

Field Emission from Bismuth and Tungsten in a Magnetic Field*

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Detailed calculations of magnetic-field-induced quantum effects in bismuth are described. In agreement with previous calculations, it is found that 10% fluctuations in the field-emission current can be expected at moderate fields if only the conduction electrons contribute to the field-emitted current. The magnitude of the fluctuations decreases significantly if other bands contribute to the field-emission current. In particular, when the contribution from the hole band is included in the calculations for a magnetic field parallel to the trigonal axes, the magnitude of the magnetic-field-induced fluctuations is reduced to 0.23%. Two experimental attempts to observe quantum effects are described. In the first, the current was measured as a function of magnetic field for fields up to 45 kG. In the second, the magnetic field was modulated and the in-phase fluctuations of the field-emission current were measured. No dc magnetic-field-induced quantum effects larger than 0.5% were observed from bismuth or tungsten and no fractional current changes larger than 2×10^{-4} were observed for a 40-G-rms field modulation. Both techniques had sufficient sensitivity to measure effects had the conduction band been the only contributor to the field-emission current. These null experimental results support the theoretical prediction that other bands besides the conduction band would reduce the relative magnitude of the magnetic-field-induced effects. Another experimental technique in which the magnetic-field-induced fluctuations would be enhanced to measurable values is proposed.

I. INTRODUCTION

Several workers have suggested the possibility of observing magnetic-field-induced quantum effects in the field-emission current from a system with low effective masses.¹⁻³ Oscillations in the Fermi energy and the density of states at the Fermi level are expected for a low-effective-mass system in a magnetic field and both of these effects could lead to fluctuations of the field-emission current in a magnetic field. The work of Blatt² predicts 10% oscillations in the field-emission current from bismuth for magnetic fields of 10 kG, and larger fluctuations at higher magnetic fields. Although numerical estimates are not made by the other workers, they obtain similar equations. No explicit theoretical calculations of the field-emission current from tungsten in the presence of a magnetic field have been made.

Experimental attempts to measure these magnetic-field-induced quantum effects have yielded conflicting results. Flood⁴ reported no fluctuations in the field-emission current larger than 1% for cathodes at 1.2°K in fields between 0 and 100 kG. Among the field-emitting materials he investigated were oriented single crystals of bismuth, and tungsten tips prepared from high-purity polycrystalline wire. Recently, Buribaev and Shishkin⁵ reported a 20% drop in the field-emission current from tungsten for fields between 0 and 5 kG, and the beginning of oscillatory behavior for fields up to 15 kG. The initial drop was observed for experiments per-

formed both at 300 and 78°K, but the oscillatory behavior only appeared at 78°K. The results of Buribaev and Shishkin are in obvious disagreement with the work of Flood.

This work considers the theoretical and experimental details of the field-emission current from bismuth in a magnetic field. Bismuth was chosen because it has extremely low effective masses, and is thus strongly influenced by a magnetic field.⁶ The calculations show that magnetic-field-induced fluctuations are relatively large if just the contribution from the conduction band is considered, but the contribution of the hole band reduces the magnitude of the fluctuations by a factor of 40. Experimental results are also given for tungsten because of the recent work done by Buribaev and Shishkin. Although two distinct experimental techniques were utilized to detect magnetic-field-induced current fluctuations, none were observed. Such null results are consistent with the theoretical results derived for bismuth. A possible explanation of the results of Buribaev and Shishkin is given. A technique is proposed which would possibly allow detection of magnetic-field-induced quantum effects using the field-emission process.

II. CALCULATION OF FIELD-EMISSION CURRENT

The electron states of bismuth are well described in terms of the effective mass approximation. For a uniform magnetic field H in the z direction, the energy of a state labeled by the quantum numbers (n, s, k_z) is given by⁷

$$E_{n,s,k_z} = (n + \frac{1}{2}) \frac{e\hbar H}{m_c^* c} + \frac{s}{2} \frac{m_0}{m_s^*} \mu_B H + \frac{\hbar^2 k_z^2}{2m_z^*} . \quad (1)$$

