Field emission from narrow bands above the Fermi level of nanometer-scale objects

S. T. Purcell and Vu Thien Binh
Département de Physique des Matériaux, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France

N. Garcia
Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, 28049 Madrid, Spain

M. E. Lin
Department of Physics, Purdue University, West Lafayette, Indiana 47907

R. P. Andres
School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

R. Reifenberger
Department of Physics, Purdue University, West Lafayette, Indiana 47907
(Received 30 November 1993)

Field emission from localized narrow bands above the Fermi level (E_F) are obtained in two nanometer-scale systems: gold nanoclusters deposited on W support tips and nanotips that are W nanoscale protrusions formed on W support tips. The shift of localized bands was used as a probe of the tunneling process. The emission above E_F is explained by considering the role of the tail of the Fermi function in supplying electrons to these localized levels. Conservation of energy is consistent with this process. The emission of hot electrons opens the possibility of local cooling of nanostructures.

In the classic picture of the field-electron emission from metal emitters, the electrons tunnel from the Fermi sea through the surface barrier and into the vacuum upon application of a sufficiently large electric field. Field-emission electron spectroscopy[1,2] (FEES) has been recently used to measure the electrons emitted from nanometer-size gold clusters deposited from a cluster beam on W field emitter tips[3] and from nanotips that consisted of nanoscale W pyramidal protrusions ending in one atom, formed under the action of temperature and field, on the W emitter.[4,5] These studies showed similar total-energy distributions[1,2] (TED's) that were strikingly different from those of macroscopic metal emitters. In both cases, the TED's consisted solely of strong multiple peaks that are generally spread over a range of several electron volts below the Fermi level (E_F) and that shifted linearly with applied electric field. In several cases, localized bands considerably above E_F were observed. This is particularly interesting because it should lead to enhanced cooling of the nanostructures during field emission by the Nottingham effect,[6] converse to the significant heating of nanotips that has been found in the presence of emission from bands below E_F.[7]

The peaks in the TED's point to the existence of localized states that are present in the clusters and the tip protrusion apexes due to the atomic size and dimensionality of the emitting systems. The general behavior found experimentally is that the peaks become more pronounced and sharper as the cluster size is reduced[8,9] or the protrusion height is increased,[10] a trend indicating that band formation is driven by the reduced coordination inherent in nanoscale objects. The linear shifting with electric field has been interpreted as due to field penetration into the nanometer scale objects.[3,5] Because of the field shifting, the position of the bands relative to E_F can be controlled by the applied voltage and they can thus be used as a probe for studying the electronic structure of the system and the related tunneling behavior. In this paper, we show how this technique can be used to obtain, in a controlled way, emission from localized levels well above E_F of the support tip. We analyze this phenomenon in terms of the partial filling of the bands by the tail of the Fermi sea, which acts as a supply function for the localized levels. In this case, energy conservation is obeyed.

The clusters and nanoprotrusions were produced and studied in separate, ultrahigh vacuum systems. The FEES measurements were made with hemispherical electron energy analyzers through a probe hole. The size of the Au clusters could be controlled by the known properties of the cluster beams. The height of the W nanoprotrusions were varied by controlling the temperature and field during their formation. As reported earlier, separated peaks that shifted linearly to lower (higher) energy with increasing (decreasing) electric field were observed in the TED's immediately after deposition of the clusters[3] or formation of high protrusions.[5] The linear shifting was used to displace the bands in order to study the behavior of the bands during the crossing of E_F. The bands could be typically shifted by ~ 0.5 eV for the ranges of applied voltages in these experiments which often allowed the complete scanning of a peak across E_F in a controlled way. It was found that in the case of nanotips, the existence of a sharp band within ± 0.3 eV of E_F was facilitated by the presence of adsorption at the W protrusion and this was used to study the emission above E_F. Fuller descriptions of the experimental details have

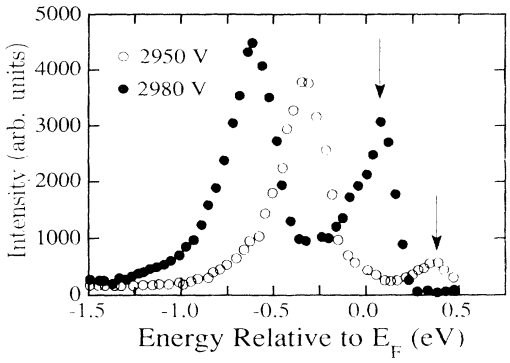

FIG. 1. FEES spectra for two different applied fields for emission from a 2-nm gold cluster deposited on a W field emitter. The higher-energy peak, marked by the arrows, is above E_F of the bulk support tip.

been given elsewhere.[3-5]

Two TED's from a 2-nm gold cluster deposited on a W field emitter tip taken for different applied voltages are shown in Fig. 1. The TED's consist of two separated peaks which shift to lower energy with increasing applied field. Most important for this article is that the higher-energy peak is significantly above E_F (0.2–0.4 eV). The intensity of the higher-energy peak increases relative to the lower-energy peak with increasing voltage. At the higher voltage a large fraction of the total emission is above E_F. The peaks are characteristically asymmetric with a sharp edge on the high-energy sides.

