14

Plasmons, Polaritons, and Polarons

NOTE: The text and problems of this chapter assume facility in the use of electromagnetic theory at the level of a good senior course.

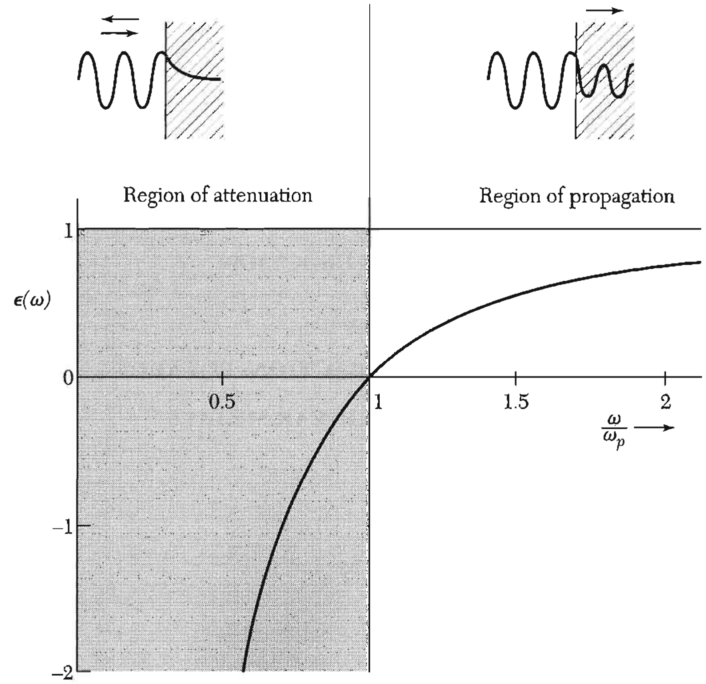


Figure 1 Dielectric function $\epsilon(\omega)$ or $\epsilon(\omega, 0)$ of a free-electron gas versus frequency in units of the plasma frequency ω_p. Electromagnetic waves propagate without damping only when ϵ is positive and real. Electromagnetic waves are totally reflected from the medium when ϵ is negative.

CHAPTER 14: PLASMONS, POLARITONS, AND POLARONS

DIELECTRIC FUNCTION OF THE ELECTRON GAS

The dielectric function $\epsilon(\omega,\mathbf{K})$ of the electron gas, with its strong dependence on frequency and wavevector, has significant consequences for the physical properties of solids. In one limit, $\epsilon(\omega,0)$ describes the collective excitations of the Fermi sea—the volume and surface plasmons. In another limit, $\epsilon(0,\mathbf{K})$ describes the electrostatic screening of the electron-electron, electron-lattice, and electron-impurity interactions in crystals.

We will also use the dielectric function of an ionic crystal to derive the polariton spectrum. Later we discuss the properties of polarons. But first we are concerned with the electron gas in metals.

Definitions of the Dielectric Function. The dielectric constant ϵ of electrostatics is defined in terms of the electric field **E** and the polarization **P**, the dipole moment density:

$$\text{(CGS)}\quad \mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = \epsilon\mathbf{E}\ ; \qquad \text{(SI)}\quad \mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P} = \epsilon\epsilon_0\mathbf{E}\ . \tag{1}$$

Thus defined, ϵ is also known as the relative permittivity.

The introduction of the displacement **D** is motivated by the usefulness of this vector related to the external applied charge density ρ_{ext} in the same way as **E** is related to the total charge density $\rho = \rho_{\text{ext}} + \rho_{\text{ind}}$, where ρ_{ind} is the charge density induced in the system by ρ_{ext}.

Thus the divergence relation of the electric field is

$$\begin{array}{ll} \text{(CGS)} & \text{(SI)} \\ \operatorname{div}\mathbf{D} = \operatorname{div}\epsilon\mathbf{E} = 4\pi\rho_{\text{ext}} & \operatorname{div}\mathbf{D} = \operatorname{div}\epsilon\epsilon_0\mathbf{E} = \rho_{\text{ext}} \qquad (2) \\ \operatorname{div}\mathbf{E} = 4\pi\rho = 4\pi(\rho_{\text{ext}} + \rho_{\text{ind}}) & \operatorname{div}\mathbf{E} = \rho/\epsilon_0 = (\rho_{\text{ext}} + \rho_{\text{ind}})/\epsilon_0\ . \qquad (3) \end{array}$$

Parts of this chapter will be written in CGS; to obtain results in SI, write $1/\epsilon_0$ for 4π.

We need relations between the Fourier components of **D**, **E**, ρ, and the electrostatic potential φ. For brevity we do not exhibit here the frequency dependence. Define $\epsilon(\mathbf{K})$ such that

$$\mathbf{D}(\mathbf{K}) = \epsilon(\mathbf{K})\mathbf{E}(\mathbf{K})\ ; \tag{3a}$$

then (3) becomes

$$\operatorname{div} \mathbf{E} = \operatorname{div} \Sigma\, \mathbf{E}(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) = 4\pi \Sigma\, \rho(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) \ , \tag{3b}$$

and (2) becomes

$$\operatorname{div} \mathbf{D} = \operatorname{div} \Sigma\, \epsilon(\mathbf{K})\mathbf{E}(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) = 4\pi \Sigma\, \rho_{\text{ext}}(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) \ . \tag{3c}$$

Each of the equations must be satisfied term by term; we divide one by the other to obtain

$$\epsilon(\mathbf{K}) = \frac{\rho_{\text{ext}}(\mathbf{K})}{\rho(\mathbf{K})} = 1 - \frac{\rho_{\text{ind}}(\mathbf{K})}{\rho(\mathbf{K})} \ . \tag{3d}$$

The electrostatic potential φ_{ext} defined by $-\nabla\varphi_{\text{ext}} = \mathbf{D}$ satisfies the Poisson equation $\nabla^2\varphi_{\text{ext}} = -4\pi\rho_{\text{ext}}$; and the electrostatic potential φ defined by $-\nabla\varphi = \mathbf{E}$ satisfies $\nabla^2\varphi = -4\pi\rho$. The Fourier components of the potentials must therefore satisfy

$$\frac{\varphi_{\text{ext}}(\mathbf{K})}{\varphi(\mathbf{K})} = \frac{\rho_{\text{ext}}(\mathbf{K})}{\rho(\mathbf{K})} = \epsilon(\mathbf{K}) \ , \tag{3e}$$

by (3d). We use this relation in the treatment of the screened coulomb potential.

Plasma Optics

The long wavelength dielectric response $\epsilon(\omega,0)$ or $\epsilon(\omega)$ of an electron gas is obtained from the equation of motion of a free electron in an electric field:

$$m\frac{d^2x}{dt^2} = -eE \ . \tag{4}$$

If x and E have the time dependence $e^{-i\omega t}$, then

$$-\omega^2 mx = -eE \ ; \qquad x = eE/m\omega^2 \ . \tag{5}$$

The dipole moment of one electron is $-ex = -e^2E/m\omega^2$, and the polarization, defined as the dipole moment per unit volume, is

$$P = -nex = -\frac{ne^2}{m\omega^2}E \ , \tag{6}$$

where n is the electron concentration.

The dielectric function at frequency ω is

(CGS)
$$\epsilon(\omega) \equiv \frac{D(\omega)}{E(\omega)} \equiv 1 + 4\pi\frac{P(\omega)}{E(\omega)} \ ; \tag{7}$$

(SI)
$$\epsilon(\omega) = \frac{D(\omega)}{\epsilon_0 E(\omega)} = 1 + \frac{P(\omega)}{\epsilon_0 E(\omega)} \ .$$

The dielectric function of the free electron gas follows from (6) and (7):

$$\text{(CGS)} \quad \epsilon(\omega) = 1 - \frac{4\pi ne^2}{m\omega^2} \; ; \qquad \text{(SI)} \quad \epsilon(\omega) = 1 - \frac{ne^2}{\epsilon_0 m\omega^2} \; . \tag{8}$$

The **plasma frequency** ω_p is defined by the relation

$$\text{(CGS)} \quad \omega_p^2 = 4\pi ne^2/m \; ; \qquad \text{(SI)} \quad \omega_p^2 \equiv ne^2/\epsilon_0 m \; . \tag{9}$$

A plasma is a medium with equal concentration of positive and negative charges, of which at least one charge type is mobile. In a solid the negative charges of the conduction electrons are balanced by an equal concentration of positive charge of the ion cores. We write the dielectric function (8) as

$$\boxed{\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \; ,} \tag{10}$$

plotted in Fig. 1.

If the positive ion core background has a dielectric constant labeled $\epsilon(\infty)$ essentially constant up to frequencies well above ω_p, then (8) becomes

$$\epsilon(\omega) = \epsilon(\infty) - 4\pi ne^2/m\omega^2 = \epsilon(\infty)[1 - \bar{\omega}_p^2/\omega^2] \; , \tag{11}$$

where $\bar{\omega}_p$ is defined as

$$\bar{\omega}_p^2 = 4\pi ne^2/\epsilon(\infty)m \; . \tag{12}$$

Notice that $\epsilon = 0$ at $\omega = \bar{\omega}_p$.

Dispersion Relation for Electromagnetic Waves

In a nonmagnetic isotropic medium the electromagnetic wave equation is

$$\text{(CGS)} \quad \partial^2\mathbf{D}/\partial t^2 = c^2\nabla^2\mathbf{E} \; ; \qquad \text{(SI)} \quad \mu_0\,\partial^2\mathbf{D}/\partial t^2 = \nabla^2\mathbf{E} \; . \tag{13}$$

We look for a solution with $\mathbf{E} \propto \exp(-i\omega t)\exp(i\mathbf{K}\cdot\mathbf{r})$ and $\mathbf{D} = \epsilon(\omega,\mathbf{K})\mathbf{E}$; then we have the dispersion relation for electromagnetic waves:

$$\text{(CGS)} \quad \epsilon(\omega,\mathbf{K})\omega^2 = c^2K^2 \; ; \qquad \text{(SI)} \quad \epsilon(\omega,\mathbf{K})\epsilon_0\mu_0\omega^2 = K^2 \; . \tag{14}$$

This relation tells us a great deal. Consider

- ϵ real and > 0. For ω real, K is real and a transverse electromagnetic wave propagates with the phase velocity $c/\epsilon^{1/2}$.
- ϵ real and < 0. For ω real, K is imaginary and the wave is damped with a characteristic length $1/|\mathbf{K}|$.
- ϵ complex. For ω real, $\mathbf{K}$ is complex and the waves are damped in space.

- $\epsilon = \infty$. This means the system has a finite response in the absence of an applied force; thus the poles of $\epsilon(\omega,\mathbf{K})$ define the frequencies of the free oscillations of the medium.
- $\epsilon = 0$. We shall see that longitudinally polarized waves are possible only at the zeros of ϵ.

Transverse Optical Modes in a Plasma

The dispersion relation (14) becomes, with (11) for $\epsilon(\omega)$,

$$\text{(CGS)} \qquad \epsilon(\omega)\omega^2 = \epsilon(\infty)(\omega^2 - \bar{\omega}_p^2) = c^2K^2 \ . \tag{15}$$

For $\omega < \bar{\omega}_p$ we have $K^2 < 0$, so that K is imaginary. The solutions of the wave equation are of the form $\exp(-|K|x)$ in the frequency region $0 < \omega \leq \bar{\omega}_p$. Waves incident on the medium in this frequency region do not propagate, but will be totally reflected.

An electron gas is transparent when $\omega > \bar{\omega}_p$, for here the dielectric function is positive real. The dispersion relation in this region may be written as

$$\text{(CGS)} \qquad \omega^2 = \bar{\omega}_p^2 + c^2K^2/\epsilon(\infty) \ ; \tag{16}$$

this describes transverse electromagnetic waves in a plasma (Fig. 2).

