tance minimum can be controlled by impurities rather than lattice defects, which should be negligible for this ternary system. With the Au-Ge doping complex introduced into the crystal, we find both a photosensitive extra ("inelastic") current channel and a photosensitive zero-bias anomaly in $Ga_{1-x}Al_xAs$ tunnel diodes. Both phenomena are caused by the Au-Ge impurity complex which establishes an acceptor state ~ 150 mV above the valence-band edge in $Ga_{1-x}Al_xAs$ (and, of course

GaAs). This state is fixed relative to the valence-band edge as the band gap is increased with increase in crystal Al composition.

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Proposal for Experiments for the Direct Verification of the Size-Quantization Effect

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Based on a simple pictorial construct in E-$\vec{k}$ space, we analyze the interactions of external excitations with electrons in thin films and propose three new experiments for the direct verification of the size-quantization effect. Two of these involve intersubband transitions, and the third is predicted to give results analogous to the giant quantum oscillations observed in solids under the action of a magnetic field. Excitations suitable for these experiments are shown to be ultrasonic waves.

Considerable work of a theoretical as well as an experimental nature has been done[1-4] in recent times, on the interesting subject of size quantization in thin films. Most of the experimental results, however, have been fairly indirect in nature from the viewpoint of exhibiting the structure of these quantum levels. Thus a large number of the observations are primarily concerned with the oscillations of the thermodynamic and kinetic parameters (such as susceptibility and resistivity) with variations in the film thickness. The work of Ogrin *et al.*[5-7] and of Komnik and Bukhshtab[8,9]

falls in this category. The least indirect experiment observation of size quantization has been in connection with the tunneling of electrons between thin films.[10] Based on a simple pictorial analysis of the effect, we present here a proposal for some experiments that would verify the existence of the quantized levels in a film in a quite direct manner.

One of the present authors has shown[4] that, using the fact that one has a thin film and not a bulk sample, an approximate separation of the Schrödinger equation can be carried out. One may then treat the z problem (the z direction is the thickness
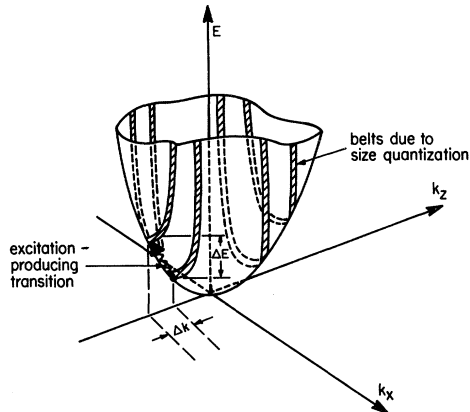
FIG. 1. Slashed paraboloid showing the belts due to size quantization and explicitly indicating the requirements of energy *and* momentum conservation in a transition process.

direction of the film) independently of the x-y problem. Distinctly quantized levels appear in the solution of the z problem, and we propose in this paper that the existence of these levels be observed by resonance methods analogous to spectroscopic analysis in atomic physics.

For the sake of simplicity, we analyze the simple model of free electrons with a modified isotropic effective mass m^*. The analysis is further simplified by considering a two-dimensional problem by eliminating a dimension which is not crucial to the problem (e.g., the y direction). The energy surfaces which form a paraboloid for a bulk sample (x and z unrestricted) take the form of the "slashed paraboloid" of Fig. 1, when the z direction is restricted as in a film. Possible states then exist only on narrow belts (the slashes) on the paraboloid. These belts are finite in size (and in fact even spread outside the paraboloid surface) due to the collisional broadening. Size-quantization effects become undetectable when the film thickness becomes too large, with a resulting strong overlap between the belts. If these belts are projected onto the ϵ-k_x plane [see Figs. 1 and 2(a)], one obtains the "subbands" displayed and discussed by other authors.[1,11] The simple (albeit obvious) picture of the slashed paraboloid we provide here allows a clear insight into the situation and immediately suggests the possibility of obtaining a resonance whenever the film is bombarded by excitations which simultaneously provide the $\Delta\epsilon$ and the Δk needed to lift an electron into the "next subband" [see Fig. 2(b)]. What these excitations should be will depend on the values of $\Delta\epsilon$ and Δk.

