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PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Properties of Image-Potential-Induced Surface States of Insulators*†

Milton W. Cole ‡
Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 6 July 1970)

The strongly repulsive interaction between electrons and He or Ne atoms, or H_2 molecules, gives rise to the existence of electronic states localized near a condensed medium consisting of such units. The attractive image potential binds the electrons weakly near the surface; the binding energy ranges from 0.4 meV for liquid He^3 to 22 meV for solid D_2. Motion parallel to the surface is nearly free-electron–like. An exploration of the interaction between electrons and oscillations of the medium's surface reveals a breakdown in perturbation theory which may be remedied by correct treatment of long-wavelength oscillations. A determination is made of the temperature-dependent mobility of electrons for fields parallel to the surface. We find that the surface waves scatter more for the liquid than for the solid. A transition occurs in the mobility as the temperature increases to a point where scattering by atoms of the vapor becomes dominant over other mechanisms. A second transition occurs when the electron in the vapor becomes localized in the bubble state, and the present treatment loses its validity.

I. INTRODUCTION

This paper attempts to elaborate the characteristics of a new kind of electronic state recently proposed by Cohen and the author.[1] The electrons are localized near, but primarily external to, a condensed insulating medium which satisfies certain criteria. The media we shall discuss are composed of atoms which have a primarily repulsive interaction with electrons. Outside of the medium, the interaction is the attractive image potential. The balance between these opposing forces results in localization of excess electrons in the vicinity of the surface. Motion parallel to the surface is essentially unrestricted and, in fact, becomes two-dimensional in character.

The question of the existence and character of electronic surface states in general has been investigated theoretically and experimentally for nearly forty years.[2] Tamm[3] and later Shockley[4] showed that termination of a one-dimensional Kronig-Penney model potential of a one-dimensional crystal may yield solutions for electronic states localized near the "surface" in addition to the usual delocalized states of the bulk material. Bardeen subsequently hypothesized[5] that surface electronic states played an important role in determining the electrostatic-potential configuration at the inter-

face between a semiconductor and another material (or vacuum). More recently, Schrieffer[6] described a kind of surface state localized in discrete energy levels with respect to motion normal to the surface but delocalized with respect to parallel motion. This general description has been appropriate to a variety of systems of current interest. These include states localized in inversion layers at semiconductor surfaces, [7-11] and magnetic-field-induced surface states. [12,13] An important question in all surface-state investigations is the relationship between properties of the bulk material, for example, electronic band structure, [14] bonding, [15] and transport, [16] and their manifestation at the surface.

The electronic states under discussion were used in I as a basis for explaining experimental results on electron ejection from liquid helium. [17] We presently believe that another explanation is appropriate to that phenomenon. The type of state proposed then and discussed here should nevertheless exist and be observable at surfaces of liquid and solid helium, neon, and hydrogen.

In Sec. II we develop an explanation of the origin of the image-potential-induced surface bands in terms of interaction between an electron and an isolated atom. Section III describes the eigenfunctions and eigenvalues of the surface states. In Sec. IV, we study the effect for the liquid problem of the interaction between the electrons and quantized capillary-gravity waves at the liquid surface. We discuss as well the electron–Rayleigh-surface-wave interaction for the solid. In Sec. V, we calculate the mobility of the electrons in an electric field parallel to the surface. Section VI summarizes our results.

II. ORIGIN OF SURFACE STATES

In this section, we describe the interaction between an electron and an isolated neutral nonpolar atom[18] of the kind under consideration. We then describe the modification of this interaction in the presence of other atoms in a condensed medium. [19] These characteristics will be important in understanding the origin and properties of the surface states.

We shall consider as specific examples helium, neon, and hydrogen, although other systems may satisfy the criteria we develop. These atoms have a tightly bound core in the ground state and a large excitation energy to higher states. They are nonpolar and only weakly polarizable. When an electron is incident upon the isolated atom, the scattering is determined by competition between a short-range repulsion and a long-range attraction. [20] The repulsion arises from the requirement of the exclusion principle of orthogonality of the scattering-electron wave function ψ_e to the atomic core orbitals. This forces ψ_e to oscillate rapidly in the core region, contributing a large positive term to the energy. An effective repulsion results[21] with a range approximately equal to the Hartree-Fock atomic radius.

At large interparticle separation r, the electric field of the electron polarizes the atom; the induced dipole moment attracts the electron with a polarization potential

$$V_p(r) = -\alpha e^2/2(r^2+r_0^2)^2 \ , \tag{1}$$

where α is the atomic polarizability. [22,23] We have introduced the parameter r_0 to provide a reasonable extrapolation of V_p to the region of small r.

Experiments in which an electron is scattered by an atom in the gas phase are capable of revealing the delicate balance between these two opposing effects. The low-energy cross section is given by

$$\sigma_s = 4\pi a_s^2 \ . \tag{2}$$

Both theory and experiment[20] find that the scattering length a_s decreases monotonically among the rare gases from a fairly large, positive value in He to a large and negative value for Xe, primarily because of increasing polarizability. For the systems we are considering, He and Ne, the repulsion predominates in determining a_s.

In the transition to a condensed phase, the long-range term is considerably modified, but the repulsive term is not. An excess electron injected into a rare-gas solid is subject to a periodic potential in the absence of lattice distortion. [24] It occupies a state $\psi_{\vec{k}}(\vec{r})$ in a conduction band, where $\vec{k}$ determines the translational properties required of this delocalized state by the Bloch theorem. Because of the large energy gap between valence and conduction bands, the effective-mass sum rule gives an effective mass reduced to only slightly less than the free-electron mass m_0. Those nearly free-electron states centered about the conduction-band minimum at the point Γ of the Brillouin zone have an isotropic parabolic dispersion relation, [25]

$$E(k) = V_0 + \hbar^2 k^2/2m \ . \tag{3}$$

The quantity V_0, the negative of the electron affinity, represents the minimum energy required for electron injection into the medium. Calculations which we describe later reveal that V_0 is positive for both He and Ne.

We next review briefly the present picture of the electronic states of disordered systems. Foldy[26] and later Lax[27] and Levine and Sanders[28] have treated the problem of an electron moving through a hypothetical random lattice of n scattering centers per unit volume. In the weak-scattering approximation ($na_s^3 \ll 1$), they find that the real part of the

electron energy increases because of scattering by [redacted] to include dynamic behavior, as has been employed

TABLE I. Description of wave functions for normal motion.

