Electrical Conductivity and Thermodynamics of the Narrow-Half-Filled-Band Hubbard Model

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We consider the question: Is there a semiconductor-to-metal transition (smooth or otherwise) with increasing temperature in the half-filled narrow-band Hubbard model? In the pertinent literature, with one exception, the answer has been yes. We bring to bear previous theoretical results for thermodynamic quantities, pseudoparticle density of states, our earlier variational calculation, and a new evaluation of the temperature dependence of the electrical conductivity. We are forced to conclude that there is *not* such a transition, at least in terms of standard terminology for "semiconductor" and "metal." We also briefly discuss recent experimental results of Epstein *et al.* on apparently one-dimensional systems in the light of the above consideration.

I. INTRODUCTION

The narrow-bandwidth (Δ) high-temperature regime of the Hubbard model has been studied by several authors[1-3] in the past few years. Since the Coulomb repulsion U is on the order of 10 eV in many insulating oxides,[4] the regime $(\Delta/U) \ll 1$ and $kT \approx U$ has been of somewhat academic interest only. However, recent studies[5] of complex organic systems seem to show that this regime is of experimental interest and warrants further theoretical investigation.

Historically, des Cloizeaux[1] was the first to apply Slater's band-antiferromagnetism picture to the Hubbard model. That is, he investigated the Hartree–Fock approximation to this model; he found a transition from an ordered antiferromagnetic insulator to a nonmagnetic metal at a second-order phase-transition temperature $kT \simeq \frac{1}{4}U$. He interpreted this as a transition from a state with disordered local moments to a state with no local moments (in apparent contradiction to the calculated results).

A few years ago we[2] reported that in going beyond the Hartree–Fock approximation we found a variational solution to the Hubbard model that exactly reproduced all physical predictions of the latter at $\Delta = 0$ and that gave a lower free energy than des Cloizeaux's solution in the regime $(\Delta/U) \ll 1$. We further noted that in this regime we did not find a transition to a metallic state: The localized nature of the one-electron states was maintained for all $kT > kT_N = 0(\Delta^2/U)$ and the solution exhibited only smooth thermodynamic behavior for all $T > T_N$. On the other hand, we did find a second-order transition from a paramagnetic insulator to an antiferromagnetic insulator at $T = T_N$.

In a related development Langer, Plischke, and Mattis[3] rederived some of des Cloizeaux's results by using Green's functions; in particular, they found the same second-order phase transition and again interpreted it as a nonmagnetic-insulator–to–nonmagnetic-metal transition. We had pointed out to them[6,7] that their result was in direct contradiction to the exact behavior of the Hubbard model at $\Delta = 0$, which shows no phase transition. In a later paper Langer[7] advanced a corrected form of the critical temperature, $kT = U/(4\ln U/\Delta)$, which vanished at $\Delta = 0$, consistent with the exact result at $\Delta = 0$. As Blackman and Esterling[8] pointed out, the corrected form is based on an approximation scheme that gives a spurious term of first order in Δ to the spectral weight function. Consequently, it is also difficult to have confidence in the corrected form in the region of very small Δ.

Although Hartree–Fock theory gives incorrect results in the narrow-band regime, it is worthwhile to consider whether it has any predictive value in relationship to an insulator-to-metal transition. For $\Delta = 0$, the exact constant-volume specific heat C may be obtained easily. The exact free energy[9] is very easily calculated and C is found by the simple well-known differentiation. This C is seen in Fig. 1 to exhibit a smooth maximum at $kT \simeq \frac{1}{5}U$ (slightly lower than the Hartree–Fock transition temperature). Shiba and Pincus[10] recently found a similar peak for the half-filled-band Hubbard model in numerical calculations for small numbers (2–6) of atoms when $\Delta/U = \frac{1}{8}$. They interpreted this peak as arising from a smooth insulator-to-metal transition which occurs with increasing temperature.[11] Considering the whole temperature range for small but nonzero Δ/U, their[10,11] results are in qualitative agreement with

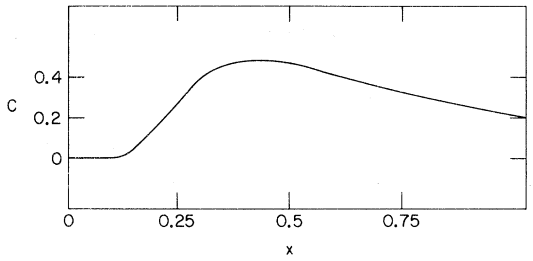

FIG. 1. Exact specific heat at zero bandwidth, $C=k(U/4kT)^2\,\mathrm{sech}^2(U/4kT)$, is plotted in units of k against $x=2kT/U$.