To analyze the phenomenon in-depth, nanotips were used in order to vary the spectra in a systematic way by controlling the height of the protrusion and the nature of the emitting atoms. Experiments with two types of nanotips are presented: (1) a high protrusion with the presence of adsorbed atoms which then gave multiple sharp peaks in the TED's, in particular, near E_F; (2) a low, clean protrusion which gave a broad single-peak TED; and (3) a high protrusion which had a narrow single-peak TED.

TED's from a high nanotip with adsorption are shown in Fig. 2. The highest energy peak of the TED's crosses E_F without change in shape or width as the applied voltage is varied. In this case, the width of the peak is quite small and the high-energy edge is particularly sharp (70 meV between 90–10 % intensity levels). As a counter example, in Fig. 3(a) we show a series of TED's when a relatively small protrusion was formed on the tip. The resulting spectra consisted of a single broad peak. At the highest voltages, the peak is shifted away from E_F and has a roughly Gaussian shape with FWHM ~0.4 eV. As the applied voltage is reduced, the peak shifts to E_F where the form of the peak changes shape, narrows and can be said to be cut by the much sharper Fermi edge.

We interpret the above behavior as a consequence of the width of the band as it crosses E_F. The band structure in the TED's can be qualitatively understood within the resonant tunneling model which was developed for tunneling through localized levels of singly adsorbed atoms.[2] This theory leads to a simple formula[11] for the emission current which is the product of the Young equation for tunneling current, $j'(\varepsilon)$, from a free-electron gas with an appropriate band function which describes the density of states at the emission site. Though the peaks generally have a distinct asymmetric shape with a sharper high-energy side, for simplicity we have used a Gaussian band in the following discussion. This question could not be examined in the original tunneling experiments on singly adsorbed atoms[12] because the observed features were not strong enough above the direct tunneling current. The tunneling current is given by

$$j_B(\varepsilon)=j'(\varepsilon)\exp\left[-\left[\frac{\varepsilon-E_B}{\alpha}\right]^2\right]$$
$$=\left[\frac{J_0}{d}\right]\frac{\exp(\varepsilon/d)}{[1+\exp(\varepsilon/kT)]}\exp\left[-\left[\frac{\varepsilon-E_B}{\alpha}\right]^2\right].$$

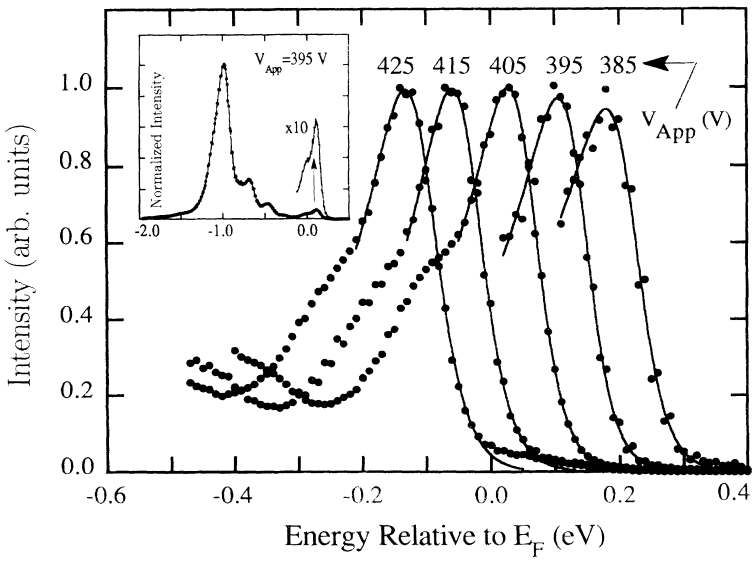

FIG. 2. The high-energy peak versus V_{App} of TED's from a high nanometric protrusion formed on a W field emitter with adsorption at the protrusion apex. Inset: full spectra for one fixed voltage. The high-energy peak passes through E_F upon variation of the applied field.