		$10^{-22}n$ (cm^{-3})	10^3Z	V_0 (eV) Theor	V_0 (eV) Expt	$10^2\eta$	$10^2\delta\kappa$	$E_\perp$ (meV)	$\langle x\rangle$ (Å)	10^4R
He^3	(liq)	1.64	5.14	0.90		1.3	4.2	0.39	103	0.9
	(sol)	2.56	8.00	1.61		1.8	5.2	0.96	66	1.3
He^4	(liq)	2.18	6.82	1.30	1.0 ± 0.2 [34,35]	1.6	4.6	0.69	78	1.2
	(sol)	3.01	9.39	2.01		2.0	5.0	1.32	56	1.5
Ne	(liq)	3.72	22.12	0.47		6.7	24.1	11.5	24	80
	(sol)	4.60	27.16	0.61		7.7	24.2	17.5	19	95
H_2	(liq)	2.17	26.00	2.20	0.3 ± 0.2 [36]	6.8	10.5	11.5	20	13
	(sol)	2.66	31.62	3.27		7.6	10.0	16.7	17	12
D_2	(liq)	2.59	30.82	3.11		7.5	10.0	16.0	17	12
	(sol)	3.08	36.37	4.44		8.3	9.4	21.9	15	11

eters we have chosen[1] and the corresponding results of the calculation. The "effective-charge" Z has been derived from the Clausius-Mossotti relation, which is valid for atoms such as these which have small polarizability. The quantity η is approximately equal to the magnitude (relative to unity) of those terms neglected when we substituted in the matching-equation Bessel and Neumann functions for the true eigenfunctions. If the classical turning point for the ground-state eigenvalue had been selected for b, η would be 1.

The quantity $\delta\kappa$ given in Table I is the shift of the eigenvalues from integral values. As we have seen, all the κ undergo the same shift. $|E_\perp|$ is the binding energy of the ground state. The quantity $\langle x\rangle$ is the expectation value of the electron coordinate. This value is approximate, having been obtained from hydrogenic wave functions. The small values of R confirm the expectation that there is little electron penetration.

We note here that the results are not sensitive to the choice of cutoff b that we have made. In all cases shown in Table I, variation in $E_\perp$ was less than 5% for variation of b between $\frac{1}{2}r_s$ and $2r_s$.

We have some basis for analyzing the calculation of V_0. Electron-injection experiments have been performed for both liquid helium and liquid hydrogen with results shown in Table I. The discrepancy for hydrogen is not surprising in view of the oversimplified model employed here. Each of the systems listed in Table I have $V_0>0$, which is certainly sufficient for localization. However, even a negative V_0 would permit localized surface states if Z is sufficient to create a bound state with $E<V_0$.

We observe that hydrogen has the strongest binding in terms of both binding energy and size of $\langle x\rangle$, which is only 20 Å. Helium has the weakest and neon falls intermediate between the two. On the other hand, we note that the fractional penetration R for Ne is the largest (0.009) as is the eigenvalue shift (~0.25). Ne is perhaps the most interesting system in this respect.

IV. SCATTERING AND LIFETIME OF SURFACE STATES

The eigenstates we have discussed arise from a static attractive interaction between the electron and a uniformly dense medium bounded by the plane $x=0$. Bulk-density fluctuations (phonons) will modify this interaction but, because of small electron penetration into the medium, will not play an important role in scattering. Additionally, the attraction may be enhanced if the surface deforms to some other configuration $u(\vec{\rho}, \vec{r}_e)$ in the presence of an electron. Here $u(\vec{\rho}, \vec{r}_e)$ denotes the amplitude of the surface displacement at a position $\vec{\rho}$ in the surface plane and $\vec{r}_e$ is the electron position. The perturbation will affect both the lifetime and the energy of the state we have disucssed.

The displacement at the surface is opposed in the liquid case by both gravity and the surface tension. In the absence of the electron, the normal modes of vibration of the free surface are known as capillary-gravity waves. Atkins[54] has discussed their quantized form as ripplons and calculated their contribution to the surface free energy, and hence surface tension, of liquid helium. In Appendix A, we quantize the ripplons and derive their dispersion relation using a technique developed by Pitaevskii.[55] The resulting eigenfrequencies are given by the classical formula

$$\omega^2(q)=gq+(\sigma/d)q^3\,, \tag{23}$$

where g is the gravitational constant, σ the surface tension, d the liquid mass density, and $\vec{q}$ the wave vector in the surface plane. The gravitational term becomes unimportant in (23) for $q>10^2$ cm^{-1}.

We note here that the Pitaevskii method is based on a hydrodynamic approximation and is hence strictly correct only for long wavelengths and low frequencies. In addition, the liquid has been considered ideal and incompressible; more realistic treatment will yield both damping and coupling to phonon modes.

The electron-ripplon interaction represents the

change in electron-fluid polarization energy which arises when the surface deforms. This change can be expressed as a sum of interactions between electron and atoms of the fluid. However, because of dielectric screening, it is not permissible simply to add up individual terms of $V_p(\vec{r})$ in the form given in Sec. II, Eq. (6). Lekner has studied[56] this screening for the case of a charge in liquid argon. For distances r greater than a small multiple of the atomic hard-core diameter, he finds that the local fields set up by atoms near the one at r reduce the potential to the value given by classical Lorentz local-field theory:

$$V_p^{\rm scr}(\vec{r}) = V_p(\vec{r})/(1+\tfrac{8}{3}\pi n\alpha) .$$

This applies to an atom deep within the medium. Near the surface, however, the screening will be incomplete. For simplicity, therefore, we completely ignore the screening and remember that subsequent work will be valid only to lowest order in the local field (i.e., n). In the cases of liquids He, Ne, and H_2, the quantity $\frac{8}{3}\pi n\alpha$ takes the values 0.03, 0.12, and 0.15, respectively, which gives some estimate of the uncertainty involved in the assumption.

