

values of $[\Delta G(V) - \Delta G(0)]/G_0(0)$ as it would give the smooth departure from $-\ln(eV/kT)$ behavior at $eV \sim E_0$ in Fig. 3.

⁶R. N. Hall, in Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961),

p. 193; R. N. Hall, J. H. Racette, and H. Ehrenreich, *Phys. Rev. Letters* **4**, 456 (1960); A. G. Chynoweth, R. A. Logan, and D. E. Thomas, *Phys. Rev.* **125**, 877 (1962).

⁷R. A. Logan and J. M. Rowell, following Letter [*Phys. Rev. Letters* **13**, 404 (1964)].

CONDUCTANCE ANOMALIES IN SEMICONDUCTOR TUNNEL DIODES

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In narrow p - n junctions, where current flow is by tunneling across the forbidden gap, the conductance at zero bias exhibits structure which corresponds to a conductance dip, peak, or combination of these shapes.¹⁻³ The detailed structure depends on the choice of semiconductor, the specific dopants and doping level, and the temperature of measurement, and varies with magnetic field strength. The conductance peaks which may be formed in both Si and Ge diodes are strikingly similar to those described in the preceding Letter by Wyatt⁴ for tunneling through an insulating film between the transition metals Nb or Ta and a metal.

At present the most extensive data have been obtained with Si diodes. These diodes were made by alloying Al or Cu containing 1% of boron into n -type wafers of Si where the p -type regrowth has an acceptor concentration of $2.3 \times 10^{19} \text{ cm}^{-3}$. The doping level in the n side was varied from $\sim 1 \times 10^{19} \text{ cm}^{-3}$ to $1.5 \times 10^{20} \text{ cm}^{-3}$ by choice of starting material, the diodes changing from backwards to Esaki diodes over this range. Reciprocal conductance vs voltage plots were obtained by applying a constant ac current to the diode and measuring the voltage developed across the diode as a function of dc bias. Typically, the ac voltage generated was less than $70 \mu\text{V}$. The diodes were immersed in liquid helium which could be pumped from 4.2 to 0.8°K.

Conductance peaks were observed in all junctions made by alloying Al-B to Sb-doped crystals. Typical results for a diode with $n = 8 \times 10^{19} \text{ cm}^{-3}$ are shown in Fig. 1 where the conductance, $G(V)$, normalized to the background conductance at zero bias, $G_0(0)$, is plotted against bias at 4.2 and 0.84°K. The value of $G_0(0)$ changes by only ~4% in this temperature range.

Wyatt⁴ has shown that the similar peak obtained with Ta structures may be explained by assuming a logarithmic singularity at the Fermi

level in the density of states of Ta. This gives rise to a conductance change $\Delta G(V) = G(V) - G_0(V)$ whose temperature dependence at $V = 0$ is given by

$$\Delta G(0)/G_0(0) = a[0.125 - \ln(kT/E_0)], \quad (1)$$

where a is a constant and E_0 is the cut-off energy for the logarithmic singularity. Using the data of Fig. 1 at 4.2 and 0.84°K, and similar data at intermediate temperatures, a plot is shown in Fig. 2(a) of $\Delta G(0)/G_0(0)$ versus $\log T$, and the reasonable fit to a straight line gives $a = 0.024$ and $E_0 = 2.3 \text{ MeV}$. The peaks observed here are considerably narrower than in the Ta and Nb structures where $E_0 = 9.4 \text{ MeV}$. As discussed by Wyatt,⁴ the data should lie on a universal curve given by

$$[\Delta G(V) - \Delta G(0)]/G_0(0) = -a[0.125 - g(eV/kT)], \quad (2)$$

where $g(eV/kT)$ is a known function whose value approaches the limit $-\ln(eV/kT)$ for $eV/kT \gg 1$. Figure 2(b) shows a plot of $[\Delta G(V) - \Delta G(0)]/G_0(0)$ against $\log(eV/kT)$ using data obtained at five

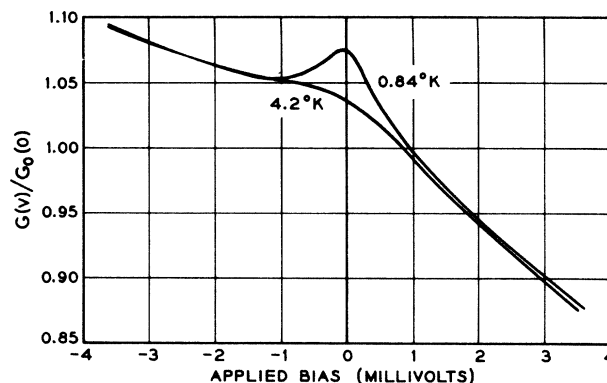


FIG. 1. The conductance $G(V)$ normalized to the zero-bias background conductance $G_0(0)$ plotted against bias at 4.2 and 0.84°K.

