lel to the c axis, the resonance is with the B exciton series in which $E_{1s} = 2.569$ eV.) The Raman efficiency of the forbidden 1LO at 4965 Å $[(E_{1s} - \omega_i)/\omega_0 = 1.8]$ may be found from Table I and absolute measurements[15] of the A_1 TO intensity at 5145 Å to be 0.6×10^{-7}/cm sr in excellent agreement with the theory.

Consider now the alternative interpretation based on extrinsic bound excitons. For I_1 or I_2 type impurity states one expects 1LO to be greatly broadened (~2LO width); this has been observed by Colwell and Klein.[3] In the present work, however, the 1LO width is invariant (2 ± 0.2 cm^{-1}) for allowed or forbidden lines at all reported ω_i. Our data could be explained (including the resonance enhancement) by a very shallow unknown impurity state of radius ~100 Å, but it would be unlikely that a state with such large oscillator strength would escape detection in absorption and luminescence. Forward scattering measurements which would also distinguish between intrinsic and extrinsic processes have not been made because of difficulties in analyzing measured intensities.

In conclusion, large forbidden 1LO Raman scattering has been observed near resonance in good agreement with theoretical calculations in which the resonant intermediate states are intrinsic hydrogenic excitons. All theoretical results are independent of crystal symmetry; consequently large forbidden 1LO lines near resonance are expected in a wide range of crystals, including many for which 1LO is completely inactive and cannot be detected in any geometry far from resonance.

We are indebted to J. F. Scott and E. O. Kane for many helpful discussions and to P. J. Colwell and M. V. Klein for a preprint of their work before publication.

[1]J. F. Scott, R. C. C. Leite, and T. C. Damen, Phys. Rev. 188, 1285 (1969) and references given there.
[2]M. V. Klein and S. P. S. Porto, Phys. Rev. Lett. 22, 782 (1969).
[3]P. J. Colwell and M. V. Klein, to be published.
[4]M. P. Fontana and E. Mulazzi, Phys. Rev. Lett. 25, 1102 (1970).
[5]R. Loudon, J. Phys. (Paris) 26, 677 (1965); A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967); D. C. Mills and E. Burstein, Phys. Rev. 188, 1465 (1969).
[6]D. C. Hamilton, Phys. Rev. 188, 1221 (1969).
[7]B. Bendow *et al.*, Optics Commun. 1, 267 (1970).
[8]E. Mulazzi, Phys. Rev. Lett. 25, 228 (1970).
[9]Explicit details are given in R. M. Martin, to be published.
[10]See, for example, A. Pinczuk and E. Burstein, Phys. Rev. Lett. 21, 1073 (1968).
[11]Polariton effects are important only very near resonance with the exciton (within ~1 meV in CdS).
[12]R. Loudon, Advan. Phys. 13, 423 (1964).
[13]Y. Toyazawa, Prog. Theoret. Phys. 20, 53, (1958).
[14]It is noteworthy that for an allowed geometry with $\vec{\epsilon}_i \perp \vec{\epsilon}_s$, the LO/TO ratio actually *decreases* near resonance because of cancelations. Thus previously published (Refs. 1, 7) unpolarized data need not have any simple theoretical form as a function of ω_i.
[15]C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. 191, 1351 (1969).

Observation of Electron Standing Waves in a Crystalline Box

R. C. Jaklevic, John Lambe, M. Mikkor, and W. C. Vassell
Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121
(Received 30 November 1970)

We have observed electron standing-wave states in thin Pb films by electron tunneling. The simple theory includes the important fact that oriented crystalline films will vary in thickness only by discrete steps. As a result, certain "commensurate" energy levels play an important role in the experiment.

The description of a particle confined to a box of finite dimensions is a basic problem in quantum mechanics. As is well known, the particle has available to it a series of energy levels whose spacing varies with the size of the box. This Letter reports a direct observation and study of these states in crystalline Pb, in the form of thin films. The term crystalline is used to emphasize that, while real metal films are not perfectly smooth, they nevertheless may vary in thickness only by discrete steps. This fact has very significant experimental consequences related to the observability of the box-quantized energy levels in Pb films. Briefly, the energy-level structure of these crystalline films is found to possess special "commensurate" lev-

els. These energy levels will be aligned so long as only discrete variations in thickness are permitted. Such states are related to momenta whose wavelengths are commensurate with the crystal lattice spacing.

The theory of quantum size effects in electron tunneling[1] can be discussed most simply in terms of standing-wave states obtained by requiring nodes of the wave function at the boundaries of the metal film. The component of the crystal momentum k normal to the film surface is restricted to the values

$$k = n\pi/t, \quad n = 1, 2, \cdots, \tag{1}$$

where t is the film thickness.

