Thermoelectric power of a Hubbard chain with arbitrary electron density: Strong-coupling limit

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We have studied the thermoelectric power of an infinite Hubbard chain with arbitrary electron density in the strong-coupling limit. Calculations were carried out for the simple Hubbard model and in the atomic limit of an extended Hubbard model having an arbitrary nearest-neighbor repulsion. We compare the results to the measured thermopower of high-conductivity complex salts of tetra-cyanoquinodimethane (TCNQ).

I. INTRODUCTION

The conducting salts of the organic compound tetracyanoquinodimethane (TCNQ) have been studied widely on the basis of a variety of models.[1] Most efforts have focused on the simple salts, particularly N-methylphenazinium-TCNQ,[1,2] and tetrathiafulvalinium-TCNQ (Ref. 3) and its analogs. This paper will be concerned with a high-conductivity complex salts of TCNQ: Q(TCNQ)$_2$, A(TCNQ)$_2$, and DTC(TCNQ)$_2$. These materials are composed of separate, uniform chains of TCNQ and, respectively, quinolinium, acridinium, and 3,3-diethyltiazolinocarbocyaninium.[1] Measurements of the electrical conductivity, magnetic susceptibility, and thermopower show marked similarities among these salts,[1,4] favoring a systematic interpretation of their properties.

The conductivity of these compounds exhibits a broad peak centered at a few hundred degrees and activated behavior at lower temperatures, reminiscent of a system undergoing a Mott-Hubbard transition.[5,6] The susceptibility data are also consistent with this picture, which predicts a uniform antiferromagnetic exchange along a chain.[7] These, of course, are the very arguments used by Epstein et al.[2] to justify the application of the simple Hubbard model[6,8] to N-methylphenazinium-TCNQ (NMP-TCNQ). Some modifications of the Hubbard model will be necessary and/or desirable to reflect the properties of the complex salts.[9-11] The primary source of inspiration here is the thermoelectric power.

Consider the thermopower calculated by one of the authors (G. B.) for a simple Hubbard chain in the atomic limit.[12] While this can be fit qualitatively to the data obtained for the simple salt NMP TCNQ by assuming, say, a filling factor ρ of 0.9 electrons per site and an on-site Coulomb repulsion U of 300°K, the data for the complex salts cannot be so satisfactorily matched. The model predicts, for a quarter-filled band, a high-temperature thermopower of -80 μV/°K with a smooth

shift to -60 μV/°K at temperatures $kT \ll U$. The data, illustrated in Figs. 1–3,[13] show a constant high-temperature value of about -60 μV/°K with a steady decline in magnitude beginning well below room temperature and persisting to the lowest temperatures measured. This implies that $U \gg kT$ in these salts for all experimental temperatures. Moreover, a more complete description of the electronic interactions is clearly necessary. Since the complex salts will have transferred about $\frac{1}{2}$ electron per TCNQ, it is reasonable to postulate that at least the Coulombic repulsion between carriers on adjacent sites must be taken into account.[14]

We therefore propose to discuss the thermopower of these systems on the basis of the extended-Hubbard-model Hamiltonian

$$H = U \sum_l n_{l\uparrow} n_{l\downarrow} + V \sum_l n_l n_{l+1} - t \sum_{l,\sigma} (C^\dagger_{l,\sigma} C_{l+1,\sigma} + \text{H. c}) ,$$

$$(1)$$

in the limit $U = \infty$. U and V are, respectively, the on-site and nearest-neighbor Coulomb interactions; t is the nearest-neighbor tight-binding transfer integral; $C^\dagger_{l,\sigma}$ ($C_{l,\sigma}$) creates (destroys) an electron of spin σ at the lth site; $n_{l\sigma} = C^\dagger_{l\sigma} C_{l\sigma}$ is the corresponding number operator; $n_l = n_{l\uparrow} + n_{l\downarrow}$. In the present calculation we shall restrict our attention to bands less than half-full. Thus the infinite on-site repulsion requires $n_l = 0$ or 1. While the limit $U = \infty$ is taken primarily because it greatly reduces the complexity of the problem, the evidence for a very strong on-site repulsion has been indicated above. Indeed, one may surmise that U should be larger here than in the simple salts, where the interaction could be reduced by the higher proportion of polarizable donors.

