Electron-Hole Coherence and Charging Effects in Ultrasmall Metallic Grains

S. Drewes and S. R. Renn
Department of Physics, University of California at San Diego, La Jolla, California 92093

F. Guinea
Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain
(Received 16 June 1997)

We consider a model for electron tunneling between a pair of ultrasmall metallic grains. Under appropriate circumstances, nonequilibrium final state effects can strongly enhance tunneling and produce electron-hole coherence between the grains. The model displays a quantum phase transition between a Coulomb blockaded state to a coherent state exhibiting sub-Ohmic tunneling conductance. The critical state of the junction exhibits a temperature independent resistance of order h/e^2. Finally we discuss the similarities between the quantum transition in our model and the metal-insulator transition in granular wires observed by Herzog *et al.* [S0031-9007(97)04521-3]

PACS numbers: 73.23.Hk, 71.10.Hf, 73.40.Gk

Recent work by Herzog *et al.* [1] has found dramatic evidence for an unusual metal-insulator (MI) transition in granular wires fabricated by *in situ* deposition through a metallic stencil onto a GaAs substrate. The transition involves an abrupt multiorder change in wire resistance as a function of the amount of deposited metal. The transition occurs in a variety of materials (including Sn, Pb, Au, Ag, $Pb_{0.85}Bi_{0.15}$). Although the transition may be observed in wires as wide as 7000 Å, the resistance gap decreases with increasing wire width and is absent in two-dimensional films.

In this paper, we wish to consider the possibility of modeling the above behavior in terms of a pair of metallic grains in close proximity. Our model will include two ingredients. The first is electrostatic charging effects. This should be important in the Herzog *et al.* experiments since the charging energy E_Q is estimated [2] to be large (100 K). The second ingredient is a nonequilibrium final state effect in which electrostatic fields between the two particles are suddenly switched on during the tunneling process. This effect is an exciton effect in which the tunneled electron is attracted to the positively charged counter electrode. We will show that the competition between the exciton effect and Coulomb blockade gives rise to a MI transition between a phase exhibiting sub-Ohmic I(V) characteristics to a phase exhibiting a Coulomb blockade. The critical state separating these two phases exhibits a temperature independent conductance. Finally, we will discuss the similarities between these results and those of Herzog *et al.* [1].

We begin our discussion by considering a pair of identical metallic grains on an insulating substrate. (See Fig. 1.) The grains are in close proximity and form an ultrasmall tunnel junction with intergrain capacitance $C < 10^{-15}$ F. (For the present argument, we will neglect the intragrain capacitance.) The two grains may be part of a granular host. However, tunneling to other grains in the host material will be ignored. Now consider a tunneling process in which an electron tunnels from grain #1 to grain #2. See Figs. 1(c) and 1(d). In the classical Coulomb blockade picture a tunneled electron causes all energy levels in the grain #2 to up-shift by $e^2/2C$ and all energies in grain #1 to down-shift by $e^2/2C$. In the diagram, we have represented the electrostatic potentials and surface confinement potential as a square well whose shape is unaffected by the tunneling process. Notice that the classical Coulomb blockade picture does not properly describe the nonequilibrium effect associated with suddenly switching on the electrostatic attraction between the two grains. See Figs. 1(e) and 1(f). Such effects can give rise to shakeup (orthogonality catastrophe) effects which can seriously effect tunneling rates [3,4], especially in small particles. To see how important these effects might be, consider the classic problem of the x-ray absorption edge [5,6]. In that problem, the absorption intensity, near threshold, could vanish at threshold due to the orthogonality catastrophe [6] or could exhibit a power law divergence known as the exciton effect [5]. *A priori* one might expect that similar effects could cause the differential conductance of a tunnel junction to vanish or diverge.

