Discontinuous Metal-Insulator Transitions and Fermi-Liquid Behavior of Correlated Electrons

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A simple thermodynamic theory is given of the metal-insulator transitions concurrent with a localization of electrons in a half-filled correlated band. The approach supplies a complete phase diagram for the system $(V_{1-x}Cr_x)_2O_3$. We show also that for an almost half-filled band the disappearance of local moments is accompanied by a transition to a heavy Fermi liquid.

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We report here on a new theory of interacting electrons in a narrow band at nonzero temperatures ($T>0$). One of the novel aspects is the prediction, for a half-filled band case, of *discontinuous* transitions as a function of T for fixed U/W, where U is the intra-atomic Coulomb energy and W the bare-particle bandwidth.[1] In place of the phenomenological two-fluid model considered earlier,[1] the present theory is based on a one-phase model of fermions, in a band narrowed by correlations, which transform into a lattice of localized spins. The theory is used to interpret the three consecutive metal-insulator transitions (MIT's) and, in particular, the reentrant metallic behavior of the $(V_{1-x}Cr_x)_2O_3$ alloy system.[2,3] The MIT in the paramagnetic phase of this system has been interpreted previously in terms of the Mott transition[4] and later,[5] within the Hubbard model, with U/W as a variable and at $T=0$. Our theory yields the previous results in the limit $T\rightarrow 0$, in addition to the reentrant features and the full phase diagram at higher temperatures. In this way, we offer a resolution of the long-standing problem of the nature of the spectacular MIT's observed in $(V_{1-x}Cr_x)_2O_3$.[2,3] Furthermore, for the case of the less than half-filled band we formulate the conditions under which the correlated metallic system with local moments transforms into a Fermi liquid with a large effective mass. Our results thus supplement earlier detailed Fermi-liquid descriptions of almost localized correlated systems; see, e.g., Anderson and Brinkman and the reviews by Vollhardt and by Ramakrishnan.[6]

Prior treatments of MIT's based on the functional-integration technique lead to continuous transitions with temperature.[7] The experimentally observed discontinuities were ascribed to lattice instabilities[8]; also, no reentrant metallic behavior was reported. An alternative six-parameter theory[9] does incorporate some of the features reported below, but the fit to observed conductivity data is very marginal. An approach to the correlated-electron liquid for an almost half-filled band has been developed recently[10] and applied to the heavy-fermion system UBe_{13}. The entropy expression of Rice *et al.*[10] interpolates phenomenologically between the Fermi-liquid and localized-moment regimes.

As is well-known, when $U\simeq W$, the band energy $E_B<0$ and correlation energy $E_c>0$ become comparable. In the present theory[1] $E_c=U\eta$, as well as the balance of the energies, is determined variationally by optimizing of the two-electron correlation function $\eta\equiv\langle n_{i\uparrow}n_{i\downarrow}\rangle$ which describes the probability that a typical site is doubly occupied by electrons of opposite spin. The band energy E_B is characterized by a band-narrowing factor $\Phi(\eta)$ which attends to the suppression as U/W increases of the hopping processes involving doubly occupied states. We discuss first the transitions in the paramagnetic phase for the half-filled band case ($n=1$).

Following the procedure of I which is a reformulation of the Gutzwiller approach,[5] we write the total energy at $T=0$ as $E_B+E_c=\Phi(\eta)\bar{\epsilon}+U\eta$, where $\bar{\epsilon}$ is the average bare-band energy per particle and where $\Phi(\eta)=8\eta(1-2\eta)$. As implicit in the later analysis, Φ may be identified[5] with the inverse effective-mass enhancement m^*/m_0, which derives in the Gutzwiller approach from the slow variation of the electron energy shift with momentum. On minimizing the total energy with respect to η one obtains $\eta\equiv\eta_0=\frac{1}{4}(1-U/8|\bar{\epsilon}|)$ for $U<8|\bar{\epsilon}|$, and $\eta_0=0$ for $U\geq 8|\bar{\epsilon}|$; the cases $\eta>0$ and $\eta=0$ correspond to the paramagnetic metallic (PM) and paramagnetic insulating states. Hence, at $T=0$ we recover the well-known result of Brinkman and Rice.[5]