Here n has integer values greater than or equal to zero, and $s = \pm 1$. The cyclotron effective mass is given by m_c^* , m_s^* is the spin effective mass, and m_z^* is the z -directional effective mass. For a system in a magnetic field, the spatial density of states is given by the sum

$$N = \frac{eH}{2\pi\hbar c} \sum_{s=\pm 1} \sum_{n=0}^{\infty} \int_0^{\infty} dk_z f_0(E_{n,s,k_z}) , \quad (2)$$

where

$$f_0(x) = (1 + e^{(x-\mu)/k_B T})^{-1} . \quad (3)$$

Here μ is the Fermi energy. Since the velocity of an electron incident on the surface is $\hbar k_z/m_z^*$, the total field-emission current is given by the expression

$$J = \frac{e^2 H}{2\pi\hbar c} \sum_{s=\pm 1} \sum_{n=0}^{\infty} \int dk_z \frac{\hbar k_z}{m_c} f_0(E_{n,s,k_z}) D(E_{n,s,k_z}) , \quad (4)$$

where $D(E)$ is the field-emission tunneling probability.

The field-emission tunneling probability was first calculated by Fowler and Nordheim.⁸ For the one-dimensional model they considered, the tunneling probability is given to a good approximation⁹ by

$$D(E) = \exp \left[-\frac{4}{3} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{(\phi - E)^{3/2}}{eF} \right] \quad (5)$$

$$= e^{-a} e^{bE} , \quad (6)$$

where

$$a = \frac{4}{3} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{\phi^{3/2}}{eF} , \quad (7)$$

$$b = 2 \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{\phi^{1/2}}{eF} . \quad (8)$$

Here E is the energy of the electron with respect to the Fermi energy, ϕ is the work function, and F is the applied electric field.

In the usual Fowler-Nordheim theory, the energy entering into the tunneling probability is taken to be the z component of the total energy. A certain ambiguity arises over what expression to use for the energy which enters the tunneling probability when field emission from a low-effective-mass system is considered. For a typical work function of 4 eV and an electric field of 20 MV/cm which gives an appreciable field-emission current, the width of the barrier through which an electron must tunnel to be field emitted is 20 Å. The wave function of the electron is thus not influenced by the lattice for most of the length of the barrier. Thus it seems likely that the appropriate mass associated with the motion of the electron in the barrier is the free-electron mass rather than the effective mass inside

the solid. The angular momentum of a state with quantum number n whose energy is given by Eq. 1 is simply $n\hbar$. The ratio of the cyclotron orbital energy associated with the quantum number n in a low-effective-mass system to the energy associated with this same angular momentum quantum number in a free-electron system is just m_0/m^* . If angular momentum is conserved during the field-emission process, the energy associated with the orbital energy of the wave function in the solid must be transferred to the z -directional energy associated with the free-electron wave function in the barrier. Thus it is possible that the *total* energy of the electron state in the solid enters the tunneling probability rather than just the energy in the z direction.

Combining Eqs. (4) and (6) and performing the sum at zero temperature, the field-emission current density can be calculated in closed form.

These calculations were performed using both the total energy and the energy in the z direction in the tunneling probability. Both of these results were applied to bismuth. The effective-mass parameters, as well as the self-consistent technique used to calculate the Fermi energy of the conduction band of bismuth given by Smith, Baraff, and Rowell,⁷ were used. These parameters yield a spin effective mass of $0.024m_0$, cyclotron effective mass of $0.014m_0$, and z -directional effective mass of $0.0044m_0$ for a single crystal of bismuth oriented such that the applied magnetic field is parallel to its trigonal axis. Figure 1 shows the calculated field-emission current from the conduction band as a function of magnetic field. The magnitude of the magnetic-field-induced current variations increases as the magnetic field increases. The variation in the field-emission current between 32 and

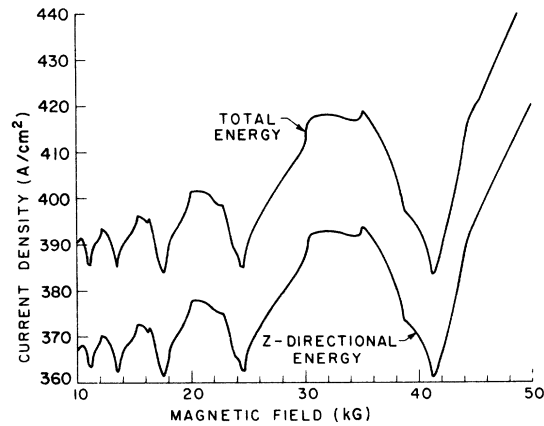


FIG. 1. Field-emitted current from the conduction band of bismuth. The upper curve results when the total energy of an electron state is used in the tunneling probability, and the lower when the Z component is used. The oscillations are the result of quantum phenomena.