For our simple model,

$$\epsilon = \frac{\hbar^2}{2m^*} \left(k_x^2 + \frac{\pi^2 n^2}{d^2} \right), \quad n = 1, 2, \ldots \quad (1)$$

where d is the thickness of the film. The simplest and the most direct form of the resonance experiment would be one involving no change in k_x. The estimates of the values of the relevant quantities are as follows. Defining $\Delta\omega$ as $\Delta\epsilon/\hbar$, where $\Delta\epsilon$ is the energy separation of the electron states,

$$\Delta\omega \approx [5(m/m^*)\gamma(1/\alpha^2)] \times 10^{12} \text{ rad/sec}, \quad (2)$$

$$\Delta k \approx [3/\alpha] \times 10^6 \text{ cm}^{-1}, \quad (3)$$

$$c = \Delta\omega/\Delta k \approx [\tfrac{5}{3}(m/m^*)\gamma(1/\alpha)] \times 10^6 \text{ cm/sec}. \quad (4)$$

Here the thickness of the film is taken to be $\alpha(100 \text{ Å})$, and γ is a factor that depends upon which "subbands" contain the states that are to be connected by the external excitations. Thus if they are the first two, γ equals $2^2 - 1^2 = 3$, and for higher "subbands" γ can easily be 10 or more. The most important equation above is (4) which describes what c, the "speed" of the external excitations, should be. It is thus clear that if external excitations of speed given by (4) are collimated as to be incident on the thin film in the z direction (i.e., perpendicular to the film plane), sharp resonance absorption is expected to result at certain frequencies given by (2).

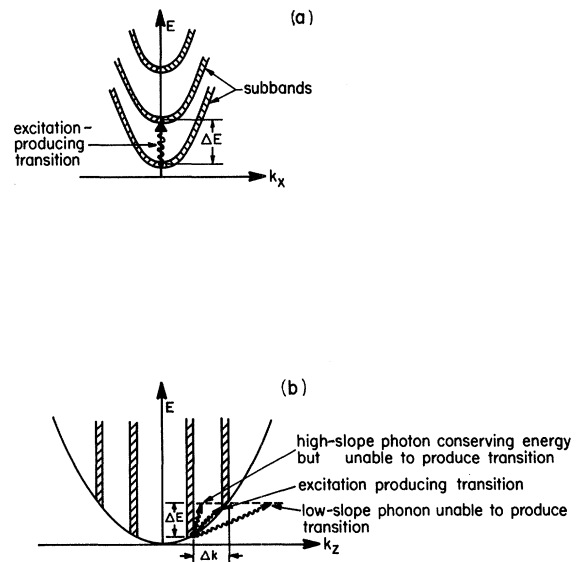This is the first and the most direct experiment that we propose for the observation of the size-

FIG. 2. (a) Projection on ϵ-k_x plane showing the "subbands" discussed in the literature; note that momentum conservation is not displayed. (b) Projection on ϵ-k_z plane showing explicitly the requirements for the conservation of momentum *as well as* of energy.

quantization effect. However, there are several difficulties associated with it. For the success of the experiment it is necessary that one vary the various parameters appearing in Eqs. (2)–(4), so as to keep the $\Delta\omega$ much larger than the collisional and the thermal broadenings. If that is not satisfied, distinct quantized levels no longer have any meaning. One may estimate the collisional broadening as

$$\omega_{coll} \approx 1/\tau = \beta \times 10^{12} \text{ rad/sec,} \qquad (5)$$

when one assumes a relaxation time τ of the order of 10^{-12} sec (this is the experimentally observed value) at room temperatures, and β is a factor which varies with temperature, and which at low temperatures could be made as low as 10^{-2}. The thermal broadening ω_{th} is given by

$$\omega_{th} \approx [(1.4)T] \times 10^{11} \text{ rad/sec ,} \qquad (6)$$

where T is in degrees Kelvin. At very low temperatures (e.g., 50 mdeg) the ω_{th} can thus be made as small as 10^9 rad/sec.