our[2] variational solution; e.g., the specific heat shows both a low-T ($kT\approx\Delta^2/U$) and a high-T ($\simeq\frac{1}{5}U$) peak. Further, their speculation[10,11] that even for large three-dimensional crystals there would be only smooth thermodynamic behavior at $T>T_N$ is of course consistent with our prediction[2] of the absence of a high-T transition. There does appear to be some disagreement between our statement that there is no high-T transition and theirs that there is a smooth insulator-metal transition. We present arguments that, according to common usage, the high-T behavior is not that of a metal, in agreement with our original claim,[2] while the more recent description[10,11] as an insulator-metal transition is misleading. Also, we shall see that Hartree–Fock theory, while suggestive, is quite misleading as to the physics.[12]

In reaching these conclusions, we were helped by the results of Sec. II. There we study the electrical conductivity as a function of temperature and frequency in the narrow-band regime. The conductivity in this regime has been studied previously by other authors. Brinkman and Rice[13] studied the mobility of a single hole in a half-filled band at infinite U (Ohata and Kubo[14] considered this mobility in the further limit, $T=\infty$). Bari, Adler, and Lange[15] utilized the degeneracy of the $\Delta=0$ ground state to obtain the conductivity for $kT\ll\Delta\ll U$ as a function of electron concentration.

In this paper we are strictly concerned with the conductivity of the half-filled band in the regimes $kT_N<kT\lesssim U$ and $kT\gtrsim U\gg\Delta$. Accordingly, the result of most interest to us is that of Kubo.[16] Kubo used a Green's-function decoupling scheme which originated from Hubbard[17] to obtain a two-particle Green's function and an expression for $\sigma(\omega)$ that can be adapted to the regime of interest. $\sigma(\omega)$ is a function of T and electron concentration and contains a dc part as well as optical peaks at $\omega\approx\pm U$. In this approximation scheme, the optical peaks are broadened but the dc part contains a δ-function peak in ω. Kubo emphasized the behavior of the optical conductivity at $T=0\,^\circ\mathrm{K}$, whereas we are mainly concerned with the temperature dependence of the dc part for a half-filled band.

The idea of Hubbard's[17] decoupling scheme is to treat the zero-bandwidth problem exactly and make approximations only in quantities that vanish with bandwidth. Since the conductivity explicitly contains a product of two current operators [see Eqs. (1) and (2)], the ratio σ/Δ^2 can be obtained exactly in the limit of zero bandwidth. In Sec. II we obtain the expression for $\sigma(\omega)$ to this order by straightforward statistical averaging. The result agrees with Kubo's Green's-function approximation to this order. Further, we find that the higher corrections found by Kubo do not qualitatively alter our analysis, and therefore we use the simpler expression [Eq. (6)] for $\sigma(\omega)$. For comparison, we also consider a simple two-band model of a semiconductor with no electron-electron interactions.

In Sec. III we use the results of Sec. II to help us reach the conclusions mentioned above and present further discussion. One consequence of these conclusions is that the very recent papers[10,11] do not enlarge our physical understanding of the narrow-band regime of the Hubbard model beyond the picture that had been presented earlier.[2]

II. CONDUCTIVITY CALCULATION

From the Kubo formula[18] the dissipative part of the conductivity is written

$$\sigma(\omega)=\frac{1}{2\Omega}\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}\int_0^\beta d\lambda\,\mathrm{Tr}(\rho J e^{iH(\tau+i\lambda)}Je^{-iH(\tau+i\lambda)})\,, \tag{1}$$

where J is the current operator. For the single-band Hubbard model

$$J=\frac{-ie}{\hbar}\sum_{i,j,\sigma}(R_i-R_j)t_{ij}c_{i\sigma}^\dagger c_{j\sigma}\,, \tag{2}$$

where R_i are the components of the lattice-site position vectors parallel to the external electric field, t_{ij} is the hopping integral, $c_{i\sigma}^\dagger$ and $c_{j\sigma}$ are the electron creation and annihilation operators, Ω is the crystal volume, and ρ is the density operator appropriate to the Hubbard Hamiltonian,

$$H=\sum_{i,j,\sigma}t_{ij}c_{i\sigma}^\dagger c_{j\sigma}+U\sum_i n_{i\uparrow}n_{i\downarrow}\,. \tag{3}$$

Equation (2) is based on the assumption that the Wannier function $w(\vec{r})$ associated with the lattice point at the origin satisfies $w(\vec{r})=w^*(\vec{r})=w(-\vec{r})$.

