(1966).

[6]For examples, see A. Abragam, in *Principles of Nuclear Magnetism* (Oxford Univ. Press, New York, 1961); C. P. Slichter, in *Principles of Magnetic Resonance*, edited by F. Seitz (Harper, New York, 1963).

[7]D. Davidov, V. Zevin, R. Levin, D. Shaltiel, and K. Babeschke, Phys. Rev. B 45, 277 (1977), and references therein.

[8]J. M. Bloch, D. Davidov, and H. D. Dokter, Physica (Utrecht) 101B, 189 (1980).

[9]It should be noted that the use of the absorption line shape for the truncation procedure does not imply that the resultant line shape is due entirely to the density of states confined by the linewidth but it just determines the states over which the matrix elements in the moment equation will be evaluated.

[10]The same truncation procedure applies to the discrete and continuous extreme and has been shown to yield correct results in an intermediate case $\Delta E_i \sim \hbar\omega_0$ (see J. M. Bloch, to be published).

[11]Bloch, Ref. 10.

[12]L. L. Hirst, Phys. Rev. 181, 597 (1969).

[13]R. Orbach and H. J. Spencer, Phys. Lett. 26A, 457 (1968).

[14]H. J. Spencer and S. Doniach, Phys. Rev. Lett. 18, 994 (1967).

[15]For the Redfield equation (for example, see Ref. 6) $dG_{\alpha\alpha'}*/dt = \Sigma_{\beta\beta} R_{\alpha\alpha'\beta\beta'} G_{\beta\beta'}*$; the density matrix G must not change too much during the correlation time of the bath variables τ_c. This means that $R_{\alpha\alpha'\beta\beta'} \ll 1/\tau_c$. The correlation time τ_c is inversely proportional to the interaction within the bath. The condition implies that in order for this perturbation method to hold, the interaction within the bath must be considerably stronger than that of the bath to the resonant system.

[16]Such a case is quite common. It is encountered, for example, in the evaluation of the excitation spectrum of Van Vleck excitation where the random-phase approximation Green's function approach yields infinitely long excitation lifetimes.

Electron Glass

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Numerical calculations on a model of localized interacting electrons are reported. A Coulomb gap is found in the density of states for bare and dressed single-particle excitations, which fills with increasing temperature. By making an analogy with a random-field Ising spin-glass with $1/r$ interactions, evidence is found, in a modified Edwards-Anderson order parameter, of glasslike order at low temperatures.

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The spatial distribution of electrons in localized states is strongly influenced by the long-ranged Coulomb repulsion between them. This causes a depletion of the single-particle density of states (DOS) near the Fermi energy. At zero temperature this density of states vanishes at the Fermi energy but is nonzero elsewhere. This "soft" gap is known as the Coulomb gap,[1-4] and at low temperatures it leads to deviations from Mott's $T^{1/4}$ law which assumes a flat density of states. In this Letter, we report calculations of the DOS for both bare and dressed single-particle excitations from the ground state and examine the evolution of the bare single-particle DOS with temperature. We also explore the analogy between this model and a spin-glass, and have calculated the susceptibility, order parameter, and specific heat as a function of temperature.

A simplified Hamiltonian for a system of localized electrons, for example in the impurity band of a doped, compensated semiconductor, has the form (in dimensionless units)

$$H = \sum_i n_i \varphi_i + \tfrac{1}{2} \sum_{i \neq j} n_i n_j / r_{ij}, \tag{1}$$

where n_i is the number operator and φ_i is the site energy including the potential of the neutralizing charge. Following Efros and Shklovskii[3] we have simplified the Hamiltonian by neglecting spin and tunneling between sites. Since the latter is short ranged it can be neglected in studying the low-energy and long-range behavior.

Efros and Shklovskii have shown that the distribution of single-site energies defined by $E_i = \varphi_i + \sum_j n_j / r_{ij}$ is required to have a Coulomb gap. Their deviation is based on the stability of the ground state against all excitations which move an electron from site i to j, with energy change $E_{ji} = E_j - E_i - 1/r_{ij}$. This leads to a bound on the bare single-particle DOS $n_b(E)$ near the Fermi energy μ of the form

$$n_b(E) \propto |E|^{D-1} \tag{2}$$

in D dimensions, where E is measured from μ. By considering the stability of the ground state against excitations in which the surrounding electrons were allowed to relax, Efros[4] obtained a sharper bound of $n_b(E) \propto \exp\{-|E_0/E|^{1/2}\}$ for $D=3$.