Values of the plasma frequency ω_p and of the free space wavelength $\lambda_p \equiv 2\pi c/\omega_p$ for electron concentrations of interest are given below. A wave will propagate if its free space wavelength is less than λ_p; otherwise the wave is reflected.

n, electrons/cm^3	10^{22}	10^{18}	10^{14}	10^{10}
ω_p, s^{-1}	5.7×10^{15}	5.7×10^{13}	5.7×10^{11}	5.7×10^{9}
λ_p, cm	3.3×10^{-5}	3.3×10^{-3}	0.33	33

Transparency of Metals in the Ultraviolet. From the preceding discussion of the dielectric function we conclude that simple metals should reflect light in the visible region and be transparent to light at high frequencies. A comparison of calculated and observed cutoff wavelengths is given in Table 1. The reflection of light from a metal is entirely similar to the reflection of radio waves from the ionosphere, for the free electrons in the ionosphere make the dielectric constant negative at low frequencies. Experimental results for InSb with $n = 4 \times 10^{18}$ cm^{-3} are shown in Fig. 3, where the plasma frequency is near 0.09 eV.

Longitudinal Plasma Oscillations

The zeros of the dielectric function determine the frequencies of the longitudinal modes of oscillation. That is, the condition

$$\epsilon(\omega_L) = 0 \tag{17}$$

determines the longitudinal frequency ω_L near $K = 0$.

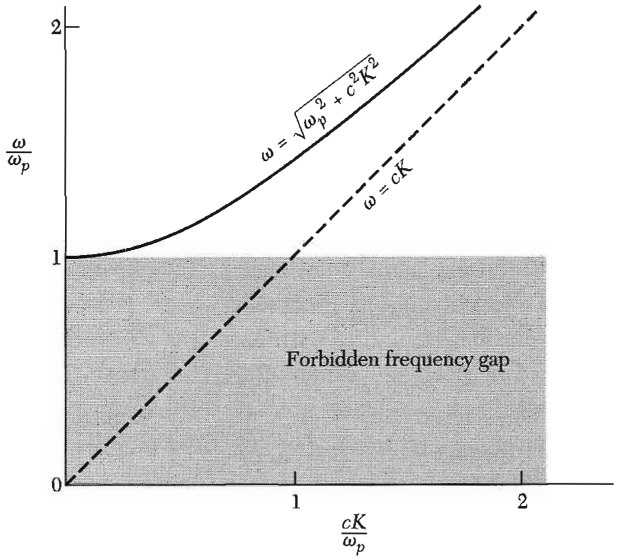


Figure 2 Dispersion relation for transverse electromagnetic waves in a plasma. The group velocity $v_g = d\omega/dK$ is the slope of the dispersion curve. Although the dielectric function is between zero and one, the group velocity is less than the velocity of light in vacuum.

Table 1 Ultraviolet transmission limits of alkali metals, in Å

	Li	Na	K	Rb	Cs
λ_p, calculated	1550	2090	2870	3220	3620
λ_p, observed	1550	2100	3150	3400	—

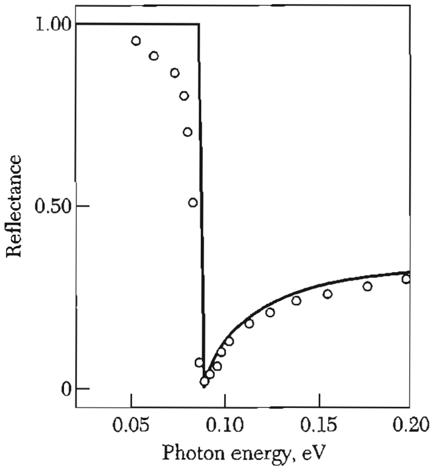


Figure 3 Reflectance of indium antimonide with $n = 4 \times 10^{18}$ cm^{-3}. (After J. N. Hodgson.)

By the geometry of a longitudinal polarization wave there is a depolarization field $\mathbf{E} = -4\pi\mathbf{P}$, discussed below. Thus $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = 0$ for a longitudinal wave in a plasma or more generally in a crystal. In SI units, $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P} = 0$.

For an electron gas, at the zero (17) of the dielectric function (10)

$$\epsilon(\omega_L) = 1 - \omega_p^2/\omega_L^2 = 0 \ , \tag{18}$$

whence $\omega_L = \omega_p$. Thus there is a free longitudinal oscillation mode (Fig. 4) of an electron gas at the plasma frequency described by (15) as the low-frequency cutoff of transverse electromagnetic waves.

A longitudinal plasma oscillation with $K = 0$ is shown in Fig. 5 as a uniform displacement of an electron gas in a thin metallic slab. The electron gas is moved as a whole with respect to the positive ion background. The displacement u of the electron gas creates an electric field $E = 4\pi neu$ that acts as a restoring force on the gas.

The equation of motion of a unit volume of the electron gas of concentration n is

(CGS)
$$nm\frac{d^2u}{dt^2} = -neE = -4\pi n^2e^2u \ , \tag{19}$$

or

(CGS)
$$\frac{d^2u}{dt^2} + \omega_p^2u = 0 \ ; \qquad \omega_p = \left(\frac{4\pi ne^2}{m}\right)^{1/2} \ . \tag{20}$$

This is the equation of motion of a simple harmonic oscillator of frequency ω_p, the plasma frequency. The expression for ω_p is identical with (9), which arose in a different connection. In SI, the displacement u creates the electric field $E = neu/\epsilon_0$, whence $\omega_p = (ne^2/\epsilon_0m)^{1/2}$.

A plasma oscillation of small wavevector has approximately the frequency ω_p. The wavevector dependence of the dispersion relation for longitudinal oscillations in a Fermi gas is given by

$$\omega \cong \omega_p\,(1 + 3k^2v_F^2/10\omega_p^2 + \cdots) \ , \tag{21}$$

where v_F is the electron velocity at the Fermi energy.

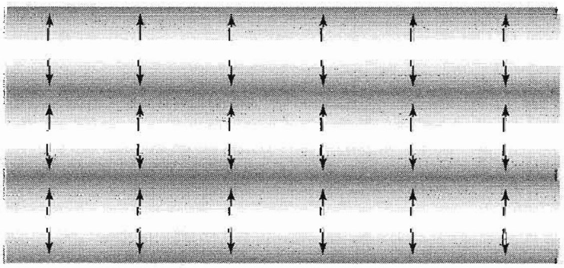


Figure 4 A plasma oscillation. The arrows indicate the direction of displacement of the electrons.

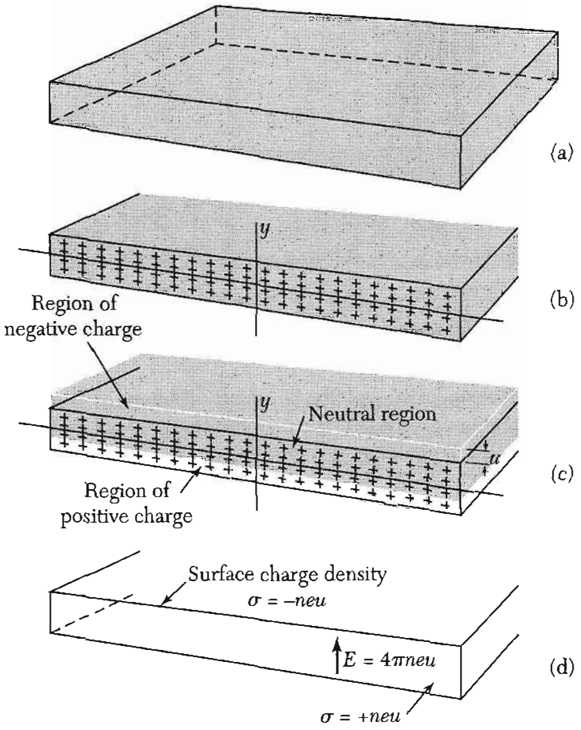


Figure 5 In (a) is shown a thin slab or film of a metal. A cross section is shown in (b), with the positive ion cores indicated by + signs and the electron sea indicated by the gray background. The slab is electrically neutral. In (c) the negative charge has been displaced upward uniformly by a small distance u, shown exaggerated in the figure. As in (d), this displacement establishes a surface charge density $-neu$ on the upper surface of the slab and $+neu$ on the lower surface, where n is the electron concentration. An electric field $E = 4\pi neu$ is produced inside the slab. This field tends to restore the electron sea to its equilibrium position (b). In SI units, $E = neu/\epsilon_0$.

PLASMONS

A plasma oscillation in a metal is a collective longitudinal excitation of the conduction electron gas. A **plasmon** is a quantum of a plasma oscillation; we may excite a plasmon by passing an electron through a thin metallic film (Figs. 6 and 7) or by reflecting an electron or a photon from a film. The charge of the electron couples with the electrostatic field fluctuations of the plasma oscillations. The reflected or transmitted electron will show an energy loss equal to integral multiples of the plasmon energy.

Experimental excitation spectra for Al and Mg are shown in Fig. 8. A comparison of observed and calculated values of plasmon energies is given in Table 2; further data are given in the reviews by Raether and by Daniels. Recall that $\bar{\omega}_p$ as defined by (12) includes the ion core effects by use of $\epsilon(\infty)$.

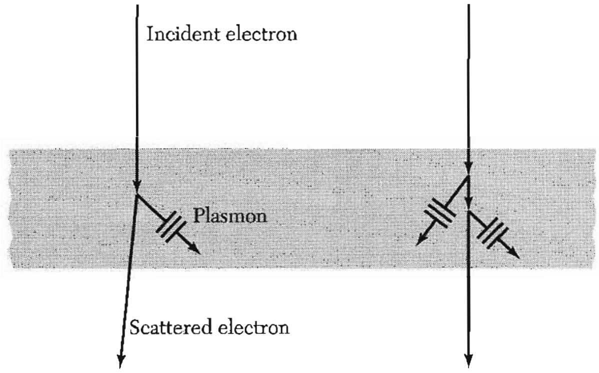


Figure 6 Creation of a plasmon in a metal film by inelastic scattering of an electron. The incident electron typically has an energy 1 to 10 keV; the plasmon energy may be of the order of 10 eV. An event is also shown in which two plasmons are created.

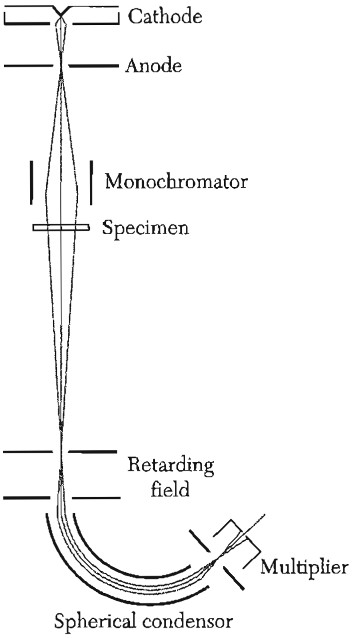
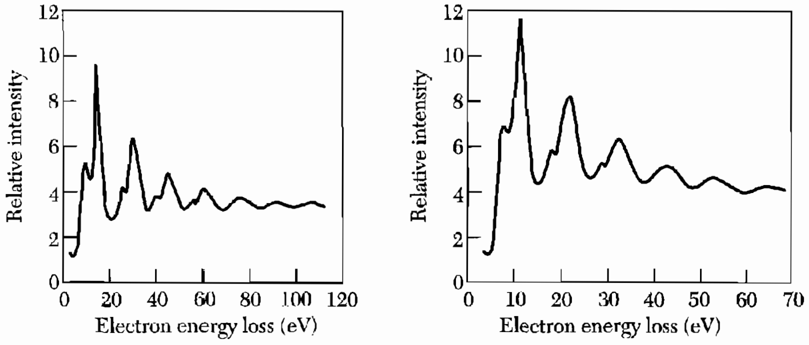


Figure 7 A spectrometer with electrostatic analyzer for the study of plasmon excitation by electrons. (After J. Daniels et al.)