The additional electron-surface interaction $V_{\rm int}$ in the presence of surface perturbation is then

$$V_{\rm int}(\vec{r}_e) = -C\int d^2\vec{\rho}\,' \int_0^{u(\vec{\rho}\,')} dx' \{1/[(\vec{r}_e-\vec{r}\,')^2+r_0^2]^2\} ,$$
$$C = \tfrac{1}{2}n\alpha e^2 .$$

We may expand the integrand in a Taylor's series in powers of $x'/x_e = \Delta$, valid if $|\Delta|<1$. Only the first two terms will be considered, a valid approximation since the wave function is small in that region anyway. Similarly we shall take $r_0 = 0$. The result is

$$V_{\rm int}(\vec{r}_e) = -C\int d^2\vec{\rho}\,' \frac{1}{[(\vec{\rho}_e-\vec{\rho}\,')^2+x_e^2]^2} \times\left\{u(\vec{\rho}\,') + \frac{2u^2(\vec{\rho}\,')}{x_e\{1+[(\vec{\rho}_e-\vec{\rho}\,')/x_e]^2\}}+\cdots\right\} . \quad (24)$$

We expand the surface displacement in ripplon normal modes as described in Appendix A:

$$u(\vec{\rho}) = A^{-1/2}\textstyle\sum_{\vec{k}} Q_{\vec{k}}\, e^{i\vec{k}\cdot\vec{\rho}} ,$$

where $\vec{k}$ is a wave vector and ρ a radius vector in the surface plane of area A. The lowest-order interaction term is

$$V_{\rm int}^{(1)} = A^{-1/2}\textstyle\sum_{\vec{k}} Q_{\vec{k}}\int d^2\vec{\rho}\,'\{e^{i\vec{k}\cdot\vec{\rho}\,'}/[(\vec{\rho}_e-\vec{\rho}\,')^2+x_e^2]^2\}$$
$$= A^{-1/2}\textstyle\sum_{\vec{k}} Q_{\vec{k}} e^{i\vec{k}\cdot\vec{\rho}_e}\int d^2\vec{\rho}[e^{i\vec{k}\cdot\vec{\rho}}/(\vec{\rho}^2+x_e^2)^2] .$$

The integral becomes

$$\int d^2\vec{\rho}\,\frac{e^{i\vec{k}\cdot\vec{\rho}}}{(\rho^2+x_e^2)^2} = 2\pi\int d\rho\,\rho\,\frac{J_0(k\rho)}{(\rho^2+x_e^2)^2}$$
$$= (\pi k/x_e)K_1(kx_e) , \quad (25)$$

where we have used the integral representation of the zero-order Bessel function:

$$J_0(y) = (1/\pi)\int_0^{\pi} d\theta\cos(y\cos\theta)$$

and a representation of the modified Bessel function of the second kind[57] (for positive argument):

$$K_1(u) = K_{-1}(u) = 2u\int_0^{\infty} dt[tJ_0(t)/(t^2+u^2)^2] .$$

The second term requires evaluation of

$$V_{\rm int}^{(2)}(\vec{r}_c) = -C2\int d^2\vec{\rho}\,' \frac{u^2(\vec{\rho}\,')}{[(\vec{\rho}_e-\rho')^2+x_e^2]^2(x_e\{1+[(\vec{\rho}_e-\vec{\rho}\,')/x_e]^2\})}$$
$$= \left(\frac{2C}{Ax_e}\right)\sum_{\vec{k},\vec{k}'} Q_{\vec{k}}Q_{\vec{k}'} \times\int d^2\vec{\rho}\,' \frac{e^{i\vec{k}''\cdot\vec{\rho}\,'}}{[(\vec{\rho}_e-\vec{\rho}\,')^2+x_e^2]^2\{1+[(\vec{\rho}_e-\vec{\rho}\,')/x_e]^2\}}$$
$$= \frac{4\pi x_e}{A}C\sum_{\vec{k},\vec{k}'} Q_{\vec{k}}Q_{\vec{k}'}e^{i\vec{k}''\cdot\vec{\rho}_e}\{[(k'')^2/8x_e^2]K_{-2}(k''x_e)\} , \quad (26)$$

where

$$\vec{k}'' = \vec{k}+\vec{k}' .$$

We arrive at the total electron-ripplon interaction term from (25) and (26):

$$(-1/C)V_{\rm int} = A^{-1/2}\sum_{\vec{k}} Q_{\vec{k}}e^{i\vec{k}''\cdot\vec{\rho}_e}[(\pi k/x_e)K_1(kx_e)] + A^{-1}\sum_{\vec{k},\vec{k}'} Q_{\vec{k}}Q_{\vec{k}'}\,e^{i\vec{k}''\cdot\vec{\rho}_e} \times\{[(\pi(k'')^2/2x_e]K_2(k''x_e)\}+\cdots .$$

The boson amplitude operators $Q_{\vec{k}}$ are replaced by creation ($a_{\vec{k}}^{\dagger}$) and annihilation ($a_{\vec{k}}$) operators via the transformation developed in Appendix A, Eq. (A7b):

$$Q_{\vec{k}} = (\hbar k/2d\omega_k)^{1/2}(a_{-\vec{k}}^{\dagger}+a_{\vec{k}}) .$$

The first-order term in the electron-ripplon interaction is then, in second-quantized notation,

$$H_{\rm int} = -\sum_{\substack{\vec{q},\vec{k}\\ l,m}} M_{\vec{q},\vec{k}}^{l,m}\,(c_{\vec{k}+\vec{q},l}^{\dagger}a_{-\vec{q}}^{\dagger}+c_{\vec{k}+\vec{q},l}^{\dagger}a_{\vec{q}})c_{\vec{k},m} , \quad (27)$$

$$M_{\vec{q},\vec{k}} = \pi C(\hbar q^3/2dA\omega_q)^{1/2}\langle\vec{k}+\vec{q},l|[K_1(qx)/x]e^{i\vec{q}\cdot\vec{\rho}_e}|\vec{k},m\rangle . \quad (28)$$

Here $c_{\vec{k},m}^{\dagger}$ and $c_{\vec{k},m}$ are creation and annihilation operators for the electronic states $\psi_{\vec{k},m} = |\vec{k},m\rangle$. Note that the interaction term is Hermitian and conserves quasimomentum in the parallel direction, given by

$$\vec{P}_{\parallel} = -i\hbar\nabla_{\parallel}+\textstyle\sum_{\vec{q}} a_{\vec{q}}^{\dagger}a_{\vec{q}}\hbar\vec{q} ,$$

where $\nabla_{\parallel}$ denotes differentiation with respect to $\vec{\rho}_e$. Thus, $\vec{P}_{\parallel}$ is a good quantum number and may be

used to characterize eigenstates of the full problem. All possible single-boson processes are included. Higher-order processes arise from the neglected terms $H_{\rm int}^{(i)}$, $i \geq 2$, which the present treatment ignores.

The matrix elements M may be calculated by numerical integration of the expression (28) using known series expansions for $K_1(qx)$. Subsequent calculations we shall perform tend to depend most sensitively on small values of the argument. In particular, the characteristic wave vector for perpendicular motion in the unperturbed problem is

$$q_0 = 2Z/a_0 \equiv 2Zme^2/\hbar^2 .$$

For $q/q_0 \ll 1$, we may then use the small argument expansion for K_1 when computing M:

$$K_1(qx) \approx (qx)^{-1}, \quad qx \ll 1 . \tag{29}$$

If we make the (approximate) substitution of "hydrogenic" wave functions for the true ones, it follows that

$$\langle \varphi_0 | K_1(qx)/q | \varphi_0 \rangle \cong q_0^2/2q, \quad q \ll q_0. \tag{30}$$

No cutoff of the interaction for small x is necessary in this calculation because of the vanishing of the approximate wave function in that region.

