decay and consequently leads to a decay width to the high energy plasmaron, at any wavelength.

The matrix element for two-body decay of a plasmaron may be extracted from eq. (55). For the sake of analytic simplicity, let us study the decay of the lower energy plasmaron, and treat it simply as a surface phonon. The decay, however, will only occur if an accumulation layer exists.

The matrix element is now given by eq. (38).

$$M = -\left[\frac{2\pi e^2 \hbar\omega_s}{A k_{/\!/}}\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\right]^{1/2} . \tag{58}$$

The decay rate is given by the Fermi golden rule

$$\Gamma_s = \frac{2\pi}{\hbar}\sum_{ps} f_p^{(-)} \sum_{p's'} f_{p'}^{(+)} \frac{2\pi\omega_s e^2\hbar}{k_{/\!/}}\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)$$
$$\times\, \delta_{ss'}\delta_{\boldsymbol{p}',\boldsymbol{p}+\boldsymbol{k}_{/\!/}}\delta(\hbar\omega_s + \epsilon_{\boldsymbol{p}} - \epsilon_{\boldsymbol{p}+\boldsymbol{k}_{/\!/}}) . \tag{59}$$

The (two-dimensional) wave-vectors of the electrons and holes have been denoted by $\boldsymbol{p}$ and $\boldsymbol{p}'$, respectively. The Fermi factors have been denoted by $f^{(\pm)}$ and the spin index is s. The integrals may be evaluated trivially and we find

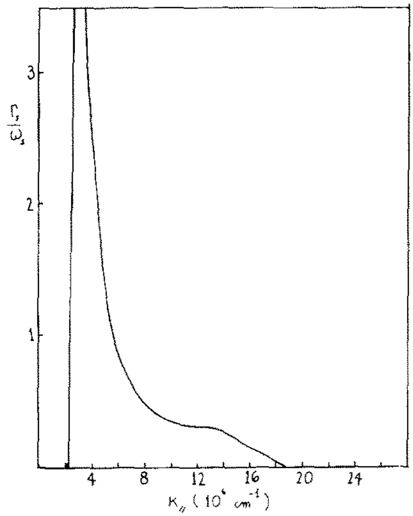
$$\frac{\Gamma_s}{\omega_s} = \frac{2m^*e^2}{\hbar^2 k_{/\!/}^2}\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\left\{\left[P_F^2 - \left(\frac{m^*\omega}{\hbar k_{/\!/}} - \tfrac{1}{2}k_{/\!/}\right)^2\right]^{1/2}\right.$$
$$\left. - \left[P_0^2 - \left(\frac{m^*\omega}{\hbar k_{/\!/}} - \tfrac{1}{2}k_{/\!/}\right)^2\right]^{1/2}\right\}\Theta(P_F - P_0) , \tag{60}$$

where

$$P_0 = \begin{cases} \left|\tfrac{1}{2}k_{/\!/} - \dfrac{m^*\omega}{\hbar k_{/\!/}}\right| , & \text{if } \hbar P_F^2 < 2m^*\omega , \\ \max\left[\left|\tfrac{1}{2}k_{/\!/} - \dfrac{m^*\omega}{\hbar k_{/\!/}}\right| , \left(P_F^2 - \dfrac{2m^*\omega}{\hbar}\right)^{1/2}\right] , & \text{otherwise} . \end{cases} \tag{61}$$

Two-body decay is only possible when the plasmaron penetrates the shaded region of figs. 1 and 2. Similar formulas may be written for the decay of the two-dimensional plasmon or for the full-dressed plasmarons. The ratio of the decay width to the phonon frequency is plotted in fig. 5 for a density $N = 10^{13}\ \mathrm{cm}^{-2}$.

The case of three-body decay is complicated by the fact that one must go to one higher order in perturbation theory. We shall restrict our attention here to the case where a plasmon decays to a phonon and an electron–hole pair. The method may be extended to the case of interplasmaron decay. In fig. 6 the various Feynman diagrams associated with the decay are shown. The coupling constants are obtained



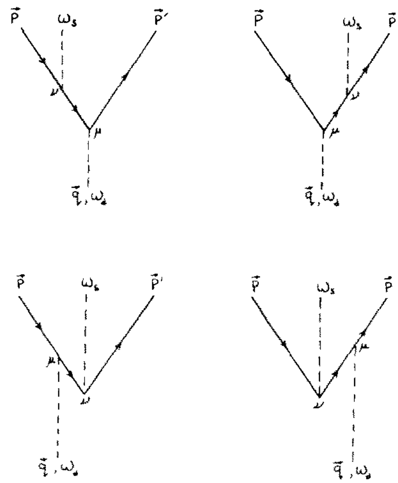


Fig. 5. The ratio of the two-body decay width of a phonon to its frequency as a function of wave-vector for an electron density $N_0 = 10^{13}$ cm^{-2}.