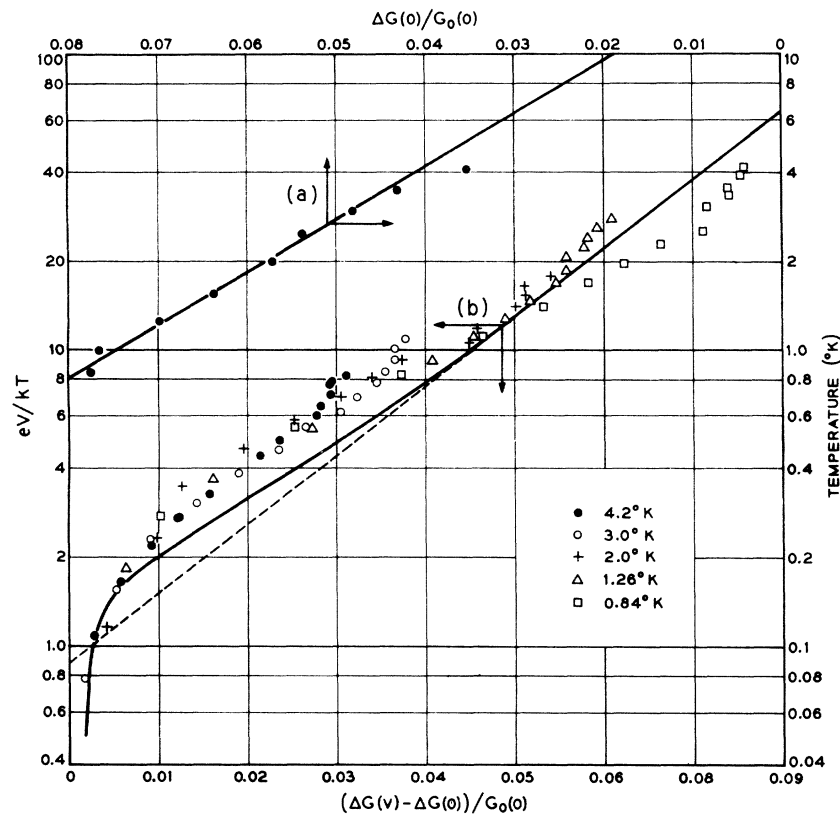


FIG. 2. (a) $\Delta G(0)/G_0(0)$ plotted against $\log T$, and (b) the quantity $[\Delta G(V) - \Delta G(0)]/G_0(0)$ plotted against eV/kT , using data obtained at the five temperatures listed in the Figure. The solid curve is a plot of Eq. (2) using $a = 0.019$, while the dashed curve is limiting form of Eq. (2) for $eV/kT \gg 1$.

temperatures between 0.84 and 4.2°K. Also shown in Fig. 2(b) are the calculated curve of Eq. (2) and the asymptotic limit (dashed line) where $g(eV/kT) \sim -\ln(eV/kT)$, obtained with $a = 0.019$. The consistency of the value of a is good considering the problem of estimating the background conductance. The results suggest that the anomaly in conductance at zero bias in the semiconductor diodes can also be explained in terms of a logarithmic singularity in the density of states at the Fermi level, and perhaps any explanation should be applicable to both the diodes and the Ta and Nb structures.

A similar peak in conductance is observed in diodes made by alloying Al-B wires into As- or P-doped Si if $n \geq 5 \times 10^{-19} \text{ cm}^{-3}$. However, if $n \leq 5 \times 10^{-19}$, one observes a dip in conductance of similar size and shape to the peak described above. It may be significant that diodes which show dips also have relatively high prephonon current⁵ ($V < 18.6 \text{ mV}$). Dips can also be produced in diodes doped with Sb if the diode is made by alloying Cu-1% B instead of the Al-1%

B. Diodes made with the Cu alloy have relatively high prephonon current, presumably due to an increased density of deep states associated with Cu. Qualitatively similar behavior was observed in Ge diodes made by alloying Al or GaIn alloys to n -type crystals where lightly doped (low current density) diodes showed conductance dips and heavily doped diodes showed conductance peaks. If diodes are made in III-V materials, the conductance anomaly is always a dip with $\Delta G(0)/G_0(0)$ as large as 0.6 in InAs junctions.³

The effect of a magnetic field, H , on the dip in III-V materials was most marked in an InAs junction where we believe a good planar junction geometry existed. When a field of 88 kG was applied with H perpendicular to the current, I , the dip was approximately doubled in size; but with $H \parallel I$ no change was observed. In III-V diodes of poorer geometry the magnetic field in any direction increased the dip. In Si and Ge diodes the effect is also to increase dips and in diodes of heavily doped material the peak is re-

duced by the magnetic field.