Since close to the metal-insulator transition $\Phi|\bar{\epsilon}|$ and $U\eta$ are of comparable magnitude, the balance between them at $T>0$ will be affected by the much smaller entropy contribution. The basic postulate introduced at this point is that the same factor also enters the expression for the quasiparticle energy $E_{\mathbf{k}}=\Phi\epsilon_{\mathbf{k}}$, where $\epsilon_{\mathbf{k}}$ is the energy of state $\mathbf{k}$ in the uncorrelated band. By this device we maintain **k** as a good quantum number under the restrictions on the hopping of electrons imposed by intra-atomic interactions. This allows us to start from the following expression for the Helmholtz free energy per site:

$$\frac{F}{N}=\frac{\Phi}{N}\sum_{\mathbf{k}\sigma}\epsilon_{\mathbf{k}}f_{\mathbf{k}}+U\eta+\frac{k_BT}{N}\sum_{\mathbf{k}\sigma}[f_{\mathbf{k}}\ln f_{\mathbf{k}}+(1-f_{\mathbf{k}})\ln(1-f_{\mathbf{k}})], \qquad (1)$$

where $f_{\mathbf{k}}\equiv\{\exp[(\epsilon_{\mathbf{k}}-\mu)/k_BT^*]+1\}^{-1}$ is the Fermi-Dirac distribution function for quasiparticles representing the correlated electrons (the Fermi level $\mu=0$ coincides with the zero of energy), $T^*=T/\Phi$ is an effective temperature, and N is the number of sites. One sees that Eq. (1) represents the free-energy functional for a Fermi liquid with quasiparticle energies $E_{\mathbf{k}}$ and with the Landau term for particle scattering replaced by $U\eta$. Furthermore, the effective-mass renormalization $m^*/m_0=1/\Phi$ is calculated self-consistently by minimization of F with respect to η. The expansion (1) may be rewritten as

$$F(T)/N=\Phi(\eta)F_0(T^*)/N+U\eta, \qquad (2)$$

where $F_0(T^*)$ is the free energy of the electron gas at temperature T^*. Strictly speaking, the validity of Eq. (1) is limited to the low-T regime $k_BT\ll\Phi|\bar\epsilon|$, since for interacting systems only the electrons near the Fermi surface can be regarded as obeying the Fermi-Dirac distribution $f_{\mathbf{k}}$. In this limit, we can disregard the additional solution $\eta\simeq0$, $s\simeq2k_BN\ln2$ appearing when we minimize (1) numerically with respect to η. Hence, Eq. (1) is discussed in terms of a Sommerfeld-type expansion to the order T^2:

$$F/N=\Phi\bar\epsilon+U\eta-(\gamma_0/2\Phi)T^2, \qquad (3)$$

$\gamma_0\equiv2\pi^2\rho_0(\mu_0)k_B^2/3$ being the linear specific-heat coefficient for bare electrons; $\rho_0(\mu_0)$ is the density of states per spin and per site at the bare Fermi level μ_0. Minimizing Eq. (3) with respect to η we find that $\eta(T)=\eta_0-aT^2$, and $\Phi=\Phi_0-UaT^2/|\bar\epsilon|$, where $a=U\gamma_0/64\Phi_0^2\bar\epsilon^2$ and $\Phi_0\equiv\Phi(\eta_0)$. Substituting these expressions back into Eq. (3) we obtain the free energy as

$$F(T)/N=\bar\epsilon(1-U/U_c)^2-\tfrac{1}{2}(\gamma_0/\Phi_0)T^2, \qquad (4a)$$

where $U_c=8|\bar\epsilon|$. Similarly, the internal energy is given by

$$E(T)/N=\bar\epsilon(1-U/U_c)^2+\tfrac{1}{2}(\gamma_0/\Phi_0)T^2, \qquad (4b)$$

with $\Phi_0=1-(U/U_c)^2$. Clearly, the bare-particle electronic specific heat is enhanced by a factor $1/\Phi_0$ which can become large if $\eta\to0$. This also means that the leading contribution to the thermal energy at low T gives rise to excitations in the narrowed by correlations band of fermions.