Fig. 6. Diagrams corresponding to the three-body decay of a two-dimensional plasmon into a phonon and an electron–hole pair.

from eqs. (38) and (45):

$$\nu = e\left[\frac{2\pi\hbar\omega_s}{Q}\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\right]^{1/2}, \tag{62}$$

$$\mu = -\frac{4\pi e}{\epsilon_\infty + 1}\left(\frac{\hbar N_0 e^2}{2m^*\omega_d}\right)^{1/2}. \tag{63}$$

The matrix element for the decay is

$$M = \nu\mu\left(-f^{(-)}_{p-Q}\frac{1}{\hbar\omega_d + \epsilon_{p-Q} - \epsilon_p} + f^{(+)}_{p-Q}\frac{1}{\epsilon_p - \hbar\omega_s - \epsilon_{p-Q}}\right.$$
$$\left. - f^{(-)}_{p+q}\frac{1}{\epsilon_{p+q} - \epsilon_{p'} - \hbar\omega_s} + f^{(+)}_{p+q}\frac{1}{\hbar\omega_d + \epsilon_p - \epsilon_{p+q}}\right). \tag{64}$$

By employing the energy conservation criterion

$$\epsilon_p + \hbar\omega_d = \epsilon_{p'} + \hbar\omega_s, \tag{65}$$

this reduces to

$$M = \nu\mu\left\{\frac{1}{\epsilon_p - \epsilon_{p-Q} - \hbar\omega_s} + \frac{1}{\hbar\omega_d + \epsilon_p - \epsilon_{p+q}}\right\}. \tag{66}$$

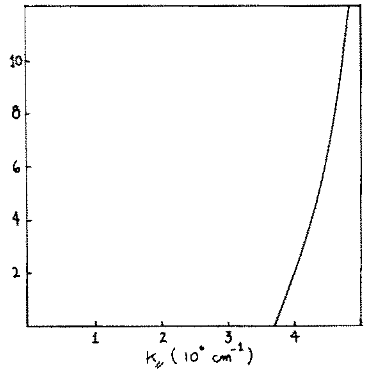


Fig. 7. The ratio of the three-body decay rate for a surface plasmon to the plasmon frequency, as a function of its wave vector. The curve is for ZnO with an accumulation layer density of $N_0 = 10^{13}$ cm^{-2}.

The decay rate is

$$\Gamma_d = \frac{2\pi}{\hbar} \sum_{ps} \sum_{p's'} \delta_{ss'} |M|^2 f_p^{(-)} f_{p'}^{(+)} \delta(\epsilon_p + \hbar\omega_d - \epsilon_{p'} - \hbar\omega_s) , \tag{67}$$

where we have imposed momentum conservation

$$\boldsymbol{p} + \boldsymbol{q} = \boldsymbol{p}' + \boldsymbol{Q} . \tag{68}$$

This may be reduced to the following expression

$$\frac{\Gamma}{\omega_d} = \frac{64 e^6 m^{*2} N_0}{\hbar^5} \frac{\omega_s}{\omega_d^2} \left(\frac{1}{\epsilon_\infty + 1}\right)^2 \left[\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right] S , \tag{69}$$

where

$$S = \int_{p_1}^{p_F} \mathrm{d}p\, p \int_0^{2\pi} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\phi' \frac{[\boldsymbol{q} \cdot (\boldsymbol{p}' - \boldsymbol{p} - \boldsymbol{q})]^2}{|\boldsymbol{p}' - \boldsymbol{p} - \boldsymbol{q}|}$$

$$\times \left[2\boldsymbol{p}' \cdot \boldsymbol{q} - \boldsymbol{q}^2 - \frac{2m^*\omega_d}{\hbar}\right]^{-1} \left[2\boldsymbol{p} \cdot \boldsymbol{q} + \boldsymbol{q}^2 - \frac{2m^*\omega_d}{\hbar}\right]^{-1} , \tag{70}$$

where

$$p_1 = \begin{cases} [p_F^2 - 2m^*(\omega_d - \omega_s)/\hbar]^{1/2} , & \text{if argument} > 0 , \\ 0 , & \text{otherwise} , \end{cases} \tag{71}$$

and

$$p' = \left(\frac{2m^*}{\hbar^2} [\epsilon_p + \hbar(\omega_d - \omega_s)]\right)^{1/2} . \tag{72}$$

The quantity Γ/ω_d is plotted as a function of wave-vector in fig. 7. While three body decay exists for all values of $k_{/\!/}$ (which is energetically accessible), it is seen to be important only for larger values of $k_{/\!/}$.

The natural experimental tool to study surface plasmarons is electron loss spectroscopy [7]. We have seen from our previous analysis that plasmarons are characterized by their being highly dispersive in some regions of the frequency–wave-vector plane and strongly damped in other regions. This makes the task of detecting them rather difficult. One must work at conditions of high energy and angular resolution to overcome the fact that their frequency varies rapidly with wavelength.

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Note added in proof

The referee has brought to my attention related work by Nakayama [8]. It is concerned only with dispersion curves for the surface plasmarons in the sheet charge approximation but not with the problem of coupling strengths or stability.

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