PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

Gutzwiller theory of electron correlation at finite temperature

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(Received 15 April 1975; revised manuscript received 26 April 1976)

The Gutzwiller's scheme is extended to finite temperature in order to study the properties of electrons in strongly correlated metals. Using the quasichemical approximation we have constructed an orthogonal set of trial functions. These functions have a one-to-one correspondence to the Slater determinants with Bloch states. Our scheme for constructing this set of basis functions is independent of the perturbation theory. Based on this orthogonal set, the entropy of the correlated electrons has been derived from the thermodynamic equations. It has the correct behavior in the metallic phase except in the vicinity of the metal-nonmetal phase boundary. The electron effective mass and the Pauli spin susceptibility are found to be enhanced in a way similar to the Brinkman-Rice result for a correlated ground state. The Knight shift is also enhanced but the enhancement factor is much less than that for the susceptibility. However, the electronic specific heat is enhanced only for $k_B T/\Delta \gtrsim 0.11$ (Δ is the bare bandwidth). For $k_B T/\Delta \lesssim 0.11$ we need to consider the collective excitations such as paramagnons in order to have a complete treatment of the specific heat. Using an ellipsoidal density of states we have performed model calculations for a nonmagnetic state in order to illustrate the characteristic features of the strongly correlated electron system.

I. INTRODUCTION

In 1963, Hubbard,[1] Gutzwiller,[2] and Kanamori[3] proposed a simple Hamiltonian to investigate the magnetic ordering and the Mott transition[4] in highly correlated metals with narrow energy bands. The model Hamiltonian, which is usually referred to as the Hubbard Hamiltonian, includes the intra-atomic Coulomb repulsion and the one-electron hopping energy. The Hubbard model, although simple in form, is not easy to handle mathematically. The ground-state properties have been extensively studied by many authors[5] with various assumptions. Many of these treatments closely follow Hubbard's Green's-function decoupling scheme.[1]

Another approach, which is basically different from Hubbard's is Gutzwiller's scheme.[2] Though very different in mathematical structure, the mechanism for the metal-nonmetal (MNM) transition is the same in both types of approaches. Brinkman and Rice[6] have used Gutzwiller's method to show that a half-filled band becomes nonconducting when the number of doubly occupied atoms becomes zero due to strong correlation. In Hubbard's approach some atoms are doubly occupied because the two subbands overlap. As soon as the Mott-Hubbard gap opens under strong correlation a MNM transition occurs and all the atoms become singly occupied.

Brinkman and Rice[6] were also the first to show that for zero temperature the variational method gives simultaneous enhancements of the Pauli susceptibility and the electronic effective mass by the same order of magnitude as the MNM transition is approached from the paramagnetic metallic side. Furthermore, they suggested that the electronic specific heat is enhanced in a similar manner. This property is important for highly correlated metals as Mott[7] has pointed out.

The finite-temperature regime of the Hubbard model was first investigated by des Cloizeaux.[8] His results derived from the Hartree-Fock approximation have been largely extended by Langer, Plischke and Mattis,[9] Kaplan and Bari,[10] Blackman and Esterling,[11] and Bari and Kaplan.[12] At large U/Δ (U is the Hubbard parameter and Δ is the bandwidth) Kaplan and Bari,[10] Kimball and Schrieffer[13] and Plischke[14] found a Néel temperature $kT_N \sim \Delta^2/U$. Ramirez, Falicov, and Kimball[15] have given a discussion of an entropy-driven MNM transition in a related model as the temperature rises. Nevertheless, none of these works describes the important features of the enhancements of the susceptibility, the specific heat, and the electronic mass, as well as the effect of electron correlation on the Knight shift in the metallic phase.

It is therefore an important problem to generalize Gutzwiller's approach to finite temperatures as well as to extend the Brinkman-Rice results to this case. This is the main purpose of the present paper.[16] Since we are interested in the highly correlated metallic phase, we will not consider the antiferromagnetic ordering which often appears in the insulating phase of the half-filled-band Hubbard model. We should point out that in the variational scheme, the original Gutzwiller's trial functions should be drastically modified in order to take into account the antiferromagnetic ordering due to the electron virtual hoppings.[17] Therefore our results for paramagnetic state are not valid when the antiferromagnetic state is approached at the low-temperature and large U/Δ limit.

In Sec. II we briefly summarize Gutzwiller's scheme for the ground state. Its generalization to finite temperatures is given in Sec. III for the general case. We then consider the special case of a paramagnetic state with one electron per atom, and perform a model calculation using an ellipsoidal density of states. In terms of this model calculation the validity of our generalized finite-temperature Gutzwiller's scheme will be discussed in details. The Pauli susceptibility, the Knight shift, and the electronic specific heat are derived in Secs. IV–VI, respectively, together with numerical calculations to illustrate the electron correlation effect. A short discussion is given in Sec. VII.

II. REVIEW OF GUTZWILLER'S SCHEME FOR THE GROUND STATE

Gutzwiller's scheme[2] was originally formulated for the ground state in an orbitally nondegenerate narrow band. It has been generalized to include the orbital degeneracy,[18] and subsequently used to treat the low-lying excitations.[19] In the finite temperature version to be discussed in Sec. III we will, however, only consider the case of a simple s band. In view of previous results[18] generalizations to more complicated band structures are straightforward. Already the simplified s-band theory is useful, however, and can be applied to realistic system, such as phosphorus-doped silicon. The impurity band in Si : P is a narrow nondegenerate band separated from the conduction band by about 20–40 meV, depending on the impurity concentration. For example, the susceptibility of Si : P has been measured through a temperature range[20] from 1 to 77 °K (equivalent to about 10 meV) and shows enhancements suggestive of strong electron-electron interactions. Hence the relevant theory should be able to cope with effects of electron correlation in a wide range of temperature.

The mathematical structure as well as some of the fundamental physical concepts in our generalized finite-temperature Gutzwiller approach are similar to those in the ground-state Gutzwiller method. It is therefore instructive to first summarize Gutzwiller's ground state scheme. The reader is referred to the original works for details.

Consider the s-band Hubbard Hamiltonian

$$H=\sum_{gg'\sigma} t_{gg'} a^\dagger_{g\sigma} a_{g'\sigma} + U\sum_g n_{g\uparrow} n_{g\downarrow}, \tag{1}$$

where the sum g, g' is over all lattice sites and $a^\dagger_{g\sigma}$, $a_{g\sigma}$, and $n_{g\sigma}$ are the creation, annihilation, and number operators for an electron of spin σ at lattice site g. The quantity $t_{gg'}$ is the electron hopping energy and U the Coulomb repulsion between the electrons on the same site.

We assume that there are N electrons in a simple lattice of L sites. N can be arbitrary except that $N \leq L$ (if $N > L$ we can consider the holes instead of electrons). Among them let $N(\sigma)$ electrons have σ spin, and $N(\sigma)$ is also arbitrary as long as $N(\uparrow)+N(\downarrow)=N$. To describe the wave function of these N electrons, we use a set of lattice sites $G(\sigma)=[g(\sigma)_1, \ldots, g(\sigma)_{N(\sigma)}]$ to specify $N(\sigma)$ Wannier functions $\phi_\sigma(r-g)$ through the relation $g\in G(\sigma)$. If G represents both $G(\uparrow)$ and $G(\downarrow)$, then the many-electron wave functions in the localized representation have the general form

$$\Psi_c=\sum_G A_c(G)\Phi(G), \tag{2}$$

where

$$\Phi(G)=\prod_\sigma \prod_{g\in G(\sigma)} a^\dagger_{g\sigma}|0\rangle. \tag{3}$$

The summation in Eq. (2) runs over all possible configurations G.