A superficially similar model has been suggested by Buravov et al.[15] as being appropriate to these complex salts. $U = \infty$ is implicitly assumed in the restriction of the carrier number to zero or one per site. The intersite electronic interaction con-
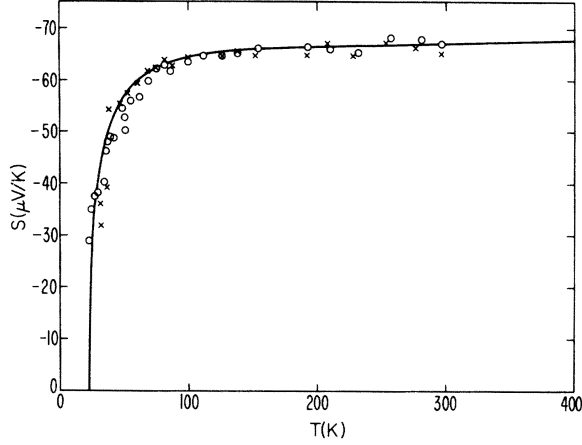
FIG. 1. Absolute thermopower of $Q(TCNQ)_2$. $\times$, $\circ$, single-crystal data. Solid curve is the result of Eq. (28) for $\rho = 0.475$, $V = 80\,°K$.

FIG. 3. Absolute thermopower of $DTC(TCNQ)_2$. $\circ$, single-crystal data. Solid curve is the result of Eq. (28) for $\rho = 0.485$, $V = 450\,°K$.

sidered, however, is attractive. This was intended to represent the chemical bonding of the molecules, which is more likely owing to the formation of elec- electron bands. These authors also assume that the spin degeneracy of the carriers is quenched, appealing for justification to the behavior of the magnetic susceptibility at high temperatures. The observed small, somewhat constant susceptibility[1] does not require such a conclusion, which is in fact inconsistent with the Heisenberg model discussed in Ref. 1. Thus, we believe that the extended Hub- bard model, although still very schematic, does present an improved description of the physics in- volved.

In this connection one additional point should be mentioned. Both the model of Buravov et al. and
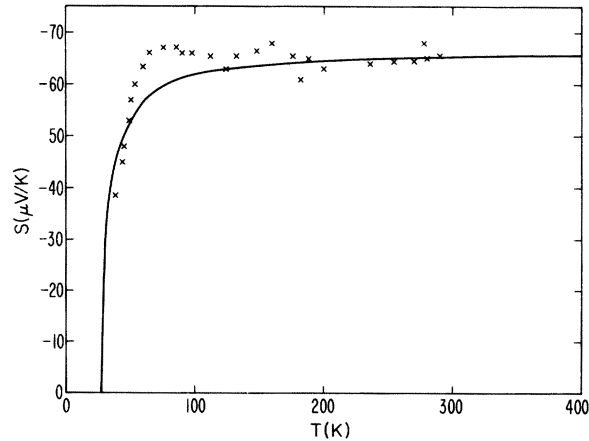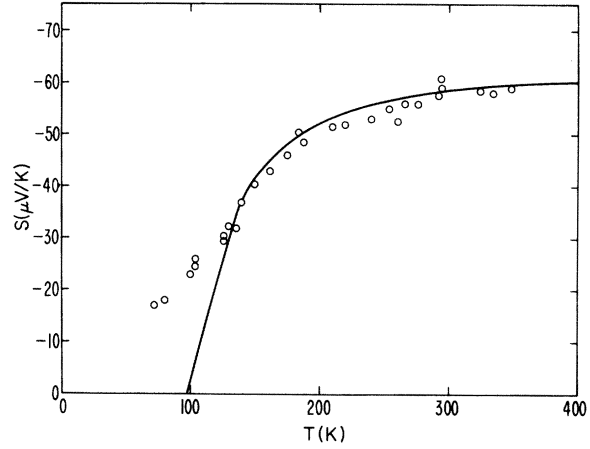