The real and imaginary energy shifts caused by the electron-ripplon interaction may be investigated using perturbation theory. This investigation turns out to yield anomalous and interesting results which arise from both the ripplon dispersion relation and the dimensionality of the calculation.

The rate of scattering by interactions in which a single ripplon is created is

$$\begin{aligned}\Gamma^C(k, T) &= (2\pi/\hbar)\textstyle\sum_{\vec{q}} |M_{\vec{q}}|^2 (n_q + 1) \\ &\quad \times \delta(\tfrac{1}{2}a[k^2 - (\vec{k} - \vec{q})^2] - \hbar\omega_q) \\ &= (A/2\pi\hbar)\textstyle\int_0^{q_m} dq\, q(n_q + 1)|M_q|^2 \\ &\quad \times \int_0^{2\pi} d\theta\, \delta(akq\cos\Theta - aqS_+(q)) ,\end{aligned}$$

where a, n_q, and $S_+(q)$ are given by

$$\begin{aligned} a &= \hbar^2/m , \\ n_q &= (e^{\beta\hbar\omega_q} - 1)^{-1}, \quad \beta^{-1} = k_B T \\ S_\pm(q) &= \tfrac{1}{2}q \pm m\omega_q/\hbar q . \end{aligned} \tag{31}$$

Integration over θ gives the general result,

$$\begin{aligned}&\int_0^{2\pi} d\theta\, \delta(akq\cos\theta - S_\pm(q)) \\ &\quad = 2\Theta(k^2 - S_\pm^2(q))/aq(k^2 - S_\pm^2(q))^{1/2} , \end{aligned} \tag{32}$$

$$\Gamma^C(k, T) = (Am/\pi\hbar^3)\int_{q_1}^{q_2} dq\,(n_q + 1)|M_q|^2/ (k^2 - S_+^2(q))^{1/2} , \tag{33}$$

where the limits of integration correspond to the range of ripplon wave vector that can be created. If the denominator has zeros for q less than the Debye cutoff q_m, then these define $\{q_i\}$ through

$$|S(q_i)| = k , \quad i = 1, 2 .$$

This case is depicted schematically in Fig. 2. Otherwise, the integration is carried to the limits 0 and/or q_m. For the ripplon case, there are two q_i satisfying this equation only if k exceeds a threshold value k_0, which equals the minimum of $S_+(q)$ as a function of q (see Fig. 2). For the acoustic phonon case, in contrast, the emission threshold occurs for phonons having $q = 0$, so $q_1 = 0$ and the sound velocity becomes the threshold, as is well known.[33]

Integration of Eq. (33) indicates that as k passes from below to above k_0, Γ^C jumps discontinuously from zero to a finite value

$$\Gamma^C(k_0^+, T) = Am(n_{q_0} + 1)|M_{q_0}|^2/\pi\hbar^3[2k_0 S_+''(q_0)]^{1/2} ,$$

where the primes indicate differentiation. The discontinuity occurs because of the zero of the denominator at threshold. It does not occur in three dimensions because there the $\sin\theta$ phase-space term suppresses it at the emission threshold ($\theta = 0$). Unfortunately, the discontinuity that occurs in the present case is not experimentally accessible because k_0 corresponds to much less than thermal energies.

The rate Γ^A at which the electron scatters via ripplon-annihilation processes is obtained similarly:

$$\Gamma^A(k, T) = (mA/\pi\hbar^3)\int_{q_1^-}^{q_2^-} dq\{n_q |M_q|^2/[k^2 - S_-^2(q)]^{1/2}\} ,$$

where the $\{q_i^-\}$ are defined with respect to S_-. Since the minimum of $|S_-|$ is zero, no threshold occurs, and the process will always occur for finite T.

We have numerically evaluated the rates Γ^A and Γ^C. For temperatures of most experimental interest ($T \gtrsim 0.1\,^\circ$K), the most important contributions to the scattering of thermal electrons ($k \approx 10^5$ cm^{-1}) arise from ripplon wave vectors $10^1 < q < 10^4$

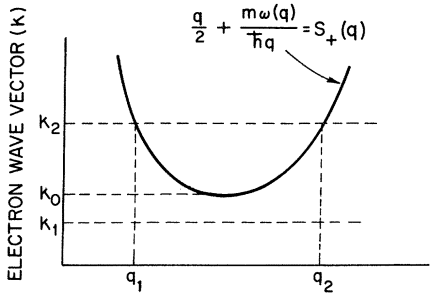

FIG. 2. Schematic depiction of wave-vector relationship which determines ripplon emission. Electron having wave vector k_1 is below the emission threshold. With wave vector k_2, it can emit ripplons with wave vector q between q_1 and q_2.

cm^{-1}. For these q and T, the distribution function reaches its classical high-temperature limit

$$n_q \approx k_B T/\hbar\omega_q \gg 1,$$

and Γ^A becomes identical to Γ^C. The total scattering rate can then be evaluated analytically:

$$\Gamma(k, T) = 2\Gamma^C = (T/k)[m\pi^2 C^2 q_0^4 k_B/8\hbar^3(gd\sigma)^{1/2}]. \quad (34)$$

For $T = 1\ ^\circ$K and $k = 10^5\ cm^{-1}$, we obtain an extremely high scattering rate $\Gamma \approx 10^{14}\ sec^{-1}$. This is a consequence of the small excitation energy associated with the ripplons. In fact, the author has shown elsewhere[58] that the modes are so "soft" that in the thermodynamic limit only the weak gravitational force prevents a long-wavelength divergence predicted by Widom[59] for the surface-vibration amplitudes.

Two comments are appropriate here. The result we have obtained relies on perturbation theory, a situation we explore below. Additionally, since the important q's are much smaller than k, the momentum-transfer rate important for mobility calculations will be much less than $k\Gamma$. In Sec. V we evaluate the mobility more realistically.