For the paramagnetic insulator (PI) with localized moments the free energy (per site) is $F'/N=-k_BT\ln2$. *The MIT in this case takes place at the coexistence boundary determined by* $F=F'$ which gives rise to the two solutions

$$k_BT_\pm=[3\Phi_0/2\pi^2\rho_0(\mu_0)]\{\ln2\pm[(\ln2)^2-\tfrac{4}{3}\pi^2\rho_0(\mu_0)|\bar\epsilon|(1-U/U_c)^2/\Phi_0]^{1/2}\}. \qquad (5)$$

Thus, in the range where Eq. (4) is valid there are two transitions at $T=T_-$ (PM → PI) and at $T=T_+$ (PI → PM′). Hence, reentrant metallic behavior is encountered for $T\gtrsim T_+$. These two transition lines meet at a critical point: The lower critical value of $U=U_{lc}$ is given by

$$\frac{U_{lc}}{U_c}=1-\frac{\sqrt{3}\ln2}{2\pi}\frac{1}{[\rho_0(\mu_0)|\bar\epsilon|]^{1/2}}, \qquad (6)$$

and the corresponding critical temperature $T=T_c$ is specified by

$$k_BT_c=\frac{3\ln2}{2\pi^2\rho_0(\mu_0)}\left[1-\left(\frac{U_{lc}}{U_c}\right)^2\right]. \qquad (7)$$

For $U\le U_{lc}$ the Fermi-liquid state is stable for all T.

To take antiferromagnetic (AF) ordering effects into account we assume that the interaction between cation sites is represented by the kinetic exchange invoked by Anderson for Mott insulators and extended later to strongly correlated metals.[11] Consistent with our earlier procedure (see I), only the portion $1-\Phi$ of electrons in a correlated metallic system ($U<U_c$) is affected by this exchange. We specify the exchange constant by $J=(W^2/Z^2U)(1-\Phi)$, where Z is the number of nearest neighbors ($Z=4$ for V_2O_3). The above reduces to $J=4t^2/U$ in the insulating phase for which $\eta=\Phi=0$. In general, the kinetic exchange Hamiltonian has the form

$$H_{\rm ex}=J\sum_{\langle i,j\rangle}[\mathbf{S}_i\cdot\mathbf{S}_j-\tfrac{1}{4}(1-2\eta_i)(1-2\eta_j)], \qquad (8)$$

in which the summation $\langle i,j\rangle$ is restricted to nearest-neighboring pairs (each counted once), and $\eta_i=n_{i\uparrow}n_{i\downarrow}$. The exchange part (8), when added to the band and correlation parts

$$E(T)/N=(1/N)\sum_{\mathbf{k}\sigma}\Phi(\eta)\epsilon_{\mathbf{k}}f_{\mathbf{k}\sigma}+U\eta, \qquad (9)$$

leads in the mean-field approximation (and if we keep η as a variational variable) to the *Slater splitting* of the band narrowed by correlation effects. For quasiparticles in subbands of the form $\pm[(\Phi\epsilon_{\mathbf{k}})^2+\Delta^2]^{1/2}$ the band gap is given by $2\Delta=JZ\langle S^z\rangle$; at low temperature the material is then an *antiferromagnetic Slater insulator* (AFS) for $n=1$. For the rectangular density of states both the magnetic moment $\langle S^z\rangle \equiv \langle n_{i\uparrow} - n_{i\downarrow}\rangle/2$ at $T=0$ and the ground-state energy E_G can be calculated explicitly. One finds that

$$\langle S^z\rangle = (\Phi W/JZ)/\sinh(2\Phi W/JZ), \tag{10}$$

and

$$E_G^{\mathrm{AFS}}/WN = \tfrac{1}{4}\,[\Phi^2 + (JZ\langle S^z\rangle/W)^2]^{1/2} + (U/W)\eta - (JZ/8W)(1-2\eta)^2. \tag{11}$$