The coefficients $A_c(G)$ must satisfy two conditions: In the atomic limit where all the atoms are neutral, $A_c(G)$ is a finite constant if G does not contain doubly occupied sites and zero otherwise. On the other hand, in the band limit where $U=0$, Ψ_c reduces to an antisymmetrized product of Bloch states Ψ. Let $K(\sigma)$ be a set of k vectors such that the Bloch state $\psi_k(r)$ with the $k\in K(\sigma)$ is occupied by a σ-spin electron, and K represents $K(\uparrow)$ and $K(\downarrow)$. Then the corresponding wave function at this band limit is simply

$$\Psi(K)=\prod_\sigma \prod_{k\in K(\sigma)} a^\dagger_{k\sigma}|0\rangle. \tag{4}$$

By means of the transformation

$$a^\dagger_{k\sigma}=L^{-1/2}\sum_g e^{ikg} a^\dagger_{g\sigma} \tag{5}$$

$\Psi(K)$ can be decomposed into

$$\Psi(K)=\sum_G A(K,G)\Phi(G), \tag{6}$$

in which the coefficients $A(K,G)$ are well defined and known.

To construct $A_c(G)$ for the general case of finite U, we note that the configuration G is characterized by the number of doubly occupied atoms, ν. As the correlation energy U increases, the configurations which have large value of ν are more likely to be projected out. Accordingly we propose the trial form

$$A_c(K,G)=\eta^\nu B(K,G)A(K,G), \tag{7}$$

where $0 \leqslant \eta \leqslant 1$ is a parameter which measures the intra-atomic correlation strength: $\eta = 1$ at the band limit and $\eta = 0$ at the atomic limit. The factor $B(K, G)$ is introduced to account for the less important interatomic interactions. They satisfy the condition $B(K, G) = 1$ when there is no correlation. The correlated wave function can then be written

$$\Psi_c(K) = \sum_{\nu} \eta^{\nu} \sum_{G}{}' B(K, G) A(K, G) \Phi(G), \tag{8}$$

where the primed sum includes the configurations which have the same value of ν. Note that at the band limit $\Psi_c(K)$ reduces to $\Psi(K)$.

In this section we consider the ground state only. Let K_F be the set of k vectors which specify the Fermi sea. Then the trial function for the correlated ground state is

$$\Psi_c(K_F) = \sum_{\nu} \eta^{\nu} \sum_{G}{}' B(K_F, G) A(K_F, G) \Phi(G). \tag{9}$$

The expectation value of the energy with respect to this function

$$\langle K_F | H | K_F \rangle_c = \langle \Psi_c(K_F) | H | \Psi_c(K_F) \rangle / \langle \Psi_c(K_F) | \Psi_c(K_F) \rangle \tag{10}$$

will be computed in the quasichemical approximation[21] (QCA). We compute only one hopping matrix element

$$\langle K_F | t_{gg'} a^{\dagger}_{g\sigma} a_{g'\sigma} | K_F \rangle_c = \sum_{\nu'\nu} \eta^{\nu+\nu'} \sum_{G,G'}{}' B^*(K_F, G) B(K_F, G') A^*(K_F, G) A(K_F, G') \langle \Phi(G) | t_{gg'} a^{\dagger}_{g\sigma} a_{g'\sigma} | \Phi(G') \rangle \tag{11}$$

as an illustrative example. The matrix element on the right-hand side describes the hopping of an electron from site g' to site g, changing the initial configuration G' to the final configuration G. Depending on the atomic configurations at g and g' this hopping alters the number of double occupancies from the initial value ν' to the final value ν. Therefore, due to the intra-atomic Coulomb repulsion, the bare hopping probability is modified.

The bare hopping probability is also affected by the interaction between the hopping electron and the surrounding electrons not localized on either g or g'. Such a long-range interaction is measured by the factors $B(K_F, G)$. As an example, let us consider the electron hopping from a singly occupied site g' into another singly occupied site g, increasing the number of double occupancies by one (i.e., $\nu = \nu' + 1$). The motion of the surrounding $N - 2$ electrons is so restricted that when they move around they cannot localize on either g or g'. That is, they are restricted to a lattice of $L - 2$ sites. Accordingly, QCA is the exact treatment of a correlated two-site system embedded in a medium which is treated by the "restricted" random-phase approximation. Instead of knowing the exact form of $B(K_F, G)$, this approach imposes certain conditions on $B(K_F, G)$. It has been proved that QCA gives exact solutions at both the band limit and the atomic limit, and that it is a good approximation for the case of narrow energy bands in general.

The main feature of QCA is that the "correlated" hopping probability remains invariant with respect to translations by a lattice vector. Therefore, a band picture is preserved though the electrons are correlated. It has been proved that for given correlation strength η, the sum over ν in Eq. (11) is sharply peaked at the most probable number of double occupancies ν_0. Hence we can approximate the sum by this dominant term. We note that this particular value of ν_0 is the same as the optimum number of double occupancies in Van Vleck's theory.[22]

The QCA result for energy can then be expressed as

$$\langle K_F | H | K_F \rangle_c = \sum_{\sigma} \sum_{k \in K_F(\sigma)} \epsilon_c(\sigma k) + \nu_0 U, \tag{12}$$

where

$$\epsilon_c(\sigma k) = \epsilon_0 + \frac{1}{L} \sum_{g'g} D(\sigma) t_{gg'} e^{ik(g-g')} \tag{13}$$

and

$$\begin{aligned} D(\sigma) = \{ N(\sigma) [L - N(\sigma)] \}^{-1} & \\ \times \{ [N(\sigma) - \nu_0]^{1/2} (L - N + \nu_0)^{1/2} & \\ + \nu_0^{1/2} [N(-\sigma) - \nu_0]^{1/2} \}^2 \leqslant 1. & \end{aligned} \tag{14}$$

The quantity $\epsilon_c(\sigma k)$ in Eq. (13) has the form of a spin-polarized energy band centered at ϵ_0, the energy of an electron in the atomic limit. This energy ϵ_0 spreads into a "band" due to the correlated hopping which is reduced from the bare hopping by a factor $D(\sigma)$. Accordingly this "band" should be narrower than the bare energy band. We can adjust the zero-energy reference so that $\epsilon_0 = 0$. From now on we will therefore drop ϵ_0.