To examine these effects in detail, we consider a model [3,4,7,8] which describes tunneling between the two grains

$$H = H_L + H_R + H_T + \frac{Q^2}{2C}, \qquad (1)$$

where $H_T = \sum_{kp}[T_{kp}e^{i\phi}c_k^+ c_p + \text{H.c.}]$ and where ϕ is defined in terms of the voltage difference $V_L - V_R$ across the grains via the relation $\dot{\phi} = e(V_L - V_R)/\hbar$. Finally, the H_L and H_R are given by

$$H_\alpha = \sum_k \epsilon_{k,\alpha}^0 c_{k\alpha}^+ c_{k\alpha} + Q \sum_{kk'} V_{kk'}^\alpha c_{k\alpha}^+ c_{k'\alpha}, \qquad (2)$$

where $V_{kk'}^\alpha$ represents the sudden change of surface and electrostatic potentials on grain $\alpha = L, R$ which occurs

 0031-9007/98/80(5)/1046(4)$15.00

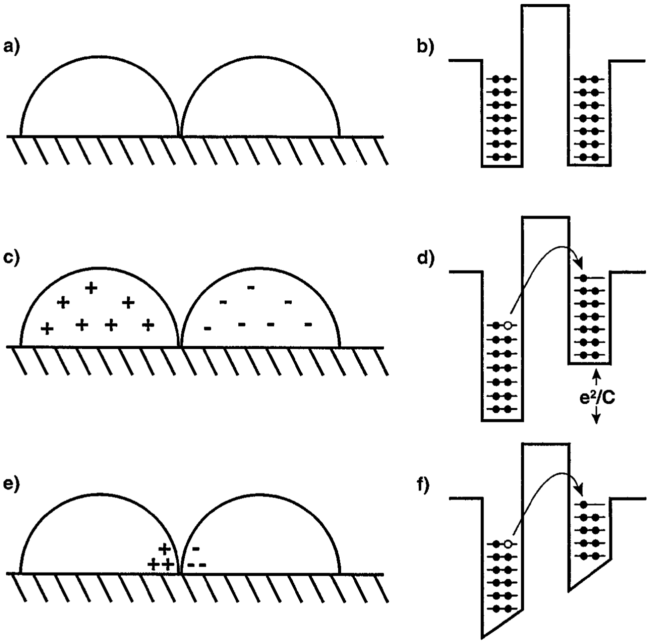

FIG. 1. (a) An illustration of two nearby metallic grains on an insulating substrate. The two grains form an ultrasmall tunnel junction. Although the grains may be part of a composite granular material, coupling to other grains in the host material will be ignored. (b) Energy levels and confinement potential associated with (a). (c) Metallic grains after tunneling event. An unrealistic charge distribution is obtained when $V^{\alpha}_{kk'}$ is set to zero. (d) The energy levels and confinement potentials associated with (c). (e) Metallic grains after tunneling event. Charges localized at the tunneling site give rise to long range electrostatic interactions which act as a suddenly switched-on potential $V^{L}_{kk'} = V^{R}_{kk'}$. (f) The nonequilibrium energy levels and confinement potential associated with (f).

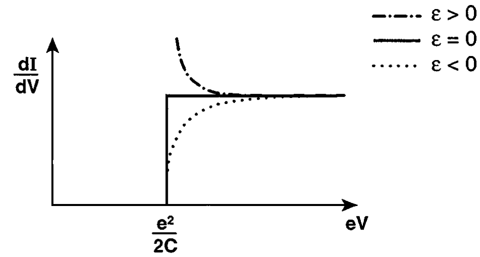

FIG. 2. Differential conductance for $\epsilon > 0$ (dot-dashed line), $\epsilon = 0$ (solid line), and $\epsilon < 0$ (dotted line). $\epsilon > 0$ curve assumes exciton effect dominates the orthogonality catastrophe.

during the tunneling process. If $V^{\alpha}_{kk'} = 0$, we recover the standard model [7] [see Figs. 1(c), 1(d), and 2(a)] which describes the effects of particle-hole excitations induced by tunneling processes in ultrasmall tunnel junctions. $V^{L}_{kk'} = V^{R}_{kk'} \neq 0$ would be chosen to include shakeup and other final state effects in symmetric tunnel junctions.

