obtain the lattice constants reported in this article.

The difference between the lattice constants of the end member LiH and LiD is 0.0146 Å, one of the largest known for systems of this type. Several attempts[4,7] have been made to calculate this difference theoretically using the Einstein and Debye models, but poor agreement has been obtained.

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Magnetoplasma Surface Waves in Metals*

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The effect of a dc magnetic field of arbitrary magnitude and orientation on surface plasmons in a metal or degenerate semiconductor is studied in the "nonretarded" limit.

Recently, there has been a reawakening of interest in the problem of surface plasmons[1] in metals and degenerate semiconductors. The frequency of a surface plasmon depends in an essential way on the dielectric function of the solid. Since the dielectric function is strongly affected by the presence of a dc magnetic field, it is interesting to inquire how such a field affects the surface plasmons. Such knowledge could be of considerable value in the experimental study of surface plasmons, particularly in semiconductors where the plasma frequency and the electron cyclotron frequency can easily be of comparable magnitude. In this paper we investigate the dependence on orientation and strength of an applied magnetic field of surface plasma waves in the "nonretarded" or short-wavelength limit.[2]

We consider a model consisting of a free-electron gas moving through a medium of background dielectric constant ϵ_L and bounded by an insulator of dielectric constant ϵ' ($\epsilon'=1$ if the solid is bounded by vacuum). We choose the z axis of a Cartesian coordinate system normal to the interface, and let the insulator fill the space $z<0$. A dc magnetic field $\vec{B}_0=(B_{ox}, B_{oy}, B_{oz})$ is oriented in an arbitrary direction. Without loss of generality we can choose the propagation vector $q=(0, q_y, q_z)$ to lie in the yz plane. The electron gas is described by a dielectric tensor[2]

$$\epsilon_{ij}(\omega)=\epsilon_L\delta_{ij}-\omega^{-2}\omega_p^2(\omega^2-\omega_c^2)^{-1} \times(\omega^2\delta_{ij}-\omega_{ci}\omega_{cj}-i\delta_{ijk}\omega_{ck}\omega)\ . \quad (1)$$

In this equation ϵ_L is the background dielectric constant of the lattice. The plasma frequency $\omega_p=(4\pi ne^2/m)^{1/2}$, where n is the electron concentration and the cyclotron-frequency vector $\vec{\omega}_c$ is defined by $\vec{\omega}_c=(e/m)\vec{B}_0$. The symbol δ_{ij} is the Kronecker δ, and δ_{ijk} is the third-rank antisymmetric tensor defined by

$$\begin{aligned}\delta_{ijk}&=+1 \quad \text{if } ijk \text{ is an even permutation}\\ &=-1 \quad \text{if } ijk \text{ is an odd permutation}\\ &=0 \quad \text{otherwise.}\end{aligned} \quad (2)$$

The surface plasmon is a solution of the wave equation

$$\begin{pmatrix} \epsilon_{xx}-\omega^{-2}q^2 & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy}-\omega^{-2}q_z^2 & \epsilon_{yz}+\omega^{-2}q_yq_z \\ \epsilon_{zx} & \epsilon_{zy}+\omega^{-2}q_yq_z & \epsilon_{zz}-\omega^{-2}q_y^2 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} = 0 , \tag{3}$$

which is obtained from the Maxwell equations. In the limit $q_y \gg \omega$ considered in this paper it is permissible to neglect the off-diagonal components[3] ϵ_{xy}, ϵ_{xz}, ϵ_{yx}, and ϵ_{zx}. The secular equation obtained in this approximation can be written

$$(q^2-\omega^2\epsilon_{xx})[\epsilon_{zz}q_z^2+\epsilon_{yy}q_y^2+(\epsilon_{yz}+\epsilon_{zy})q_yq_z]=0 . \tag{4}$$

The two factors correspond to two independent polarizations. It can easily be demonstrated that the solution of $q^2-\omega^2\epsilon_{xx}=0$ does not lead to a surface plasmon.[4] The second factor in Eq. (4) is a quadratic equation in q_z/q_y whose solution is

$$\frac{q_z}{q_y} = -\frac{\epsilon_{yz}+\epsilon_{zy}}{2\epsilon_{zz}} \pm \left[\left(\frac{\epsilon_{yz}+\epsilon_{zy}}{2\epsilon_{zz}}\right)^2 - \frac{\epsilon_{yy}}{\epsilon_{zz}}\right]^{1/2} . \tag{5}$$

In order to have surface waves which decay exponentially with distance from the surface it is necessary that

$$\epsilon_{yy}\epsilon_{zz} > [\tfrac{1}{2}(\epsilon_{yz}+\epsilon_{zy})]^2 . \tag{6}$$