Since it is possible to perform the experiment at low temperatures, one thus requires the $\Delta\omega$ in (2) to be of the order of 10^{11} rad/sec or larger.

We shall examine the various parameters appearing in Eqs. (2)–(4). The ratio m/m^* of the free-electron mass to the effective electron mass varies from about 1 for ordinary metals to 10^2 for semimetals such as bismuth, and one can in fact raise it up to 10^3 for certain semimetallic alloys; it is also possible to have it as low as 0.3 for some transition metals. Fermi statistics dictate that the observable transitions be only from filled states to unfilled states, and this has an influence on the value of γ. For ordinary metals, the high carrier concentration causes many "belts" to be filled and γ must perforce be large. (If the transitions are between neighboring "belts," $\gamma \approx 2n$, where the highest filled "belt" is the nth.) For such substances as bismuth where it is possible to have only one or two levels filled, γ will be only slightly larger than 1. Since the thinnest films that can be made comfortably and conveniently are of the order of tens of Å in thickness, α varies from 10^{-1} to higher values.

Choosing a substance for which the factor $(m/m^*)\gamma$ is of the order of unity, we get from (2) and (4)

$$\Delta\omega \approx 10^{11} \text{ rad/sec ,} \qquad (7)$$

$$c \approx 10^5 \text{ cm/sec} \qquad (8)$$

if $\alpha \approx 1$. Thus for films of a thickness of 100 Å, we see that phonons are an excellent candidate for the excitations. The first experiment we propose thus consists of bombarding a thin film [chosen as to have $(m/m^*)\gamma \sim 1$] of a thickness of about 100 Å

with ultrasonic waves collimated as to be normal to the film plane. Resonance absorption should be observed as one varies either the phonon frequency or the film thickness.

It should be noted in this connection that for the above choice of the film, photons cannot be used to excite the electrons. This is because they cannot satisfy both energy *and* momentum conservation in the excitation process due to their high speed, or equivalently their steep ω-k slope. This is shown in Fig. 2(b). It is interesting to examine the possibility of using photons in conjunction with Umklapp processes. While such a transition can occur in ordinary solids when a phonon is lifted from its acoustic branch to its optical branch, it is easy to prove that it is forbidden in the present context. The smallest reciprocal-lattice vector that an Umklapp process can provide, is of the order of $1/a$, where a is a lattice constant. And this is much larger than the Δk required for our transition, since the latter is of the order of $1/d$, and the film thickness is much larger than a lattice constant. Photons, even if assisted by Umklapp processes, are therefore unable to cause the desired transitions. Photons assisted by phonons can cause transitions, but such double processes are much less probable than single processes and we do not consider them here.

If we are to employ electromagnetic waves as the excitation, we must change the values of the film parameters to make the c in Eq. (4) of the order of 10^{10} cm/sec. This is highly improbable and difficult but may be achieved if special alloys yielding $m/m^* \approx 10^3$ are used (we assume $\gamma \approx 1$) to make very thin films of the order of 10 Å ($\alpha \approx 10^{-1}$). Under such conditions resonance absorption will be observed for photons of frequency of the order of 10^{17}. This is in the far ultraviolet range.