FIG. 2. Absolute thermopower of $A(TCNQ)_2$. $\times$, single-crystal data. Solid curve is the result of Eq. (28) for $\rho = 0.480$, $V = 100\,°K$.

the atomic limit of the extended Hubbard model, treated in Sec. III of this paper, ultimately neglect the carriers' kinetic energy in comparison to the off-site correlations. While on the basis of the other transport properties this may be a reason- able hypothesis, there is no possibility of testing it within the diffusion formalism used in Ref. 15. Our model, on the contrary, can be studied for the case where t is arbitrary and V is zero in order to establish the plausibility of this assumption. This is done in Sec. II. In Sec. III we derive our main result, the thermoelectric power of the extended Hubbard model in the atomic limit. Finally, in Sec. IV numerical results are presented and com- pared to the experimental data.

II. THERMOPOWER: $V = 0$, t ARBITRARY

We first rewrite Hamiltonian (1) so as to take full advantage of the restriction $n_l = 0$, 1. The terms $n_{l\uparrow}n_{l\downarrow}$ vanish identically. In addition,

$$\sum_\sigma C^\dagger_{l\sigma}C_{l+1,\sigma}$$

can be replaced by $C^\dagger_l C_{l+1}$, which transfers carriers of either spin but cannot result in a doubly occupied site. We have

$$H = V\sum_l n_l n_{l+1} - t\sum_l (C^\dagger_l C_{l+1} + H.c.)\,, \qquad (2)$$

with $n_l = 0$, 1. It is important to keep in mind that the carrier spins are still doubly degenerate.

Consider now the case $V = 0$ and t arbitrary. Upon a Fourier transform of the remaining term, the Hamiltonian becomes

$$H = -2t\sum_k n_k \cos(ka)\,, \qquad (3)$$

where a is the lattice spacing and the wave vectors k assume the allowed values $2\pi n/N_a a$ in the first Brillouin zone. N_a is the total number of sites.

The thermopower for this tight-binding model could be calculated using ordinary Boltzmann theory.[16] We, however, shall proceed by means of the Kubo formalism[17] so as to lay the foundation for the calculation in Sec. III of this paper. The Seebeck coefficient S is given by

$$eTS = -eS^{(2)}/S^{(1)} + \mu . \tag{4}$$

T is the temperature, e the absolute value of the electronic charge, μ the chemical potential, and

$$S^{(1)} = \tfrac{1}{2}\beta e^2 \int_0^\infty \langle vv(\tau) + v(\tau)v \rangle\, d\tau , \tag{5}$$

$$S^{(2)} = \tfrac{1}{2}\beta e \int_0^\infty \langle Qv(\tau) + v(\tau)Q \rangle\, d\tau , \tag{6}$$

where $v(\tau) = e^{iH\tau}$. In (5) and (6), $\beta = (kT)^{-1}$, $\langle \ldots \rangle$ denotes a thermal average, and v and Q are, respectively, the velocity-flux and energy-flux operators given by