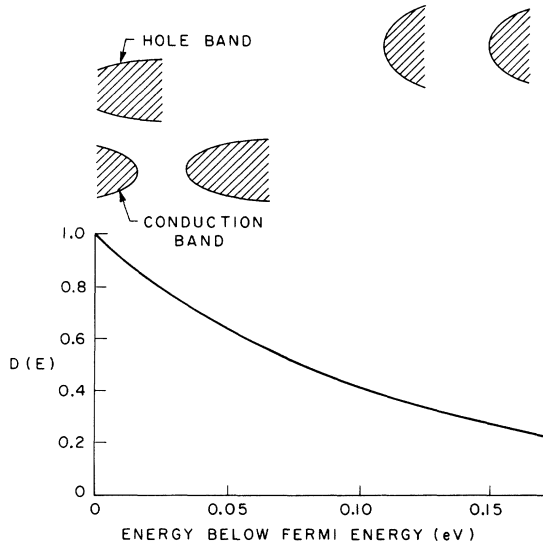


FIG. 2. Field-emission transmission probability and the band structure of bismuth. The bottom half of the figure shows the field-emission tunneling probability for electrons with different energies below the Fermi surface. The top part of the figure shows the bands of bismuth plotted on the same horizontal energy scale. It is apparent that the field-emission current has contributions from several bands.

41 kG is approximately 10%. The calculated field-emission currents inserting both the total energy and E_z in the tunneling probability are very similar, indicating that this is not an important consideration.

According to these calculations, variations in the field-emission current from bismuth would be easily measurable if just the conduction band contributed to the field-emission current. This result is consistent with the results of earlier workers. The possibility, however, of obtaining substantial field-emission current from other bands besides the conduction band, which had not been considered by previous workers, can have important effects on the field-emission current. Figure 2 shows the field-emission transmission probability plotted as a function of energy beneath the Fermi surface. On the same energy scale, the band structure of bismuth is shown.¹⁰ Electrons from the hole band and other lower-lying bands which are not strongly influenced by a magnetic field will also be field-emitted. The contribution of this current to the field-emission current will severely reduce the magnitude of the magnetic-field-induced quantum effects. The transmission probability illustrated is for an electric field of 21 MV/cm. Even for such a modest field, however, the contribution from lower-lying bands is not negligible.

The contribution to the field-emission current from the electrons in the hole band was calculated.

The energy levels of the electron states in the hole band are given in the effective-mass approximation by⁷

$$E = E_0 - \frac{\hbar^2 k_z^2}{2m_z^*} - (n + \frac{1}{2}) \frac{e\hbar H}{m_c^* c} - \frac{s}{2} \frac{m_0}{m_s^*} \mu_B H. \quad (9)$$

Here E_0 is the energy between the bottom of the conduction band and the top of the hole band, which is 38.5 meV for bismuth. An expression for the total field-emitted current from this band using the total energy in the tunneling probability was derived. The derivation proceeded directly from Eqs. (4) and (6), using the energies in the tunneling probability given by Eq. (9). Figure 3 shows the total field-emission current, including contributions from both bands as a function of magnetic field. The relative magnitude of the magnetic-field-induced fluctuations is reduced by approximately a factor of 40 when the contribution from the hole band is included into the calculation. Other bands which were not considered in the calculation would also be expected to make a contribution to the field-emission current.

III. EXPERIMENTS

Experiments were performed in an effort to observe magnetic-field-induced current fluctuations in tungsten and bismuth. Field emission was performed in a specially constructed ceramic tube which was evacuated at room temperature to a pressure less than 10^{-9} Torr, sealed, and totally immersed in liquid helium. This tube was placed inside of a superconducting magnet. Figure 4 shows the electronics used. The current leaving the tip was measured to avoid any problems associated with secondary-electron emission at the collector and electron-optical problems associated

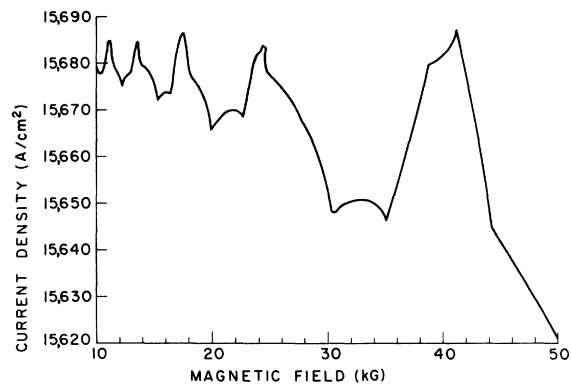


FIG. 3. Field-emitted current from the conduction and hole bands of bismuth as a function of magnetic field. A comparison of Figs. 1 and 3 shows the presence of electron states near the Fermi energy in the hole band reduces the magnitude of quantum effects by a factor of 40.

with the collection process.