The energy levels are $E_n = E(k) + E(k_\parallel)$, where $k_\parallel$ is the component of momentum parallel to the film. It would be expected that such a series of quantized energy levels would be observable as a series of peaks in the tunneling conductance $G = dI/dV$. For specular tunneling only states with small $k_\parallel$ and small $E(k_\parallel)$ will be involved. The successful observation of these states would require good orientation of all crystal grains and a mean free path at least comparable with the film thickness. These requirements can be met, it appears, to a satisfying degree. It would also appear that film smoothness of a fraction of an electron wavelength is required, a difficult achievement. In this regard, however, it is essential to note that the thickness of a crystalline box is given by

$$t = Nd, \tag{2}$$

where N is an integer and d is the appropriate lattice spacing for the particular orientation of the film. (For the [111] orientation $d = a/\sqrt{3}$, where a is the lattice constant.) Equation (1) then will be

$$k = n\pi/Nd. \tag{3}$$

Therefore, a real metal film composed of sections of differing N values will yield a tunneling spectrum which is a sum of the conductances contributed by those areas of different N values. In general the energy levels of a given N will not line up with those of any other N value. However, there are certain states, which we call commensurate states, whose energy levels are independent of the value of N. These states are those whose wavelength is commensurate with the lattice spacing d. For example, the state $k = \frac{1}{2}\pi/d$ will exactly "fit" in the crystalline box for all even values of N. Therefore the energy levels $E(\frac{1}{2}\pi/d)$ are the same for any even value of N. This level, and nearby levels, will tend to line up and be resolved in the tunneling measurement with the level $E(\frac{1}{2}\pi/d)$ being the most prominent. Other levels near this commensurate one will be observed, since their values will depend only weakly on N. The peaks will gradually die out in intensity away from the commensurate one. Also, those film sections of odd N will yield a set of states which just interleave those from the even set. For example if the average $\bar{N}$ is 100, then N might range between 95 and 105 for typical surface roughness. It is easy to do a simple graphical summation for this model and see these general features. If such a commensurate point is observed by a tunneling experiment, states in the band structure related to well-defined k values can be located with respect to the Fermi level. Also, the observed spacing yields a value of the group velocity

$$v_g = \frac{1}{\hbar}\frac{\partial E}{\partial k} = Q\left(\frac{2\Delta V t}{h}\right), \quad Q = 1, 2, 3, \cdots,$$

where ΔV is the observed spacing in the tunneling spectrum. The proper value of Q depends upon the commensurate state around which the spectrum is observed. For simplicity, consider the commensurate states for which $Q = 1$ or 2. $Q = 1$ corresponds to the commensurate state $k = \pi/d$ which is, of course, the zone boundary. Here energy levels for states of any N will line up. $Q = 2$ corresponds to the commensurate state $k = \frac{1}{2}\pi/d$ which was discussed above. For higher Q values, a greater amount of interleaving of the levels from different N will occur and hence will make observability more and more difficult.

The tunneling experiments were carried out with Al-(Al oxide)-Pb or Mg-(Mg oxide)-Pb tunneling diodes fabricated according to established procedures.[2] The Al or Mg films (1000-Å thickness) were vacuum deposited on glazed alumina or fused silica substrates, and the oxide layer was formed by exposure to a gas discharge. To promote smoothness, the Pb was deposited with the substrate cooled to about 100°K and then warmed up to room temperature in vacuum in about one-half hour. The vacuum system was oil free and pressures below 5×10^{-8} Torr were maintained during Pb deposition. X-ray examination of the Pb films revealed a strong [111] texture which is characteristic of fcc films.[3] Optically, the Pb films were quite smooth and did not show the obvious roughness usually obtained for room-temperature-deposited films. The