Thus, due to the requirement of the simultaneous conservation of energy and momentum, electromagnetic absorption cannot occur except under the very special conditions described above. This point, which is made very clear by the "slashed paraboloid" (Fig. 1), and by its projection on the ϵ-k_z plane [Fig. 2(b)], seems to have been overlooked in an earlier treatment of the subject. [12]

Difficulties exist in the ultrasonic absorption experiment we have proposed. The phonons required are very energetic [see Eq. (7)], and the only known manner of generating them is by using superconducting tunnel junctions [13] or by light scattering. [14] Until experimental techniques for collimating these phonons are developed, this experiment is difficult to perform, unless one can reduce the collisional broadening and rearrange the film parameters.

In view of this fact, we propose two other ex-

periments. We remove the restriction that there should be no change in k_x in the transitions, and we may therefore employ uncollimated phonons produced by the methods of Ref. 13. These will then be absorbed if their energy equals the energy difference between the relevant electron states. If one thus varies the energy of the uncollimated phonons from a low value, an "edge effect" will be observed, i.e., absorption will start at a definite value corresponding to the energy difference between the highest filled states and the lowest energy states of the next "subband." If the Fermi energy as measured from the bottom of the highest filled "subband" is known from other experiments, the experimental result in this edge effect can be used directly to calculate the energy difference between "subbands." The latter is merely the sum of the Fermi energy and the energy of the phonons at which the "edge" appears.

While the above experiments involve intersubband transitions, an interesting experiment involving intrasubband transitions would also be very useful to perform. It is in exact analogy with the experiments on giant quantum oscillations.[15] The theoretical treatment is completely parallel to the one[15] for the case when the quantization is due to a magnetic field, and it will not therefore be given here. Suffice it to say that if ordinary low-energy phonons of a definite frequency are made to be incident on the film, energy and momentum conservation requires that the intrasubband transition be from a definite point on the subband. On the other hand, Fermi statistics and the fact that the phonon energies are of the order of kT at the temperature of the experiment, dictate that the point be within an interval of kT of the Fermi level. It is easy to show that these two conditions can be satisfied only for certain specific locations of the various subbands, relative to the energy axis. By varying the film thickness, the conditions can be made to be met periodically, and large periodic peaks will thus be observed in the absorption of the sound waves. It should, however, be noticed that in this experiment one has two quantities that one can vary: the film thickness *and* the direction of the sound waves. This is particularly important in the present context because the film thickness cannot be varied in as easy and simple a manner as

the magnetic field of Ref. 15.

The preceding analysis thus shows that a direct verification of the size-quantization effect and the experimental observation of the structure of the quantized levels can be accomplished with the help of the three simple experiments we have described above. We believe it will be interesting and worthwhile to perform these experiments.

Note added in proof. The manner in which we have presented the structure of the electron states through the "slashed paraboloid" and the relevant discussion could lead the reader to believe that we claim that those states are k_z eigenstates. This is not true, and the following clarification is perhaps in order. Whenever the free (or quasifree) electron gas is contained in a box of finite (however large) dimensions, the Hamiltonian eigenstates must perforce correspond to standing waves and each eigenstate must thus be an equal mixture of states with equal but opposite k's. Only infinite boxes or boxes with Born–von Karman conditions imposed on them will have electron eigenstates which are truly k eigenstates. While these are precisely the boundary conditions used for bulk samples, they cannot be used (in the z direction) for thin films. Surely an infinite extension is excluded by definition, and replacing the true boundary conditions by periodic ones might distort the physics of this particular problem, since the boundary conditions are a crucial part of the system. Our pictorial analysis should therefore be read with this fact in mind. This observation does not clash with any of our results in the article, and resonances will appear exactly as predicted by our analysis. (Perhaps we should draw the reader's attention to additional resonances which have not been mentioned in the body of the paper but which will appear at phonon frequencies and wave vectors equaling the sums of the electron frequencies and wave vectors, respectively, since the electron eigenstates are equal mixtures of states with equal but opposite k_z's.)

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Comment on the Fong-Cohen d Pseudopotential

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We show that a d pseudopotential which is a constant A_2 for $|\vec{r}-\vec{R}_j| \leq R_s$ and equal to the exact crystal potential for $|\vec{r}-\vec{R}_j| > R_s$ has the shortcoming that A_2 is a strong function of the energy of the various d states. The implications for the Fong-Cohen empirical pseudopotential which is based on this rigorous pseudopotential are discussed.