Tips of bismuth were formed by electrolytically removing material from oriented single crystals to form a small field-emission tip with radius of approximately 10^{-4} cm. This was done by rubbing the tip on an uninked rubber-stamp pad which had been impregnated with a saturated KI, 0.06-mole % HCl solution. The tip was held at a potential of 6 V relative to the pad. Experiments were performed on bismuth single crystals oriented so that the magnetic field was parallel to the trigonal axis, binary axis, and bisectrix axis. Tips of tungsten were constructed using the standard electropolishing techniques¹¹ out of high-purity polycrystalline wire which had been annealed at 2200 °C. For all experiments performed, the magnetic field was parallel to the applied electric field, and the magnetic field was perpendicular to the surface of the emitting tip.

Two methods were used to search for the magnetic-field-induced current changes: The first method accurately measured the current as a function of the magnetic field; the second electronically measured the derivatives of the functional relationship between the current and the magnetic field.

The first type of experiment was performed by recording the field-emission current as a function of magnetic field for fields between 0 and 45 kG. By sweeping the magnetic field back and forth over a given region, systematic variations of the current larger than 0.5% were visible. No such variations were seen. The accuracy of these experiments was limited by noise intrinsic to the field-emission process. A different experimental technique was therefore attempted.

Experiments were performed using the ac-modulated magnetic field and the phase-sensitive detection scheme shown in Fig. 5. Such a technique measures the in-phase fluctuations of the field-

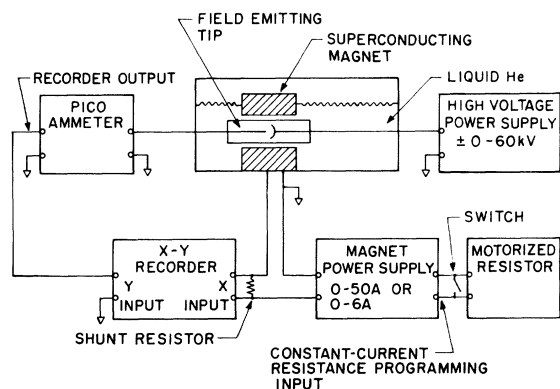


FIG. 4. Electronics for field-emission in a dc magnetic field.

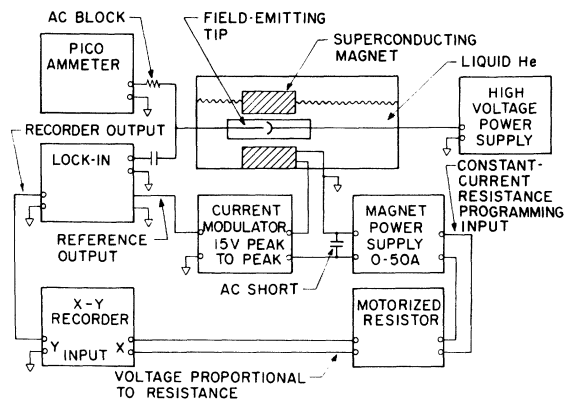


FIG. 5. Electronics for field-emission in an ac magnetic field.

emission current caused by the modulated magnetic field, and is sensitive to large slopes in the relationship between the current and the magnetic field. The discontinuities and thus large slopes which are present in Figs. 1 and 2 motivated such a technique. Furthermore, such a technique allows averaging to be performed for long times in order to raise the signal-to-noise ratio. For a 40 G-rms magnetic field modulation, no effects which gave rms modulations of the field-emission current larger than 2×10^{-4} of the total field-emission current were observed. These measurements were made at average fields between 0 and 35 kG. Total field-emission currents of between 5 and 10 nA were used. These were the smallest currents possible which gave a tolerable signal-to-noise ratio. It is desirable to use the smallest possible total field-emission current because then the contribution from the conduction-electron states is proportionally larger. The sensitivity of the experiments was limited by the noise intrinsic to the field-emission process.¹²

The experiments performed in the dc magnetic field had sufficient sensitivity to detect the predicted 10% current fluctuations in the current coming from the conduction-electron states. The failure to observe these fluctuations, which is consistent with the work of Flood,⁴ suggests that the presence of bands other than the conduction band obscures the magnetic-field-induced quantum effects present in the current from the conduction band. Similarly, the null result of the modulated magnetic field experiment also indicates the presence of other bands. Unfortunately, the sensitivity of these experiments was not sufficient to indicate how many additional bands were contributing to the field-emission process.