Now consider the zero temperature tunnel conductance to leading order in $T_{kp} = T$. One may calculate the tunneling current using $I = -2e\,\mathrm{Im}[X_{ret}(-eV)]$ where $X_{ret} = |T|^2 \int_0^\infty d\tau\, G^e_R(\tau) G^h_L(\tau) \exp i\omega\tau$ is the retarded response function associated with the nonequilibrium production of the R electron and L hole. Now the nonequilibrium electron and hole propagators associated with the suddenly switched on $V^{\alpha}_{kk'}$ are given by $G^{h,e}_R(t) \propto N_R t^{-(1\pm\delta_R/\pi)^2} \exp -iE^R_f t$ where N_α is the density of states at the Fermi level in the $\alpha = L, R$ electrode and δ_α is a phase shift associated with the scattering of electrons off the potential $V^{\alpha}_{kk'}$. In the above result, $+$ is used for hole and $-$ for electrons in the right electrode. Similarly $G^{h,e}_L(t) \propto N_L t^{(1\mp\delta_L/\pi)^2} \exp -iE^L_f t$ for the left electrode. Because of intergrain charging energy, the electrons tunnel to a nonequilibrium state characterized by Fermi levels shifted such that $E^R_f - E^L_f = e^2/2C$. Combining these results one obtains $dI/dV \propto (1/R_T)\{(e^2/C)/[(eV - e^2)/2C]\}^{\epsilon}$ where $\epsilon = 2(\delta_R/\pi + \delta_L/\pi) - (\delta_R/\pi)^2 - (\delta_L/\pi)^2$ and $R_T^{-1} = 4\pi e^2 N_L N_R |T|^2$. For small positive δ_α, there is a competition between excitonic effects associated with $2(\delta_R/\pi + \delta_L/\pi)$ and orthogonality effects associated with $-(\delta_R/\pi)^2 - (\delta_L/\pi)^2$. Depending on which terms dominate, one can obtain [Fig. 2(b)] a divergent differential conductance [9] at threshold $V_T = e^2/2C$ or [Fig. 2(c)] a vanishing conductance at threshold.

In general, the form of the final state interactions $V^{\alpha}_{kk'}$ is not important to the following discussion and is difficult to calculate. However, there are several observations which can be made: First we observe that one can estimate [10,11] $|\delta_{L,R}| \sim \pi/k$ where k is the number of transverse channels available for intergrain tunneling. Next, we observe that δ_R will be positive if $V^{\alpha}_{kk'}$ is a potential which tends to keep the tunneled electron in the electrode near the tunneling site, i.e., if the electron is attracted to the positively charged electrode. Similarly δ_L will be positive if the hole is attracted to the negatively charged electrode. Hence the electrostatic interaction between a pair of grains with a small number of accessible tunneling channels is expected to give a positive δ_α large enough to make exciton effects observable.

To some readers it may be surprising that the repulsive Coulomb interactions would enhance tunneling between the grains. The behavior is not unusual and can be found in several simple models. For instance, consider a pair of semi-infinite 1D spinless chains described by the Hamiltonian $H = [t' c^{+}_{L0} c_{R0} + \mathrm{H.c.}] + \sum_{i=0}[t c^{+}_{Li+1} c_{Li} + \mathrm{H.c.}] + U[c^{+}_L(0)c_L(0) - \frac{1}{2}][c^{+}_R(0)c_R(0) - \frac{1}{2}]$. This model is equivalent to a 1D Anderson impurity model. The interchain tunneling is associated with a transverse magnetic field acting on the impurity. For $U > 0$ the magnetic susceptibility and transverse magnetization $\langle c^{+}_L c_R \rangle$ will be rapidly enhanced with increasing U. Hence, the differential tunneling conductance will be significantly increased by a large positive U.

The above discussion of the exciton effect has been performed to leading order in $|T|^2$. We will now go beyond leading order in $|T|^2$ and show that if $|T|$ large and $\epsilon > 0$, the Coulomb blockade is destroyed. To do this, we integrate out the particle-hole excitations within the grains. This gives an effective action in imaginary time of the form

$$S = \int_0^{\beta\hbar} d\tau \frac{C}{2e^2}\dot{\phi}^2 + \tau_Q^{-\epsilon}\int_0^{\beta\hbar} d\tau\, d\tau'\, \alpha(\tau - \tau') \times \{1 - \cos[\phi(\tau) - \phi(\tau')]\},$$

where $\alpha(\tau) = \alpha_0[\pi k_B T/\sin(\pi k_B T\tau)]^{2-\epsilon}$ and $\alpha_0 = \hbar/(2\pi e^2 R_T)$. This is a one-dimensional XY model with long range interactions. This model had been studied within the framework of the renormalization group by Kosterlitz [12] who found an order-disorder transition at $\alpha_0 = \alpha_c = 2/\epsilon\pi^2$ for $\epsilon \geq 0$. The model is disordered for $\epsilon \leq 0$, although the absence of an ordered phase when $\epsilon = 0$ was a source of controversy [13–15].