It is equally possible to excite collective plasma oscillations in dielectric films; results for several dielectrics are included. The calculated plasma energies of Si, Ge, and InSb are based on four valence electrons per atom. In a dielectric the plasma oscillation is physically the same as in a metal; the entire valence electron gas oscillates back and forth with respect to the ion cores.



(a) (b)

Figure 8 Energy loss spectra for electrons reflected from films of (a) aluminum and (b) magnesium, for primary electron energies of 2020 eV. The 12 loss peaks observed in Al are made up of combinations of 10.3 and 15.3 eV losses, where the 10.3 eV loss is due to surface plasmons and the 15.3 eV loss is due to volume plasmons. The ten loss peaks observed in Mg are made up of combinations of 7.1 eV surface plasmons and 10.6 eV volume plasmons. Surface plasmons are the subject of Problem 1. (After C. J. Powell and J. B. Swan.)

Table 2 Volume plasmon energies, in eV

		Calculated	
Material	Observed	$\hbar\omega_p$	$\hbar\bar{\omega}_p$
Metals			
Li	7.12	8.02	7.96
Na	5.71	5.95	5.58
K	3.72	4.29	3.86
Mg	10.6	10.9	
Al	15.3	15.8	
Dielectrics			
Si	16.4–16.9	16.0	
Ge	16.0–16.4	16.0	
InSb	12.0–13.0	12.0	

ELECTROSTATIC SCREENING

The electric field of a positive charge embedded in an electron gas falls off with increasing r faster than $1/r$, because the electron gas tends to gather around and thus to screen the positive charge. The static screening can be described by the wavevector dependence of the static dielectric function $\epsilon(0,\mathbf{K})$. We consider the response of the electrons to an applied external electrostatic field. We start with a uniform gas of electrons of charge concentration $-n_0e$ superimposed on a background of positive charge of concentration n_0e. Let the positive charge background be deformed mechanically to produce a sinusoidal variation of positive charge density in the x direction:

$$\rho^+(x) = n_0e + \rho_{\mathrm{ext}}(K)\sin Kx \ . \tag{22}$$

The term $\rho_{\mathrm{ext}}(K)\sin Kx$ gives rise to an electrostatic field that we call the external field applied to the electron gas.

The electrostatic potential φ of a charge distribution is found from the Poisson equation $\nabla^2\varphi = -4\pi\rho$, by (3) with $\mathbf{E} = -\nabla\varphi$. For the positive charge we have

$$\varphi = \varphi_{\mathrm{ext}}(K)\sin Kx \ ; \quad \rho = \rho_{\mathrm{ext}}(K)\sin Kx \ . \tag{23}$$

The Poisson equation gives the relation

$$K^2\varphi_{\mathrm{ext}}(K) = 4\pi\rho_{\mathrm{ext}}(K) \ . \tag{24}$$

The electron gas will be deformed by the combined influences of the electrostatic potential $\varphi_{\mathrm{ext}}(K)$ of the positive charge distribution and of the as yet unknown induced electrostatic potential $\varphi_{\mathrm{ind}}(K)\sin Kx$ of the deformation of the electron gas itself. The electron charge density is

$$\rho^-(x) = -n_0e + \rho_{\mathrm{ind}}(K)\sin Kx \ , \tag{25}$$

where $\rho_{\mathrm{ind}}(K)$ is the amplitude of the charge density variation induced in the electron gas. We want to find $\rho_{\mathrm{ind}}(K)$ in terms of $\rho_{\mathrm{ext}}(K)$.

The amplitude of the total electrostatic potential $\varphi(K) = \varphi_{\mathrm{ext}}(K) + \varphi_{\mathrm{ind}}(K)$ of the positive and negative charge distributions is related to the total charge density variation $\rho(K) = \rho_{\mathrm{ext}}(K) + \rho_{\mathrm{ind}}(K)$ by the Poisson equation. Then, as in Eq. (24),

$$K^2\varphi(K) = 4\pi\rho(K) \ . \tag{26}$$

To go further we need another equation that relates the electron concentration to the electrostatic potential. We develop this connection in what is called the Thomas-Fermi approximation. The approximation consists in assuming that a local internal chemical potential can be defined as a function of the electron concentration at that point. Now the total chemical potential of the electron gas is constant in equilibrium, independent of position. In a region where there is no electrostatic contribution to the chemical potential we have

$$\mu = \epsilon_F^0 = \frac{\hbar^2}{2m}(3\pi^2 n_0)^{2/3} \tag{27}$$

at absolute zero, according to (6.17). In a region where the electrostatic potential is $\varphi(\mathrm{x})$, the total chemical potential (Fig. 9) is constant and equal to

$$\mu = \epsilon_F(x) - e\varphi(x) \simeq \frac{\hbar^2}{2m}[3\pi^2 n(x)]^{2/3} - e\varphi(x) \cong \frac{\hbar^2}{2m}[3\pi^2 n_0]^{2/3} \ , \tag{28}$$

where $\epsilon_F(x)$ is the local value of the Fermi energy.

The expression (28) is valid for static electrostatic potentials that vary slowly compared with the wavelength of an electron at the Fermi level;

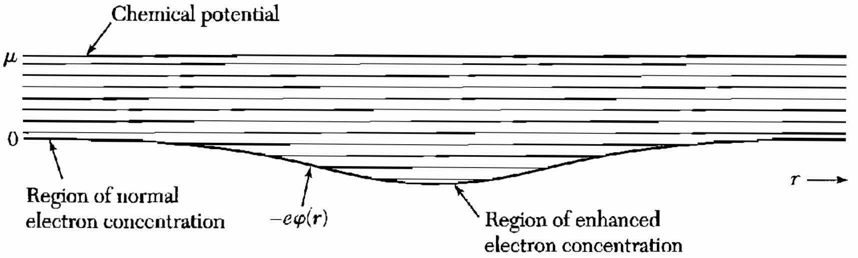


Figure 9 In thermal and diffusive equilibrium the chemical potential is constant; to maintain it constant we increase the electron concentration in regions of space where the potential energy is low, and we decrease the concentration where the potential is high.

specifically, the approximation is $q \ll k_F$. By a Taylor series expansion of ϵ_F, Eq. (28) may be written as

$$\frac{d\epsilon_F}{dn_0}[n(x) - n_0] \cong e\varphi(x) \ . \tag{29}$$

From (27) we have $d\epsilon_F/dn_0 = 2\epsilon_F/3n_0$, whence

$$n(x) - n_0 \cong \frac{3}{2} n_0 \frac{e\varphi(x)}{\epsilon_F} \ . \tag{30}$$

The left-hand side is the induced part of the electron concentration; thus the Fourier components of this equation are

$$\rho_{\text{ind}}(K) = -(3n_0e^2/2\epsilon_F)\varphi(K) \ . \tag{31}$$

By (26) this becomes

$$\rho_{\text{ind}}(K) = -(6\pi n_0 e^2/\epsilon_F K^2)\rho(K) \ . \tag{32}$$

By (3d) we have

$$\epsilon(0,K) = 1 - \frac{\rho_{\text{ind}}(K)}{\rho(K)} = 1 + k_s^2/K^2 \ ; \tag{33}$$

here, after some rearrangement,

$$k_s^2 = 6\pi n_0 e^2/\epsilon_F = 4(3/\pi)^{1/3} n_0^{1/3}/a_0 = 4\pi e^2 D(\epsilon_F) \ , \tag{34}$$

where a_0 is the Bohr radius and $D(\epsilon_F)$ is the density of states for a free electron gas. The approximation (33) for $\epsilon(0,K)$ is called the Thomas-Fermi dielectric function, and $1/k_s$ is the Thomas-Fermi screening length, as in (40) below. For copper with $n_0 = 8.5 \times 10^{22}$ cm^{-3}, the screening length is 0.55 Å.

We have derived two limiting expressions for the dielectric function of an electron gas:

$$\epsilon(0,K) = 1 + \frac{k_s^2}{K^2} \ ; \qquad \epsilon(\omega,0) = 1 - \frac{\omega_p^2}{\omega^2} \ . \tag{35}$$

We notice that $\epsilon(0,K)$ as $K \rightarrow 0$ does not approach the same limit as $\epsilon(\omega,0)$ as $\omega \rightarrow 0$. This means that great care must be taken with the dielectric function near the origin of the ω-K plane. The full theory for the general function $\epsilon(\omega,K)$ is due to Lindhard.[1]

Screened Coulomb Potential. We consider a point charge q placed in a sea of conduction electrons. The Poisson equation for the unscreened coulomb potential is

$$\nabla^2\varphi_0 = -4\pi q\delta(\mathbf{r}) \ , \tag{36}$$

and we know that $\varphi_0 = q/r$. Let us write

$$\varphi_0(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{K}\ \varphi_0(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) \ . \tag{37}$$

We use in (36) the Fourier representation of the delta function:

$$\delta(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{K} \exp(i\mathbf{K}\cdot\mathbf{r}) \ , \tag{38}$$

whence $K^2\varphi_0(K) = 4\pi q$.

By (3e),

$$\varphi_0(K)/\varphi(K) = \epsilon(K) \ ,$$

where $\varphi(K)$ is the total or screened potential. We use $\epsilon(K)$ in the Thomas-Fermi form (33) to find

$$\varphi(\mathbf{K}) = \frac{4\pi q}{K^2 + k_s^2} \ . \tag{39}$$

The screened coulomb potential is the transform of $\varphi(\mathbf{K})$:

$$\begin{aligned}\varphi(r) &= \frac{4\pi q}{(2\pi)^3}\int_0^\infty dK \frac{2\pi K^2}{K^2 + k_s^2}\int_{-1}^{1} d(\cos\theta)\exp(iKr\cos\theta) \\ &= \frac{2q}{\pi r}\int_0^\infty dK \frac{K\sin Kr}{K^2+k_s^2} = \frac{q}{r}\exp(-k_s r) \qquad (40)\end{aligned}$$

as in Fig. 10a. The screening parameter k_s is defined by (34). The exponential factor reduces the range of the coulomb potential. The bare potential q/r is obtained on letting the charge concentration $n_0 \to 0$, for then $k_s \to 0$. In the vacuum limit $\varphi(K) = 4\pi q/K^2$.

One application of the screened interaction is to the resistivity of certain alloys. The atoms of the series Cu, Zn, Ga, Ge, As have valences 1, 2, 3, 4, 5. An atom of Zn, Ga, Ge, or As added substitutionally to metallic Cu has an excess charge, referred to Cu, of 1, 2, 3, or 4 if all the valence electrons join the conduction band of the host metal. The foreign atom scatters the conduction electrons, with an interaction given by the screened coulomb potential. This scattering contributes to the residual electrical resistivity, and calculations by Mott of the resistivity increase are in fair agreement with experiment.

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[1] A good discussion of the Lindhard dielectric function is given by J. Ziman, *Principles of the theory of solids*, 2nd ed., Cambridge, 1972, Chapter 5. The algebraic steps in the evaluation of Ziman's equation (5.16) are given in detail by C. Kittel, Solid state physics **22**, 1 (1968), Section 6.

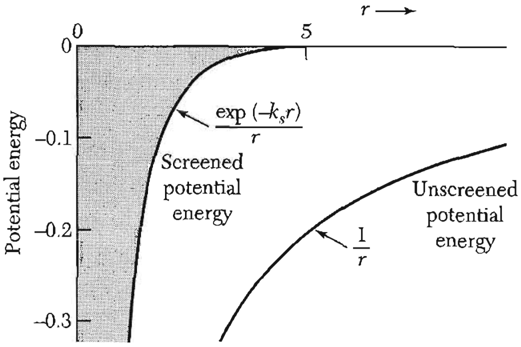


Figure 10a *Comparison of screened and unscreened* coulomb potentials of a static unit positive charge. The screening length $1/k_s$ is set equal to unity. The static screened interaction is taken in the Thomas-Fermi approximation, which holds for low wavevectors $q \ll k_F$; More complete calculations with all wavevectors included exhibit spatial oscillations, called **Friedel oscillations**, in $2k_F r$ and are plotted in QTS, p. 114.