$$v = \lim_{q \to 0} \frac{1}{\hbar q} \sum_l [n_l, H] e^{iqla} \tag{7}$$

and

$$Q = \lim_{q \to 0} \frac{1}{\hbar q} \sum_l [h_l, H] e^{iqla} , \tag{8}$$

where

$$\sum_l h_l = H \quad \text{and} \quad \sum_l n_l = N ,$$

the total number operator. For the Hamiltonian (3) we obtain

$$v = \frac{2ta}{\hbar} \sum_k n_k \sin(ka) \tag{9}$$

and

$$Q = -\frac{2t^2 a}{\hbar} \sum_k n_k \sin(2ka) . \tag{10}$$

Since $[v, H] = 0$, $v(\tau) = v$, and

$$eTS = -\langle Qv \rangle / \langle vv \rangle + \mu$$

$$= 2t \sum_k f_k(1 - f_k) \sin^2(ka)\cos(ka)\Big/$$

$$\times \sum_k f_k(1 - f_k)\sin^2(ka) , \tag{11}$$

where $f_k = \langle n_k \rangle$ and μ is determined by

$$\rho N_a = \langle N \rangle = \sum_k f_k . \tag{12}$$

Since the states are spin degenerate but only singly occupiable,[18] f_k is not the usual Fermi function:

$$f_k = \langle n_k \rangle = 2e^{-\beta(\epsilon_k - \mu)}/(1 + 2e^{-\beta(\epsilon_k - \mu)})$$

$$= (1 + \tfrac{1}{2}e^{\beta(\epsilon_k - \mu)})^{-1} , \tag{13}$$

where $\epsilon_k = -2t\cos ka$. If, however, we explicitly account for the spin term in μ by taking

$$\mu = \mu_0 - kT \ln 2 , \tag{14}$$

then

$$f_k = (1 + e^{\beta(\epsilon_k - \mu_0)})^{-1} . \tag{15}$$

μ_0 is seen from Eq. (12) to be the chemical potential for an ordinary tight-binding band of spin-$\tfrac{1}{2}$ carriers with density 2ρ. Finally, the thermopower is

$$S = S_0 - (k/e)\ln 2 , \tag{16}$$

where S_0 is the thermopower in the ordinary tight-binding model and has been calculated by Bernstein.[19] This result is plotted as a function of ρ and kT/t in Fig. 4. One sees, on comparison with Figs. 1–3, that the observed thermopower cannot be represented well by Eq. (16). We conclude, therefore, that off-site correlations must be taken into account.

III. THERMOPOWER: $t = 0$, V ARBITRARY

We return to the Hamiltonian (2) and proceed to calculate the thermopower to lowest order in the transfer. The flux operators are

$$v = \frac{ita}{\hbar} \sum_l C_l^\dagger C_{l+1} + \text{H. c.} , \tag{17}$$

$$Q = \frac{it^2 a}{\hbar} \sum_l C_l^\dagger C_{l+2}$$

$$+ \frac{iVta}{\hbar} \sum_l C_l^\dagger C_{l+1}(n_{l-1} + n_{l+2}) + \text{H. c.} \tag{18}$$
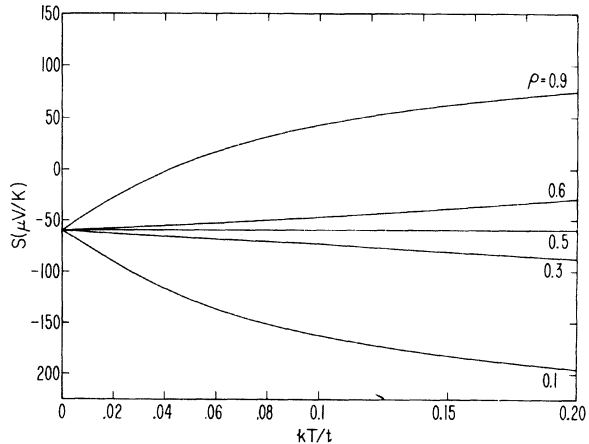

FIG. 4. Thermopower as a function of temperature and electron density for $V = 0$ and t arbitrary.