Pseudopotentials can be either rigorous[1,2] (the eigenvalues of the pseudo-Hamiltonian identical to the true Hamiltonian) or empirical (parametrized) to fit previously determined features of the energy bands). In order that an empirical pseudopotential with only a few adjustable parameters be able to reproduce all the features of the energy bands, it must be closely related to a rigorous pseudopotential. The first empirical pseudopotentials[3,4] for transition and noble metals were based on expansions containing both atomiclike d functions and plane waves and contained nine[4] and ten[3] parameters for the d states (including s-d hybridization) plus additional parameters for the s-p bands. Fong and Cohen[5] used the much simpler pseudopotential

$$\overline{V}_{ps}(\vec{r}) = V_L(\vec{r}) + \sum_j P_2^\dagger \overline{V}_2(\vec{r} - \vec{R}_j)P_2 \quad, \tag{1}$$

where $\vec{R}_j$ is the lattice vector, P_2 is the d projection operator and

$$\overline{V}_2(\vec{r} - \vec{R}_j) = \overline{A}_2 \quad \text{for} \quad |\vec{r} - \vec{R}_j| \leq R_s$$
$$= 0 \quad \text{otherwise} \quad. \tag{2}$$

The first few Fourier transforms of the local pseudopotential $V_L(\vec{r})$ are taken as parameters. If these are determined from the s-p bands, then the Fong-Cohen pseudopotential can be said to contain only two d parameters, namely, A_2 and R_s.

If $V_L(\vec{r})$ is taken to be zero for $|\vec{r} - \vec{R}_j| \leq R_s$ and to be the exact crystal potential $V(\vec{r})$ for $|\vec{r} - \vec{R}_j| > R_s$, which according to the cancellation theorem[6] is what one would expect for an s-p pseudopotential, then one sees that the empirical

pseudopotential (1) is based on the rigorous pseudopotential

$$V_{ps}(\vec{r}) = \sum_{jl} P_l^\dagger V_l(\vec{r} - \vec{R}_j)P_l \quad, \tag{3}$$

where $V_0(\vec{r} - \vec{R}_j)$ and $V_1(\vec{r} - \vec{R}_j)$ are Phillips-Kleinman[1] pseudopotentials and

$$V_2(\vec{r} - \vec{R}_j) = A_2 \quad \text{for} \quad |\vec{r} - \vec{R}_j| \leq R_s$$
$$= V(\vec{r}) \quad \text{otherwise} \quad. \tag{4}$$

This pseudopotential is rigorous providing only that the true crystal potential within the inscribed sphere may be accurately approximated by its spherical average.[7] For $|\vec{r} - \vec{R}_j| \leq R_s$ the d eigenfunctions of this pseudopotential are $\psi_d = j_2(kr)Y_{lm}(\hat{r})$ where j_2 is a spherical Bessel function and $Y_{lm}(\hat{r})$ is a spherical harmonic. The energy of ψ_d, which of course must be equal to the eigenvalue of the crystal Hamiltonian, is[8]

$$E = A_2 + k^2 \quad, \tag{5}$$

where k (which is not to be confused with a wave vector) is determined from

$$\frac{1}{j_2(kR_s)}\left(\frac{dj_2}{dr}\right)_{R_s} = \frac{1}{f_2(R_s)}\left(\frac{df_2}{dr}\right)_{R_s} \tag{6}$$

and where $f_2(r)$ is the d eigenfunction of the spherically average crystal potential. Thus A_2 is a uniquely determined function of E, but R_s may take any value less than the largest inscribed-sphere radius. Note that our d pseudopotential is very similar to that of Heine and Abarenkov[9] except that theirs is not strictly rigorous because their A_l are determined from atomic term values and the poten-