If we use Eq. (2) in Eq. (1) we obtain

$$\sigma(\omega)=-\frac{e^2}{\Omega\hbar^2}\sum_{\substack{i,j\bar{\sigma}\\ l,m,\sigma}}(R_i-R_j)(R_l-R_m)t_{ij}t_{lm}\times\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}\int_0^\beta d\lambda\times\mathrm{Tr}\left(\frac{e^{-\beta(H-\mu N)}}{z}c_{i\bar{\sigma}}^\dagger c_{j\bar{\sigma}}e^{iH(\tau+i\lambda)}c_{l\sigma}^\dagger c_{m\sigma}e^{-iH(\tau+i\lambda)}\right)\,; \tag{4}$$

here $z = \mathrm{Tr}(e^{-\beta(H-\mu N)})$, $N = \sum_l (n_{l\uparrow}+n_{l\downarrow})$, and μ is the chemical potential (equal to $\frac{1}{2}U$ in the half-filled-band case); also we take $t_{ij} = \Delta$ if $|\vec{R}_i - \vec{R}_j| = a$ (lattice spacing) and $t_{ij} = 0$ otherwise. We see the explicit appearance of a product of two hopping parameters, as mentioned above. The difficulty comes in evaluating the trace in Eq. (4) and it is for this reason that approximation schemes must be developed.

We note, however, that the trace can be performed straightforwardly at zero bandwidth (it can, of course, also be done at $U = 0$). Thus, with $\tilde{H} = U\sum_l n_{l\uparrow}n_{l\downarrow}$, we have

$$e^{i\tilde{H}(\tau+i\lambda)} c^{\dagger}_{l\sigma} e^{-i\tilde{H}(\tau+i\lambda)} = e^{iU(\tau+i\lambda)n_{l-\sigma}} c^{\dagger}_{l\sigma} .$$

Equation (4) reduces to

$$\sigma(\omega) = \frac{e^2a^2\Delta^2}{\hbar^2} q\eta \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \int_0^{\beta} d\lambda\, \mathrm{Tr}\left(\frac{e^{-\beta(\tilde{H}-\mu N)}}{z} \times e^{iU(\tau+i\lambda)(n_{l-\sigma}-n_{m-\sigma})} n_{m\sigma}(1-n_{l\sigma})\right), \quad (5)$$

where q is the number of nearest neighbors, η is the number density, $n_{m\sigma}$ is the occupation number for a *given* site and spin, and l refers to its nearest neighbors. The trace is easily calculated in the Wannier basis using the grand canonical ensemble, and the following identities are found:

$$\frac{1}{z}\mathrm{Tr}[e^{-\beta(\tilde{H}-\mu N)} e^{\xi n_{l-\sigma}}(1-n_{l\sigma})] = \frac{1+e^{\xi}e^{\beta U/2}}{2(1+e^{\beta U/2})}$$

and

$$\frac{1}{z}\mathrm{Tr}(e^{-\beta(\tilde{H}-\mu N)} e^{\xi n_{m-\sigma}} n_{m\sigma}) = \frac{e^{\xi}+e^{\beta U/2}}{2(1+e^{\beta U/2})} .$$

Thus the conductivity becomes

$$\sigma(\omega) = \pi q \frac{ne^2a^2\Delta^2\hbar^2}{2(1+e^{\beta U/2})^2}\left(2\beta e^{\beta U/2}\delta(\omega) + \frac{e^{\beta U}-1}{U}[\delta(\omega+U)+\delta(\omega-U)]\right). \quad (6)$$

It is easy to verify that Eq. (3.14) of Ref. 16 reduces to Eq. (6) for the half-filled-band case. The former qualitatively differs from Eq. (6) only in that the optical peaks are broadened. The δ-function peak in the dc part is common to both expressions and the T dependence is qualitatively the same for $\Delta \ll U$. Thus for simplicity we shall concentrate our discussion on Eq. (6). The optical conductivity does not vanish as $T \to 0$, and corresponds to optical excitations across the Mott–Hubbard gap, in analogy to optical excitations in band semiconductors. Although Kubo[16] stressed the differences between the two types of optical processes, it is interesting to note that (for $U \gg kT$) the thermal gap in the dc conductivity is equal to half the optical gap, in agreement with the analogous situation in band semiconductors (see below).