We may calculate the real energy shift from perturbation theory. To lowest order, the energy shift is

$$\Delta E^{(2)} = \mathcal{P}\sum_{\vec{q}}\left\{\frac{n_q+1}{\frac{1}{2}a[k^2-(\vec{k}-\vec{q})^2]-\hbar\omega_q} + \frac{n_q}{\frac{1}{2}a[k^2-(\vec{k}+q)^2]+\hbar\omega_q}\right\}|M_q|^2 .$$

The integration over θ is a principal-part integral:

$$\int_0^{2\pi} d\theta/[k\cos\theta - S(q)] = 0, \qquad k^2 > S^2(q)$$
$$= \frac{-\pi\,\mathrm{sgn}(S(q))}{(S^2-k^2)^{1/2}}, \qquad k^2 < S^2(q) .$$

For a thermalized electron of wave vector k, the approximate result is

$$\Delta E^{(2)} = (-\pi C^2 m q_0^4/16\hbar^2\sigma\beta k^2)(1-4k^2/q_m^2)^{1/2} ,$$

which is a very small value, of order a few millidegrees in energy. This occurs because the q vectors of long wavelength that contribute strongly to Γ do not contribute at all to $\Delta E^{(2)}$, because of the angular integration above. To check if this is accidental, we may explore the next term of perturbation theory, which is of fourth order and of the form

$$\Delta E^{(4)} = \sum_{l,m,n} \frac{V_{kl}V_{lm}V_{mn}V_{nk}}{(E_k-E_l)(E_k-E_m)(E_k-E_n)} .$$

Examination of these terms reveals that one kind of term (corresponding to a "crossing" diagram) contributes very strongly to the energy shift. For this term, the states $|l\rangle$ and $|n\rangle$ include ripplons of different wave vector. The other kind of term contributes little for the same reasons that made $\Delta E^{(2)}$ small.

We conclude that this simple perturbation approach does not provide a good description of these scattering processes. A more realistic treatment is currently under investigation. This uses time-dependent wave functions which adjust adiabatically to the long-wavelength low-frequency surface oscillations which created difficulty for the method used here.

The same failure of perturbation theory occurs in the solid case, except here an actual divergence occurs. We consider in particular Rayleigh surface waves.[60] The interaction-matrix element can be obtained by analogy to the ripplon case:

$$M_R(q) = B_R C\pi q_0^2[\hbar q/8dA\omega_R(q)]^{1/2} , \qquad \omega_R(q) = c_R q, \quad c_R = C_t\xi . \quad (35)$$

Here B_R and ξ are constants of order unity, and C_t is the bulk transverse sound velocity. Except for the modified dispersion relation, this is of the same form as the ripplon matrix element. Integration of the scattering rate here gives a logarithmic divergence arising from $q \to 0$ modes. Thus, the same problem occurs for the solid case as we encountered previously for the liquid.

V. MOBILITY

In this section, we determine the mobility of electrons in image-potential-induced surface states for dc electric field, parallel to the surface . The scattering arises from several mechanisms we have not described as well as from ripplons and Rayleigh waves for liquid and solid, respectively.

First we modify the transition-rate calculations of Sec. IV to obtain a result appropriate to mobility determinations. We define a fractional momentum-transfer rate λ which is a sum of the rates for all momentum-transfer processes, weighted by the fraction (with respect to k) of momentum transferred in the direction of the electron velocity vector:

$$\lambda = (2\pi/\hbar)\sum_{\vec{q}}(-\vec{q}\cdot\vec{k}/k^2)|M_q|^2\{(n_q+1)\delta(aq[k\cos\theta - S_+(q)]) + n_q\delta(aq[k\cos\theta - S_-(q)])\} . \quad (36)$$

The angular integration gives

$$\int_0^{2\pi} d\theta\cos\theta\,\delta(aq[k\cos\theta - S_\pm(q)]) = [-2S_\pm(q)/akq][k^2 - S_\pm^2(q)]^{-1/2}\Theta[k^2 - S_\pm^2(q)] .$$

The result of the integration over q for the ripplon case is

$$\lambda_1 = (m\pi^2 C^2 q_0^4/8\hbar^3\sigma)(1/\beta k^2) . \quad (37)$$

This result depends mostly on large q values, for which the present treatment is valid, so it should

yield the correct mobility. The rate λ_I is of order 10^{10} sec^{-1}, much smaller than Γ itself. For the Rayleigh wave case appropriate to the solid, we obtain

$$\lambda_s = \frac{m\pi C^2 q_0^4 B_R^2}{2d\hbar^3 c_R^2} \frac{[k^2 - (mc_R/\hbar)^2]^{1/2}}{\beta k^2} , \quad (38)$$

which is only of order 10^6 sec^{-1} for typical values of the parameters. We obtain the interesting result that the liquid surface reduces the mobility more than the solid surface does. Although we have not included other modes present at the solid surface, similar small values occur for these because of the linear dispersion relation at long wavelengths.

One contribution to the mobility that we have not discussed yet arises from perturbation of the potential V_0 itself, which contributes a direct short-range interaction with the electron. Similar problems have been considered by Greene and O'Donnell[61] and Prange and Nee.[13] Those treatments, however, take V_0 to be infinite, to keep electrons in the medium, and the formulation is somewhat different. The matrix element $M_d(q)$ for scattering an electron from a state $|\vec{k}, n\rangle$ to a state $|\vec{k}+\vec{q}, m\rangle$ is

$$M_d(q) = A^{-1} \int d^2\vec{\rho} \int_\infty^\infty dx\, \phi_m^*(x)\, \phi_n(x)\, V_c(\vec{\rho}, x)\, e^{i\vec{q}\cdot\vec{\rho}} ,$$

$$V_c(\vec{\rho}, x) = V_0[\Theta(x) - \Theta(x - u(\vec{\rho}))] .$$

If the ϕ_n, and ϕ_m vary slowly near $x = 0$, we may expand the integrand and find

$$M_d(q) = V_0 \sum_{\alpha=1}^{\infty} A_{n,m}^{\alpha} I_\alpha(q) ,$$

$$A_{n,m}^{\alpha} = \frac{1}{\alpha!} \left[\frac{d^{(\alpha-1)}}{dx^{(\alpha-1)}} \phi_m^*(x)\, \phi_n(x)\right]_{x=0} ,$$

$$I_\alpha(q) = A^{-1} \int d^2\vec{\rho}\, e^{i\vec{q}\cdot\vec{\rho}}\, u^\alpha(\vec{\rho}) .$$

We may examine these equations for several kinds of deformation. For both liquid and solid cases, we may expand the u's as before in the normal modes of surface oscillation. The matrix element for lowest-order scattering becomes

$$M_d(q) = A^{-1/2}\, V_0\, |\, \phi(0)\,|^2\, Q_{-q} . \quad (39)$$

A comparison with the comparable expression developed earlier for the long-range polarization term shows that $M_d(q)$ is a factor of 10^{-2} smaller than the previous expression for wave vectors of interest, given the eigenfunctions obtained earlier. Higher-order terms turn out to contribute negligibly as well, so we shall consider this direct interaction no further.