We neglect the direct tunneling and interference terms in agreement with experiment. J_0 is the zero temperature Fowler Nordheim current density expression, d is the field/work function parameter given by $d(\text{eV}) \approx F(\text{V/Å})\phi(\text{eV})^{1/2}$, and F is the applied field given by $F = \beta V_{\text{App}}$ with β being the geometrical factor. E_B depends linearly on field[5] and can, therefore, be written as $E_B = E_{B0} - \gamma V_{\text{App}}$ with V_{App} the applied voltage, E_{B0} the band position at zero field and γ the field shift coefficient, all of which are obtained from experiment. α defines the Gaussian bandwidth.

The effect of the bandwidth on the evolution of a band as it crosses E_F is shown in Fig. 4. Calculations were made for a narrow [4(a)] and wide band [4(b)] with all other parameters fixed except the bandwidth. The field-dependent prefactor of the Young equation was divided out. When the narrow band passes E_F it continues to shift linearly, does not change in form or width but its intensity drops rapidly. In contrast, for the wide band the emission remains at E_F, the TED changes to an asymmetric shape, its width narrows and its intensity drops less quickly. The resulting TED appears to stick at E_F because the Fermi-Dirac cutoff is so sharp, even if the true band position is shifted above E_F. Thus the emission from a peak above E_F is possible if the peak or related band is sharper than the Fermi edge itself. Its intensity drops rapidly as it is shifted across E_F since it is supplied by the bulk Fermi sea but it can continue to emit above the Fermi edge because of the high energy tail of the Fermi function.

In Fig. 3(b) we show a calculation with the measured values of the field shift and bandwidth of the data from 3(a). All the essential features of the experimental data are reproduced including the band narrowing, change to an asymmetric shape and the apparent band sticking at E_F. In Fig. 5(a), we compare the position of the measured and calculated peak maxima for the data of Figs. 2(b) and 3 versus E_B. It is worthwhile to emphasize that there is a difference between the band position E_B found from the linear shift of the peaks when they are below E_F, and the positions of the peak maxima which depend also on how the band crosses E_F. The agreement is quite good for the wide band but a theoretical bandwidth of only 70 meV is needed to get reasonable agreement with the experimental shifts of the narrow peak. However, the accuracy of the measurement for such a narrow peak is limited by the resolution of the electron analyzer. The point is that the narrow peak shifts right through the Fermi edge without being noticeably deformed.

In Fig. 5(b) we show a semilog plot of the experimental

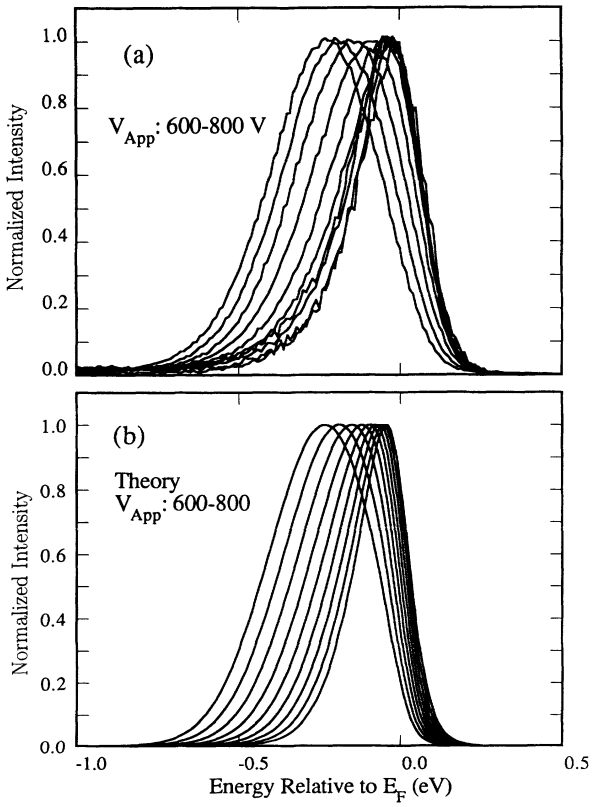

FIG. 3. (a) FEES spectra as a function of applied field from a relatively small nanometric protrusion formed on a W field emitter. (b) Calculation of TED's using equation in the text and parameters determined from Fig. 3(a).