The dc conductivity exhibits the temperature dependence (as shown in Fig. 2)

$$f(\tfrac{1}{2}\beta U) = \tfrac{1}{8}\beta U \,\mathrm{sech}^2\tfrac{1}{4}\beta U . \quad (7)$$

We now consider the simple two-band noninteracting-electron model of a standard semiconductor (a band-model semiconductor). The Hamiltonian is

$$H_{2\text{-band}} = \sum_{\nu=1}\sum_{\vec{k}\sigma} \epsilon_{\nu\vec{k}} n_{\nu\vec{k}\sigma} , \quad (8)$$

where $n_{\nu\vec{k}\sigma}$ are the occupation numbers for Bloch functions with band index ν, wave vector $\vec{k}$, spin σ; there are two electrons per site or per $\vec{k}$ vector. Neglecting interband transitions for the purpose of calculating the low-frequency response, the current operator appropriate here is an obvious generalization of Eq. (2):

$$J = \frac{-ie}{\hbar}\sum_{\nu ij\sigma}(R_i - R_j) t^{\nu}_{ij} c^{\dagger}_{\nu i\sigma} c_{\nu j\sigma} . \quad (9)$$

Here the hopping integral $t^{\nu}_{ij} = N_0^{-1}\sum_{\vec{k}} \epsilon_{\nu\vec{k}} \exp[i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)]$ and $c^{\dagger}_{\nu i\sigma}$ is the Wannier-function creation operator for band ν. But then J commutes with Eq. (8), so that Eq. (1) gives directly

$$\sigma(\omega) = \frac{\pi\delta(\omega)}{\Omega}\beta\langle J^2\rangle = \frac{2\pi e^2}{\Omega}\beta\sum_{\nu\vec{k}} v^2_{\nu\vec{k}} f_{\nu\vec{k}}(1-f_{\nu\vec{k}})\delta(\omega) ,$$

where $v_{\nu\vec{k}}$ is the component of the group velocity $\hbar^{-1}\nabla_{\vec{k}}\epsilon_{\nu\vec{k}}$ parallel to the external electric field and $f_{\nu\vec{k}}$ is the Fermi–Dirac distribution. If both bands are narrow and if we call the gap U, then the above becomes, to lowest order in the bandwidths,

$$\sigma(\omega) = \frac{8\pi e^2\langle v^2\rangle}{U}\eta f\left(\frac{\beta U}{2}\right)\delta(\omega) , \quad (10)$$

where $\langle v^2\rangle$ is the average of $v_{\nu\vec{k}}$ over both bands and $f(\frac{1}{2}\beta U)$ is given by Eq. (7).

III. DISCUSSION

Referring to Eqs. (6), (7), and (10), we see that the dc conductivities of the two models show the

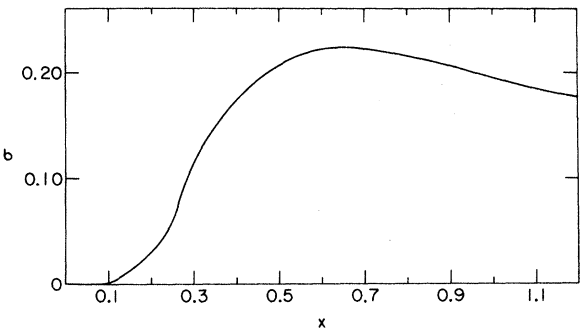

FIG. 2. Temperature dependence of the dc conductivity, as given by Eq. (7), is plotted against $x = 2kT/U$.

same temperature dependence, contained in $f(\frac{1}{2}\beta U)$. From the plot of this function in Fig. 2, we see that the conductivity starts at small values at low T, rises to a smooth maximum at $kT \simeq \frac{1}{3}U$, and then approaches zero slowly (as $1/T$) as $T \to \infty$.