Therefore, we find it convenient to write the solution in the conductor as

$$\frac{q_z}{q_y} = \mp i\left[\frac{\epsilon_{yy}}{\epsilon_{zz}} - \left(\frac{\epsilon_{yz}+\epsilon_{zy}}{2\epsilon_{zz}}\right)^2\right]^{1/2} - \frac{\epsilon_{yz}+\epsilon_{zy}}{2\epsilon_{zz}} , \tag{7}$$

where the $\mp$ sign is taken, depending upon whether q_y is positive or negative, in such a way as to obtain an exponentially decaying wave in the metal. For convenience we introduce the subscript 1 to denote quantities in the metal and the subscript 0 to denote quantities in the dielectric. The electric field $\vec{E}_1$ in the metal must be an eigenvector of the matrix appearing in Eq. (3), and the magnetic field $\vec{B}_1 = i\omega^{-1}\vec{\nabla}\times\vec{E}_1$. Thus the waves in the metal are of the form

$$\vec{E}_1 = (0,\ E_{y1},\ E_{y1}q_{z1}/q_y)\, e^{-iq_{z1}z}\eta , \qquad \vec{B}_1 = 0 \tag{8}$$

in the nonretarded limit. Here η stands for $e^{i\omega t - iq_y y}$. In the dielectric the waves must be of the form

$$\vec{E}_0 = (0,\ E_{y0},\ E_{y0}q_{z0}/q_y)\, e^{-iq_{z0}z}\eta , \quad \vec{B}_0 = 0 . \tag{9}$$

Furthermore $q_{z0} = \pm iq_y$ is the solution of the secular equation in the dielectric. The boundary conditions at the plane $z=0$ are the standard ones of continuity of the tangential components of $\vec{E}$ and $\vec{H}$ and of the normal components[5] of $\vec{D}$ and $\vec{B}$. Application of the boundary conditions leads to the dispersion relation

$$\pm i\epsilon' = \epsilon_{zz}(q_{z1}/q_y) + \epsilon_{zy} . \tag{10}$$

The real part of ϵ_{zy} exactly cancels the real part of $\epsilon_{zz}(q_{z1}/q_y)$ and Eq. (10) simply becomes

$$\epsilon' + \epsilon_{zz}\left[\frac{\epsilon_{yy}}{\epsilon_{zz}} - \left(\frac{\epsilon_{yz}+\epsilon_{zy}}{2\epsilon_{zz}}\right)^2\right]^{1/2} \pm \frac{\omega_p^2\omega_{cx}\omega^{-1}}{\omega^2-\omega_c^2} = 0 , \tag{11}$$

where the $\pm$ sign corresponds to propagation in the positive-y or negative-y direction. If we introduce the symbol $\lambda = \omega_p^2\omega^{-2}/(\omega^2-\omega_c^2)$, then Eq. (11) can be rewritten

$$\lambda^2\omega^2(\omega^2-\omega_c^2) - \lambda[2\epsilon_L\omega^2 - \epsilon_L(\omega_c^2-\omega_{cx}^2) \pm 2\epsilon'\omega_{cx}\omega] + \epsilon_L^2 - \epsilon'^2 = 0 . \tag{12}$$

For the particular case where $\epsilon_L = \epsilon'$, i.e., the background dielectric constant of the conductor is equal to the dielectric constant of the insulator, this equation simplifies to

$$\omega^2 - \omega_c^2 + (\omega \pm \omega_{cx})^2 = \epsilon_L^{-1}\omega_p^2 . \tag{13}$$

In the absence of a magnetic field, Eq. (13) gives the standard result $\omega^2 = \frac{1}{2}\epsilon_L^{-1}\omega_p^2$; remember that the bulk plasmon occurs at the frequency[6] $\epsilon_L^{-1/2}\omega_p$ so that the surface-wave frequency is smaller by the factor $2^{1/2}$. If the magnetic field is normal to the x axis, the two roots given by Eq. (13) become identical and are given by $\omega = (\epsilon_L^{-1}\omega_p^2 + \omega_c^2)^{1/2}2^{-1/2}$, with $\epsilon_L^{-1}\omega_p^2 > \omega_c^2$. When $\vec{B}_0$ is parallel to the x axis, the two roots corresponding to propagation in the $\pm y$ direction are given by

$$\omega = (\epsilon_L^{-1}\omega_p^2 + \tfrac{1}{2}\omega_c^2)^{1/2}2^{-1/2} \mp \tfrac{1}{2}\omega_c . \tag{14}$$

The dependence of the surface-plasmon frequency on both the orientation and strength of an applied magnetic field is given by Eq. (12) or (13). In experiments in metals and semiconductor where surface plasmons are observed propagating in a particular direction (normal to a grating ruled on the surface) this dependence on orientation and strength of the applied magnetic field should be readily observable and very useful in interpreting experimental results.