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¹R. N. Hall, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Ac-

ademic Press, New York, 1961), p.193.

²A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).

³R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters **4**, 456 (1960).

⁴A. F. G. Wyatt, preceding Letter [Phys. Rev. Letters **13**, 401 (1964)].

⁵R. A. Logan and A. G. Chynoweth, Phys. Rev. **131**, 89 (1963).

ELECTRON PAIRS IN THE QUASICHEMICAL-EQUILIBRIUM AND BARDEEN-COOPER-SCHRIEFFER THEORIES

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The notion of a Fermi pair or pairon has played a key role in recent discussions of superconductivity and will undoubtedly become increasingly important in various aspects of fermion physics. However, it is apparent from the current controversy between Blatt¹ and Girardeau² and from much of the literature about superconductivity that there is some ambiguity concerning the definition of the pairons of a given system and misconceptions about their statistics. It is the author's belief that it is most cogent to associate, to a system of N fermions, $\frac{1}{2}N(N-1)$ pairons distributed over the natural geminals of the state or ensemble. A geminal is a two-particle function as an orbital is a one-particle function. Natural orbitals and natural geminals are, respectively, eigenfunctions of the one- or two-particle reduced density matrix of the state or ensemble. Adopting Löwdin's normalization,³ we denote the 1 matrix by $\Gamma_1 = \rho_1$ and the 2 matrix by $\Gamma_2 = \frac{1}{2}\rho_2$ so that $\text{Tr}(\Gamma_1) = N$ and $\text{Tr}(\Gamma_2) = \frac{1}{2}N(N-1)$.

It has been known to the author for several years (7 ± 1) that, in this normalization, no natural geminal can be occupied by as many as $\frac{1}{2}N$ pairons. Recently, Sasaki⁴ and Yang⁵ proved, independently, that the occupation of a natural geminal could be arbitrarily close to $\frac{1}{2}N$. Thus, not quite one ($N-1$)th of the pairons can occupy any one geminal. This is as close as pairons can get to the complete Bose-Einstein (B-E) condensation which Blatt⁶ seems to believe is predicted by the quasicheical-equilibrium (QCE) theory of superconductivity. However, even this minute condensation of pairons permits an occupancy of one natural geminal proportional to the volume and this, rather than something which could be called complete B-E

condensation, is what the QCE theory really needs.

In the course of his proof⁶ that the BCS ground state is an antisymmetrized ($\frac{1}{2}N$) power of a single geminal (denoted by g^N and discussed in our recent paper⁷), Blatt argues, "There are $\frac{1}{2}N$ pairs altogether, accounting for all N electrons and every pair goes into the same pair quantum state... The statement that all electron pairs are in the same state is manifestly gauge invariant." Such an interpretation of pairons might be appropriate for distinguishable particles but certainly not for fermions. Indeed, Blatt's definition of extreme condensation is consistent with no condensation at all. The reductio ad absurdum of Blatt's interpretation is provided by a wave function whose rank is equal to N so that it is a single Slater determinant. For example, with $N=4$, let φ_i be orbitals and φ_{ij} ($i \neq j$) the normalized Slater geminal formed with φ_i and φ_j . Setting $g = a\varphi_{12} + b\varphi_{34}$, then, according to Blatt, if A_4 is the antisymmetrizer, $\Psi \equiv A_4[g(12)g(34)]$ is an instance of extreme B-E condensation with all pairons in the geminal g and this is "manifestly gauge invariant." However, except for normalization, $\Psi \equiv A_4[\varphi_{ij}\varphi_{kl}]$ where i, j, k, l is any permutation of 1, 2, 3, 4, so this "manifestly invariant" case of extreme B-E condensation is also susceptible of analysis as two pairons distributed equally between any of six pairs of strongly orthogonal geminals! This example, which generalizes immediately to arbitrary macroscopic N , suggests that Girardeau is correct and that much of the intuitive talk of Chap. III of Blatt's book⁸ is distinctly misleading.

However, this does not invalidate Blatt's very significant thesis that the QCE theory is equiva-