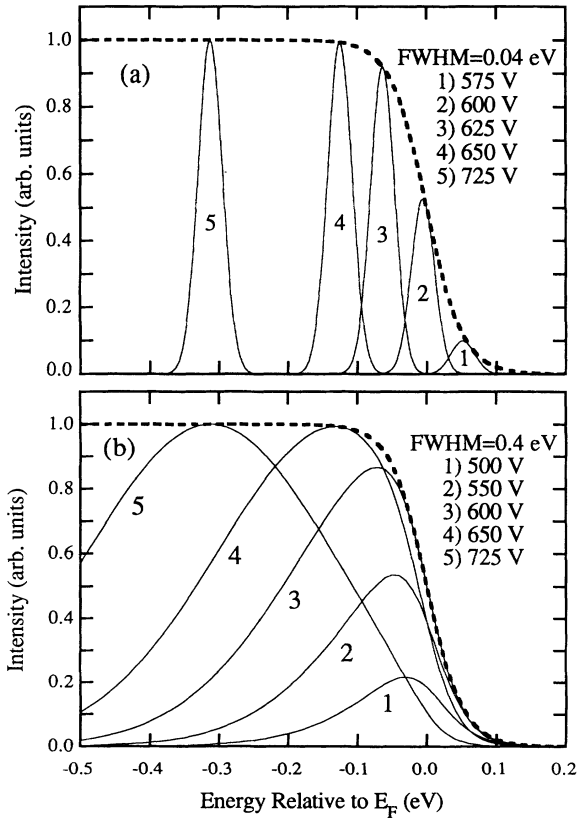

FIG. 4. Simulation of the dependence of band TED's on applied voltage for (a) a narrow and (b) a wide Gaussian band. This demonstrates how narrow bands pass through E_F while for a wide band, the emission remains near E_F. ($E_{B0} = 1.5$ eV, $\gamma = 0.0025$ eV/V, $T = 300$ K).

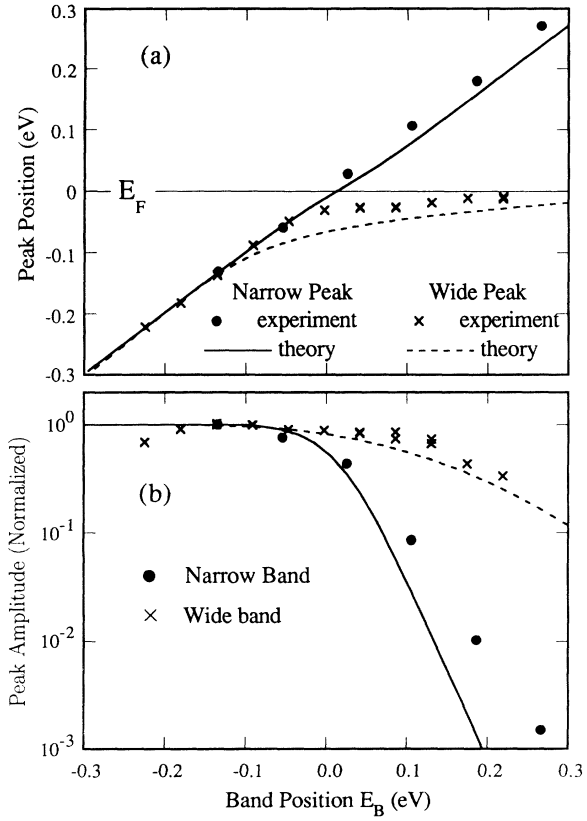

FIG. 5. (a) Measured and calculated peak positions for the data of Figs. 2 and 3. (b) Intensities of the peaks of Figs. 2 and 3 against their positions relative to E_F. The normalization of the intensities are discussed in the text (narrow band—$E_{B0}=3.36$ eV, $\gamma=0.0041$ eV/V, $T=300$ K; wide band—$E_{B0}=1.20$ eV, $\gamma=0.00178$ eV/V, $T=300$ K.)

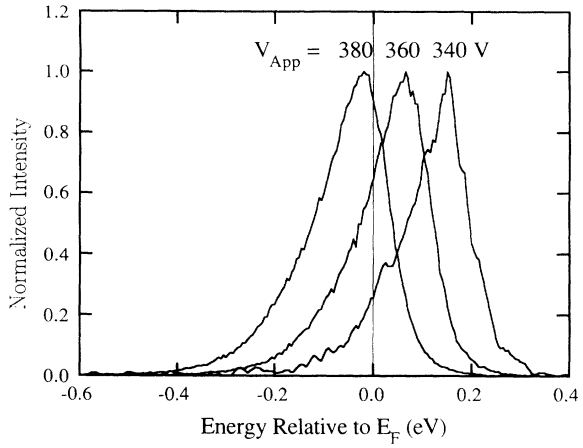

FIG. 6. FEES spectra as a function of applied field from a high clean nanometric protrusion formed on a W field emitter. For the lower voltages the peak shifts to above E_F.