Finally, we apply the variational method to minimize the energy by varying ν_0. The condition

$$\frac{\partial}{\partial \nu_0} \Big(\sum_{\sigma} \sum_{k \in K_F(\sigma)} \epsilon_c(\sigma k) + \nu_0 U \Big) = 0 \tag{15}$$

determines ν_0 as a function of the correlation energy U. Here we must point out that because of the QCA, the calculated minimum energy has not been shown to be an upper bound on the exact ground-state energy. For this reason, this scheme is referred to as the Gutzwiller variational method after the pioneering work of Gutzwiller.[2]

Before we proceed to the finite-temperature version we note that the total energy Eq. (12) may be written in the more general form[23]

$$E_c = \sum_\sigma D(\sigma) \sum_k f_k \epsilon(k) + \nu_0 U, \tag{16}$$

where $\epsilon(k)$ are bare band energies and f_k occupation numbers specifying the uncorrelated state Ψ. Evidently the sum of f_k must equal the total number of electrons also when the system is correlated. For Sec. III it is also important to note that within QCA the correlated wave functions satisfy the orthogonality condition[18,19]

$$\langle K | K' \rangle \propto \delta_{K,K'} . \tag{17}$$

Furthermore, it is noteworthy that the interaction term in Eq. (16) does not depend explicitly on occupation numbers. This is because only intra-atomic interactions are considered. Different configurations $\{f_k\}$ associated with a particular Hartree-Fock energy and $N(\uparrow)/N(\downarrow)$ ratio therefore give the same correlation energy through Eq. (15).

III. GUTZWILLER'S SCHEME AT FINITE TEMPERATURE

In order to extend the previous results to finite temperature we will assume that we are dealing with only one kind of states, normally nonmagnetic ones. Our results are valid for the strongly correlated metallic regime where the system does not show antiferromagnetic ordering. In order to cope with the antiferromagnetic state, the Gutzwiller trial function should be much modified[17] and will be outside the interest of the present paper. In this respect our formalism has similarities with the thermal Hartree-Fock theory in which the same assumption is usually made.

Let the energy of the system be sharply peaked at a specific value E_c, i.e., we assume a microcanonical ensemble. The energy is then given by an expression similar to Eq. (16) in which the occupation numbers f_k are now some kind of mean occupation numbers. f_k will be treated as the variational parameters which minimize the free energy. The free energy of the correlated system can consequently be expressed as

$$F_c(T, \nu(T)) = E_c(T, \nu(T)) - TS_c(T, \nu(T)). \tag{18}$$

The entropy S_c and the energy E_c must satisfy the thermodynamic equation

$$\frac{\partial E_c}{\partial T} = T \frac{\partial S_c}{\partial T} \tag{19}$$

or

$$\left.\frac{\partial E_c}{\partial T}\right|_\nu + \left.\frac{\partial E_c}{\partial \nu}\right|_T \frac{\partial \nu}{\partial T} = T\left(\left.\frac{\partial S_c}{\partial T}\right|_\nu + \left.\frac{\partial S_c}{\partial \nu}\right|_T \frac{\partial \nu}{\partial T}\right). \tag{20}$$

But the free energy must have a minimum at the optimum number of double occupancy $\nu(T)$. This condition yields

$$\left.\frac{\partial F_c}{\partial \nu}\right|_T = \left.\frac{\partial E_c}{\partial \nu}\right|_T - T \left.\frac{\partial S_c}{\partial \nu}\right|_T = 0, \tag{21}$$

and consequently Eq. (20) simplifies to

$$\left.\frac{\partial E_c}{\partial T}\right|_\nu = T \left.\frac{\partial S_c}{\partial T}\right|_\nu . \tag{22}$$

This equation has a special solution as

$$E_c(T, \nu(T)) = \sum_\sigma D(\sigma, \nu(T)) \sum_k f(T, \epsilon(k))[\epsilon(k) - \mu] + \nu(T) U \tag{23}$$

and

$$S_c(T, \nu(T)) = -k_B \sum_\sigma D(\sigma, \nu(T)) \sum_k \{ f(T, \epsilon(k)) \ln f(T, \epsilon(k)) + [1 - f(T, \epsilon(k))] \ln[1 - f(T, \epsilon(k))] \} + S_I(\nu(T)), \tag{24}$$

where $S_I(\nu(T))$ depends on T implicitly through $\nu(T)$, and

$$f(T, \nu(T)) = (\exp\{[\epsilon(k) - \mu]/k_B T\} + 1)^{-1}. \tag{25}$$

It is easy to check that when Eqs. (23)–(25) are substituted into Eq. (18) the free energy satisfies exactly the conditions $\partial F_c(T, \nu(T))/\partial f(T, \epsilon(k)) = 0$ for all k. This is crucial since as in the thermal Hartree-Fock theory our free energy should be minimized with respect to the occupation numbers $f(T, \epsilon(k))$. We should point out that as $T \to 0$, the energy expression Eq. (23) reduces to Eq. (16) if the energy is so normalized that a completely filled band has zero total energy. Since $D(\sigma, \nu(T)) \to 1$ for either small U or large T, hence both $E_c(T, \nu(T))$ and $S_c(T, \nu(T))$ approach to their correct band limits if we require $S_l(\nu(T))$ approaching to zero with sufficiently small U or large T.

The physical interpretation for the solution Eqs. (23)–(25) finds its origin in Gutzwiller's original work.[2] With QCA, the occupation probability $n(\sigma, k)$ in the reciprocal space at $T=0$ has been derived by Gutzwiller as

$$n(\sigma, k) = [1 - D(\sigma)] N(\sigma)/L + D(\sigma) f_k . \tag{26}$$

Since we are dealing with only one kind of states the energies of which are sharply peaked at a specific value E_c, we can readily extend Gutzwiller's zero-temperature results to finite temperatures as

$$n(T, \sigma, k) = [1 - D(\sigma, \nu(T))] N(\sigma)/L + D(\sigma, \nu(T)) f(T, \epsilon(k)). \tag{27}$$

$n(\sigma,k)$ or $n(T,\sigma,k)$ then consists of two parts: a constant $[1 - D(\sigma)] N(\sigma)/L$ or $[1 - D(\sigma, \nu(T))] N(\sigma)/L$ throughout the whole band corresponding to the localized properties of electrons due to the strong correlation, and a scaled Fermi distribution function $D(\sigma) f_k$ or $D(\sigma, \nu(T)) f(T, \epsilon(k))$ corresponding to the correlation-reduced electron hopping. The entropy in a correlated system is determined by this dual localized-itinerant characteristics and should reduce to its correct values at both the band limit and the atomic limit. Accordingly, the physical meaning of Eq. (24) is very clear: The first term in due to the delocalization of electrons, and the second term $S_l(\nu(T))$ accounts for the spin degeneracy when the electrons become localized.

A qualitative analysis of the entropy of a correlated system for different values of T/Δ (Δ is the bare bandwidth) and U/Δ will help us to determine $S_l(\nu(T))$. For simplicity, let us assume one electron per atom. At the atomic limit $U/\Delta \to \infty$, the spin degeneracy yields an entropy per electron $S = k_B \ln 2$. For $U/\Delta \neq 0$ the degeneracy is lifted and the energy of the many-electron system spreads into a band. At $T=0$ only the nondegenerate ground state is occupied and therefore $S=0$. If U/Δ is sufficiently large, this nondegenerate ground state should be antiferromagnetic insulating.[10,13,14,17] As T/Δ rises, the correlated electron system goes either (a) first to paramagnetic insulating and then to paramagnetic metallic or (b) directly to paramagnetic metallic, depending on whether U/Δ is greater or less than a critical value.[10,17] For case (a) the entropy S will first rise rapidly even at rather low temperature from zero to $k_B \ln 2$, the value for an insulating nonmagnetic state as T/Δ increases. Around $k_B T/\Delta \sim U/\Delta$ the entropy will rise again and approach to the limiting value $2k_B \ln 2$ as predicted from the band theory. For case (b) the entropy should increase smoothly with temperature from zero to $2k_B \ln 2$.