The first term in (18) does not contribute to lowest order in t and henceforward is disregarded. The time-developed operator $v(\tau)$ becomes, to lowest order,

$$v(\tau) = \frac{ita}{\hbar} \sum_l \exp[iV\tau$$

$$\times (n_{l+1} + n_{l-1} - n_l - n_{l+2} + 1)] C_l^\dagger C_{l+1} + \text{H. c.}$$

(19)

Referring to Eqs. (4)–(6), which relate the thermopower of the thermal averages $\langle vv(\tau) \rangle$ and $\langle Qv(\tau) \rangle$, we obtain, after carrying out the necessary commutations and using the diagonality of the traces,

$$\frac{\mu - eTS}{V} = \left(\sum_{l,\pm} \int_0^\infty d\tau \, \text{Tr}\{e^{-\beta K} n_l (1 - n_{l\pm1})(n_{l\pm2} + n_{l\mp1}) \exp[iV\tau(n_{l\mp1} + n_{l\pm1} - n_l - n_{l\pm2} + 1)]\} \right) \Big/$$

$$\times \sum_{l,\pm} \int_0^\infty d\tau \, \text{Tr}\{e^{-\beta K} n_l (1 - n_{l\pm1}) \exp[iV\tau(n_{l\pm1} + n_{l\mp1} - n_l - n_{l\pm2} + 1)]\} ,$$

(20)

where $K = H_0 - \mu N$, with H_0 the off-site interaction.

The time exponentials are simplified and removed from the trace by use of the identity

$$e^{n_l x} = (1 - n_l) + n_l e^x .$$

(21)

Now the integrations may be performed. Terms in which a net time exponential survives contribute a factor $\delta(V)$ upon integration. As we are interested in nonzero V, we discard these terms and are left with

$$\frac{\mu - eTS}{V} = \left(\sum_{l\pm} \text{Tr}[e^{-\beta K} n_l (1 - n_{l\pm1}) 2 n_{l\pm2} n_{l\mp1}] \right) \Big/ \sum_{l\pm} \text{Tr}\{e^{-\beta K} n_l (1 - n_{l\pm1})[(1 - n_{l\mp1})(1 - n_{l\pm2}) + n_{l\mp1} n_{l\pm2}]\} .$$

(22)

Rewriting the traces in terms of the transfer matrix,[20] we have

$$\frac{\mu - eTS}{V} = 2 \frac{\text{Tr}[P^{l-2} \tilde{n} P \tilde{n} P (I - \tilde{n}) P \tilde{n} P^{N_a - l - 1}]}{\text{Tr} P^{l-2}[(I - \tilde{n}) P \tilde{n} P (I - \tilde{n}) P (I - \tilde{n}) + \tilde{n} P (I - \tilde{n}) P \tilde{n} P \tilde{n}] P^{N_a - l - 1}} ,$$

(23)

where I is the identity matrix,

$$\tilde{n} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} , \quad P = \begin{pmatrix} 1 & \sqrt{x} & \sqrt{x} \\ \sqrt{x} & xy & xy \\ \sqrt{x} & xy & xy \end{pmatrix} \quad x = e^{\beta\mu}, \quad y = e^{-\beta V} .$$

(24)

The traces are evaluated in the diagonal representation of the transfer matrix P. The eigenvalues and eigenvectors of P are given by

$$\lambda_{1,2} = \tfrac{1}{2}\{1 + 2xy \pm [(1 - 2xy)^2 + 8x]^{1/2}\} , \quad \lambda_3 = 0 ,$$

(25)

$$|1, 2\rangle = \frac{1}{N_{1,2}} \begin{pmatrix} \lambda_{1,2} - 2xy \\ \sqrt{x} \\ \sqrt{x} \end{pmatrix} , \quad |3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} ,$$

(26)

where

$$N_{1,2}^2 = 2\lambda_{1,2}^2 - (1 + 6xy)\lambda_{1,2} + 2xy(1 + 2xy) .$$

(27)