One unrelated contribution to the lifetime that should be considered here is scattering by isolated atoms of the vapor. The Clausius-Clapeyron equation along the phase-equilibrium curve gives for the saturated vapor pressure

$$P = P_0\, e^{-\beta L} ,$$

where L is the energy of vaporization (sublimation in the solid case) per particle, and P_0 is a relatively slowly varying function of T which, in the low-temperature limit, can be obtained by integrating this equation in conjunction with the ideal-gas law:

$$P_0 = g_s (M / 2\pi\hbar^2)^{3/2}\, \beta^{-5/2} ,$$

where M is the atomic mass and g_s the spin degeneracy.

Interaction with the vapor atoms has the effect of raising the zero of energy according to Eq. (4), as well as scattering of the electrons. The first effect is unimportant to lowest order[10] because the gas density is uniform. The second contribution, however, becomes the dominant scattering mechanism for T greater than some T_1. We can anticipate this with confidence because we know that for He the dynamic electron-atom interaction in the gas phase[28] at densities of order 10^{21} cm^{-3} causes localization of electrons in a cavity (bubble) from which the He atoms are evacuated. This density occurs in the saturated vapor of He^4 at a temperature of 3.5 °K and for He^3 at 2.3 °K. This important difference between results for the two isotopes should be experimentally observable.

Scattering of surface-state electrons from impurity potentials has been discussed by Kawaji and Kawaguchi[11] and Stern and Howard[8] for the Coulomb potential. We will employ instead the coherent-parallel-plane theory of Duke.[62] In this model, self-energy diagrams corresponding to the electron-atom interaction at a fixed distance from the surface are analyzed to include multiple scattering within each plane of constant x. Then an integration over x is performed. The interaction is taken to be a contact pseudopotential interaction

$$V(\vec{r} - \vec{r}_i) = (\hbar^2/m)\, 2\pi a_s\, \delta(\vec{r} - \vec{r}_i) .$$

The scattering rate that results is given in the present notation as

$$\lambda_v = (2n_v/\hbar)[\hbar^2/m 2\pi a_s]^2 \int_0^\infty dx\, |\, \phi_n(x)|^2$$

$$\times \sum_m |\, \phi_m(x)\,|^2\, \pi \mathfrak{N}_m(E) .$$

Because of orthogonality of the eigenfunctions, the term $m = n$ in the sum will contribute most. Taking only this term and using hydrogenic eigenfunctions, we find

$$\lambda_v = 3\pi^2\, n_v\, a_s^2\, \hbar q_0 / 16m .$$

For the example of liquid He^4 at 1 °K, this gives a rate of order 10^{10} sec^{-1}, which is comparable to rates for scattering by surface waves discussed earlier.

In Appendix B, the mobility of a two-dimensional

electron gas is calculated using the Boltzmann equation and a relaxation-time (τ) approximation. The resulting mobility is given in Eq. (B4) as

$$\mu=\frac{e}{2m}\int_0^\infty dk\, k^3\tau(k)e^{-\beta\hbar^2k^2/2m}/\int_0^\infty dk\, k^3 e^{-\beta\hbar^2k^2/2m}\ .$$

We have calculated in this section several contributions to the scattering rate. For both liquid and solid, the quantity can be expressed as the inverse of a sum of scattering contributions from gas-phase atoms and surface oscillations which we have separately evaluated.

In Fig. 3 we show the mobility for electronic states at the surface of liquid He^3, liquid He^4, and solid He^4. These suffice to illustrate the various regions of interest. At low T, surface-wave scattering dominates. For the solid case, this becomes very small as few electrons exceed the emission-velocity threshold. In the liquid case, the mobility is T independent because of the form of (37). As the temperature increases, the transition occurs to scattering primarily by vapor atoms, so the mobility becomes approximately exponentially T dependent. At some point, in the vicinity of the vertical arrows in Fig. 3, this treatment fails as the electron becomes localized in a "bubble" state and the mobility drops rapidly.[28]

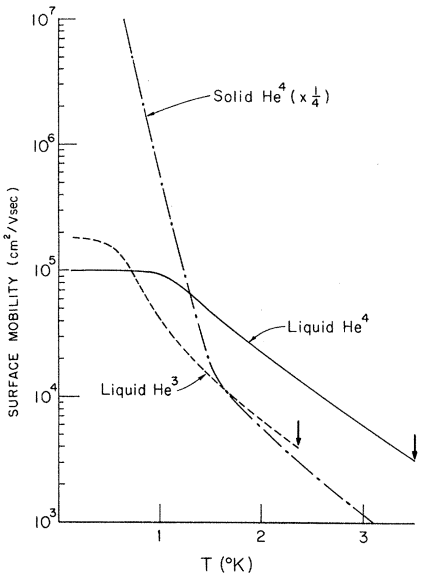

FIG. 3. Mobility as function of temperature for electrons bound near the surface of liquid and solid He^4 and liquid He^3. The vertical arrows indicate a transition to the localized bubble state of much lower mobility. Note reduction by a factor of 4 of the mobility shown for solid He^4.

VI. DISCUSSION AND CONCLUSIONS

We have explored in detail the image-potential-induced surface bands. In particular, we have found that the wave functions for normal motion correspond closely to those of simple form which solve the hydrogenic problem. The fractional penetration of the wave function into the medium is small. It increases, however, for the most strongly bound states.

We have obtained results for the interaction between the surface electrons and oscillatory modes of the liquid surface which are important for the present study in addition to being of more general theoretical interest.

Experiments are currently being performed in several laboratories to test for the existence and properties of these states. In particular, we have made predictions regarding the mobility which should be readily accessible to experiment.

We note that further theoretical work is in progress with the aim of improving upon the perturbation method employed here. In addition, the theory is being extended to apply to the dielectric film on a metal substrate, for which case the binding is strongly enhanced.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor Morrel H. Cohen whose guidance, encouragement, and stimulation made an invaluable contribution to this work. In addition, he is particularly grateful to Dr. J. Sak and Dr. E. Economou. Thanks are due to the Xerox Corporation for a generous fellowship received during the course of this work.

APPENDIX A: RIPPLON QUANTIZATION

Ripplons are quantized capillary-gravity waves at and near a liquid surface, the motion extending to a depth of order the inverse of the wave vector k. No density oscillation is associated with these modes, which are well-known classically. The present derivation describes an ideal incompressible semi-infinite fluid bounded by the plane $x=0$ of area A. We shall impose periodic boundary conditions to quantize k. The hydrodynamic technique we employ was used earlier by Pitaevskii[55] to derive the density-fluctuation excitation spectrum of liquid helium.