It is then clear that in order to determine the entropy, one must know exactly how the many-electron eigenfunctions evolve from the atomic limit where the Wannier states are exact to the band limit where the Bloch picture is correct. Deep in the metallic region where $D(\sigma, \nu(T))$ is close to one, $S_l(\nu(T))$ is negligibly small and therefore can be dropped. Later we will show that the role of $S_l(\nu(T))$ becomes important only when the system is very near to the metal-nonmetal transition. However, the variational method does not give an accurate description on the detailed coupling of different configurations in the vicinity of the metal-nonmetal transition. Without such crucial informations, it is impossible to obtain the correct $S_l(\nu(T))$ for all values of U/Δ and T/Δ. Instead of using different approximate forms of $S_l(\nu(T))$ for different regions in the $U/\Delta - T/\Delta$ phase diagram we found that it is sufficient to use the simple "metallic solution" $S_l(\nu(T)) = 0$ and determine the conditions for its validity. This is not unreasonable because our main interest is the correlated metallic properties which happens to be not depending crucially on a very accurate entropy. In fact, the following numerical results indicate that for the physical quantities we are interested in, this simple "metallic solution" is valid even for very strong electron correlation.

From now on we will restrict ourselves to the metallic solution $S_l(\nu(T)) = 0$. The free energy Eq. (18) can then be written

$$F_c(T, \nu(T)) = \sum_\sigma D(\sigma, \nu(T)) F(\sigma, T) + \nu(T) U, \tag{28}$$

where $F(\sigma, T)$ is the free energy of the uncorrelated σ-spin electrons. If we define $\bar{\epsilon}(\sigma, T)$ as the average bare band energy per σ-spin electron and $S(\sigma, T)$ the entropy of the uncorrelated σ-spin electrons, then

$$F(\sigma, T) = N(\sigma)\bar{\epsilon}(\sigma, T) - TS(\sigma, T). \tag{29}$$

In Secs. IV–VI we will investigate the Pauli spin susceptibility, the Knight shift, and the electronic specific heat in a half-filled narrow band with no magnetic ordering. Hence we must first justify the validity of the "metallic solution" for this special case of one electron per atom. It is most convenient and convincing to justify it with a very general model calculation. For the nonmagnetic state with one electron per atom, $N(\uparrow) = N(\downarrow) = \frac{1}{2}L$. Then $D(\uparrow, \nu(T)) = D(\downarrow, \nu(T)) = D(T)$,

$\bar{\epsilon}(\uparrow, T) = \bar{\epsilon}(\downarrow, T) = \bar{\epsilon}(T)$, $S(\uparrow, T) = S(\downarrow, T) = S(T)$, and $F(\uparrow, T) = F(\downarrow, T) = F(T)$. For convenience, we will normalize $\nu(T)$ by dividing it with $N = L$, and redefine $S(T)$, $F(T)$, and $S_c(T)$ and $F_c(T)$ as the entropy and the free energy per electron of the uncorrelated and the correlated system, respectively. They can be written

$$S(T) = -\frac{2k_B}{N}\sum_k \{f(T, \epsilon(T)) \ln f(T, \epsilon(T)) + [1 - f(T, \epsilon(T))] \times \ln[1 - f(T, \epsilon(T))]\}, \tag{30}$$

$$F(T) = \bar{\epsilon}(T) - TS(T), \tag{31}$$

$$S_c(T) = D(T)S(T) \tag{32}$$

and

$$F_c(T) = D(T)F(T) + \nu(T)U. \tag{33}$$

The reduction factor $D(T)$ is computed from Eq. (14) as

$$D(T) = 8\nu(T)[1 - 2\nu(T)]. \tag{34}$$

If we define the quantity

$$U_0(T) = -8F(T) \geq 0, \tag{35}$$

then the optimum number of double occupancy takes the simple form

$$\nu(T) = \tfrac{1}{4}[1 - U/U_0(T)]. \tag{36}$$

The corresponding $D(T)$ and $F_c(T)$ are easily calculated as

$$D(T) = 1 - [U/U_0(T)]^2 \tag{37}$$

and

$$F_c(T) = F(T)[1 - U/U_0(T)]^2. \tag{38}$$

These expressions are similar to Brinkman and Rice's results[6] for orbitally nondegenerate ground state, and to the results obtained earlier by one of the authors[18] for a degenerate ground state. For a given temperature, the critical correlation energy $U_0(T)$ is a well-defined number. As the electron correlation increases the optimum number of double occupation $\nu(T)$ decreases monotonically to zero at $U = U_0(T)$ according to Eq. (36). If the "metallic solution" is correct also for small values of $\nu(T)$, then $\nu(T) = 0$ defines a boundary between the metallic and the nonmetallic phases. However, as we pointed out in the previous discussion, the entropy Eq. (32) does not approach to the correct limit $k_B \ln 2$ as $\nu(T) \to 0$. Hence in the vicinity of $\nu(T) = 0$, or near the metal-nonmetal boundary our results become doubtful.

We would clarify what we mean by saying "$\nu(T) = 0$ defines a boundary between the metallic and the nonmetallic phase." For the true wave function the *exact* number of doubly occupied atoms, $\nu_{\text{ex}}(T)$ vanishes only at $\Delta/U = 0$. In Gutzwiller's scheme only the direct hoppings of electrons are considered. It was pointed out in Ref. 17 that the ν in Gutzwiller's scheme is only the number of double occupancies in the zeroth-order wave function. It has been shown there by second-order perturbation theory which is valid for large U/Δ (or for small ν) that when the virtual hoppings of electrons are included, ν_{ex} is very small but finite even at $\nu = 0$. Although Ref. 17 is for $T = 0$, the same conclusion should also hold for finite temperature. For $\nu_{\text{ex}}(T) = 0$, the correct value of entropy is $S_c(T) = k_B \ln 2$ since the number of quantum states is 2^N all of which have the same expectation value of the Hamiltonian Eq. (1). Therefore, the correct value of entropy as $\nu(T) \to 0$ should be very close to $k_B \ln 2$.