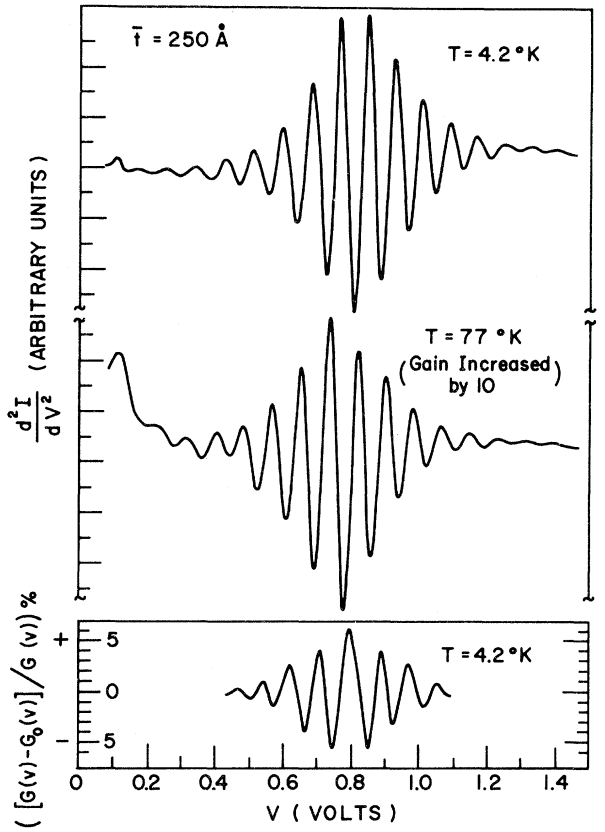

FIG. 1. Experimental traces of dI/dV and d^2I/dV^2 for an Al-(Al oxide)-Pb (250 Å) showing the strong size-dependent structure. Peak spacing ΔV is nearly uniform over the voltage range. A small amount of background has been subtracted from the d^2I/dV^2 curves.

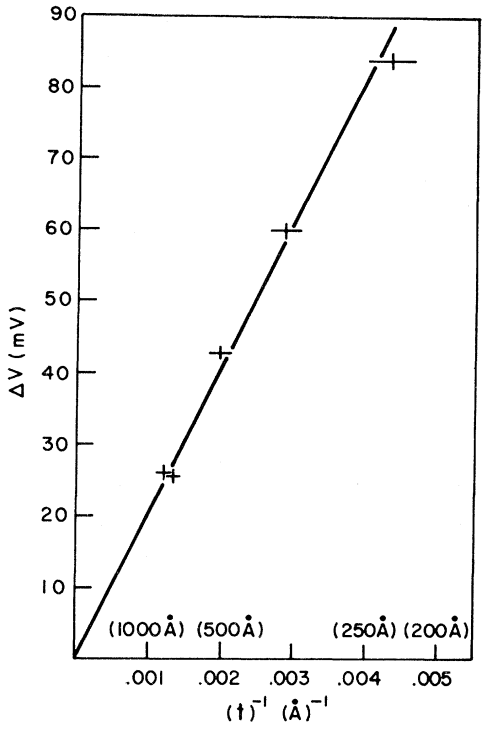

FIG. 2. Plot of experimental peak spacings ΔV in the vicinity of 0.8 V versus $\bar{t}^{-1}$ for several diodes at 4°K. These were made on fused-silica substrates to facilitate thickness measurement. By simple standing-wave theory, the straight line corresponds to a group velocity of 2×10^8 cm/sec.

actual roughness could not be measured, but examination with an electron microscope showed the grain size to be several hundred angstroms. Film thicknesses were determined by optical interferometry. Tunneling resistances in the range 50-1000 Ω were obtained for areas of several square millimeters. Measurements of $G = dI/dV$ and d^2I/dV^2 versus V were made at 4 and 77°K using an established ac technique.[2]

Experimental traces of dI/dV and d^2I/dV^2 versus V are shown in Fig. 1 for an Al-(Al oxide)-Pb diode with a Pb film of 250-Å thickness. The evenly spaced structure is observed with the Pb positive with respect to the Al electrode over a voltage range from about 0.1 to 1.5 V. This means that the energy levels located above the Fermi level of Pb are involved. The peak spacing varies inversely with thickness, a clear indication of a size effect. Although weaker, the structure is present at 77°K, which rules out size effects related to superconductivity.[4] These structures have been observed for Pb thicknesses from 250 to 900 Å and the effects exist independently of whether the counterelectrode is Mg or Al. In magnitude, the largest peaks correspond to a 10% change in diode conductance. Magnetic fields up to 10 kG do not affect the structure.

A significant fact is that the dI/dV spectra at 4°K are nearly symmetric about the prominent peak near 0.8 V. For spectra taken from different Pb thicknesses, this peak remains fixed, while the others move about. Thus, the positions of peaks in the wings of the spectra are much more sensitive to thickness than the 0.8-V line. A slight shift of this central line occurs on warming to 77°K.

The spacing ΔV of the structure varied with thickness according to the data shown in Fig. 2 where ΔV is plotted versus $\bar{t}^{-1}$. The points shown are obtained from diodes made on fused silica substrates in order that the film thicknesses could be measured as accurately as possible. The straight line is a reasonable fit to the data. All the diodes studied produced a ΔV which fitted this line, within experimental accuracy.