Pseudopotential Component $U(0)$. In the legend to Fig. 9.22b we stated a result that is important in pseudopotential theory: "For very small k the potential approaches $-\frac{2}{3}$ times the Fermi energy." The result, which is known as the screened ion limit for metals, can be derived from Eq. (39). When converted to the potential energy of an electron of charge e in a metal of valency z with n_0 ions per unit volume, the potential energy component at $k = 0$ becomes

$$U(0) = -ezn_0\varphi(0) = -4\pi zn_0e^2/k_s^2 \ . \tag{41}$$

The result (34) for k_s^2 in this situation reads

$$k_s^2 = 6\pi zn_0e^2/\epsilon_F \ , \tag{42}$$

whence

$$U(0) = -\tfrac{2}{3}\epsilon_F \ . \tag{43}$$

Mott Metal-Insulator Transition

A crystal composed of one hydrogen atom per primitive cell should always be a metal, according to the independent-electron model, because there will always be a half-filled energy band within which charge transport can take place. A crystal with one hydrogen molecule per primitive cell is a different matter, because the two electrons can fill a band. Under extreme high pressure, as in the planet Jupiter, it is possible that hydrogen occurs in a metallic form.

But let us imagine a lattice of hydrogen atoms at absolute zero: will this be a metal or an insulator? The answer depends on the lattice constant, with small values of a giving a metal and large values giving an insulator. Mott made an early estimate of the critical value a_c of the lattice constant that separates the metallic state from the insulating state: $a_c = 4.5a_0$, where $a_0 = \hbar^2/me^2$ is the radius of the first Bohr orbit of a hydrogen atom.

On one approach to the problem, we start in the metallic state where a conduction electron sees a screened coulomb interaction from each proton:

$$U(r) = -(e^2/r)\exp(-k_s r) \ , \tag{44}$$

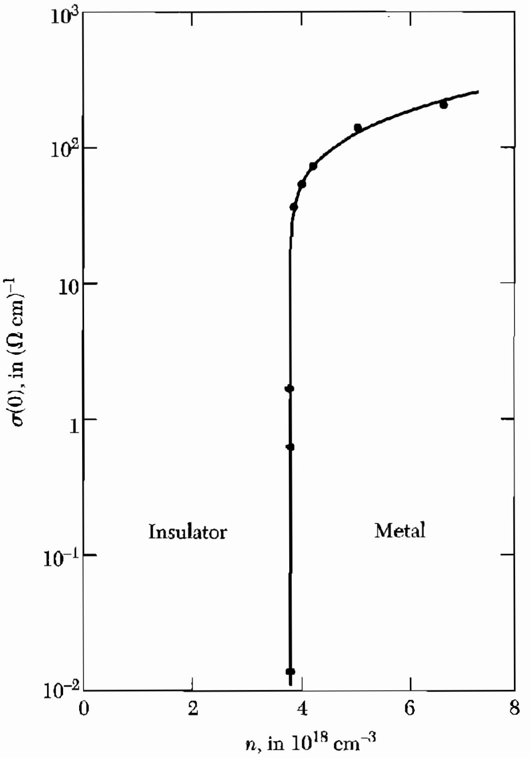


Figure 10b Semilog plot of observed "zero temperature" conductivity $\sigma(0)$ versus donor concentration n for phosphorous donors in silicon. (After T. F. Rosenbaum, et al.)

where $k_s^2 = 3.939 n_0^{1/3}/a_0$, as in (34), where n_0 is the electron concentration. At high concentrations k_s is large and the potential has no bound state, so that we must have a metal.

The potential is known to have a bound state when k_s is smaller than $1.19/a_0$. With a bound state possible the electrons may condense about the protons to form an insulator. The inequality may be written in terms of n_0 as

$$3.939 n_0^{1/3}/a_0 < 1.42/a_0^2 \ . \tag{45}$$

With $n_0 = 1/a^3$ for a simple cubic lattice, we may have an insulator when $a_c > 2.78 a_0$, which is not far from the Mott result $4.5 a_0$ found in a different way.

The term *metal-insulator transition* has come to denote situations where the electrical conductivity of a material changes from metal to insulator as a function of some external parameter, which may be composition, pressure, strain, or magnetic field. The metallic phase may usually be pictured in terms of an independent-electron model; the insulator phase may suggest important electron-electron interactions. Sites randomly occupied introduce new and interesting aspects to the problem, aspects that lie within percolation theory. The percolation transition is beyond the scope of our book.

When a semiconductor is doped with increasing concentrations of donor (or acceptor) atoms, a transition will occur to a conducting metallic phase.

Experimental results for P atoms in silicon are shown in Fig. 10b. Here the insulator-metal transition takes place when the concentration is so high that the ground state wavefunctions of electrons on neighboring impurity atoms overlap significantly.

The observed value of the critical concentration in the Si : P alloy system is $n_c = 3.74 \times 10^{18}\ \mathrm{cm}^{-3}$, as in the figure. If we take 32×10^{-8} cm as the radius of the ground state of a donor in Si in the spherical approximation, then by the Mott criterion $a_c = 1.44 \times 10^{-6}$ cm. The P atoms are believed to occupy lattice sites at random, but if instead their lattice were simple cubic, the critical Mott concentration would be

$$n_c = 1/a_c^3 = 0.33 \times 10^{18}\ \mathrm{cm}^{-3} \ , \tag{46}$$

appreciably less than the observed value. It is usual in the semiconductor literature to refer to a heavily-doped semiconductor in the metallic range as a **degenerate semiconductor**.

Screening and Phonons in Metals

An interesting application of our two limiting forms of the dielectric function is to longitudinal acoustic phonons in metals. For longitudinal modes the total dielectric function, ions plus electrons, must be zero, by (17). Provided the sound velocity is less than the Fermi velocity of the electrons, we may use for the electrons the Thomas-Fermi dielectric function

$$\epsilon_{el}(\omega,K) = 1 + k_s^2/K^2 \ . \tag{47}$$

Provided also that the ions are well-spaced and move independently, we may use for them the plasmon $\epsilon(\omega,0)$ limit with the approximate mass M.

The total dielectric function, lattice plus electrons, but without the electronic polarizability of the ion cores, is

$$\epsilon(\omega,K) = 1 - \frac{4\pi ne^2}{M\omega^2} + \frac{k_s^2}{K^2} \ . \tag{48}$$

At low K and ω we neglect the term 1. At a zero of $\epsilon(\omega,K)$ we have, with $\epsilon_F \equiv \frac{1}{2}mv_F^2$,

$$\omega^2 \frac{4\pi ne^2}{Mk_s^2}K^2 = \frac{4\pi ne^2}{M} \cdot \frac{\epsilon_F}{6\pi ne^2}K^2 = \frac{m}{3M}v_F^2K^2 \ , \tag{49}$$

or

$$\omega = vK \ ; \qquad v = (m/3M)^{1/2}\, v_F \ . \tag{50}$$

This describes long wavelength longitudinal acoustic phonons.

In the alkali metals the result is in quite good agreement with the observed longitudinal wave velocity. For potassium we calculate $v = 1.8 \times 10^5\ \mathrm{cm\ s}^{-1}$; the observed longitudinal sound velocity at 4 K in the [100] direction is $2.2 \times 10^5\ \mathrm{cm\ s}^{-1}$.

There is another zero of $\epsilon(\omega,K)$ for positive ions imbedded in an electron sea. For high frequencies we use the dielectric contribution $-\omega_p^2/\omega^2$ of the electron gas:

$$\epsilon(\omega,0) = 1 - \frac{4\pi ne^2}{M\omega^2} - \frac{4\pi ne^2}{m\omega^2} \ , \tag{51}$$

and this function has a zero when

$$\omega^2 = \frac{4\pi ne^2}{\mu} \ ; \quad \frac{1}{\mu} = \frac{1}{M} + \frac{1}{m} \ . \tag{52}$$

This is the electron plasma frequency (20), but with the reduced mass correction for the motion of the positive ions.

POLARITONS

Longitudinal optical phonons and transverse optical phonons were discussed in Chapter 4, but we deferred treatment of the interaction of transverse optical phonons with transverse electromagnetic waves. When the two waves are at resonance the phonon-photon coupling entirely changes the character of the propagation, and a forbidden band is established for reasons that have nothing to do with the periodicity of the lattice.

By resonance we mean a condition in which the frequencies and wavevectors of both waves are approximately equal. The region of the crossover of the two dashed curves in Fig. 11 is the resonance region; the two dashed curves are the dispersion relations for photons and transverse optical phonons in the absence of any coupling between them. In reality, however, there always is coupling implicit in Maxwell's equations and expressed by the dielectric function. The quantum of the coupled phonon-photon transverse wave field is called a **polariton**.

In this section we see how the coupling is responsible for the dispersion relations shown as solid curves in the figure. All takes place at very low values of the wavevector in comparison with a zone boundary, because at crossover $\omega(\text{photon}) = ck(\text{photon}) = \omega(\text{phonon}) \approx 10^{13}\,\text{s}^{-1}$; thus $k \approx 300\,\text{cm}^{-1}$.

An early warning: although the symbol ω_L will necessarily arise in the theory, the effects do not concern longitudinal optical phonons. Longitudinal phonons do not couple to transverse photons in the bulk of a crystal.

The coupling of the electric field E of the photon with the dielectric polarization P of the TO phonon is described by the electromagnetic wave equation:

(CGS) $$c^2K^2E = \omega^2(E + 4\pi P) \ . \tag{53}$$

At low wavevectors the TO phonon frequency ω_T is independent of K. The polarization is proportional to the displacement of the positive ions relative to the negative ions, so that the equation of motion of the polarization is like that of an oscillator and may be written as, with $P = Nqu$,

$$-\omega^2P + \omega_T^2P = (Nq^2/M)E \ , \tag{54}$$

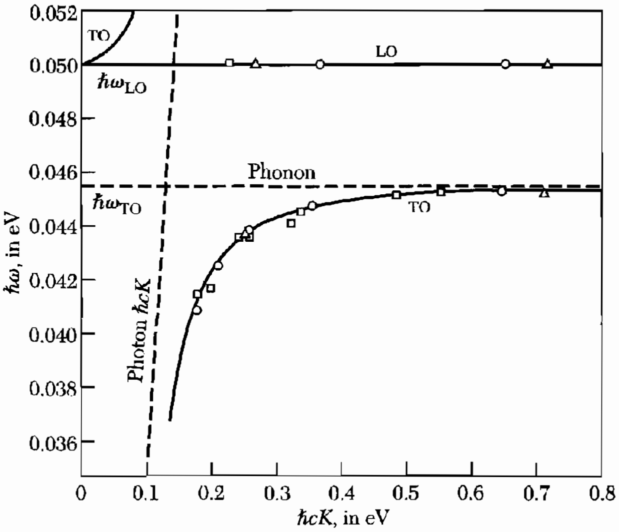


Figure 11 A plot of the observed energies and wavevectors of the polaritons and of the LO phonons in GaP. The theoretical dispersion curves are shown by the solid lines. The dispersion curves for the uncoupled phonons and photons are shown by the short, dashed lines. (After C. H. Henry and J. J. Hopfield.)

where there are N ion pairs of effective charge q and reduced mass M, per unit volume. For simplicity we neglect the electronic contribution to the polarization.

The equations (53) and (54) have a solution when

$$\begin{vmatrix} \omega^2 - c^2K^2 & 4\pi\omega^2 \\ Nq^2/M & \omega^2 - \omega_T^2 \end{vmatrix} = 0 \ . \tag{55}$$

This gives the polariton dispersion relation, similar to that plotted in Figs. 11 and 12. At $K = 0$ there are two roots, $\omega = 0$ for the photon and

$$\omega^2 = \omega_T^2 + 4\pi Nq^2/M \tag{56}$$

for the polariton. Here ω_T is the TO phonon frequency in the absence of coupling with photons.