The null experimental results obtained for the experiments performed on tungsten disagree with the results of Buribaev and Shishkin.⁵ The magnet-

ic-field-induced effects observed by Buribaev and Shishkin are thought to be the result of a process other than magnetic-field-induced quantum effects in the bulk emitter material. The presence of an adsorbed-atom layer on the surface of a field-emission tip can enhance the field-emission current from the tip by several orders of magnitude.¹³ For field-emission tips covered with adsorbed atoms, current decreases similar to those seen by Buribaev and Shishkin were observed. These experiments are described in detail in a separate paper.¹⁴ In these experiments, however, magnetic fields between 0.2 and 1.5 kG changed the magnitude of the emitted current by up to 50%. Furthermore, magnetic fields also changed the slope of the Fowler-Nordheim plot. Such changes in slope for data taken in the presence of a magnetic field were also seen by Buribaev and Shishkin. Tips which were cleaned by the technique of reverse field desorption^{13,15} exhibited no current changes in a magnetic field. Flood, who saw no magnetic-field-induced current changes, reported using such a technique to clean his emitters.

There are other reasons for questioning the interpretation given by Buribaev and Shishkin for their results:

(1) The lowest effective mass of the conduction electrons in tungsten is $0.2m_0$.¹⁶ At 300°K, the difference between the magnetic quantum levels is less than thermal energies. This would make observation of quantum effects impossible at room temperature. Nevertheless, Buribaev and Shishkin indicate that decreases at 300°K were seen.

(2) Tungsten has two sets of hole bands.¹⁶ The contribution to the field-emission current from these bands would reduce the relative magnitude of the quantum effects from the conduction band, just as was the case for bismuth.

(3) None of the existing theories of field-emission in a magnetic field predict large decreases in field-emission current for magnetic fields between 0 and 5 kG. In particular, such decreases are inconsistent with the relatively large effective masses of tungsten.

IV. POSSIBLE FUTURE EXPERIMENTS

A field-emission experiment sensitive to magnetic-field-induced quantum effects seems possible. Energy analyzers have been employed to study the energy distribution of the field-emitted current from various field emitters. Kuyatt and Plummer describe an energy analyzer with a resolution of 10 meV.¹⁷ Although these techniques are not directly applicable to experiments performed in a magnetic field, preliminary analysis shows that energy analysis is possible in a region surrounded by a superconducting shield. A device sensitive only to the electrons with energies near the Fermi

energy rejects the contributions to the field-emission current from the lower-lying bands which obscure the quantum effects.

Figure 6 shows the total field-emission current which comes from the states between the Fermi energy and 30 meV below the Fermi energy. The variation in the field-emission current between 32 and 41 kG is approximately 2.6%. Such a variation would be measurable.

The possibility that the field-emitted electrons would possess a net spin polarization was also investigated. Such a polarization results from the fact that a lower number of magnetic quantum levels are present in the system, and so an unequal number of spin-up and spin-down levels would be occupied. Farago mentions the possibility of using such a technique to produce a beam of polarized electrons from InSb.¹⁸

The spin polarization of the current emitted from bismuth can be calculated by performing the spin sums of Eq. (4) independently. These calculations indicate that 100% polarizations would be possible for crystals located in a magnetic field perpendicular to the trigonal axis for fields less than 50 kG if only the electrons from the conduction band contribute to the total current. The maximum polarization is reduced to 6% at 50 kG when the contribution from the hole band is included. The effect of additional bands on the polarization was not calculated.