In an ideal fluid, the velocity is the gradient of a potential φ. Incompressibility implies that φ satisfies Laplace's equation. Thus, the kinetic energy is given by

$$\begin{aligned} T&=\tfrac{1}{2}d\int(\nabla\varphi)^2\,d\tau \\ &=-\tfrac{1}{2}d\int\varphi\nabla^2\varphi\,d\tau+\tfrac{1}{2}d\int d\vec{S}\cdot\varphi\nabla\varphi \\ &=\tfrac{1}{2}d\int d\vec{S}\cdot\varphi\nabla\varphi\ , \end{aligned} \tag{A1}$$

where we have used the divergence theorem.

If we take $G(\vec{r}, \vec{r}')$ to be

$$G(\vec{r}, \vec{r}') = 1/|\vec{r} - \vec{r}'| ,$$
$$\nabla^2 G(\vec{r}, \vec{r}') = -4\pi\delta(\vec{r} - \vec{r}') . \quad \text{(A2)}$$

In the case that $\vec{r}$ lies on the boundary, the δ function in Eq. (A2) will contribute only one-half of the full value to the expression[63]

$$\varphi(\vec{r}) = (-1/2\pi) \int d^3\vec{r}' \varphi(\vec{r}') \nabla'^2 G(\vec{r}, \vec{r}') ,$$

where the prime denotes differentiation with respect to the primed coordinates. We next add a term of zero value to the right-hand side and use Green's theorem:

$$\begin{aligned}\varphi(\vec{r}) &= (-1/2\pi) \int d^3\vec{r}' [\varphi(\vec{r}') \nabla'^2 G(\vec{r}, \vec{r}') \\ &\quad - G(\vec{r}, \vec{r}') \nabla'^2 \varphi(\vec{r}, \vec{r}')] \\ &= (1/2\pi) \int d\vec{S}' \cdot G(\vec{r}, \vec{r}') \nabla' \varphi(\vec{r}, \vec{r}') \\ &= (1/2\pi) \int dS' [\dot{u}(\vec{r}')/|\vec{r} - \vec{r}'|] . \end{aligned} \quad \text{(A3)}$$

Here the dot denotes time differentiation and we have used

$$0 = [\nabla' G(\vec{r}, \vec{r}') \cdot \vec{n}']_{\vec{r}, \vec{r}' \text{ on } \vec{S}'} ,$$
$$\dot{u}(\vec{r}') = [\nabla' \varphi(\vec{r}') \cdot \vec{n}']_{\vec{r}' \text{ on } \vec{S}'} .$$

Here $\vec{n}'$ is the unit normal and $u(\vec{r})$ the surface displacement. We consider here oscillatory motion associated only with the upper-bounding surface. From Eqs. (A1) and (A3), we obtain

$$T = (d/4\pi) \int\int dS\, dS' [\dot{u}(\vec{r}) \dot{u}(\vec{r}')/|\vec{r} - \vec{r}'|] . \quad \text{(A4)}$$

The potential energy V arising from surface deviation from planarity has contributions from both gravitational and surface-tension forces:

$$\begin{aligned} V &= \int dS \int_{-\infty}^{u(\vec{r})} dz\, dg z + \sigma \int dS [1 + (\nabla u)^2]^{1/2} \\ &\approx V_g + \int dS [dg u^2/2 + (\sigma/2)(\nabla u)^2] , \end{aligned} \quad \text{(A5)}$$

where V_g is the equilibrium value, σ the surface-tension coefficient, and g the gravitational constant. We have assumed the displacement gradient small, $|\nabla u| \ll 1$.

We next expand the displacement and its time derivative in ripplon normal-mode coordinates $\vec{k}$ quantized by the requirement of periodic boundary conditions:

$$u(\vec{r}) = A^{-1/2} \sum_{\vec{k}} Q_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} ,$$
$$\dot{u}(\vec{r}) = A^{-1/2} \sum_{\vec{k}} \dot{Q}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} .$$

The Lagrangian of the system is given by

$$L = \sum_{\vec{k}} (T_{\vec{k}} - V_{\vec{k}}) ,$$
$$\sum_{\vec{k}} T_{\vec{k}} = \frac{d}{4\pi A} \sum_{\vec{k}, \vec{k}'} \dot{Q}_{\vec{k}} \dot{Q}_{\vec{k}'} \int\int dS\, dS' \frac{e^{i(\vec{k}\cdot\vec{r} + \vec{k}'\cdot\vec{r}')}}{|\vec{r} - \vec{r}'|} .$$

But from the integral representation of the Bessel function and an appropriate integration formula, we obtain

$$\begin{aligned} T_{\vec{k}} &= \frac{d}{4\pi A} \dot{Q}_{\vec{k}} \sum_{\vec{k}'} \dot{Q}_{\vec{k}'} \frac{2\pi}{k} \int dS\, e^{i(\vec{k}+\vec{k}')\cdot\vec{r}} \\ &= (d/2k) \dot{Q}_{\vec{k}} \dot{Q}_{-\vec{k}} . \end{aligned}$$

Similarly, we evaluate $V_{\vec{k}}$ and find

$$L_{\vec{k}} = (d/2k) \dot{Q}_{\vec{k}} \dot{Q}_{-\vec{k}} - \tfrac{1}{2}(dg + \sigma k^2) Q_{\vec{k}} Q_{-\vec{k}} .$$

We derive the canonical momentum $\pi_{\vec{k}}$ and Hamiltonian by the usual method:

$$\begin{aligned} &\Pi_{\vec{k}} = (d/k) \dot{Q}_{-\vec{k}} , \\ &H = \sum_{\vec{k}} [\Pi_{\vec{k}} \Pi_{-\vec{k}} (k/2d) + Q_{\vec{k}} Q_{-\vec{k}} [\tfrac{1}{2}(dg + \sigma k^2)]] . \end{aligned} \quad \text{(A6)}$$

We quantize H by imposing the boson commutation relations upon the operators Q, Π:

$$[Q_{\vec{k}}, \Pi_{\vec{k}'}] = i\hbar\delta_{\vec{k}, \vec{k}'} ,$$

and then transform to a form diagonal in creation and annihilation operators $a_{\vec{k}}^\dagger$, $a_{\vec{k}}$:

$$\Pi_{\vec{k}} = i(\hbar d\omega_{\vec{k}}/2k)^{1/2} (a_{\vec{k}}^\dagger - a_{-\vec{k}}) ; \quad \text{(A7a)}$$

$$\begin{aligned} &Q_{\vec{k}} = (\hbar k/2d\omega_{\vec{k}})^{1/2} (a_{-\vec{k}}^\dagger + a_{\vec{k}}) , \\ &H = \sum_{\vec{k}} \hbar\omega_{\vec{k}} (a_{\vec{k}}^\dagger a_{\vec{k}} + \tfrac{1}{2}) ; \end{aligned} \quad \text{(A7b)}$$

$$\omega_k^2 = gk + (\sigma/d)k^3 . \quad \text{(A8)}$$

We thus recapture the classical dispersion relation as one would expect. However, we have obtained in addition the transformation equations (A7) which provide a normalization necessary for computing electron-ripplon interaction. Furthermore, the Hamiltonian (A6) has been used elsewhere by the author[58] to study properties of the liquid-vacuum interface.