The dielectric function obtained from (54) is:

$$\epsilon(\omega) = 1 + 4\pi P/E = 1 + \frac{4\pi Nq^2/M}{\omega_T^2 - \omega^2} \ . \tag{57}$$

If there is an optical electronic contribution to the polarization from the ion cores, this should be included. In the frequency range from zero up through the infrared, we write

$$\epsilon(\omega) = \epsilon(\infty) + \frac{4\pi Nq^2/M}{\omega_T^2 - \omega^2} \tag{58}$$

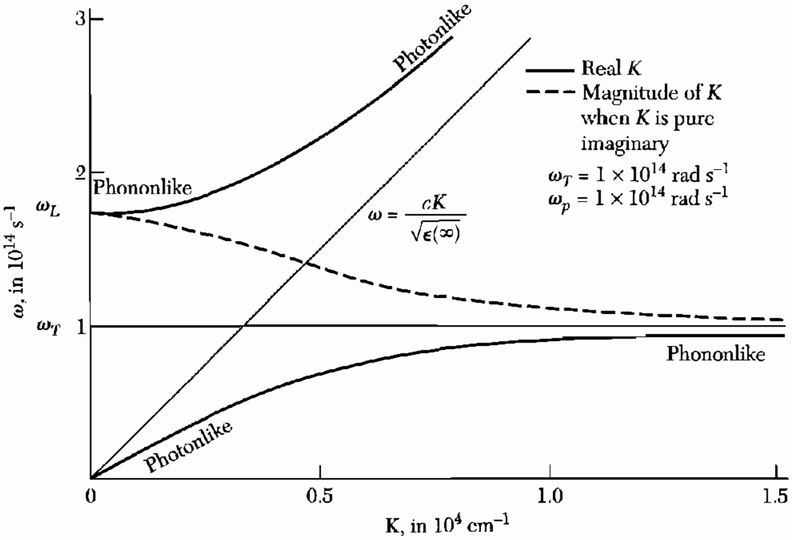


Figure 12 Coupled modes of photons and transverse optical phonons in an ionic crystal. The fine horizontal line represents oscillators of frequency ω_T in the absence of coupling to the electromagnetic field, and the fine line labeled $\omega = cK/\sqrt{\epsilon(\infty)}$ corresponds to electromagnetic waves in the crystal, but uncoupled to the lattice oscillators ω_T. The heavy lines are the dispersion relations in the presence of coupling between the lattice oscillators and the electromagnetic wave. One effect of the coupling is to create the frequency gap between ω_L and ω_T: within this gap the wavevector is pure imaginary of magnitude given by the broken line in the figure. In the gap the wave attenuates as $\exp(-|K|x)$, and we see from the plot that the attenuation is much stronger near ω_T than near ω_L. The character of the branches varies with K; there is a region of mixed electric-mechanical aspects near the nominal crossover. Note, finally, it is intuitively obvious that the group velocity of light in the medium is always $<c$, because the slope $\partial\omega/\partial K$ for the actual dispersion relations (heavy lines) is everywhere less than the slope c for the uncoupled photon in free space.

in accord with the definition of $\epsilon(\infty)$ as the optical dielectric constant, obtained as the square of the optical refractive index.

We set $\omega = 0$ to obtain the static dielectric function:

$$\epsilon(0) = \epsilon(\infty) + 4\pi Nq^2/M\omega_T^2 \ , \tag{59}$$

which is combined with (58) to obtain $\epsilon(\omega)$ in terms of accessible parameters:

$$\epsilon(\omega) = \epsilon(\infty) + [\epsilon(0) - \epsilon(\infty)]\frac{\omega_T^2}{\omega_T^2 - \omega^2}$$

or

$$\epsilon(\omega) = \frac{\omega_T^2\epsilon(0) - \omega^2\epsilon(\infty)}{\omega_T^2 - \omega^2} = \epsilon(\infty)\left(\frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2}\right) \ . \tag{60}$$

The zero of $\epsilon(\omega)$ defines the longitudinal optical phonon frequency ω_L, as the pole of $\epsilon(\omega)$ defines ω_T. The zero gives

$$\epsilon(\infty)\omega_L^2 = \epsilon(0)\omega_T^2 \ . \tag{61}$$

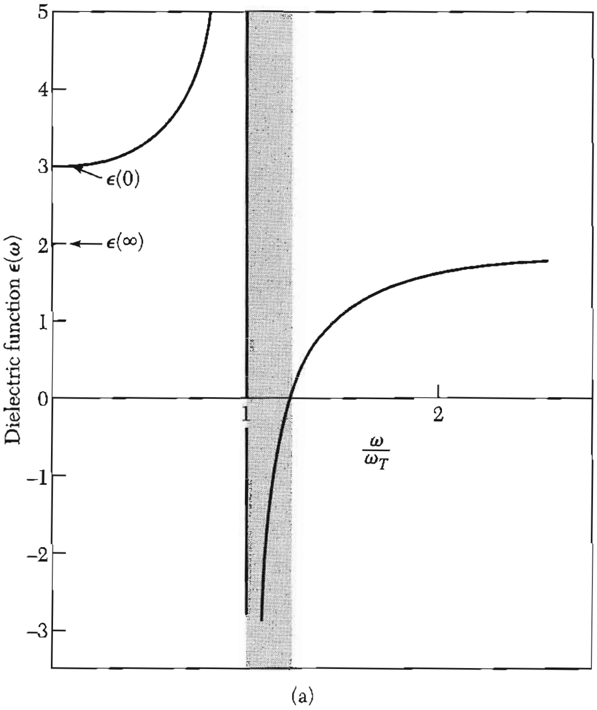


Figure 13a Plot of $\epsilon(\omega)$ from (60) for $\epsilon(\infty) = 2$ and $\epsilon(0) = 3$. The dielectric constant is negative between $\omega = \omega_T$ and $\omega_L = (3/2)^{1/2}\omega_T$; that is, between the pole (infinity) of $\epsilon(\omega)$ and the zero of $\epsilon(\omega)$. Incident electromagnetic waves of frequencies in the shaded regions $\omega_T < \omega < \omega_L$ will not propagate in the medium, but will be reflected at the boundary.

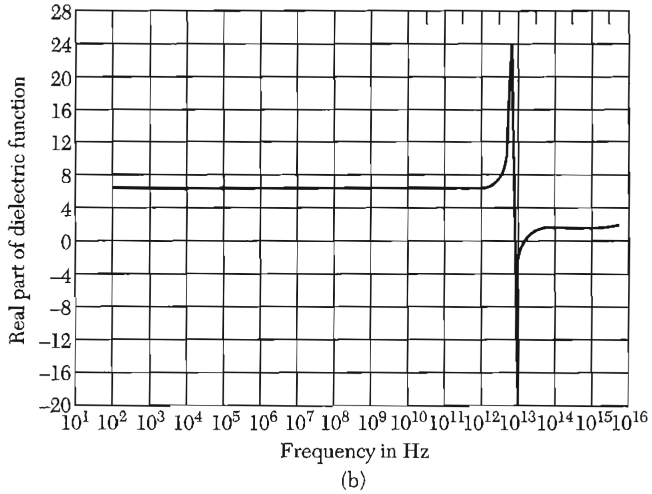
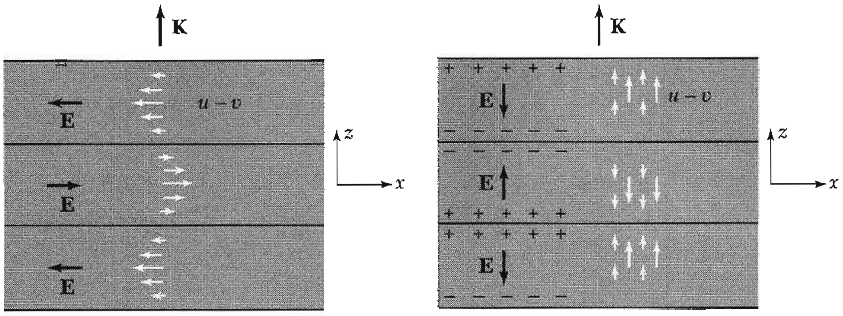


Figure 13b Dielectric function (real part) of SrF_2 measured over a wide frequency range, exhibiting the decrease of the ionic polarizability at high frequencies. (A. von Hippel.)



TO phonon

LO phonon

Figure 14 Relative displacements of the positive and negative ions at one instant of time for a wave in an optical mode traveling along the z axis. The planes of nodes (zero displacement) are shown; for long wavelength phonons the nodal planes are separated by many planes of atoms. In the transverse optical phonon mode the particle displacement is perpendicular to the wavevector $\mathbf{K}$; the macroscopic electric field in an infinite medium will lie only in the $\pm x$ direction for the mode shown, and by the symmetry of the problem $\partial E_x/\partial x = 0$. It follows that div $\mathbf{E} = 0$ for a TO phonon. In the longitudinal optical phonon mode the particle displacements and hence the dielectric polarization $\mathbf{P}$ are parallel to the wavevector. The macroscopic electric field $\mathbf{E}$ satisfies $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = 0$ in CGS or $\epsilon_0\mathbf{E} + \mathbf{P} = 0$ in SI; by symmetry $\mathbf{E}$ and $\mathbf{P}$ are parallel to the z axis, and $\partial E_z/\partial z \neq 0$. Thus div $\mathbf{E} \neq 0$ for an LO phonon, and $\epsilon(\omega)$ div $\mathbf{E}$ is zero only if $\epsilon(\omega) = 0$.

Waves do not propagate in the frequency region for which $\epsilon(\omega)$ is negative, between its pole at $\omega = \omega_T$ and its zero at $\omega = \omega_L$, as in Fig. 13. For negative ϵ, waves do not propagate because then K is imaginary for real ω, and $\exp(iKx) \rightarrow \exp(-|K|x)$, damped in space. The zero of $\epsilon(\omega)$, by our earlier argument, is the LO frequency at low K, Fig. 14. Just as with the plasma frequency ω_p, the frequency ω_L has two meanings, one as the LO frequency at low K and the other as the upper cutoff frequency of the forbidden band for propagation of an electromagnetic wave. The value of ω_L is identical at both frequencies.

LST Relation

We write (61) as

$$\boxed{\frac{\omega_L^2}{\omega_T^2} = \frac{\epsilon(0)}{\epsilon(\infty)}} \, , \tag{62}$$

where $\epsilon(0)$ is the static dielectric constant and $\epsilon(\infty)$ is the high-frequency limit of the dielectric function, defined to include the core electron contribution. This result is the Lyddane-Sachs-Teller relation. The derivation assumed a cubic crystal with two atoms per primitive cell. For soft modes with $\omega_T \rightarrow 0$ we see that $\epsilon(0) \rightarrow \infty$, a characteristic of ferroelectricity.

Undamped electromagnetic waves with frequencies within the gap cannot propagate in a thick crystal. The reflectivity of a crystal surface is expected to be high in this frequency region, as in Fig. 15.

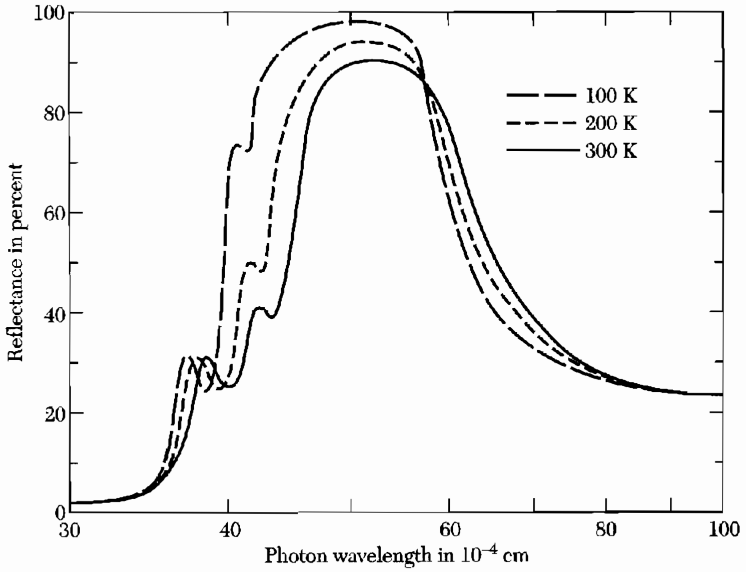


Figure 15 Reflectance of a crystal of NaCl at several temperatures, versus wavelength. The nominal values of ω_L and ω_T at room temperature correspond to wavelengths of 38 and 61 × 10^{-4} cm, respectively. (After A. Mitsuishi et al.)