Energy-analysis techniques would also increase the spin polarization which could be obtained from

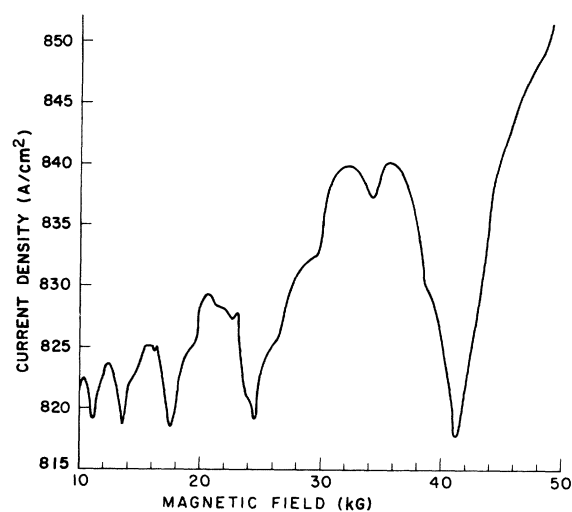


FIG. 6. Field-emitted electrons from bismuth with energies between the Fermi energy and 30 meV below the Fermi energy. An experiment which was sensitive only to electrons with energies near the Fermi energy would measure enhanced quantum fluctuations.

the field-emission process. Figure 7 shows the polarization of the field-emission current from those states within 30 meV of the Fermi energy for a single crystal of bismuth oriented with the trigonal axis parallel to the applied magnetic field. Polarizations as large as 30% for fields of 50 kG are possible.

Thus an experiment in which one performs an energy analysis on the field-emission current from bismuth might be sensitive to magnetic-field-induced quantum effects. Furthermore, those electrons with energies near the Fermi energy would be polarized. A bismuth field emitter in a magnetic field combined with an energy filter would therefore be a source of polarized electrons.

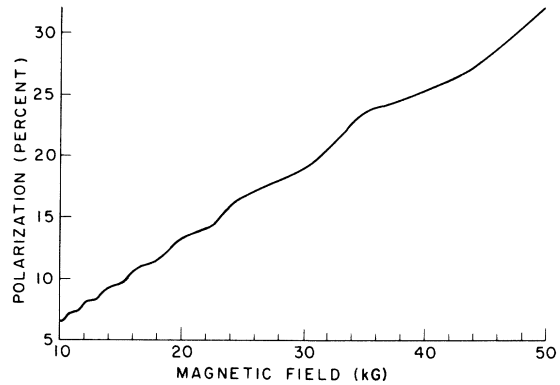


FIG. 7. Polarization of field-emitted electrons with energies near the Fermi surface for the trigonal orientation.

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¹Sh. M. Kogan and V. D. Sandorminsky, *Radio Engineering and Electron Physics* **9**, 586 (1964).

²F. J. Blatt, *Phys. Rev.* **131**, 166 (1963).

³G. A. Gogadze, F. I. Itskovich, and I. O. Kulik, **46**, 93 (1964) [*Sov. Phys. JETP* **19**, 622 (1964)].

⁴D. J. Flood, *J. Phys. Chem. Solids* **31**, 1649 (1969).

⁵I. Buribaev and B. B. Shishkin, *Fiz. Tverd. Tela* **12**, 3309 (1970) [*Sov. Phys. -Solid State* **12**, 2678 (1971)].

⁶L. A. Fal'kovskii, *Usp. Fiz. Nauk.* **94**, 3 (1968) [*Sov. Phys. Uspekhi* **94**, 1 (1968)].

⁷G. E. Smith, G. A. Baraff, and I. M. Rowell, *Phys. Rev.* **135**, A1118 (1964).

⁸R. H. Fowler and L. W. Nordheim, *Proc. Roy. Soc.*

119, 173 (1938).

⁹T. L. Martin and W. F. Leonard, Jr., *Electrons and Crystals* (Brooks-Cole, Belmont, Calif., 1970), p. 636.

¹⁰L. Esaki and P. J. Stiles, *Phys. Rev. Letters* **14**, 902 (1965).

¹¹W. P. Dyke and W. W. Dolan, *Adv. Electronics and Electron Phys.* **8**, 89 (1961).

¹²Ch. Kleint, *Surf. Sci.* **25**, 394 (1971).

¹³C. B. Duke and M. E. Alferieff, *J. Chem. Phys.* **46**, 923 (1967).

¹⁴R. F. Waites and H. A. Schwettman (unpublished).

¹⁵F. G. Allen, *J. Phys. Chem. Solids* **2**, 87 (1961).

¹⁶L. W. Swanson and L. C. Crouser, *Phys. Rev.* **163**, 622 (1967).

¹⁷C. E. Kuyatt and E. W. Plummer, *Rev. Sci. Instr.* **43**, 108 (1972).

¹⁸P. S. Farago, *Adv. Electronics and Electron Phys.* **12**, 1 (1965).