Further observational details can be listed as

follows. Films deposited in oil-pumped vacuum systems did not show the full periodic structure. However, structure still is apparent near 0.8 V. An overlayer of Ag (1000-Å thickness) extinguishes the structure while 500 Å of Sn or Ge weakens it severely. All of these observations probably relate to film purity, smoothness, grain size and texture, and boundary conditions.

These results can be understood in terms of the simple picture of electron standing waves in a Pb film of variable thickness as presented above. An examination of the Pb band structure calculated by Anderson and Gold[5] indicates that a state 0.75 eV above the Pb Fermi level would correspond to the $E(\frac{1}{2}\pi/d)$ commensurate level for a momentum halfway through the second band in the [111] direction. In Fig. 3, this portion of the $E(k)$ curve is shown together with a schematic energy level spectrum for 250- and 300-Å thicknesses. These represent the expected structure for a composite film with variations in thickness of about 10%. The spectra are constructed by adding up the contribution to the tunneling conductance from each section of the film with a given N value. A perfectly uniform film would yield a set of lines of equal amplitude with twice the spacing shown. The spectra are centered about the point $E(\frac{1}{2}\pi/d)$ which is located at 0.75 eV above the Fermi energy, in close agreement with the actual data. The lines on the wings shift with thickness, in agreement with experiment. The two important parameters for comparing this experiment to theory are v_g and the central commensurate point $E(\frac{1}{2}\pi/d)$. Theoretical values for these quantities obtained from the curve of Fig. 3 are shown in the following table:

	v_g (cm/sec)	$E(\frac{1}{2}\pi/d)$ (eV)
Theory (Ref. 5)	1.9×10^8	0.75
Experiment	2.0×10^8	0.78

The agreement is satisfactory. The measurement of these parameters is new and yields information about band structure not accessible by other methods.

Other details of the experiment agree with expectations in a reasonable manner. Since the structure vanishes for $t \gtrsim 1000$ Å, it can be estimated from mean-free-path considerations that the lifetime for a state would limit resolution for these thicknesses. Another resolution limit will be encountered as soon as the level spacing is so small that the finite angle of the tunneling cone includes more than one level. This also limits observation to thicknesses of the order of 1000 Å or less.

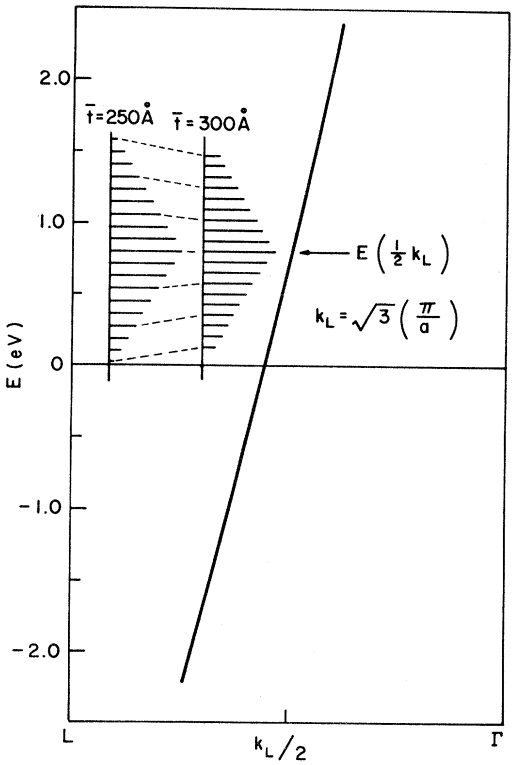

FIG. 3. Plot of a portion of the curve of $E(k)$ versus k for Pb from Anderson and Gold. The slope yields a group velocity of 1.9×10^8 cm/sec at 0.75 eV above the Fermi level. This energy level is the $E(\frac{1}{2}\pi/d)$ commensurate level. (The zone-boundary momentum is $k_L=\pi/d=\sqrt{3}\,\pi/a$.) Two schematic tunneling spectra are indicated, for two hypothetical average thicknesses with a roughness of ±10%. Note the coincidence of the $E(\frac{1}{2}\pi/d)$ level for both cases with gradual misalignment away from this level.

This discussion has not considered in any detail other aspects of this problem. For example, any significant dependence of mean free path on k would modify the predicted spectra. Similarly the specularity of tunneling and reflection plays an important role. It might be expected that the state $E(\frac{2}{3}\pi/d)$ should be observed since it is about 1.3 eV below the Fermi level. In fact it is not seen. These and other questions must be left for future work.

In summary, these experiments show directly the existence of electron standing-wave states in thin films. This is a new experimental approach to the measurement of certain characteristics of energy bands. A simple theoretical model has been presented which underscores

the fact that surface roughness consisting of discrete steps plays a vital role in these observations.