It is probably not surprising that the conductivity is very small at low T and increases with increasing T—at very low T there are essentially no "carriers" and as T increases the number of carriers increases rapidly, causing the rise in conductivity. In the band model the carriers consist of Bloch-function holes and electrons thermally excited across the band gap. In the case of the Hubbard model, it is much more difficult to give as simple and accurate a description of these carriers since the energy eigenstates are not single Slater determinants and the Hartree–Fock approximation is so poor. But we can use the thermal-single-determinant approximation (TSDA), which is the one used in Refs. 2 and 9 (and which gives, in the variational sense, the best description in terms of approximate energy eigenstates which are single Slater determinants) to give us an idea as to these carriers. The fact that the lowest-free-energy solution in this narrow-band regime that we know[2] consists of Wannier functions at all $T > T_N$ suggests that we may view these carriers as doubly occupied sites and empty sites. In fact, Eq. (6) may be viewed as a conductivity calculation for the thermodynamic state that our variational solution describes. The energy increase for each pair, doubly-occupied–empty site, is U (the Mott–Hubbard correlation gap). But once we have such a pair, there is another state of the same energy related to it by a charge transfer; hence there is a matrix element of J connecting the two states giving a contribution to the zero-frequency conductivity.

The decrease in conductivity with T at high T might be somewhat surprising since there are no phonons (or analogous excitations) to cause a scattering of the carriers, which continues to increase with T. It is seen from Eq. (1) to be a quite general property, at least for any model with a finite number of states. We believe that the physics behind this effect is simply the fact that when kT becomes the dominant parameter of the system, the random distribution of thermal velocities will eventually dominate the drift velocity in an electric field, so that as $T \to \infty$, $\sigma \to 0$.

Let us use our results [Eqs. (6) and (10)] to try to settle the controversy pointed out in the Introduction. We must first ask what we should mean by the terms semiconductor and metal—we will consider two definitions, each of which has precedence in usage.

One possibility is simply to define a material as a semiconductor when $d\sigma_{dc}/dT > 0$ and a metal when $d\sigma_{dc}/dT < 0$. This definition has empirical foundation: $d\sigma_{dc}/dT > 0$ in a semiconductor as a result of thermal population of carriers; $d\sigma_{dc}/dT < 0$ in a metal due to the T dependence of the scattering cross section (e.g., due to thermal phonons in most metals). Of course, there are no external mechanisms in the Hubbard model (by definition) to cause $d\sigma_{dc}/dT < 0$, and we have accounted for this behavior of the model in a preceding paragraph. If, however, one wished to abstract the empirical rule, then our result, Eq. (6), provides a basis for the characterization[10,11] of the narrow-band high-T regime of the Hubbard model as showing a semiconductor-to-metal transition.[19] But this definition immediately demands that the two-band model described around Eq. (8) be characterized as showing a semiconductor-to-metal transition, as seen by comparing Eqs. (6) and (10).

Such a usage is contradictory to the usual viewpoint. This viewpoint has been given explicit definition only for noninteracting-fermion models, or for electron models treated in the Hartree or Hartree–Fock approximation (where the wave functions are single Slater determinants). In these cases, this view defines a semiconductor as a material[20] for which there is a gap in the density of states at the Fermi level, and defines a metal as a nonsemiconductor. In other words, this viewpoint regards the structure of one-electron energy spectra and energy eigenstates as the basis for the distinction between a semiconductor and a metal. Clearly then the two-band model, which according to the definition of the previous paragraph shows a semiconductor-to-metal transition with increasing T, does *not* show such a transition according to the usual definition; it is rather characterized simply as being a semiconductor.

It was in the spirit of the usual definition, which we will call a microscopic definition (as opposed to the previous "macroscopic" definition, which depends entirely on the sign of $d\sigma_{dc}/dT$), that we stated[2] that there is no transition to the metallic state (when $\Delta/U \ll 1$) and characterized this narrow-band regime simply as a localized magnetic semiconductor. Our reason for these statements is that for $0 \leq \Delta/U \ll 1$ the one-electron states which gave the minimum free energy within the TSDA are *localized for all temperatures*, suggesting that the microscopic electronic structure remains essentially constant as T increases above T_N. This suggestion is strongly supported by the fact that the exact pseudoparticle density of states[17] is completely independent of T for $\Delta = 0$, and so for very small Δ we expect that the gap in this density of states (the Mott–Hubbard gap) will be very insensitive to T, certainly not approaching zero with increasing T.