To determine the minimum value of $\nu(T)$ above which the metallic solution is a good approximation, we have performed a model calculation using an ellipsoidal density of states normalized to one electron per atom. The density of states centered at $\epsilon = 0$ and has the width Δ. The detailed calculation is outlined in Appendix A. In Fig. 1 we plot the constant-$\nu(T)$ contours in the $k_BT/\Delta - \Delta/U$ plane. The numbers in the figure are the values of $\nu(T)$ for different contours. Two constant-entropy contours are also given as the dotted curves A and B. Curve A has entropy $S_c(T) = 1.6k_B \ln 2$, which is 80% of the maximum entropy an uncorrelated electron can have, namely, the high-temperature Hartree-Fock limit. Therefore, above curve A we are deep in the metallic region

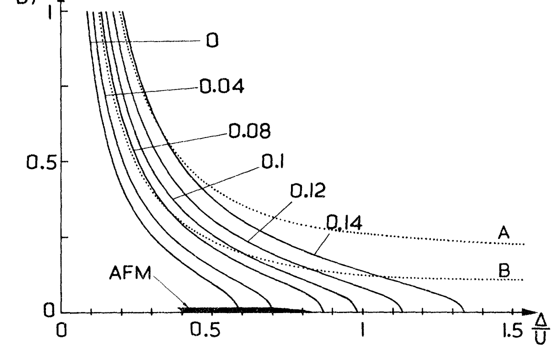

FIG. 1. Contours for constant $\nu(T)$ in the k_BT/Δ-Δ/U plane. Values of $\nu(T)$ are indicated by the numbers. The dotted curves are the constant-entropy contours and the darked area is the antiferromagnetic (AFM) phase estimated from the Ref. 17.

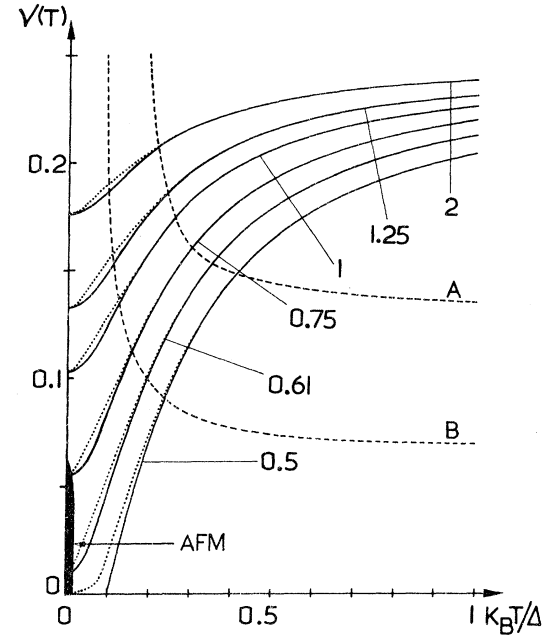

FIG. 2. Optimum number of doubly occupied atoms vs temperatures. The dashed curves are the constant-entropy contours and the dark area is the AFM phase estimated from the Ref. 17. The dotted curves are the possible alternative solutions at very low temperature.

where $S_l(\nu(T))$ should be negligibly small and the metallic solution is correct. As we mentioned before, along the contour $\nu(T)=0$ the correct value of entropy should be $S_c(T)\simeq k_B \ln 2$. However, the $S_c(T)=k_B \ln 2$ curve from the "metallic approximation" calculation is curve B while the calculated entropy along $\nu(T)=0$ contour is zero. Since $\partial S_c(T)/\partial T$ must be non-negative for given value of Δ/U, in the region to the left-hand side of curve B and for $\Delta/U<0.59$, the correct value of entropy must be substantially greater than that obtained from the metallic approximation. Consequently, the approximation breaks down in this region. For $\Delta/U>0.6$ we find that the constant-entropy contour approaches the $T=0$ axis continuously as the entropy drops to zero. So the metallic solution should be a good approximation between the curve B and the horizontal axis. From Refs. 10, 13, 14, and 17 one can estimate the Nêel temperature as a function of Δ/U and expects an antiferromagnetic phase as indicated by the darked area. The metallic solution should also break down if the electron system is sufficiently close to the antiferromagnetic-paramagnetic phase boundary. We then conclude that the metallic solution is valid for $\nu(T)>0.08$, namely in the region to the right of the $\nu(T)=0.08$ contour. Though these analyses do not precisely answer the question of where the metallic solution starts to break down, it is sure that the metallic approximation fails for small enough Δ/U.

The above discussion manifests itself to a more convincing argument in Fig. 2 where we plot the optimum number of double occupancy $\nu(T)$ in solid curves as functions of the normalized temperature for various values of Δ/U. The dashed curves A and B again correspond to $S_c(T)=1.6k_B \ln 2$ and $S_c(T)=k_B \ln 2$, respectively, and the dark area indicates the antiferromagnetic phase. At high temperature all the solid curves approach the Hartree-Fock limit $\frac{1}{4}$ as one expects. In this region above the curve A the metallic solution is certainly excellent. One should note that for $\Delta/U>0.59$ our expressions Eqs. (36)-(38) reduce to the correct Brinkman-Rice results[6] at $T=0$ where the entropy has no contribution to the free energy. Since the curves in the high-temperature region must approach their $T=0$ limits smoothly, our results should at least be good estimates in the region between the curve A and the vertical axis. The exact solutions are indicated perhaps by the dotted curves if we can obtain the correct expression for $S_l(\nu(T))$ (the dotted curve for $\Delta/U=0.5$ near $T=0$ is our conjecture and should not be taken too seriously). The difference between the dotted curves and the solid curves cannot be large because at low temperature the entropy does not contribute much to the free energy of the metallic phase. Consequently we can say that the metallic solution gives fairly accurate values of $\nu(T)$ in the metallic domain even for $\nu(T)<0.08$ as long as $\Delta/U>0.6$. On the other hand, the difference in the slopes $\partial\nu/\partial T$ between the solid curves and the corresponding dotted curves may be significant at very low temperature. This is the reason why later we discover in this temperature range our model fails to predict the correct behavior for the electronic specific heat which depends on $\partial\nu/\partial T$, in contrast to the Pauli spin susceptibility and the Knight shift which are functions of $\nu(T)$.

We have so far restricted our analysis to the case of one electron per atom. The conclusion on the validity of the metallic solution applies to the general cases $n\neq 1$ as well. Furthermore, since the correlated system can never be insulating for $n\neq 1$ and since the antiferromagnetic ordering disappears if $|n-1|>0.05$,[17] the correlated electron exhibit even stronger metallic properties. Consequently, the metallic solution works better for the general cases $n\neq 1$.

IV. ELECTRON-SPIN SUSCEPTIBILITY

In this section we investigate the enhancement of spin susceptibility in the metallic phase. In the presence of a small external magnetic field, H_0, let ζL antiparallel-spin electrons reverse their spins; $N(\uparrow)=(\frac{1}{2}+\zeta)L$ and $N(\downarrow)=(\frac{1}{2}-\zeta)L$. The value of ζ will be determined by the minimization of free energy of the electron system in the magnetic field, which then gives the spin susceptibility.

Before formally deriving the susceptibility, it is instructive to describe the effects of electron correlation in physical terms. In our correlated system there are two contributions to the susceptibility. One is from the itinerant properties of the electrons ("Pauli type") and the other is from their localized properties ("Curie type"). The intra-atomic Coulomb repulsion reduces the electron hopping probabilities by a factor $D(T)$, which results in a narrowing of the bare energy band. The density of states or the effective mass is then enhanced by a factor $D(T)^{-1}$. Therefore, besides the Stoner enhancement factor, the contribution from the band electrons should be enhanced by a factor $D(T)^{-1}$.

The optimum number of double occupancies $\nu(T)$ changes with the applied magnetic field, as a result of flipping ζL spins. In other words, the applied field increases the number of unpaired localized electrons. The enhanced Curie-like contribution from such unpaired spins is entirely due to the intra-atomic correlation. However, the localized and the itinerant contributions are not independent events. We cannot separate the electron system into two unconnected parts and say that one is localized and that the other is delocalized. We have only one system of electrons which can only be properly described by a dual itinerantlocalized picture.