For our numerical calculations, we used an even simpler model introduced by Efros[4] in which the sites are put on a square or simple cubic lattice of unit lattice parameter and the disorder is introduced by selecting the site energies φ_i from a rectangular distribution of width 2. The number of electrons was one-half the number of sites and to maintain electrical neutrality each site had a charge of $+\frac{1}{2}$. The computer program is based on the method of Baranovskii *et al.*[5] The electrons are thrown in at random, and one-electron hops which lower the total energy are made successively. Starting with different occupations but the same set of random energies, a distribution of final states resulted. A large fraction of these states were identical and had the lowest energy found, and so we believe this common state to be the ground state of the finite system. Even if it were not the ground state, it may well be the state of physical interest. We compared the DOS of the systems tested for stability against only single-electron hops, against single- and two-electron hops, and also of the selected ground states, and found very little systematic difference. The results shown have been averaged over many configurations of random energies. The samples used had mainly 16×16 or 10×10 sites; other sizes were tried but no size dependence of the properties at zero temperature was found.

The single-particle DOS is shown for two- and three-dimensional systems in Fig. 1. The form of the Coulomb gap in three dimensions (3D) is fitted well by the exponential form. For the 2D samples the curve is clearly not linear close to the Fermi energy, as predicted by (2), but has a rather stronger gap. The results agree with those obtained by Baranovskii *et al.*[5] for relatively high excitation energy, but lie below their results for energies near μ. We believe that this difference arises because they used free boundaries.[6] We used periodic boundary conditions, taking only the shortest distance between sites in the repeated lattice. This gave results which were much less sensitive to the size of the sample, and $n_p(E)$ could therefore be determined more accurately at lower energies.

It has been pointed out[1,4,7] that at low temperature the important single-particle excitations might not be bare, like those considered above, but would rather be "electronic polarons." If an electron is added to a site, the system can relax if nearby electrons move away, thereby creating a polarization cloud. Mott[7] suggested that the spectrum of such excitations should show no Coulomb gap; according to Efros[4] it should obey (2). It is difficult to define these polarons precisely, and the following method was used to calculate the polaron DOS $n_p(E)$ plotted in Fig. 1. An electron was added to a site and held there. If it was possible to move another electron and lower the system's energy, the most favorable transition was made, and this was repeated until the system was stable against all one-electron transitions. The energy of this final state above the ground state was taken to be the polaron energy. The Coulomb gap for polarons is clearly much narrower than that for bare excitations, but it is still present. For the 2D systems, the linear form (2) was a fair fit; the exponential form and the parabola fitted the curves for 3D about equally well.

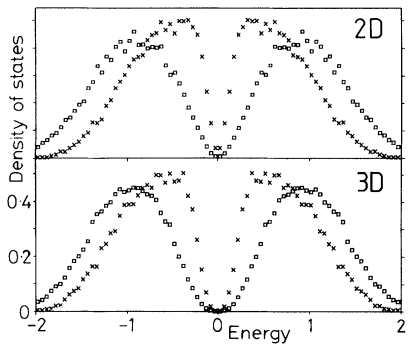

FIG. 1. Bare (squares) and polaron (crosses) single-particle densities of states for two- and three-dimensional systems.

The important point about the above definition is that a polaron is essentially localized around the selected site. In general, the ground state and low-lying excited states with the added electron will have a lower energy and many of these will have the selected site occupied. However, such states involve the rearrangement of many electrons and may therefore not be accessible from the starting state at low temperature. This picture of inaccessible configuration space is typical of a glass, a subject to which we shall return later.