We do not intend to actually develop here microscopic definitions for the terms semiconductor and

metal which would be satisfactory for general interacting-electron systems at arbitrary temperature.[21] A tentative suggestion (again limiting ourselves to normal crystalline materials) might be to follow Hubbard and consider the pseudoparticle density of states[17] at finite T as taking the place of the ordinary density of states when one "turns on" the interactions. In any case, it is clear the the recent description[10,11] of the narrow-band high-T regime of the Hubbard model as exhibiting a smooth semiconductor-to-metal transition differs from the earlier description[2] as a localized semiconductor for all T with no transition to the metallic state only by reason of the difference in definition of the words. There is no marked difference in any of the physical predictions that have been made, the correct qualitative behavior existing in the approximation (TSDA) of the earlier work.[2] (Although, for the reasons given above, the use of the term metal-insulator transition here is contrived and misleading.)

The Hartree-Fock approximation, on the other hand, gives one-electron energies which change with temperature, the gap approaching zero at a high temperature ($U/4k$ when $\Delta = 0$), thus suggesting a significant change in electronic structure, and a corresponding insulator-to-metal transition. However, this contradicts the true behavior of the density of states, as we have pointed out, and hence is quite misleading concerning this physical quantity.[22]

We comment that *if* one adopts the macroscopic definition, it should be realized that the nature of the high-T "metal" in the narrow-band regime of the Hubbard model is quite different from the usual broad-band metallic state. One reason is that at $kT \gtrsim \frac{1}{3}U$, one necessarily has $kT \gg \Delta$ in the narrow-band regime ($\Delta \ll U$), so that one certainly could not think even approximately of the transport processes or thermal quantities as resulting from Bloch-wave excitations across a well-defined Fermi surface. Furthermore, a picture of this state as a gas of free or Bloch electrons would be grossly erroneous, since e.g., this picture predicts a very small specific heat (C in this picture is *zero* at $\Delta = 0$), whereas the exact specific heat decreases quite slowly for $T \gtrsim \frac{1}{3}U$ (Fig. 1).

Concerning the smoothness of the high-T behavior we remark that our prediction[2] of the absence of a high-T transition when $0 \leq \Delta/U \ll 1$, even for infinite three-dimensional systems, lends credence to the recent speculations[10,11] to this effect. This is so because the TSDA (on which our prediction[2] was based) is quite similar to the molecular field approximation to the Heisenberg spin model, an approximation which is notorious for consistently overestimating the likelihood of the occurrence of a phase transition. In accordance with this, the TSDA gave[2] a sharp (second-order) transition at a Néel temperature T_N (as expected in three dimensions, but not so in one dimension) and yet gave smooth behavior at high T, independent of dimensionality.

We conclude with a brief discussion of the experimental results of Epstein *et al.*[5] In their interpretation of the data, they use a narrow-half-filled-band Hubbard model with a correlation gap U that renormalizes to zero above some temperature. In our studies[2] we have not found a T renormalization of the correlation gap and, further, are not aware of a theory that does predict renormalization in the narrow-band regime (and gives the correct $\Delta = 0$ behavior, of course). Epstein *et al.* also claim to observe Pauli-like behavior in the susceptibility; this too has not been evidenced in our theory or any other theory of the narrow half-filled band. Lastly, it is interesting to see if their observed conductivity can be accounted for by the simple picture of a correlated semiconductor that we have presented here. If we simply apply our result using the experimentally suggested parameters ($U = 0.17$ eV, $\Delta = 0.021$ eV), we find that the conductivity maximum T_M would occur at $\sim U/3k \simeq 670\,^\circ$K, over three times the observed[5] value of 200 °K. Actually, to determine U and Δ the conductivity at low T was assumed[5] to behave according to an activation energy equal to one-half the so-called Hubbard gap $U - 4|\Delta|$. Our result, Eqs. (5) and (6), supports that assumption in the sense that it is the same to 0 (Δ^2). This suggests that possibly the finite-Δ result may be approximated by replacing U by $U - 4|\Delta|$ everywhere; this would reduce T_M to $\sim 330\,^\circ$K, still somewhat high. One obvious modification of the model would be the introduction of lattice vibrations and their interactions with the electrons. For example, if we take a relaxation time in our dc conductivity that goes as $1/T$ (due to phonons) then this additional T dependence lowers the maximum from ~ 330 to $\sim 200\,^\circ$K.