Equation (23) therefore becomes

$$(\mu - eTS)/V = 4x^2\{\lambda_1^3(1 - 2x/N_1^2)/N_1^4 + \lambda_2^3(1 - 2x/N_2)/N_2^4 + [\lambda_1^2\lambda_2(1 - 6x/N_1^2) + \lambda_1\lambda_2^2(1 - 6x/N_2^2)]/(N_1^2 N_2^2)\}$$

$$\times \{\lambda_1^3(1 - 2x/N_1^2)(1 - 4x/N_1^2 + 8x^2/N_1^4) + 8\lambda_2^3 x^2 (1 - 2x/N_2^2)/N_2^4 - 4\lambda_1^2\lambda_2 x(1 - 6x/N_1^2 + 12x^2/N_1^4)/N_2^2$$

$$- 2\lambda_1\lambda_2^2 x[1 - 4x/N_1^2 - 4x/N_2^2 + 24x^2/(N_1^2 N_2^2)]/N_2^2\}^{-1} .$$

(28)

This expression can be computed numerically once we have the chemical potential, the equation for which is[21]

$$\frac{\partial \lambda_1}{\partial x} = \rho \frac{\lambda_1}{x} ,$$

(29)

with solution

$$8y^2 x = 2 \left(2y + \frac{(1 - 2\rho)^2}{\rho(1 - \rho)} \right) - \frac{2(1 - 2\rho)}{\rho(1 - \rho)}$$
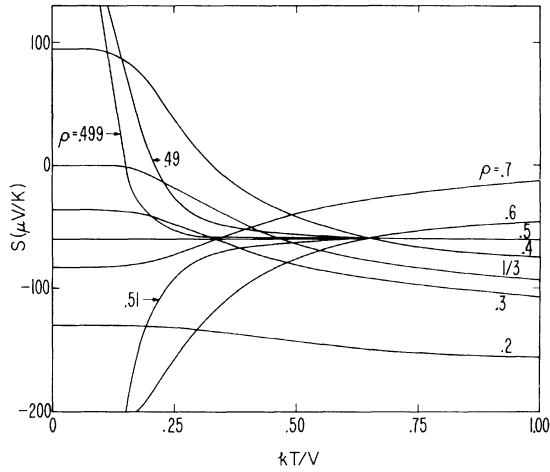
$$\times [4\rho(1 - \rho)y + (1 - 2\rho)^2]^{1/2} .$$

(30)

FIG. 5. Thermopower as a function of temperature and electron density for $t = 0$ and V arbitrary.

The thermoelectric power, a function of ρ and kT/V, is plotted in Fig. 5.

IV. COMPARISON WITH EXPERIMENT; CONCLUSIONS

The fits of the thermopower calculated in Sec. III to the data for the high-conductivity complex salts are indicated by the solid lines in Figs. 1–3. The procedure followed in obtaining these curves merits some attention. We observe that Eqs. (28) and (30) yield, for temperatures $kT \gg V$, an asymptotic value of the thermopower given by[12]

$$S(T \to \infty) = -(k/e)\ln[2(1-\rho)/\rho] .\qquad (31)$$

Note that this expression does not depend on T or V, but only on ρ. Equation (31), by the way, is the thermopower one would expect for a collection of noninteracting spin-$\frac{1}{2}$ carriers on singly occupiable sites.[22] Using (31), we have been able to fit the high-temperature observed constant thermopowers by fixing the single parameter ρ and then the low-temperature data by independent adjustment of V. These fits predict $\rho \lesssim \frac{1}{2}$ and $V \sim 100°$K.[23] The filling factor is as expected for 2:1 complex salts, and the magnitude of V is reasonable given an on-site repulsion of over $1000°$K.[2]

Of course, a more realistic model would include a finite transfer integral. In fact, the Hamiltonian (2) with V and t both arbitrary is known to be isomorphic to the anisotropic Heisenberg model,[7] for

which the ground state and first excited states have been calculated exactly.[24,25] The results, applicable to a one-quarter-filled band, show the onset of an energy gap for single-particle excitations when $V \geqslant 2t$, with $E_G = V - 4t$ for $V \gg t$. If we interpret the parameter V used in our thermopower fits as an effective interaction corresponding to this gap energy, the form of the thermopower curves is retained and an estimate can be made of the "bare" values V_0 given a value for t, from the function $E_G(V_0/2t)$ in Ref. 24. Taking $t = 240°$K,[2] we obtain for V_0 the approximate values $800°$K in $Q(TCNQ)_2$ and $A(TCNQ)_2$, and $1200°$K in $DTC(TCNQ)_2$. Thus, from the point of view of thermopower, the Hamiltonian (2) appears to be a viable representation of the electronic system in these high-conductivity complex salts.