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[2]The short-wavelength limit is defined by the inequality $q_y \gg \omega$ (throughout this paper we take the velocity of light equal to unity). However, we describe the metal by a local dielectric tensor $\underline{\epsilon}(\omega)$; this puts an upper bound on the magnitude of q. For the local theory to be valid we

must have $ql \ll 1$, where l is the electron mean free path, and $q \ll \omega_c v_F^{-1}$, where v_F is the Fermi velocity.

[3]It can easily be seen that if $\vec{B}_0$ is not parallel to the x axis, $\lim q_x^2/q_y^2 \neq -1$ as $|q_y| \to \infty$. Therefore all the terms involving q will be much larger than those in which q does not appear. If $\vec{B}_0$ is parallel to the x axis, ϵ_{xy}, ϵ_{xz}, ϵ_{yx}, and ϵ_{zx} vanish, so that our approximation is valid in any case.

[4]A number of special cases, including all retardation effects, have been investigated in detail. This more detailed work will be published elsewhere.

[5]Because we have taken $\underline{\epsilon}(\omega)$ to be independent of q, the magnetic permeability is equal to unity and $\vec{B}$ is equal to $\vec{H}$.

[6]Throughout this paper we have treated ϵ_L as a constant. In fact, Eq. (12) holds without change if $\epsilon_L = \epsilon_\infty(\omega^2 - \omega_L^2) \times (\omega^2 - \omega_T^2)^{-1}$, where ϵ_∞, ω_L, and ω_T are the high-frequency dielectric constant, longitudinal-optical-, and transverse-optical-phonon frequencies of a polar semiconductor, respectively. The solution of Eq. (12) in that case is slightly more complicated, but it gives the coupled magnetoplasma–optical-phonon surface waves. Further details on this magnetoplasmon–optical-phonon coupling will be presented elsewhere.

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High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold†

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High-resolution gold-valence-band photoemission spectra were obtained by the use of monochromatized Al $K\alpha$ radiation and a single-crystal specimen. After background and scattering corrections were made, the results were compared directly with broadened theoretical density-of-states functions. The following conclusions were drawn: (i) *Relativistic* band-structure calculations are required to fit the spectrum. (ii) Both the Korringa-Kohn-Rostoker calculation of Connolly and Johnson and the relativistic-augmented-plane-wave calculation by Christensen and Seraphin give density-of-states results that (after broadening) follow the experimental curve closely. (iii) Of the theoretical functions available to date, those with full Slater exchange agree best with experiment (perhaps because of a cancellation of errors). Fractional ($\frac{2}{3}$ or $\frac{5}{6}$) exchange gives d bands that are too wide. (iv) Eastman's 40.8-eV ultraviolet photoemission spectrum is similar to the x-ray spectrum, suggesting little dependence on photon energy above 40 eV. (v) Both (ii) and (iv) imply an absence of strong matrix-element modulation in the photoemission spectrum of gold.

I. INTRODUCTION

Electronic band structures are of fundamental importance in understanding properties of metals. A knowledge of the valence-band density of states of a metal can, in principle, yield considerable information about that metal's band structure. X-ray photoemission experiments, in which valence electrons are ejected from the specimen by photons from a monochromatic source and energy analyzed in an electron spectrometer, yield spectra that are closely related to the valence-band density of states. However, the extent to which these photoemission spectra and the density of states can be directly compared is still somewhat uncertain.

In this paper the high-resolution x-ray photoemission spectrum of the valence band in a gold single crystal is reported.[1] The spectrum is compared with lower-energy photoemission spectra and with band-structure results. The following questions are at least partially answered in the affirmative: (a) Do ultraviolet photoelectron spectroscopy (UPS) results approach x-ray photoelectron spectroscopy (XPS) data as the uv photon energy increases toward the upper end of the readily available energy range (~40 eV)? (b) Is it meaningful to compare XPS spectra directly with valence-band densities of states, or are matrix-element-modulation effects so large as to obviate such comparisons? (c) Can XPS spectra establish the necessity for relativistic band-structure calculations in heavy elements? (d) Are XPS spectra sensitive enough to distinguish critically among different theoretical band-structure calculations?

Experimental procedures are described and results presented in Sec. II. In Sec. III these results are compared with theory and addressed to the above questions.

II. EXPERIMENTAL

A gold single crystal of 99.9% purity was cut to provide samples with (100), (110), and (111) faces. These were polished, etched, and annealed. Spectra were taken at room temperature and in a sample chamber pumped to about 10^{-7} Torr, on a Hewlett-Packard ESCA spectrometer. This spectrometer