With applied magnetic field H_0 the free energy is given by the expression

$$F_c(\zeta H_0 T)=F_c(T)-2\mu_B H_0\zeta+\frac{2\mu_B^2 D(T)}{\chi_0(T)}\times\left(1-\frac{\chi_0(T)U[1+U/2U_0(T)]}{2\mu_B^2[1+U/U_0(T)]^2}\right)\zeta^2, \tag{39}$$

where $\chi_0(T)$ is the Pauli spin susceptibility per atom at $U=0$. We determine ζ from $\partial F_c(\zeta H_0 T)/\partial\zeta=0$. Then the susceptibility in a correlated system is

$$\chi_S(T)=\eta_\chi(T)\chi_0(T), \tag{40}$$

where the enhancement factor is

$$\eta_\chi(T)=D(T)^{-1}\left(1-\frac{\chi_0(T)U[1+U/2U_0(T)]}{2\mu_B^2[1+U/U_0(T)]^2}\right)^{-1}. \tag{41}$$

At $T=0$ the enhancement factor η_χ reduces to the Brinkman-Rice[6] formula.

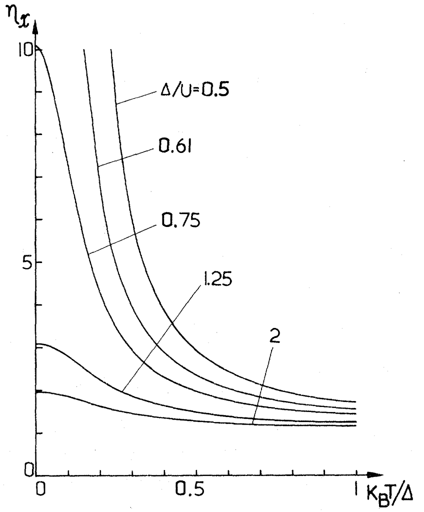

FIG. 3. Enhancement factor for the spin susceptibility vs temperature ($\eta_\chi\to 1$ as $k_BT/\Delta\to\infty$).

Figure 3 shows the enhancement factor as a function of the temperature. At sufficiently high temperature, the electrons become weakly correlated and so η_χ approaches one. As the temperature is reduced η_χ becomes large for values of Δ/U close to the critical ratio. As indicated in Fig. 2, the computed $\nu(T)$ has small uncertainty at low temperature. This uncertainty of course introduces certain error in the η_χ. However, the error is small and will not affect the over-all picture. Yet one should be aware of the fact that for $\Delta/U<0.85$ and $k_BT/\Delta<0.015$ the antiferromagnetic state sets in. In this magnetically ordered region our model is no longer valid.

V. KNIGHT SHIFT

In order to investigate the effect of electron correlation on the Knight shift, we have to calculate the spatial distribution of the σ-spin electrons in a highly correlated metal. The standard derivation starting from the correlated trial function is very tedious, but the same result can be obtained easily through the use of Eq. (27). Then the density of the σ-spin electrons is simply

$$\rho(T,\sigma,r)=\sum_k n(T,\sigma,k)|\psi_k(r)|^2, \tag{42}$$

where $\psi_k(r)$ is the Bloch state. Let us define

$$\bar{\rho}(r)=\sum_k|\psi_k(r)|^2 \tag{43}$$

and

$$\langle|\psi_k(r)|^2\rangle_\epsilon=\frac{1}{\xi(\epsilon)\,d\epsilon}\sum_k{}'|\psi_k(r)|^2, \tag{44}$$

where $\xi(\epsilon)$ is the density of states and the primed sum is restricted to those Bloch states which have the energies between ϵ and $\epsilon + d\epsilon$. Substituting Eq. (27) into Eq. (42) we have

$$\rho(T,\sigma,r)=D(\sigma,\nu(T))\int_0^{\epsilon_F}\xi(\epsilon)f(T,\epsilon)\langle|\psi_k(r)|^2\rangle_\epsilon\, d\epsilon + [1-D(\sigma,\nu(T))]\bar{\rho}(r). \tag{45}$$

The spatial distribution of electronic spins is

$$\Sigma(T,r)=\rho(T,\uparrow,r)-\rho(T,\downarrow,r). \tag{46}$$

We will consider the special case of one electron per atom with no magnetic ordering. The external magnetic field H_0 for ordinary NMR experiments is of the order of 10^4 G, and gives rise to a magnetic energy per electron much less than the Fermi energy even near the metal-nonmetal transition. With such applied magnetic field, $\Sigma(T,r)$ is readily obtained as

$$\Sigma(T,r)=\eta_K(T)\chi_0(T)H_0\langle|\psi_k(r)|^2\rangle_{\epsilon_F}, \tag{47}$$

where

$$\eta_K(T)=D(T)\eta_\chi(T)=\left(1-\frac{\chi_0(T)U[1+U/2U_0(T)]}{2\mu_B^2[1+U/U_0(T)]^2}\right)^{-1}. \tag{48}$$

The Knight shift is defined as $\alpha\Sigma(T,r)/H_0$, where α is a crystal-structure-dependent numerical factor. For cubic lattice $\alpha=\frac{8}{3}\pi$. We therefore obtain the Knight shift in strongly correlated metals as

$$K_c(T)=\eta_K(T)K_0(T), \tag{49}$$

where

$$K_0(T)=\alpha\chi_0(T)\langle|\psi_k(r)|^2\rangle_{\epsilon_F} \tag{50}$$

is the Knight shift in an uncorrelated system.

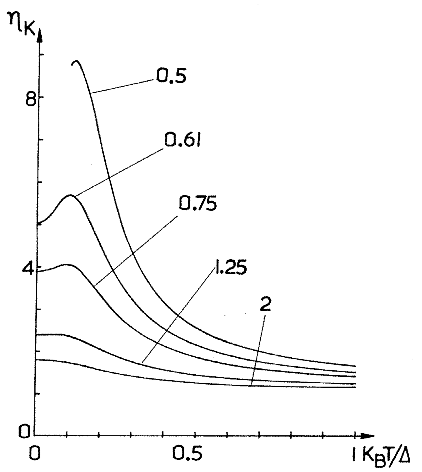

FIG. 4. Enhancement factor for the Knight shift for different values of Δ/U indicated by the numbers.

The enhancement factor for the Knight shift $\eta_K(T)$ is shown in Fig. 4. The restriction on the validity of this result is the same as that of $\eta_\chi(T)$. Though $\eta_K(T)$ and $\eta_\chi(T)$ have the same characteristic features, $\eta_K(T)$ is less than $\eta_\chi(T)$ by a factor $D(T)$. The explanation is as follows: The susceptibility and the Knight shift are enhanced due to the increased unpaired spins. As the number of unpaired spins increases, the electrons also become more localized. Since the Knight shift is essentially caused by the additional magnetic field generated by the conduction electrons at the nuclei, the localization will lower the additional magnetic field and thus reduces the Knight shift. In our model, the localization of the conduction electrons is measured by the bandwidth reduction factor $D(T)$. Therefore, $\eta_K(T)$ is less than $\eta_\chi(T)$ by a factor $D(T)$. Depending on the taste, one may find another equivalent explanation: Both the Knight shift and the susceptibility are enhanced through the enhanced density of states at the Fermi surface. However, the corresponding band narrowing only reduces the Knight shift by a factor $D(T)$. This important feature is in accord with the experimental results of the doped semiconductors, and we will discuss it later in Sec. VII.