The Monte Carlo calculations were extended to a finite temperature T by using the algorithm of

Metropolis *et al.*,[8] i.e., an electron hop requiring an energy E is made with unit probability if $E<0$ and with probability $\exp(-E/T)$ if $E>0$ ($k_B=1$). We have calculated the effect on $n_b(E)$ by starting the system in a ground state and raising the temperature T in intervals and allowing at each stage many Monte Carlo steps (about 10^3 per site) to ensure convergence. The distribution of single-particle energies was calculated for the 2D systems and the results appear in Fig. 2. At the lowest value of $T=0.05$, $n_b(E)$ has a well-defined gap. This gap has closed appreciably by $T=0.1$ until at $T=0.3$ there is only a weak remnant, and at $T=0.5$ no gap at all. This shows that the Coulomb gap is washed out at $T\approx 0.3$.

It is instructive to rewrite the lattice-gas Hamiltonian in an Ising form. Setting $\sigma_i^z = n_i - \frac{1}{2}$ we get for the half-filled band

$$H=\sum_i \Phi_i \sigma_i^z + \tfrac{1}{2}\sum_{i\neq j} \sigma_i^z \sigma_j^z / r_{ij} \qquad (3)$$

and the site energies Φ_i are now distributed about zero energy. In this form the Hamiltonian is that of an Ising model in a random field but with long-range antiferromagnetic interactions. It has been shown[9] that the random field is relevant in Ising models for $D\leq 3$ but to our knowledge this model with long-range interactions has not been studied in the spin-glass literature. We have calculated the magnetic susceptibility, χ. The density of electrons plays the role of magnetization and the chemical potential μ that of the magnetic field. However, in our system it is vital to maintain charge neutrality so upon adding (or removing) electrons we add (or subtract) compensating charge from each site. χ ($=dn/d\mu$) is calculated from $\mathrm{var}(N)/2NT$, where N is the total number of electrons. The variance was obtained from the distribution of N with time, electrons being added or removed at random sites according to the algorithm of Metropolis *et al.*[8] The activation energies were calculated including the effect of the compensating charge. The results are shown in Fig. 3. χ follows a Curie law above $T\approx 0.3$ at which point there is a change in slope. At low temperatures, $T<0.1$, there are very few electrons added or removed and the convergence rapidly worsens so that we cannot determine the limiting behavior as $T\to 0$. We expect that, because of the vanishing of $n_b(E=0, T\to 0)$, $\chi\to 0$ as $T\to 0$ but these are not simply related because of the correction to the positive charge distribution contained in χ. Note that in a glass phase, our way of calculating χ measures the change in electron density *in a restricted region of configuration space* in response to an infinitesimal change in μ. This is in contrast to the thermodynamic equilibrium value of $dn/d\mu$, which at $T=0$ is defined in terms of the ground-state energies of the $N-1$, N, and $N+1$ electron systems and is expected to be finite, but we were unable to compute a reliable value because of fluctuations from sample to sample. Parisi and Toulouse have suggested[10] that the equilibrium value of χ is independent of T and that the entropy is independent of magnetic field below the glass transition. This is consistent with a Coulomb gap which is tied to μ and whose form depends only on the temperature.

The Edwards-Anderson order parameter, $q(T)$

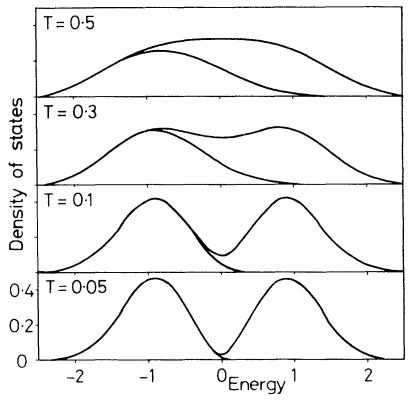

FIG. 2. Bare single-particle density of states for a two-dimensional system at various temperatures. The lower curve in each case shows the density of occupied states.