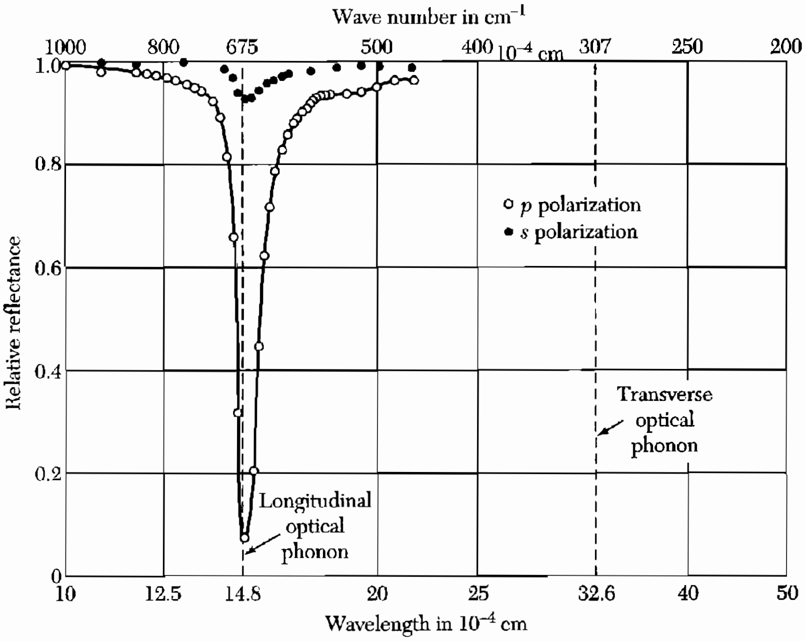


Figure 16 Reflectance versus wavelength of a LiF film backed by silver, for radiation incident near 30°. The longitudinal optical phonon absorbs strongly the radiation polarized (p) in the plane normal to the film, but absorbs hardly at all the radiation polarized (s) parallel to the film. (After D. W. Berreman.)

For films of thickness less than a wavelength the situation is changed. Because for frequencies in the gap the wave attenuates as $\exp(-|K|x)$, it is possible for the radiation to be transmitted through a film for the small values of $|K|$ near ω_L, but for the large values of $|K|$ near ω_T the wave will be reflected. By reflection at nonnormal incidence the frequency ω_L of longitudinal optical phonons can be observed, as in Fig. 16.

Experimental values of $\epsilon(0)$, $\epsilon(\infty)$, and ω_T are given in Table 3, with values of ω_L calculated using the LST relation, Eq. (62). We compare values of

Table 3 Lattice parameters, chiefly at 300 K

Crystal	Static dielectric constant $\epsilon(0)$	Optical dielectric constant $\epsilon(\infty)$	ω_T, in $10^{13}\,s^{-1}$ experimental	ω_L, in $10^{13}\,s^{-1}$ LST relation
LiH	12.9	3.6	11.	21.
LiF	8.9	1.9	5.8	12.
LiCl	12.0	2.7	3.6	7.5
LiBr	13.2	3.2	3.0	6.1
NaF	5.1	1.7	4.5	7.8
NaCl	5.9	2.25	3.1	5.0
NaBr	6.4	2.6	2.5	3.9
KF	5.5	1.5	3.6	6.1
KCl	4.85	2.1	2.7	4.0
KI	5.1	2.7	1.9	2.6
RbF	6.5	1.9	2.9	5.4
RbI	5.5	2.6	1.4	1.9
CsCl	7.2	2.6	1.9	3.1
CsI	5.65	3.0	1.2	1.6
TlCl	31.9	5.1	1.2	3.0
TlBr	29.8	5.4	0.81	1.9
AgCl	12.3	4.0	1.9	3.4
AgBr	13.1	4.6	1.5	2.5
MgO	9.8	2.95	7.5	14.
GaP	10.7	8.5	6.9	7.6
GaAs	13.13	10.9	5.1	5.5
GaSb	15.69	14.4	4.3	4.6
InP	12.37	9.6	5.7	6.5
InAs	14.55	12.3	4.1	4.5
InSb	17.88	15.6	3.5	3.7
SiC	9.6	6.7	14.9	17.9
C	5.5	5.5	25.1	25.1
Si	11.7	11.7	9.9	9.9
Ge	15.8	15.8	5.7	5.7

ω_L/ω_T obtained by inelastic neutron scattering with experimental values of $[\epsilon(0)/\epsilon(\infty)]^{1/2}$ obtained by dielectric measurements:

	NaI	KBr	GaAs
ω_L/ω_T	1.44 ± 0.05	1.39 ± 0.02	1.07 ± 0.02
$[\epsilon(0)/\epsilon(\infty)]^{1/2}$	1.45 ± 0.03	1.38 ± 0.03	1.08

The agreement with the LST relation is excellent.

ELECTRON-ELECTRON INTERACTION

Fermi Liquid

Because of the interaction of the conduction electrons with each other through their electrostatic interaction, the electrons suffer collisions. Further, a moving electron causes an inertial reaction in the surrounding electron gas, thereby increasing the effective mass of the electron. The effects of electron-electron interactions are usually described within the framework of the Landau theory of a Fermi liquid. The object of the theory is to give a unified account of the effect of interactions. A Fermi gas is a system of noninteracting fermions; the same system with interactions is a Fermi liquid.

Landau's theory gives a good account of the low-lying single particle excitations of the system of interacting electrons. These single particle excitations are called **quasiparticles**; they have a one-to-one correspondence with the single particle excitations of the free-electron gas. A quasiparticle may be thought of as a single particle accompanied by a distortion cloud in the electron gas. One effect of the coulomb interactions between electrons is to change the effective mass of the electron; in the alkali metals the increase is roughly of the order of 25 percent.

Electron-Electron Collisions. It is an astonishing property of metals that conduction electrons, although crowded together only 2 Å apart, travel long distances between collisions with each other. The mean free paths for electron-electron collisions are longer than 10^4 Å at room temperature and longer than 10 cm at 1 K.

Two factors are responsible for these long mean free paths, without which the free-electron model of metals would have little value. The most powerful factor is the exclusion principle (Fig. 17), and the second factor is the screening of the coulomb interaction between two electrons.

We show how the exclusion principle reduces the collision frequency of an electron that has a low excitation energy ϵ_1 outside a filled Fermi sphere (Fig. 18). We estimate the effect of the exclusion principle on the two-body collision $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3} + \mathbf{4}$ between an electron in the excited orbital **1** and an electron in the filled orbital **2** in the Fermi sea. It is convenient to refer all energies to the Fermi level μ taken as the zero of energy; thus ϵ_1 will be

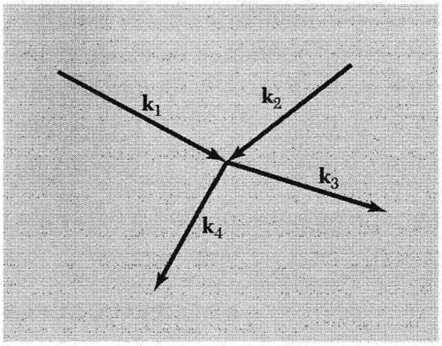


Figure 17 A collision between two electrons of wavevectors $\mathbf{k}_1$ and $\mathbf{k}_2$. After the collision the particles have wavevectors $\mathbf{k}_3$ and $\mathbf{k}_4$. The Pauli exclusion principle allows collisions only to final states $\mathbf{k}_3$, $\mathbf{k}_4$ which were vacant before the collision.

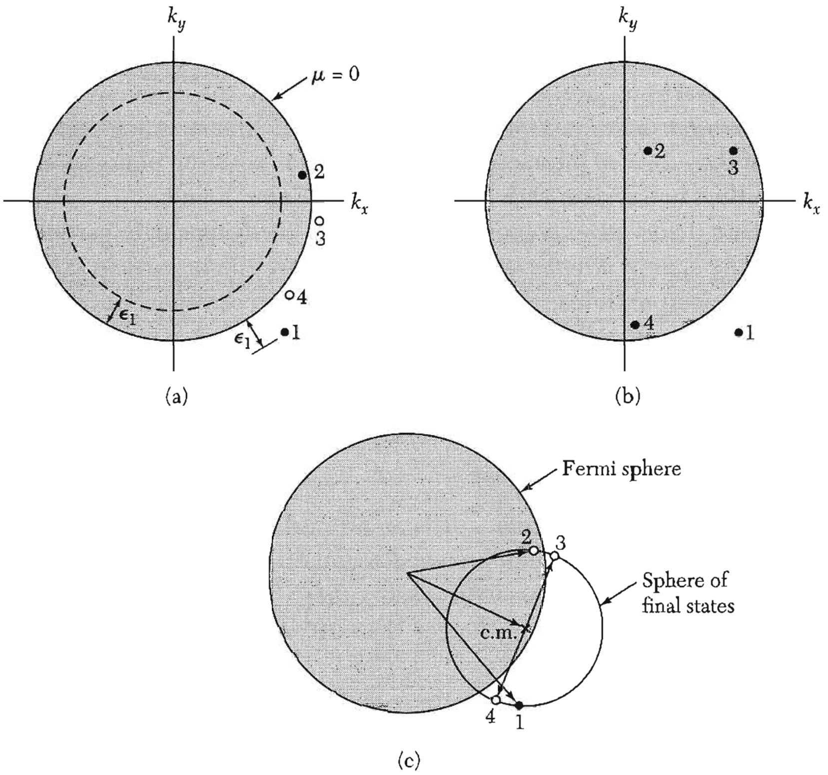


Figure 18 In (a) the electrons in initial orbitals 1 and 2 collide. If the orbitals 3 and 4 are initially vacant, the electrons 1 and 2 can occupy orbitals 3 and 4 after the collision. Energy and momentum are conserved. In (b) the electrons in initial orbitals 1 and 2 have no vacant final orbitals available that allow energy to be conserved in the collision. Orbitals such as 3 and 4 would conserve energy and momentum, but they are already filled with other electrons. In (c) we have denoted with × the wavevector of the center of mass of **1** and **2**. All pairs of orbitals 3 and 4 conserve momentum and energy if they lie at opposite ends of a diameter of the small sphere. The small sphere was drawn from the center of mass to pass through 1 and 2. But not all pairs of points 3, 4 are allowed by the exclusion principle, for both 3, 4 must lie outside the Fermi sphere; the fraction allowed is $\approx \epsilon_1/\epsilon_F$.

positive and ϵ_2 will be negative. Because of the exclusion principle the orbitals **3** and **4** of the electrons after collision must lie outside the Fermi sphere, all orbitals within the sphere being already occupied; thus both energies ϵ_3, ϵ_4 must be positive referred to zero on the Fermi sphere.

The conservation of energy requires that $|\epsilon_2| < \epsilon_1$, for otherwise $\epsilon_3 + \epsilon_4 = \epsilon_1 + \epsilon_2$ could not be positive. This means that collisions are possible only if the orbital **2** lies within a shell of thickness ϵ_1 within the Fermi surface, as in Fig. 18a. Thus the fraction $\approx\epsilon_1/\epsilon_F$ of the electrons in filled orbitals provides a suitable target for electron **1**. But even if the target electron **2** is in the suitable energy shell, only a small fraction of the final orbitals compatible with conservation of energy and momentum are allowed by the exclusion principle. This gives a second factor of ϵ_1/ϵ_F.