and theoretical intensities of the peaks of the data for Figs. 2 and 3 as a function E_B. One cannot directly compare the peak intensity variations from the different nanotips because this depends strongly on the details of the tunneling barrier, particularly through the prefactor of the Young equation. To compare the results from different nanotips we have normalized by dividing the intensities by an exponential that fits the variation of the intensities with voltage when the peaks are shifted below E_F. This is roughly equivalent to dividing by the prefactor (J_0/d). The figure shows that there is a reasonable fit to the experimental data. The important point is that the intensity of the narrow peak falls much more rapidly than the wide peak as the bands pass E_F, in agreement with the calculation. The discrepancy may be reduced if we allow for a higher temperature due to the emission induced heating effects recently found for nanotips[7] or multiparticle tunneling,[2] both of which would increase the Fermi tail above E_F.

The peaks above E_F can provide significant cooling of the tip due to Nottingham energy exchange effects. In the spectra we have presented, there is significant tunneling from bands below E_F, which will provide offsetting heating. As a counter example, in Fig. 6 we show a series of spectra from a nanotip in which the total tip emission is from a single narrow peak. The field shifting is used to cause the peak to emit from above E_F. At these peak positions the emission will exclusively cause cooling at the nanotip apex.

In conclusion, we have shown that by controlling the applied voltage, significant field emission of electrons can come from above the bulk E_F from nanometric scale objects. A consideration of the Fermi sea as a supply function showed that for these measurements, the levels are populated by the tail of the Fermi-Dirac distribution. Hence, energy conservation is obeyed in this process and more complicated inelastic mechanisms[2,13] need not be invoked. The analysis provides the necessary basis to discriminate among the different possible mechanisms which could create peaks above E_F. We have also shown how the existence of the bands and the field shifting may be used to probe the tunneling barrier and the electron density of the support tip, particularly at E_F. The emission above E_F has interesting consequences for the energy exchange processes which occur during the tunneling process. It has been shown that the spectra can be composed of a single peak (also references 9,14) and, therefore, field emission can exclusively come from above E_F. This will lead to dramatic cooling by the Nottingham effect[6] because each emitted electron will remove an average energy of $\langle E_B - E_F \rangle$ from the nanostructure which can be up to 0.4 eV per electron.

This research was sponsored by an ECC "Science" project, by French and Spanish scientific institutions and by the U.S. Department of Energy under Grant No. DE-FG0288ER45162. The Département de Physique des Matériaux is Unité Associeé au Centre National de la Recherche Scientifique.

[1]R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, 1961).
[2]J. W. Gadzuk, Rev. Mod. Phys. **45**, 487 (1973).
[3]M. E. Lin, R. P. Andres, and R. Reifenberger, Phys. Rev. Lett. **67**, 477 (1991).
[4]Vu Thien Binh and N. Garcia, J. Phys. France I **1**, 605 (1991); Ultramicroscopy **42**, 80 (1992); **43**, 80 (1992); **44**; 80 (1992).
[5]Vu Thien Binh, S. T. Purcell, N. Garcia, and J. Doglioni, Phys. Rev. Lett. **69**, 2527 (1992).
[6]W. B. Nottingham, Phys. Rev. **59**, 908 (1941).
[7]Vu Thien Binh, S. T. Purcell, G. Gardet, and N. Garcia, Surf. Sci. Lett. **279**, L197 (1992).
[8]M. E. Lin, R. Reifenberger, A. Ramachandra, and R. P. Andres, Phys. Rev. B **46**, 15 498 (1992).
[9]M. E. Lin, R. P. Andres, R. Reifenberger, and D. R. Hufman, Phys. Rev. B **47**, 7546 (1993).
[10]Vu Thien Binh, S. T. Purcell, and N. Garcia, Phys. Rev. Lett. **70**, 2504 (1993).
[11]J. W. Gadzuk, Phys. Rev. B **1**, 2110 (1969).
[12]E. W. Plummer and R. D. Young, Phys. Rev. B **1**, (1970) 2088.
[13]L. W. Swanson and L. C. Crouser, Surf. Sci. **23**, 1 (1970).
[14]Vu Thien Binh, N. Garcia, S. T. Purcell, and V. Semet, in *Nanosources and Manipulation of Atoms Under High Fields and Temperatures: Applications,* edited by Vu Thien Binh, N. Garcia, and K. Dransfeld (Kluwer, Dordrecht, 1993), Vol. 235, p. 59.