APPENDIX B: MOBILITY FOR TWO-DIMENSIONAL GAS

We investigate here two-dimensional transport for a system of electrons characterized by Maxwell-Boltzmann statistics. In steady state, the time rate of change of the distribution function $n_{\vec{k}}$ is zero:

$$0 = -\nabla_{\vec{k}} n_{\vec{k}} \cdot \frac{e\vec{E}}{\hbar} - \frac{\partial n_{\vec{k}}}{\partial t}\Big|_{\text{scatt}} , \quad \text{(B1)}$$

where $\vec{E}$ is an electric field along the z axis which perturbs an equilibrium distribution $n_0(\vec{k})$. The second term arises from scattering processes. We associate with these a relaxation time $\tau(k)$ which gives a measure of the rate at which any nonequilibrium electron distribution $n_1(\vec{k})$ would, in the absence of $\vec{E}$, relax toward equilibrium. We have

$$\begin{aligned} &-\frac{\partial n_{\vec{k}}}{\partial t}\Big|_{\text{scatt}} = \frac{n_1(\vec{k})}{\tau} , \\ &n_1(\vec{k}) = n_{\vec{k}} - n_0(\vec{k}) , \\ &n_0(\vec{k}) = (\hbar^2 \beta\pi/m) N e^{-\beta\hbar^2 k^2/2m} , \end{aligned} \quad \text{(B2)}$$

where N is the total number of electrons per unit area. If we assume that $\vec{E}$ does not strongly perturb the distrubution $n_0(\vec{k})$, then the lowest-order terms of (B1) give

$$n_1(\vec{k}) = \left(\frac{\hbar^2\beta\pi}{m}\right)^2 k_z \frac{eE\gamma(k)}{\hbar} Ne^{-\beta\hbar^2k^2/2m} . \quad \text{(B3)}$$

The current density J_z associated with this nonequilibrium distribution is

$$J_z = \int d^2\vec{k}\, e\, n_1(\vec{k})\, v(\vec{k}) .$$

We define the mobility as

$$\mu = J_z / NeE .$$

Then we obtain

$$\mu = e\int_0^\infty dk\, k^3\tau(k)e^{-\beta\hbar^2k^2/2m} / 2m\int_0^\infty dk\, k^3 e^{-\beta\hbar^2k^2/2m} . \quad \text{(B4)}$$

*Research supported in part by the National Aeronautics and Space Administration, and aided through general support of Materials Science by the Advanced Research Projects Agency.

†Submitted in partial fulfillment of the requirements for Ph. D. degree in the Department of Physics, University of Chicago.

‡Present address: Physics Department, University of Toronto, Toronto, Ont., Canada.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Isotope Splitting of the *F*-Center In-Gap Mode in KI and KBr

D. Bäuerle*†‡
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
and
R. Hübner§
Institut für theoretische Physik, der Universität Stuttgart, Germany
(Received 30 March 1970)

High-resolution measurements at the *F*-center in-gap mode in KI and KBr have revealed a threefold structure in the absorption spectrum with lines at 82.62 ± 0.02, 81.98 ± 0.02, 81.19 ± 0.05 cm^{-1} and at 99.60 ± 0.03, 99.07 ± 0.04, 98.50 ± 0.05 cm^{-1}, respectively. This structure is interpreted as due to the presence of two stable isotopes, K^{39} and K^{41}, in the crystal. In a three-dimensional-model calculation which uses as parameters changes in the force constants between the defect and the first nearest neighbors ($A01$) and changes in the force constant between the first and fourth nearest neighbors ($A14$), we found that the in-gap mode frequencies are extremely sensitive to the value of the latter. The position and splitting in the absorption lines can be explained in the calculation by using $A01 = -0.50$, $A14 = -0.060$ for KI and $A01 = -0.50$, $A14 = +0.002$ for KBr. Stress experiments on the strongest lines in KI are in agreement with our model. Extending the calculation to Cl^- and Br^- centers in KI, it is shown that the measured isotope splitting for Cl^{35}, Cl^{37} and Br^{79}, Br^{81} centers can be explained by taking into account not only changes in $A01$ but also changes in $A14$.

I. INTRODUCTION

The far-infrared absorption spectra associated with very light substitutional defects in alkali halides like H^-, D^- ions (U centers) and F, F' centers were recently reported.[1–4] These vacancy-type centers give rise to resonance absorption in the upper acoustic band for H_s^-, D_s^-, and F' centers and to gap-mode absorption in the region between the optic and acoustic phonon branches for the F center, respectively. The different absorption frequencies of these defects are mainly an effect of local force-constant changes. The amount by which the perturbed force constants differ from the unperturbed value can be obtained by fitting the experimental results to model calculations in three dimensions. Calculations of the infrared-active modes in perturbed lattices on the basis of "realistic models" for the lattice dynamics are given, e.g., by Klein,[5] Page and Strauch,[6] Benedek and Nardelli,[7] and some others. Recently, Benedek and Mulazzi[8] calculated the F-center gap-mode absorption based on one of Hardy's deformation dipole models.

The measurements and calculations reported in this paper should provide further clarification of the dependence of the optical response of perturbed lattice vibrations on mass and force-constant changes. As a "model case," we have chosen the F center for the following reasons: (a) Some lattice dynamical properties of the F center are already known. They could be studied indirectly through the electronic transition because of the electron-phonon interaction.[8–10] (b) The vibrational absorption associated with F centers in KBr and KI is in the phonon gap. Therefore, the corresponding absorption lines are sharp, and small perturbations of the surrounding lattice can be measured.

After a short description of the experimental apparatus (Sec. II), we present in Sec. III the experimental results. High-resolution measurements at the F-center in-gap mode in KI near 83 cm^{-1} have revealed a threefold structure of the absorption shape. Quite similar lines occur in KBr (Sec. III A). Stress experiments at the strongest lines in KI, those at 82.62 and 81.98 cm^{-1}, are reported in Sec. III B.