In Fig. 18c we show a small sphere on which all pairs of orbitals **3**, **4** at opposite ends of a diameter satisfy the conservation laws, but collisions can occur only if both orbitals **3**, **4** lie outside the Fermi sea. The product of the two fractions is $(\epsilon_1/\epsilon_F)^2$. If ϵ_1 corresponds to 1 K and ϵ_F to 5×10^4 K, we have $(\epsilon_1/\epsilon_F)^2 \approx 4 \times 10^{-10}$, the factor by which the exclusion principle reduces the collision rate.

The argument is not changed for a thermal distribution of electrons at a low temperature such that $k_BT \ll \epsilon_F$. We replace ϵ_1 by the thermal energy $\approx k_BT$, and now the rate at which electron-electron collisions take place is reduced below the classical value by $(k_BT/\epsilon_F)^2$, so that the effective collision cross section σ is

$$\sigma \approx (k_BT/\epsilon_F)^2\sigma_0 \ , \tag{63}$$

where σ_0 is the cross section for the electron-electron interaction.

The interaction of one electron with another has a range of the order of the screening length $1/k_s$ as in (34). Numerical calculations give the effective cross section with screening for collisions between electrons as of the order of 10^{-15} cm^2 or 10 Å^2 in typical metals. The effect of the electron-gas background in electron-electron collisions is to reduce σ_0 below the value expected from the Rutherford scattering equation for the unscreened coulomb potential. However, much the greater reduction in the cross section is caused by the Pauli factor $(k_BT/\epsilon_F)^2$.

At room temperature in a typical metal k_BT/ϵ_F is $\sim 10^{-2}$, so that $\sigma \sim 10^{-4}\sigma_0 \sim 10^{-19}$ cm^2. The mean free path for electron-electron collisions is $\ell \approx 1/n\sigma \sim 10^{-4}$ cm at room temperature. This is longer than the mean free path due to electron-phonon collisions by at least a factor of 10, so that at room temperature collisions with phonons are likely to be dominant. At liquid helium temperatures a contribution proportional to T^2 has been found in the resistivity of a number of metals, consistent with the form of the electron-electron scattering cross section (63). The mean free path of electrons in indium at 2 K is of the order of 30 cm, as expected from (63). Thus the Pauli principle explains one of the central questions of the theory of metals: how do the electrons travel long distances without colliding with each other?

ELECTRON-PHONON INTERACTION: POLARONS

The most common effect of the electron-phonon interaction is seen in the temperature dependence of the electrical resistivity, which for pure copper is 1.55 microhm-cm at 0°C and 2.28 microhm-cm at 100°C. The electrons are scattered by the phonons, and the higher the temperature, the more phonons there are and hence more scattering. Above the Debye temperature the number of thermal phonons is roughly proportional to the absolute temperature, and we find that the resistivity increases approximately as the absolute temperature in any reasonably pure metal in this temperature region.

A more subtle effect of the electron-phonon interaction is the apparent increase in electron mass that occurs because the electron drags the heavy ion cores along with it. In an insulator the combination of the electron and its strain field is known as a **polaron**, Fig. 19. The effect is large in ionic crystals because of the strong coulomb interaction between ions and electrons. In covalent crystals the effect is weak because neutral atoms have only a weak interaction with electrons.

The strength of the electron-lattice interaction is measured by the dimensionless coupling constant α given by

$$\frac{1}{2}\alpha = \frac{\text{deformation energy}}{\hbar\omega_L} , \tag{64}$$

where ω_L is the longitudinal optical phonon frequency near zero wavevector. We view $\frac{1}{2}\alpha$ as "the number of phonons which surround a slow-moving electron in a crystal."

Values of α deduced from diverse experiments and theory are given in Table 4, after F. C. Brown. The values of α are high in ionic crystals and low in covalent crystals. The values of the effective mass m^*_{pol} of the polaron are from cyclotron resonance experiments. The values given for the band effective mass m^* were calculated from m^*_{pol}. The last row in the table gives the factor m^*_{pol}/m^* by which the band mass is increased by the deformation of the lattice.

Theory relates the effective mass of the polaron m^*_{pol} to the effective band mass m^* of the electron in the undeformed lattice by the relation

$$m^*_{\text{pol}} \cong m^* \left(\frac{1 - 0.0008\alpha^2}{1 - \frac{1}{6}\alpha + 0.0034\alpha^2} \right) ; \tag{65}$$

for $\alpha \ll 1$ this is approximately $m^*(1 + \frac{1}{6}\alpha)$. Because the coupling constant α is always positive, the polaron mass is greater than the bare mass, as we expect from the inertia of the ions.

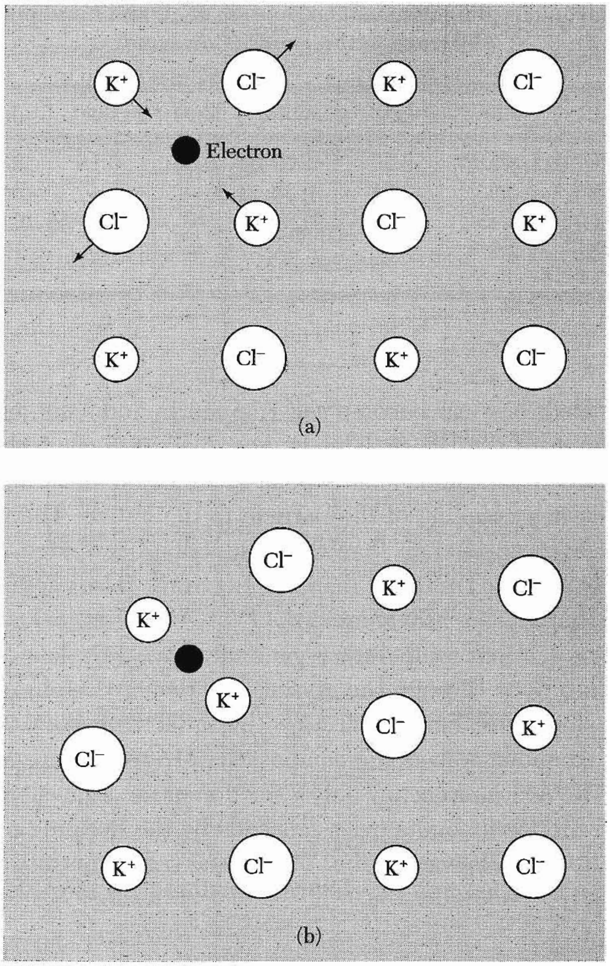


Figure 19 The formation of a polaron. (a) A conduction electron is shown in a rigid lattice of an ionic crystal, KCl. The forces on the ions adjacent to the electron are shown. (b) The electron is shown in an elastic or deformable lattice. The electron plus the associated strain field is called a polaron. The displacement of the ions increases the effective inertia and, hence, the effective mass of the electron; in KCl the mass is increased by a factor of 2.5 with respect to the band theory mass in a rigid lattice. In extreme situations, often with holes, the particle can become self-trapped (localized) in the lattice. In covalent crystals the forces on the atoms from the electron are weaker than in ionic crystals, so that polaron deformations are small in covalent crystals.

It is common to speak of large and small polarons. The electron associated with a large polaron moves in a band, but the mass is slightly enhanced; these are the polarons we have discussed above. The electron associated with a small polaron spends most of its time trapped on a single ion. At high temperatures the electron moves from site to site by thermally activated hopping; at low temperatures the electron tunnels slowly through the crystal, as if in a band of large effective mass.

Table 4 Polaron coupling constants α, masses m^*_{pol}, and band masses m^* for electrons in the conduction band

Crystal	KCl	KBr	AgCl	AgBr	ZnO	PbS	InSb	GaAs
α	3.97	3.52	2.00	1.69	0.85	0.16	0.014	0.06
m^*_{pol}/m	1.25	0.93	0.51	0.33	—	—	0.014	—
m^*/m	0.50	0.43	0.35	0.24	—	—	0.014	—
m^*_{pol}/m^*	2.5	2.2	1.5	1.4	—	—	1.0	—

Holes or electrons can become self-trapped by inducing an asymmetric local deformation of the lattice. This is most likely to occur when the band edge is degenerate and the crystal is polar (such as an alkali halide or silver halide), with *strong coupling of the particle to the lattice.* The valence band edge is more often degenerate than the conduction band edge, so that holes are more likely to be self-trapped than are electrons. Holes appear to be self-trapped in all the alkali and silver halides.

Ionic solids at room temperature generally have very low conductivities for the motion of ions through the crystal, less than 10^{-6} (ohm-cm)$^{-1}$, but a family of compounds has been reported with conductivities of 0.2 (ohm-cm)$^{-1}$ at 20°C. The compounds have the composition MAg_4I_5, where M denotes K, Rb, or NH_4. The Ag^+ ions occupy only a fraction of the equivalent lattice sites available, and the ionic conductivity proceeds by the hopping of a silver ion from one site to a nearby vacant site. The crystal structures also have parallel open channels.

PEIERLS INSTABILITY OF LINEAR METALS

Consider a one-dimensional metal with an electron gas filling all conduction band orbitals out to the wavevector k_F, at absolute zero of temperature. Peierls suggested that such a linear metal is unstable with respect to a static lattice deformation of wavevector $G = 2k_F$. Such a deformation creates an energy gap at the Fermi surface, thereby lowering the energy of electrons below the energy gap, Fig. 20. The deformation proceeds until limited by the increase of elastic energy; the equilibrium deformation Δ is given by the root of

$$\frac{d}{d\Delta}(E_{\text{electronic}} + E_{\text{elastic}}) = 0 \ . \tag{66}$$

Consider the elastic strain $\Delta \cos 2k_Fx$. The spatial-average elastic energy per unit length is $E_{\text{elastic}} = \frac{1}{2}C\Delta^2\langle\cos^2 2k_Fx\rangle = \frac{1}{4}C\Delta^2$, where C is the force constant of the linear metal. We next calculate $E_{\text{electronic}}$. Suppose that the ion

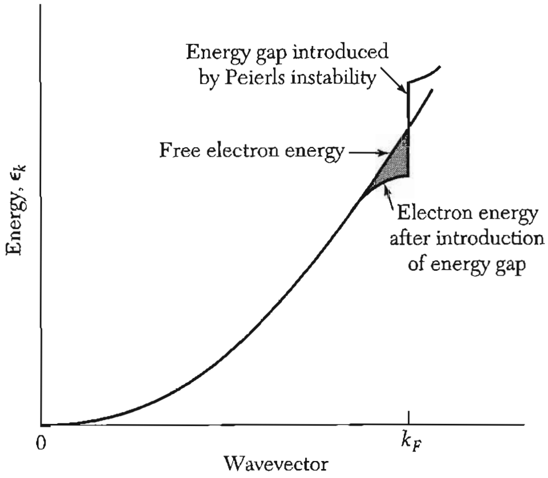


Figure 20 Peierls instability. Electrons with wavevectors near the Fermi surface have their energy lowered by a lattice deformation.

contribution to the lattice potential seen by a conduction electron is proportional to the deformation: $U(x) = 2A\Delta \cos 2k_Fx$. From (7.51) we have

$$\epsilon_K = (\hbar^2/2m)(k_F^2 + K^2) \pm [4(\hbar^2k_F^2/2m)(\hbar^2K^2/2m) + A^2\Delta^2]^{1/2} \ . \tag{67}$$

It is convenient to define

$$x_K \equiv \hbar^2K^2/m \ ; \quad x_F \equiv \hbar^2k_F^2/m \ ; \quad x \equiv \hbar^2Kk_F/m \ .$$

We retain the − sign in (67) and form

$$\frac{d\epsilon_K}{d\Delta} = \frac{-A^2\Delta}{(x_Fx_K + A^2\Delta^2)^{1/2}} \ ,$$

whence, with dK/π as the number of orbitals per unit length,

$$\frac{dE_{\text{electronic}}}{d\Delta} = \frac{2}{\pi}\int_0^{k_F} dK\,\frac{d\epsilon_K}{d\Delta} = -(2A^2\Delta/\pi)\int_0^{k_F}\frac{dK}{(x_Fx_K + A^2\Delta^2)^{1/2}}$$

$$= -(2A^2\Delta/\pi)(k_F/x_F)\int_0^{x_F}\frac{dx}{(x^2 + A^2\Delta^2)^{1/2}} = -(2A^2\Delta/\pi)(k_F/x_F)\sinh^{-1}(x_F/A\Delta) \ .$$

We put it all together. The equilibrium deformation is the root of

$$\tfrac{1}{2}C\Delta - (2A^2m\Delta/\pi\hbar^2k_F)\sinh^{-1}(\hbar^2k_F^2/mA\Delta) = 0 \ .$$

The root Δ that corresponds to the minimum energy is given by

$$\hbar^2k_F^2/mA\Delta = \sinh(-\hbar^2k_F\pi C/4mA^2) \ , \tag{68}$$

whence

$$|A|\Delta \simeq (2\hbar^2k_F^2/m)\exp(-\hbar^2k_F\pi C/4mA^2) \ , \tag{69}$$

if the argument of the sinh in (68) is $\gg 1$. We assume $k_F \leq \frac{1}{2}k_{\max}$.