In order to understand the nature of the two phases, we calculated the conductance of the model using the Kubo formula $G(\omega) = \langle |I_t(\omega)|^2\rangle/\omega$ where $I_t(\omega)$ is the tunneling current. To leading order in an expansion in powers of $1/\alpha$, a spin-wave calculation reveals that

$$G = \frac{2\sqrt{\pi}\,\alpha_0}{R_Q}\frac{\Gamma((1+\epsilon)/2)}{\Gamma(1+\epsilon/2)}\left(\frac{E_Q}{\pi k_B T}\right)^{\epsilon}, \quad (3)$$

where $E_Q = e^2/2C$ and $R_Q = \hbar/e^2 = 4.11\ \mathrm{k}\Omega$. We see that G diverges at $T \to 0$. Hence one identifies the ordered phase as sub-Ohmic. One can also calculate the conductance to leading order in α_0. In this case one finds $G \sim (\alpha_0^2/R_Q)(\pi k_B T/E_Q)^{2(1-\epsilon)}$ which vanishes as $T \to 0$, indicating that the disordered phase is insulating.

To understand the transition in greater detail, we have evaluated the dc conductance using a Monte Carlo (MC) simulation [16]. Using [14]

$$G = \frac{2\pi\alpha_0}{\hbar\beta R_Q}\int_0^{\hbar\beta}\gamma_\epsilon(\tau)\langle\cos[\phi(\tau) - \phi(0)]\rangle\, d\tau, \quad (4)$$

where $\gamma_\epsilon(\tau) = [\pi(k_B T/E_Q)/\sin(\pi k_B T\tau\hbar)]^{-\epsilon}$, we evaluate G using $\langle\cos[\phi(\tau) - \phi(\tau')]\rangle$ obtained from a series of simulations including the 64 and 128 time slice systems. The results for $\epsilon = 0.2$ are presented in Fig. 3. The transition between the sub-Ohmic (high α_0) phase to the insulating (low α_0) phase is evident. Interestingly, one observed the conductance curves cross at a single point. This point identifies a transition at a critical value of $\alpha_c = 0.9$ which compares well to $\alpha_c = 1.01$ obtained by Kosterlitz renormalization group (RG) treatment.

The fact that curves intersect at all indicates that α_c separates metallic from insulating behavior. However, the observation that all lines cross at $G_c \approx 11e^2/h \approx 1/2.3\ \mathrm{k}\Omega$ seems to indicate that the critical state has a finite temperature independent conductance. The existence of a critical state with a finite resistance can be understood as follows. In general, finite size scaling theory implies that the critical states exhibit correlations of the form $\langle \exp i\phi(\tau)\exp -i\phi(0)\rangle = (\tau_Q/\tau)^{d-2+\eta}F(\hbar\beta/\tau)$ where $\tau_Q = \hbar/E_Q$ is the width of the time slices, $d = 1$ is the space-time dimensionality, and $F(x)$ is a universal scaling function which is finite as $x \to 0$. According to Fisher, Ma, and Nickel [17], $\eta = 1 + \epsilon$ is exact for our model. It follows that

$$G_c = b(\epsilon)\frac{e^2}{h} \quad (5)$$

at criticality. Since the dc conductance depends only on the $\omega \to 0$ limit of the model, the above result is a universal but ϵ dependent result. Typically simulations for other values of ϵ reveal that $1/G_c \sim 10^5\ \Omega$ except in the $\epsilon \to 0$ limit where $G_c \to \infty$. It should be mentioned that the Herzog data reveal that the highest resistance metallic state in Au (width: 400 Å), $Pb_{0.85}Bi_{0.15}$ (width: 575 and 850 Å), and Sn (width: 550 Å) wires have critical resistances of 2 kΩ, 2 kΩ, 4 kΩ, and 4 kΩ, respectively. Such values of G_C^{-1} are consistent with Eq. (5).