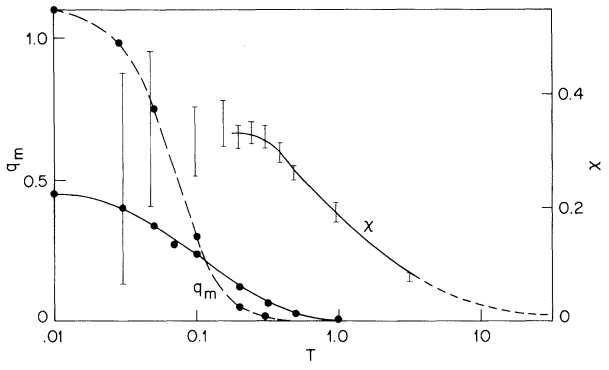

FIG. 3. Susceptibility χ and order parameter q_m for $B=2$ (full line); the broken line is the order parameter for $B=0.5$. The dotted curve for χ is the high-temperature Curie law, and the vertical bars cover the range of values obtained from different samples.

$= \langle\langle 2\sigma_i^z\rangle_t^2\rangle_S$, where the t denotes a Monte Carlo time average and S an average over samples, is unsatisfactory in a system with random fields since some spins are strongly preferentially oriented by the random field.[11] We have therefore modified this definition to give an order parameter which vanishes in the absence of the Coulomb interactions: $q_m = \langle[\langle 2\sigma_i^z\rangle_t - f(\Phi_i)]^2\rangle_S$, where $f(\Phi_i)$ is the average value of the spin at site i in the absence of interaction. We calculated q_m in Monte Carlo runs in which the number of electrons was kept fixed and electron hops were made as discussed previously. The results are shown in Fig. 3 for two choices of the bandwidth of random energies, $B = 2$ and $B = 0.5$. For the narrower bandwidth there is a rapid rise in q_m at $T \approx 0.1$. In the other case, where the Coulomb interactions are relatively less important, this rise is less marked. q_m is similar to the spin-glass order parameter proposed by Morgenstern, Binder, and Hornreich[11] for a random-field, short-range Ising model. They interpreted a nonzero value of q_m as evidence of spin-glass order.

Lastly, we have calculated the specific heat c_v for our system (Fig. 3). At low temperatures we find $c_v = \alpha T$. The value of α is quite large and corresponds to a DOS of ≈ 0.4 per site. One contribution will be from particle-hole excitations which because of the Coulomb interaction appear in our calculations to have a finite DOS at zero energy (≈ 0.2 per site).[12] The remaining contribution to c_v presumably comes from correlated two-electron and more complicated hops. These low-lying excitations cause q_m to vary strongly with temperature down to low temperatures.

In conclusion, our results show that the Coulomb interaction between localized electrons leads to a minimum in the single-particle density of states at the Fermi energy at temperatures less than 0.3. The nonzero value of the spin-glass order parameter q_m at low temperatures suggests that a glass transition has occurred, although we do not have direct evidence of a long-ranged cooperative effect. This glass state may also appear in a dependence of the electrical conductivity on the sample's history, with differences between samples cooled in an electric field and without. Experiments to test this would be most welcome.

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[1]M. Pollak, Discuss. Faraday Soc. 50, 13 (1970), and Proc. Roy. Soc. London, Ser. A 325, 383 (1971).

[2]G. Srinivasan, Phys. Rev. B 4, 2581 (1971).

[3]A. L. Efros and B. I. Shklovskii, J. Phys. C 8, L49 (1975).

[4]A. L. Efros, J. Phys. C 9, 2021 (1976).

[5]S. D. Baranovskii, A. L. Efros, B. L. Gelmont, and B. I. Shklovskii, J. Phys. C 12, 1023 (1979).

[6]S. D. Baranovskii *et al.*, private communication.

[7]N. F. Mott, J. Phys. C 8, L239 (1975).

[8]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).

[9]E. Pytte, Y. Imry, and D. Mukamel, Phys. Rev. Lett. 46, 1173 (1981).

[10]G. Parisi and G. Toulouse, J. Phys. (Paris), Lett. 41, L361 (1980).

[11]I. Morgenstern, K. Binder, and R. M. Hornreich, Phys. Rev. B 23, 287 (1981).

[12]S. D. Baranovskii, B. I. Shklovskii, and A. L. Efros predict {Zh. Eksp. Teor. Fiz. 78, 395 (1980) [Sov. Phys. JETP 51, 199 (1980)]} that the DOS for one-particle hops does in fact vanish logarithmically at zero energy, but we are unable to test this.