VI. ELECTRONIC SPECIFIC HEAT

The electronic specific heat also contains the same two contributions as the susceptibility. If only single-particle aspects are considered, one would expect the specific heat to be increased by a factor $[D(T)]^{-1}$ due to the enhanced density of states, as suggested by Brinkman and Rice.[6] However, with increasing temperature the electrons become less correlated and so results in a less enhanced density of states. When one considers this effect together with the thermal excitations of the electrons in a self-consistent calculation, the enhancement of the specific heat gets more complicated. One can arrive to the same conclusion from considering the motion of electrons in the real space. As the temperature is raised, electrons gain more kinetic energy. On the other hand, it creates more doubly occupied atoms each of which costs an energy U. Consequently there is a delicate interplay between the band and the localized contributions in the present model.

From the energy per electron

$$E_c(T)=D(T)\bar{\epsilon}(T)+\nu(T)U, \tag{51}$$

the specific heat of a correlated electron system is obtained as

$$C_e(T)=\frac{\partial E_c(T)}{\partial T}=D(T)C_0(T)+\frac{16U^2S(T)^2T}{U_0(T)^3}, \tag{52}$$

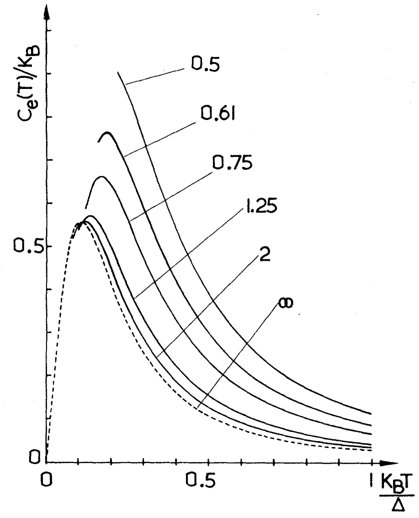

FIG. 5. Electronic specific heat in the metallic phase where the metallic solution is valid. The dashed curve is for the uncorrelated electrons.

where $C_0(T)$ is the specific heat for $U=0$. Since

$$\frac{\partial E_c(T)}{\partial T}=\left.\frac{\partial E_c(T)}{\partial T}\right|_{\nu(T)}+\left.\frac{\partial E_c(T)}{\partial \nu}\right|_{T}\frac{\partial \nu}{\partial T},$$

the slope of the $\nu(T)$-vs-T curve for constant Δ/U plays an important role in the electron correlation effect on the specific heat. As indicated in Fig. 2, the metallic solution may introduce a non-negligible error in $\partial\nu/\partial T$ in the region to the left-hand side and below the curve B. Therefore, this region is excluded from our computed specific heat plotted in Fig. 5. The dashed curve is the specific heat $C_0(T)$ of an uncorrelated electron gas. Under the condition that our model is valid, an enhancement of the specific heat is observed. One should note that the enhancement is much less than η_χ.

Another way to view the electron correlation effects on the specific heat is to compare the energy $E_c(T)$ with the energy per electron in the Hartree-Fock approximation $E_{\text{HF}}(T)$. For fixed $\Delta/U, E_c(T)<E_{\text{HF}}(T)$ at all temperatures due to the restriction on the number of doubly occupied atoms by correlation. However, $E_c(T)\rightarrow E_{\text{HF}}(T)\rightarrow\frac{1}{4}U$ as $T\rightarrow\infty$. Accordingly the specific heat must be enhanced.

In the region to the left-hand side and below the curve B of Fig. 2, we find $C_e(T)<C_0(T)$ when $k_BT/\Delta\lesssim 0.11$. This can be understood from Mott's[7] conjecture as illustrated in Fig. 6. This figure shows schematically three different density of states. The split-band Mott-Hubbard type of density of states (dashed curve) is associated with the single-particle excitations of current carriers. The excitations from the lower band to the upper band correspond to the creation of double occupancies. We may say that our metallic solution refers to this kind of density of states. For k_BT smaller than the pseudogap, $C_e(T)<C_0(T)$ because the gap suppresses thermal excitations and hence $\nu(T)$ increases very slowly with T. For k_BT greater than the pseudogap thermal excitations readily take place and the specific heat gains from the enhanced density of states in the upper band. However, collective excitations like paramagnons are ignored in our model. Their density of states is the dotted curve in Fig. 6. At low temperatures the collective excitations should give a large contribution to the specific heat in a strongly correlated metal. The third density of states represented by the solid curve refers to the free electrons.

VII. DISCUSSION

We have extended Gutzwiller's scheme[2] for a highly correlated metal to finite temperatures. Our treatment is based on: (i) the general expression for the total energy in Eq. (16) and the assumption that only one kind of states contributes to the thermodynamic properties of the system, and (ii) the metallic solution for the entropy which is justified when the number of doubly occupied sites $\nu\geq 0.08$. As expected, the variational approach is found to reduce ν at low temperatures. Also at $T=0$ our results reduce to the Brinkman and Rice[6] formula which does not depend on the entropy. At high temperatures, on the other hand, the electron correlation becomes less important so the ν approaches its Hartree-Fock value $\frac{1}{4}$. Our model becomes doubtful when the system is near the metal-nonmetal phase boundary. As we argued in Sec. III, this is due to the lack of sufficient knowledge on the exact quantum states which is essential for the

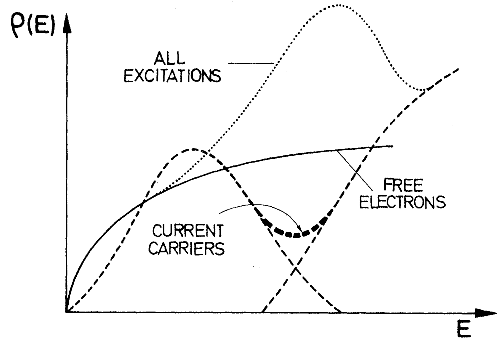

FIG. 6. Density of states for a highly correlated metal as conjectured by Mott (Ref. 7).

determination of the entropy. However, in the metallic region, especially for $\Delta/U > 0.6$, our calculated $\nu(T)$ is accurate enough for a numerical computation of the susceptibility and the Knight shift.

The expression for the spin susceptibility Eqs. (40) and (41) is a generalization of Brinkman and Rice's previous results[6] for the zero temperature case. Our χ_S shows a strong temperature dependence, a behavior which is in agreement with Mott's conjecture[7] for highly correlated metals as well as with certain measurements on Si : P.[16,20] An important feature of Gutzwiller's method is the explicit treatment of the localized electronic properties, as indicated by the fact that our model is justified even for $\nu(T)$ reduced to less than $\frac{1}{3}$ of its Hartree-Fock value. For those physical quantities which do not depend on $d\nu/dT$, our calculation is reliable within almost the entire metallic phase if $\Delta/U > 0.6$. This particular treatment is missing in Hubbard's original Green's-function decoupling scheme. For example, Kanehisa and Kamimura[24,25] have used Hubbard's approach to compute the spin susceptibility and found a sharp drop at the MNM transition in contrast to the present work. In Hubbard's scheme an energy gap opens at the MNM transition and consequently the susceptibility becomes zero. In the present approach the enhancement is mainly due to the appearance of unpaired localized spins.