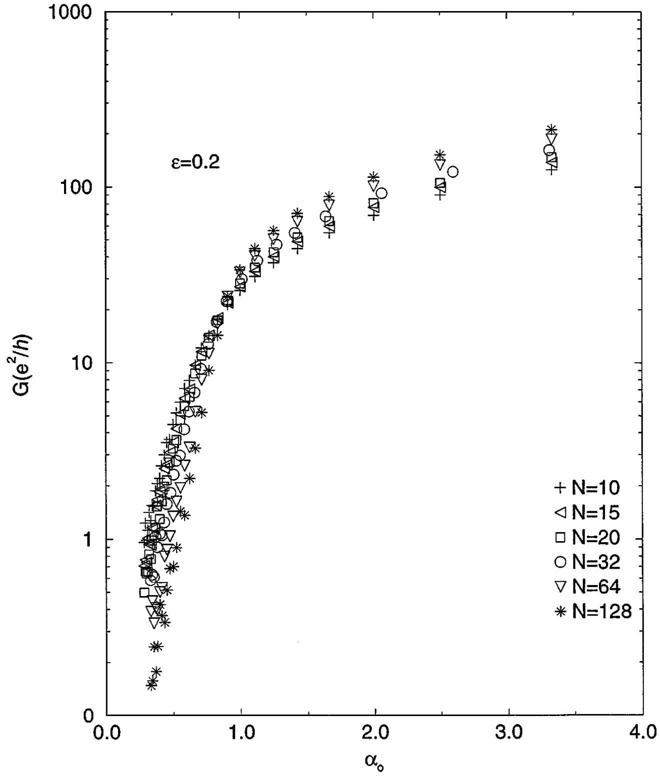

FIG. 3. Conductance obtained from a MC simulation. Notice $G(\alpha_0)$ curves intersect at $G_c \approx 11e^2/h$. This suggests that the conductance of the critical state is a universal, temperature independent constant.

We wish to consider the relevance of our tunnel junction to the MI transition observed by Herzog *et al.* [1]. Herzog's MI transition occurs in many different materials and exhibits a resistance gap which depends on the wire width, 500–6000 Å. This suggests that the transition does not involve some microscopic phenomenon in the interior or surface of the grains, but, instead, involves some low energy collective behavior which requires two or more grains. At this point, one might model the wire as a disordered network of tunnel junctions where Coulomb blockade effects could produce an insulating phase. This is reasonable since charging energies are estimated [2] to be ~100 K. Assuming the tunnel junction conductances to be broadly distributed, the wire resistance will be dominated by the tunnel junctions with highest resistance [18].

Now consider the dependence of the wire resistance on the wire width. Let l_ϕ be the phase coherence length, i.e., the length scale that correlations $\langle e^{i\phi(\vec{r})} e^{-i\phi(0)} \rangle$ die off in the disordered phase. Then for wire widths $w \ll l_\phi$, the low frequency behavior of the obstruction will be described by the tunnel junction model with a charging energy which decreases with increasing wire width. For instance, in a narrow wire ($w \ll l_\phi$) phase difference across multiple tunneling sites spanning a crack or weak link will be equal. (See Fig. 4.) Hence, the capacitances comprising the weak link add in parallel. This is a useful observation since the decreasing charging energy associated with increasing wire width will cause the resistance of the noncritical sub-Ohmic states to increase like $(T/E_Q)^\epsilon$ [Eq. (3)] similar to the behavior observed by Herzog *et al.* The increase of the metallic wire resistance with wire width is a unique phenomenon which is difficult to obtain from alternative models. The model also predicts that the resistance of insulating wires will *decrease* with increasing wire width. Consequently the resistance gap will decrease until $w \sim l_\phi$ where the crossover to two dimensional transport will occur.

We should mention that one should also be able to search for the sub-Ohmic to insulator transition in double quantum dot systems of the sort considered by Waugh *et al.* [19]. The double-dot systems have several useful features including (1) a small number of tunneling channels which implies the large phase shifts [10] required for an exciton effect, (2) small intergrain capacitances [19], and (3) precise control of the tunneling barrier between dots. Unfortunately, the Waugh experiment itself could not distinguish between a crossover and a phase transition. However, this is not an inherent limitation of the experimental method. So an attempt to search for this quantum phase transition in the double dot should be feasible and would certainly be most welcome.