[1]C. B. Duke, *Tunneling in Solids* (Academic, New York, 1969).
[2]J. Lambe and R. C. Jaklevic, Phys. Rev. 165, 821 (1968).
[3]E. Bauer, in *Single-Crystal Films*, edited by M. H. Francombe and H. Sato (Pergamon, New York, 1964), p. 43.
[4]W. J. Tomasch, Phys. Rev. Lett. 15, 672 (1965); W. L. McMillan and P. W. Anderson, Phys. Rev. Lett. 16, 85 (1966); J. M. Rowell and W. L. McMillan, Phys. Rev. Lett. 16, 453 (1966).
[5]J. R. Anderson and A. V. Gold, Phys. Rev. 139, A1459 (1965). We wish to thank Professor Anderson for providing us with an enlargement of Fig. 11 of this reference.

Hot-Hole–Electron Cascades in Field Emission from Metals

J. W. Gadzuk and E. W. Plummer
National Bureau of Standards, Washington, D. C. 20234
(Received 12 November 1970)

Recent field-emission tunneling experiments have shown a current-dependent tail in the energy distribution for energies above the Fermi energy. This tail can be understood in terms of the products of a cascade process initiated by the injection of hot holes (removal of electrons by field emission) into the interacting electron gas or metal conduction band. The derived shapes of the tails, numerical values of the high-energy distributions, and field dependences of the current in the tails are in good agreement with our experimentally observed results.

Measurements of the total-energy distribution (TED) of electrons which are field emitted from metal electrodes have provided useful information pertaining to the electronic states of both the surface and interior of the metal.[1-4] In these studies, aside from the thermal field-emission work,[3] only electronic states with energies less than the Fermi energy have been accessible to measurements. Recently Plummer[5] and also Lea and Gomer[6] have observed unexpected high-energy tails in TED's from tungsten. The usual expression for the TED or incremental change in current per unit change in energy is[1]

$$\frac{dj}{d\epsilon} = j'(\epsilon) = \frac{J_0}{d} e^{\epsilon/d} f(\epsilon), \tag{1a}$$

and the total current

$$J_0 = (4\pi med^2/h^3) e^{-c}, \tag{1b}$$

with $\epsilon = E - E_F$ the energy relative to the Fermi level; $1/d = 1.025\varphi^{1/2} t(F, \varphi)/F$ eV^{-1}, $f(\epsilon)$ the Fermi function, $c = 0.68\varphi^{3/2} v(F, \varphi)/F$, t and v tabulated elliptic functions accounting for the image potential rounding of the surface barrier,[3,7] φ the electron work function given in electron volts, and F the applied field in volts per angstrom. Some experimentally observed TED's from the (111) plane of tungsten are shown in Fig. 1 for various fields, and thus current densities. For energies 7 eV $\leq \epsilon \leq 0$, the behavior of the TED is what one would expect from Eq. (1). At lower energies band-structure and surface-state effects give rise to the added structures.[2] The dotted line above the Fermi energy is the Boltzmann tail predicted at 78 K. The rather striking departure from the Boltzmann tail at high energies,

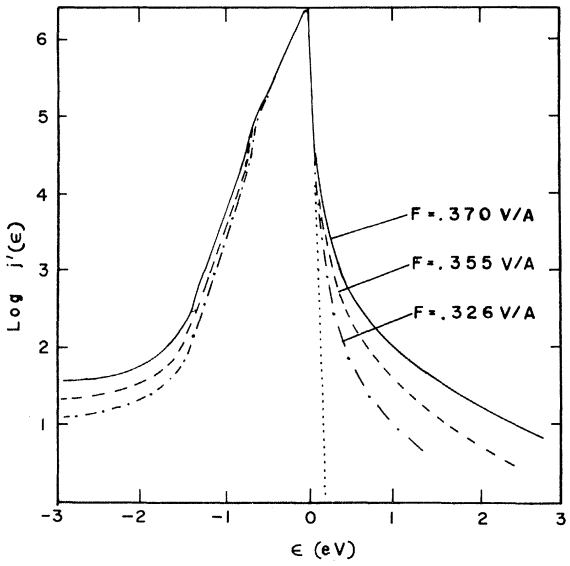

FIG. 1. TED from (111) W at 78 K. The fields and current densities calculated from the slope of the Fowler-Nordheim (FN) plot are 0.326, 0.355, and 0.37 V/Å and 4.7×10^3, 2.5×10^3, and 5.2×10^3 A/cm^2. The curves are normalized properly from FN plots.