Our predicted difference between the enhancement factors for the susceptibility η_χ and for the Knight shift η_K is supported by the experimental measurements on Si : P.[20,26,27] Figure 4 shows that η_K is less than 10 in the region of our interest. When the electrons become more and more localized, $\langle |\psi_k(r)|^2\rangle_{\epsilon_F}$ in Eq. (50) starts to have sharp peaks around ^{31}P nuclei. Therefore, the shift of the ^{31}P NMR line is much larger than that of the ^{29}Si line. The Knight shift of ^{29}Si eventually diminishes when the insulating phase is approached, as was predicted theoretically first by Mott.[28] Kamimura[29] also obtained a vanishing ^{29}Si Knight shift from the Green's-function decoupling scheme. His argument is based on the zero density of states in the energy gap similar to what he did for the susceptibility.[24,25] Therefore, Kamimura's work fails to explain the large shift of the ^{31}P line observed under exactly the same experimental conditions.

Apparently it seems that we have been successful in computing the realistic spin susceptibility and Knight shift. Our results for the electronic specific heat at low temperatures $k_B T/\Delta \lesssim 0.11$ are, however, disappointing since one would rather expect enhanced values also for this case. Our results clearly indicate that excitations of single-particle type cannot alone account for the electronic specific heat, but that collective effects like paramagnons would have to be considered. We may therefore say that our results support Mott's conjectured density of states as shown in Fig. 6.

One may ask which remedy could be found for the electronic specific heat. The expression for the free energy in Eq. (18) and the subsequent metallic solution Eqs. (23) and (24) were constructed under the assumptions that only one kind of states contributes to the thermodynamic properties and that the energy is sharply peaked at some particular value E_c. As mentioned, such a construction corresponds to a density matrix

$$\hat{\rho} = \sum_K |K\rangle \rho_K \langle K| \tag{53}$$

in which ρ_K is defined by the microcanonical ensemble. Such assumptions may be justified when dealing with the spin susceptibility and the Knight shift. In those cases the dominant mechanism behind the enhancement are the development of localized spins which can respond freely to an applied magnetic field. For the case of the electronic specific heat, however, the collective aspects are more important. Evidently the restricted summation in Eq. (53) is an oversimplification. At finite temperatures there is a set of magnetic solutions with the same energy as the nonmagnetic ones. If such states were to be included the total magnetization is still zero but the number of excitation modes is increased, covering the gap in the Mott-Hubbard density of states as in Fig. 6. This thermodynamic way of phrasing the problem of collective modes is similar to Shiba and Pincus's treatment[30] of finite rings. By including all kinds of states these authors did indeed find an enhanced electronic specific heat.

ACKNOWLEDGMENTS

We wish to thank Dr. M. C. Gutzwiller for helpful discussions and correspondence. We are also indebted to Dr. T. M. Rice for the stimulating discussion on the properties of entropy in a correlated system.

APPENDIX A: MODEL CALCULATION WITH ELLIPSOIDAL DENSITY OF STATES

We consider noninteracting electrons in a symmetric, orbitally nondegenerate band which is centered at $\epsilon = 0$ and has the width Δ. If the band is half filled, the chemical potential is then equal to zero at all temperatures T. Let $\rho(\epsilon)$ be the density of states normalized to one. The average bare band energy per electron is

$$\bar{\epsilon}(T) = -2\int_0^{\Delta/2} d\epsilon\,\rho(\epsilon)\tanh\left(\frac{\epsilon}{2k_BT}\right). \tag{A1}$$

The corresponding entropy is

$$\frac{S(T)}{k_B} = 2\ln 2 + \frac{\bar{\epsilon}(T)}{k_BT} + 4\int_0^{\Delta/2} d\epsilon\,\rho(\epsilon)\ln\left[\cosh\left(\frac{\epsilon}{2k_BT}\right)\right] \tag{A2}$$

and the electronic specific heat

$$C_0(T) = \frac{1}{k_BT^2}\int_0^{\Delta/2} d\epsilon\,\rho(\epsilon)\epsilon^2\,\mathrm{sech}^2\left(\frac{\epsilon}{2k_BT}\right). \tag{A3}$$

The Pauli susceptibility per electron is

$$\chi_0(T) = \frac{\mu_B^2}{k_BT}\int_0^{\Delta/2} d\epsilon\,\rho(\epsilon)\,\mathrm{sech}^2\left(\frac{\epsilon}{2k_BT}\right). \tag{A4}$$

With our particular choice of an ellipsoidal density of states,

$$\rho(\epsilon) = \begin{cases} (4/\pi\Delta)[1-(2\epsilon/\Delta)^2]^{1/2} & \text{if } |\epsilon| < \tfrac{1}{2}\Delta, \\ 0 \quad \text{if } |\epsilon| > \tfrac{1}{2}\Delta, \end{cases} \tag{A5}$$

the quantities in Eqs. (A1)–(A4) are easily evaluated at intermediate temperatures by numerical integration.

At low temperatures they may be expanded as

$$\bar{\epsilon}(T) \simeq (\Delta/3\pi)(-2 + z^2 - \tfrac{7}{20}z^4 - \tfrac{31}{168}z^6), \tag{A6}$$

$$S(T) \simeq \tfrac{4}{3}k_Bz(1 - \tfrac{7}{30}z^2 - \tfrac{31}{280}z^4), \tag{A7}$$

$$C_0(T) \simeq \tfrac{4}{3}k_Bz(1 - \tfrac{7}{10}z^2 - \tfrac{31}{56}z^4), \tag{A8}$$

$$\chi_0(T) \simeq 4\mu_B^2[2 - \tfrac{1}{3}z^2(1 + \tfrac{7}{20}z^2 + \tfrac{31}{56}z^4)]/\pi\Delta, \tag{A9}$$

where $z = 2\pi k_BT/\Delta$. For high temperatures one obtains

$$\bar{\epsilon}(T) \simeq -\tfrac{1}{8}\Delta z(1 - \tfrac{1}{6}z^2), \tag{A10}$$

$$S(T) \simeq 2k_B\ln 2 - \tfrac{1}{4}k_Bz^2(1 - \tfrac{1}{4}z^2), \tag{A11}$$

$$C_0(T) \simeq \tfrac{1}{2}k_Bz^2(1 - \tfrac{1}{2}z^2), \tag{A12}$$

$$\chi_0(T) \simeq \mu_B^2(1 - \tfrac{1}{4}z^2)/2k_BT, \tag{A13}$$

where $z = \Delta/4k_BT$. Because there is only one band of finite width, the classical limit gives $\bar{\epsilon} \to 0$ and $C_0 \to 0$. For the same reason the classical expression for χ_0 differs from the corresponding free-electron gas expression by a factor of $\frac{1}{2}$.

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