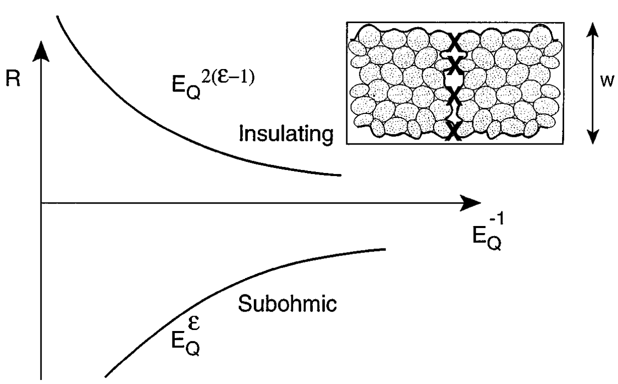

FIG. 4. Modeling a crack as a series of parallel tunnel junctions; see inset. Observe that the charging energy decreases with increasing wire width. The decreasing E_Q causes the resistance gap to close and the resistance of noncritical sub-Ohmic wires to increase.

The authors would like to acknowledge support from NSF Grant No. DMR 91-13631 (S. R.), the Hellman foundation (S. R.), and the Alfred P. Sloan Foundation (S. R.). We would like to acknowledge useful conversations with D. Arovas, R. C. Dynes, M. Ueda, F. Waugh, and P. Xiong.

[1] A. V. Herzog, P. Xiong, F. Sharifi, and R. C. Dynes, Phys. Rev. Lett. **76**, 668 (1996).

[2] Herzog *et al.* estimate typical grain sizes of 150 Å radius on a GaAs substrate. A spherical conductor of radius R imbedded at the surface of GaAs has a charging energy $E_Q = e^2/4\pi\epsilon_0(1+\kappa)R$ where $\kappa = 13$ is dielectric constant of the substrate. This gives a charging energy of about 80 K.

[3] M. Ueda and F. Guinea, Z. Phys. B **85**, 413 (1991).

[4] M. Ueda and S. Kurihara, in *Macroscopic Quantum Phenomena*, edited by T. D. Clark, H. Prance, R. J. Prance, and T. P. Spiller (World Scientific, Singapore, 1990), p. 143.

[5] G. D. Mahan, Phys. Rev. **153**, 882 (1967); **163**, 612 (1967).

[6] P. Noziéres and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).

[7] E. Ben-Jacob, E. Mottola, and G. Schön, Phys. Rev. Lett. **51**, 2064 (1983).

[8] T. Strohm and F. Guinea, Nucl. Phys. **B487**, 795 (1997).

[9] The possibility of a divergent conductance is in contrast to a previous result by one of us [3] which concluded that the exciton effect vanished for symmetric tunnel junctions. That result was based on the assumption that the electrostatic potentials acting on the electron and hole were identical. This is not the case since the electron and hole propagate in different grains and experience electrostatic potentials of opposite polarity. [See Figs. 1(e) and 1(f).]

[10] K. A. Matveev, L. I. Glazman, and H. U. Baranger, Phys. Rev. B **53**, 1034 (1996); **54**, 5637 (1996).

[11] Gerald D. Mahan, *Many-Particle Physics* (Plenum Press, New York, 1981).

[12] J. M. Kosterlitz, Phys. Rev. Lett. **37**, 1577 (1977).

[13] V. Scalia, G. Falci, R. Fazio, and G. Giaquinta, Z. Phys. B **85**, 427–433 (1991).

[14] R. Brown and E. Simanek, Phys. Rev. B **34**, 2957 (1986).

[15] W. Hofstetter and W. Zwerger, Phys. Rev. Lett. **78**, 3737 (1997).

[16] S_{eff} without the charging term was simulated on a 1D lattice of spacing $\tau_0 = \hbar/E_Q$.

[17] M. E. Fisher, Shang-keng Ma, and B. G. Nickel, Phys. Rev. Lett. **29**, 917 (1972).

[18] See D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, London, 1994), 2nd ed., Chap. 5.

[19] F. Waugh, M. J. Berry, D. J. Mar, R. M. Westervelt, K. L. Campman, and A. C. Gossard, Phys. Rev. Lett. **75**, 705 (1995); F. Waugh, M. J. Berry, C. H. Crouch, C. Livermore, D. J. Mar, R. M. Westervelt, K. L. Campman, and A. C. Gossard, Phys. Rev. B **53**, 1413 (1996); F. R. Waugh, Ph.D. thesis, Harvard University, 1994.