Is the model also consistent with the other known physical properties? We cannot give a definitive answer to this question, but there are indications in favor of the model. The transition temperatures and activation energies of the measured electrical conductivities are in qualitative agreement with the predictions of the model. Of course, an accurate consideration of the conductivity must proceed from a more sophisticated model which would include loss mechanisms neglected in the present treatment. While the magnetic susceptibility predicted on the basis of the Hamiltonian (2) would obey the Curie law,[21] the observed susceptibility might be recovered by considering a finite, but still large, on-site repulsion.

In conclusion, we have seen that the strongly correlated extended Hubbard model quantitatively fits the measured thermopowers of a class of high-conductivity complex salts of TCNQ and may be qualitatively consistent with other physical properties of these compounds. The prospect therefore appears encouraging for the comprehensive theoretical description of these systems, with its basis given by the Hamiltonian (1). Further work, particularly a detailed conductivity calculation and continued experimental studies, will provide a test for the validity of the model as applied to these systems.

[1]I. F. Shchegolev, Phys. Status Solidi A 12, 9 (1972).
[2]A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952 (1972).
[3]A. J. Heeger and A. F. Garito, in Low-Dimensional

Cooperative Phenomena, edited by H. J. Keller (Plenum, New York, 1975), p. 89.
[4]J. F. Kwak, G. Beni, and P. M. Chaikin, second preceding paper, B 13, 641 (1975).
[5]N. F. Mott, Proc. Phys. Soc. Lond. A 62, 416 (1949).
[6]J. Hubbard, Proc. Roy. Soc. Lond. A 276, 238 (1963);

<u>281</u>, 401 (1964).

[7]C. Herring, *Exchange Interaction Among Itinerant Electrons* in *Magnetism* (Academic, New York, 1966), Vol. IV.

[8]J. Kanamori, Prog. Theor. Phys. <u>30</u>, 275 (1963).

[9]A. A. Ovchinnikov, Sov. Phys. -JETP <u>30</u>, 1160 (1970).

[10]R. A. Bari, Phys. Rev. B <u>3</u>, 2662 (1971).

[11]G. Beni and P. Pincus, Phys. Rev. B <u>9</u>, 2963 (1974).

[12]G. Beni, Phys. Rev. B <u>10</u>, 2186 (1974).

[13]The data in Fig. 1 are from Ref. 4, while the others were reproduced from figures in Ref. 1.

[14]A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. <u>64</u>, 342 (1975) [Sov. Phys. -JETP <u>37</u>, 176 (1973)].

[15]L. I. Buravov, D. N. Fedutin, and I. F. Shchegolev, Sov. Phys. -JETP <u>32</u>, 612 (1971).

[16]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1972), Chap. 7.

[17]R. Kubo, J. Phys. Soc. Jpn. <u>12</u>, 1203 (1957).

[18]The restriction on momentum state occupation follows easily from the similar restriction on-site occupation.

[19]U. Bernstein (private communication).

[20]G. F. Newell and E. W. Montroll, Rev. Mod. Phys. <u>25</u>, 353 (1953).

[21]Solved independently by J. P. Gallinar, Phys. Rev. B <u>11</u>, 4421 (1974).

[22]P. Chaikin and G. Beni, first preceding paper, B <u>13</u>, 647 (1975).

[23]Fitting the data to within 5%, we estimate the limits of error on ρ and V to be 2 and 10%, respectively.

[24]J. des Cloizeaux and M. Gaudin, J. Math. Phys. <u>7</u>, 1384 (1966).

[25]J. des Cloizeaux, J. Math. Phys. <u>7</u>, 2136 (1966).