The foregoing analysis suggests that the observed conductivity vs T might be understandable[23] on the basis of the Hubbard model modified by the inclusion of phonon scattering; however, there is as yet no theoretical evidence that this model would explain the susceptibility data. Further, present theoretical results suggest, as discussed in this paper, that this model is not consistent with the believed[5] mechanisms for the observed behavior—namely a temperature renormalization of the gap and a consequent metal-insulator transition. (In particular, the theoretical arguments[5] advanced for these mechanisms were shown here[12] to be completely incorrect.)

Note added in proof. A recent exact calculation [D. Cabib and T. A. Kaplan, Phys. Rev. (to be published)] for the four-site four-electron Hubbard

model showed no sign of the experimentally observed[5] leveling of the inverse susceptibility at high T. Further, this work shows that a pronounced minimum in the inverse susceptibility should be expected to occur at lower T ($\approx \Delta^2/U$), in contradiction to the observed behavior, and concludes that the Hubbard model is probably seriously deficient as a model for the experimental system.[5]

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[11]J. Kimball and J. R. Schrieffer, in a postdeadline paper presented at the International Conference on Magnetism and Magnetic Materials, Chicago, 1971 (unpublished), also found a similar smooth high-T peak; they further found a smooth semiconductor-to-metal transition at high T. Unfortunately, an approximation introduced within their functional integral technique caused their results to be wrong in the $\Delta = 0$ limit [R. A. Bari, Phys. Rev. B 5, 2736 (1972)], so the reliability of their results in the narrow-band regime would appear to be questionable.

[12]The theoretical discussion of Epstein *et al.*, Ref. 5, also led them to conclude that there is a transition from insulator to metal. However, they based their conclusion on a crossing of two entropies (that of the antiferromagnetic Heisenberg chain with that of the simple metal) at a given T although transitions are governed by the free energy $F = U(T) - TS(T)$. As shown in Ref. 2, the *free energy* of the simple localized state is lower than that of the simple metallic state (the same one considered in Ref. 5) for all T at the value of Δ/U considered by Epstein *et al.* Even if they had compared the free energies corresponding to their calculations, they would still have found a crossing since at $T = 0$, $F_{\text{Heis}} < F_{\text{metal}}$, while at large enough T $F_{\text{Heis}} \sim -kT\ln 2 > F_{\text{metal}} \sim -kT\ln 4$ (but it would have occurred at a much higher temperature). This disagrees with our result (Ref. 2) and the essential reason is that the entropy due to the various occupancies (aside from spin) of the localized one-electron states is arbitrarily omitted from F_{Heis} but included in our free energy for what we called the localized state (the free energy for this state $F_L \sim -kT\ln 4$ at high T, so $F_{\text{metal}} \to F_L$ as $T \to \infty$, which is consistent with our (Ref. 2) no-crossing result).

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[17]J. Hubbard, Proc. Roy. Soc. (London) A276, 238 (1963).

[18]R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[19]The bases for this characterization given in Refs. 10 and 11 are questionable. One of these is the statement that the localized moments gradually disappear with increasing T. But this apparently contradicts the easily verified fact that the spin susceptibility is given by a Curie law when $kT \gg U \gg \Delta$ [see T. A. Kaplan and S. D. Mahanti, Bull. Am. Phys. Soc. 17, 292 (1972)]; furthermore, the mathematical quantity L_0 defined in Ref. 10 as the localized moment does not approach zero as $T \to \infty$. The other basis given in Ref. 10 is that once an empty or doubly occupied state is formed it moves rather freely; it will be noted below that it would be difficult to use this property to distinguish between a metal and a semiconductor.

[20]For simplicity, we consider only crystalline materials.

[21]Related attempts seem to be limited to zero temperature [W. Kohn, Phys. Rev. 133, A171 (1964); C. Herring, in *Magnetism*, Vol. IV, edited by G. Rado and H. Suhl (Academic, New York, 1966)].

[22]An approximation different from Hartree–Fock, but also having a T-dependent gap at $\Delta = 0$, and therefore also misleading, has been given by S. Doniach, Advan. Phys. 18, 819 (1969).

[23]In a preliminary account of the present work [R. A. Bari and T. A. Kaplan, Bull. Am. Phys. Soc. 17, 358 (1972)] we stated that our analysis "suggests that the Hubbard model is not sufficient to explain the observed behavior." In citing this preliminary account, H. R. Zeller [Phys. Rev. Letters 28, 1452 (1972)] exaggerated our statement by saying that "it (the Hubbard model) fails to explain the T dependence of σ." The text of the present work gives a more precise statement of our conclusions.