The result is of the form of the energy gap equation in the BCS theory of superconductivity, Chapter 10. The deformation Δ is a collective effect of all the electrons. If we set $W = \hbar^2 k_F^2/2m$ = conduction band width; $N(0) = 2m/\pi\hbar^2 k_F$ = density of orbitals at Fermi level; $V = 2A^2/C$ = effective electron-electron interaction energy, then we can write (69) as

$$|A|\Delta \simeq 4W \exp[-1/N(0)V] \ , \tag{70}$$

which is analogous to the BCS energy gap equation. An example of a Peierls insulator is TaS_3.

SUMMARY
(In CGS units)

- The dielectric function may be defined as

  $$\epsilon(\omega,\mathbf{K}) = \frac{\rho_{\mathrm{ext}}(\omega,\mathbf{K})}{\rho_{\mathrm{ext}}(\omega,\mathbf{K}) + \rho_{\mathrm{ind}}(\omega,\mathbf{K})} \ ,$$

  in terms of the applied and induced charge density components at $\omega,\mathbf{K}$.

- The plasma frequency $\bar{\omega}_p = [4\pi ne^2/\epsilon(\infty)m]^{1/2}$ is the frequency of the uniform collective longitudinal oscillation of the electron gas against a background of fixed positive ions. It is also the low frequency cutoff for propagation of transverse electromagnetic waves in the plasma.
- The poles of the dielectric function define ω_T and the zeroes define ω_L.
- In a plasma the coulomb interaction is screened; it becomes $(q/r)\exp(-k_s r)$, where the screening length $1/k_s = (\epsilon_F/6\pi n_0 e^2)^{1/2}$.
- A metal-insulator transition may occur when the nearest-neighbor separation a becomes of the order of $4a_0$, where a_0 is the radius of the first Bohr orbit in the insulator. The metallic phase exists at smaller values of a.
- A polariton is a quantum of the coupled TO phonon-photon fields. The coupling is assured by the Maxwell equations. The spectral region $\omega_T < \omega < \omega_L$ is forbidden to electromagnetic wave propagation.
- The Lyddane-Sachs-Teller relation is $\omega_L^2/\omega_T^2 = \epsilon(0)/\epsilon(\infty)$.

Problems

1. ***Surface plasmons.*** Consider a semi-infinite plasma on the positive side of the plane $z = 0$. A solution of Laplace's equation $\nabla^2\varphi = 0$ in the plasma is $\varphi_i(x,z) = A\cos kx\, e^{-kz}$, whence $E_{zi} = kA\cos kx\, e^{-kz}$; $E_{xi} = kA\sin kx\, e^{-kz}$. (a)Show that in the vacuum $\varphi_0(x,z) = A\cos kx\, e^{kz}$ for $z < 0$ satisfies the boundary condition that the tangential component of $\mathbf{E}$ be continuous at the boundary; that is, find E_{x0}. (b) Note that $\mathbf{D}_i = \epsilon(\omega)\mathbf{E}_i$; $\mathbf{D}_o = \mathbf{E}_o$. Show that the boundary condition that the

normal component of **D** be continuous at the boundary requires that $\epsilon(\omega) = -1$, whence from (10) we have the Stern-Ferrell result:

$$\omega_s^2 = \tfrac{1}{2}\omega_p^2 \tag{71}$$

for the frequency ω_s of a surface plasma oscillation.

2. ***Interface plasmons.*** We consider the plane interface $z = 0$ between metal 1 at $z > 0$ and metal 2 at $z < 0$. Metal 1 has bulk plasmon frequency ω_{p1}; metal 2 has ω_{p2}. The dielectric constants in both metals are those of free-electron gases. Show that surface plasmons associated with the interface have the frequency

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

3. ***Alfvén waves.*** Consider a solid with an equal concentration n of electrons of mass m_e and holes of mass m_h. This situation may arise in a semimetal or in a compensated semiconductor. Place the solid in a uniform magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$. Introduce the coordinate $\xi = x + iy$ appropriate for circularly polarized motion, with ξ having time dependence $e^{-i\omega t}$. Let $\omega_e = eB/m_ec$ and $\omega_h = eB/m_hc$. (a) In CGS units, show that $\xi_e = eE^+/m_e\omega(\omega + \omega_e)$; $\xi_h = -eE^+/m_h\omega(\omega - \omega_h)$ are the displacements of the electrons and holes in the electric field $E^+ e^{-i\omega t} = (E_x + iE_y) e^{-i\omega t}$. (b) Show that the dielectric polarization $P^+ = ne(\xi_h - \xi_e)$ in the regime $\omega \ll \omega_e, \omega_h$ may be written as $P^+ = nc^2(m_h + m_e)E^+/B^2$, and the dielectric function $\epsilon(\omega) = \epsilon_l + 4\pi P^+/E^+ = \epsilon_l + 4\pi c^2\rho/B^2$, where ϵ_l is the dielectric constant of the host lattice and $\rho = n(m_e + m_h)$ is the mass density of the carriers. If ϵ_l may be neglected, the dispersion relation $\omega^2\epsilon(\omega) = c^2K^2$ becomes, for electromagnetic waves propagating in the z direction, $\omega^2 = (B^2/4\pi\rho)K^2$. Such waves are known as Alfvén waves; they propagate with the constant velocity $B/(4\pi\rho)^{1/2}$. If $B = 10$ kG; $n = 10^{18}$ cm^{-3}; $m = 10^{-27}$ g, the velocity is $\sim 10^8$ cm s^{-1}. Alfvén waves have been observed in semimetals and in electron-hole drops in germanium (Chapter 15).

4. ***Helicon waves.*** (a) Employ the method of Problem 3 to treat a specimen with only one carrier type, say holes in concentration p, and in the limit $\omega \ll \omega_h = eB/m_hc$. Show that $\epsilon(\omega) = 4\pi pe^2/m_h\omega\omega_h$, where $D^+(\omega) = \epsilon(\omega)E^+(\omega)$. The term ϵ_l in ϵ has been neglected. (b) Show further that the dispersion relation becomes $\omega = (Bc/4\pi pe)K^2$, the helicon dispersion relation, in CGS. For $K = 1$ cm^{-1} and $B = 1000$ G, estimate the helicon frequency in sodium metal. (The frequency is negative; with circular-polarized modes the sign of the frequency refers to the sense of the rotation.)

5. ***Plasmon mode of a sphere.*** The frequency of the uniform plasmon mode of a sphere is determined by the depolarization field $\mathbf{E} = -4\pi\mathbf{P}/3$ of a sphere, where the polarization $\mathbf{P} = -ne\mathbf{r}$, with $\mathbf{r}$ as the average displacement of the electrons of concentration n. Show from $\mathbf{F} = m\mathbf{a}$ that the resonance frequency of the electron gas is $\omega_0^2 = 4\pi ne^2/3m$. Because all electrons participate in the oscillation, such an excitation is called a collective excitation or collective mode of the electron gas.

6. ***Magnetoplasma frequency.*** Use the method of Problem 5 to find the frequency of the uniform plasmon mode of a sphere placed in a constant uniform magnetic field **B**. Let **B** be along the z axis. The solution should go to the cyclotron

frequency $\omega_c = eB/mc$ in one limit and to $\omega_0 = (4\pi ne^2/3m)^{1/2}$ in another limit. Take the motion in the xy plane.

7. ***Photon branch at low wavevector.*** (a) Find what (56) becomes when $\epsilon(\infty)$ is taken into account. (b) Show that there is a solution of (55) which at low wavevector is $\omega = cK/\sqrt{\epsilon(0)}$, as expected for a photon in a crystal of refractive index $n^2 = \epsilon$.

8. ***Plasma frequency and electrical conductivity.*** An organic conductor has been found by optical studies to have $\omega_p = 1.80 \times 10^{15}\ \mathrm{s}^{-1}$ for the plasma frequency, and $\tau = 2.83 \times 10^{-15}$ s for the electron relaxation time at room temperature. (a) Calculate the electrical conductivity from these data. The carrier mass is not known and is not needed here. Take $\epsilon(\infty) = 1$. Convert the result to units $(\Omega\ \mathrm{cm})^{-1}$. (b) From the crystal and chemical structure, the conduction electron concentration is $4.7 \times 10^{21}\ \mathrm{cm}^{-3}$. Calculate the electron effective mass m^*.

9. ***Bulk modulus of the Fermi gas.*** Show that the contribution of the kinetic energy to the bulk modulus of the electron gas at absolute zero is $B = \frac{1}{3}nmv_F^2$. It is convenient to use (6.60). We can use our result for B to find the velocity of sound, which in a compressible fluid is $v = (B/\rho)^{1/2}$, where $v = (m/3M)^{1/2}v_F$, in agreement with (46). These estimates neglect attractive interactions.

10. ***Response of electron gas.*** It is sometimes stated erroneously in books on electromagnetism that the static conductivity σ, which in gaussian units has the dimensions of a frequency, measures the response frequency of a metal to an electric field suddenly applied. Criticize this statement as it might apply to copper at room temperature. The resistivity is $\sim 1\,\mu$ohm-cm; the electron concentration is $8 \times 10^{22}\ \mathrm{cm}^{-3}$; the mean free path is ~400 Å; the Fermi velocity is $1.6 \times 10^8\ \mathrm{cm\ s}^{-1}$. You will not necessarily need all these data. Give the order of magnitude of the three frequencies σ, ω_p, and $1/\tau$ that might be relevant in the problem. Set up and solve the problem of the response $x(t)$ of the system to an electric field $E(t < 0) = 0$; $E(t > 0) = 1$. The system is a sheet of copper; the field is applied normal to the sheet. Include the damping. Solve the differential equation by elementary methods.

*11. ***Gap plasmons and the van der Waals interaction.*** Consider two semi-infinite media with plane surfaces $z = 0, d$. The dielectric function of the identical media is $\epsilon(\omega)$. Show that for surface plasmons symmetrical with respect to the gap the frequency must satisfy $\epsilon(\omega) = -\tanh(Kd/2)$, where $K^2 = k_x^2 + k_y^2$. The electric potential will have the form

$$\varphi = f(z)\exp(ik_xx + ik_yy - i\omega t)\ .$$

Look for nonretarded solution—that is, solutions of the Laplace equation rather than of the wave equation. The sum of the zero-point energy of all gap modes is the nonretarded part of the van der Waals attraction between the two specimens—see N. G. van Kampen, B. R. A. Nijboer, and K. Schram, Physics Letters **26A**, 307 (1968).

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*This problem is somewhat difficult.