Because of inclusion of the band-narrowing factor Φ in (10) and (11), *the present formulation connects the standard Slater band-insulator to the localized (Mott) antiferromagnetic insulator (AFI),* the latter representing the limiting case $\eta \to 0$. In this way we unify the two historically different descriptions of antiferromagnetism in a narrow band.

For V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ systems with the magnetic moment $\mu_m \simeq 1\mu_B$ one has the Curie-Weiss temperature $k_B\theta_N/W = \frac{1}{4}JZ/W = 0.023$ and 0.031 for $U/W = 1.65$ and 2.0, respectively. Setting $W \cong 1$ eV one obtains $\theta_N = 300$ and 450 K, as compared to $\theta_N = 350$ K for the alloys with $x \geq 0.035$. The temperature of the AF → PM transition (T_{MIT}) is in the range 150–200 K, i.e., well below θ_N; furthermore, a discontinuous change in susceptibility occurs at the transition.[12] These and other data show that the AF → PM transition intervenes, well before the actual Néel temperature T_N is reached.

As before, we redefine the AF → PM phase boundary by the coexistence condition $F_{\mathrm{AF}} = F_{\mathrm{PM}}$. For the case of interest, $T_{\mathrm{MIT}} \ll T_N$, we assume for the sake of simplicity that $F_{\mathrm{AF}} \simeq E_G^{\mathrm{AF}}$, i.e., we neglect the spin-wave contribution ($\sim T^4$) to the free energy, which should not qualitatively change the results. The transition temperature T_{MIT} is then given by

$$\frac{k_B T_{\mathrm{MIT}}}{W} = \left(\frac{2\Phi}{\gamma_0}\right)^{1/2} \left[\bar{\epsilon}\left(1 - \frac{U}{U_c}\right)^2 - E_G^{\mathrm{AF}}\right]^{1/2}. \tag{12}$$

The phase diagram resulting from comparison of the free energies of PM, PI, and AF phases is plotted in Fig. 1. The rectangular form of the density of states has been chosen. One observes several interesting features. First, there appear two metallic phases: one bounded by the two insulating phases (AFS and PI) and one exemplifying reentrant metallic behavior at high temperatures. Second, the AFS, AFI, PM, and PI meet at a tricritical point (TCP); the other two were discussed above. All those features are observed in $(V_{1-x}Cr_x)_2O_3$ alloy systems,[3] as is shown in the inset of Fig. 1.

There is one qualitative discrepancy between the theory and experiment: The transition line PI → PM′ is of first order, whereas experimentally a continuous transition is encountered.[3] We believe that the difference is due to the fact that we have neglected entirely the lattice effects which may be important and tend to smear out the weakly discontinuous PI → PM′ transition which takes place above 500 K. Additionally, we have used the low-temperature expansion which may not be appropriate for $T \gtrsim T_+$, particularly for larger values of U/W.

Finally, we determine the stability of a paramagnetic Fermi liquid (PM phase) for the band slightly less than half filled ($n<1$); the system should be then always metallic, even for $U/W \gg 1$. This can be demonstrated by our noting that for $n<1$ the band-narrowing factor for $\eta = 0$ is (see I) $\Phi = (1-n)/(1-n/2) \neq 0$. However, then a metallic phase with local moments present is conceivable,[13] particularly at high correlations, which corresponds to the PI phase for $n=1$. In order to construct the free energy F_m for such a phase with the local moments (the PLM phase) we write down the entropy S_m in this case in the form[14]

$$S_m/Nk_B = n\ln 2 - n\ln n - (1-n)\ln(l-n). \tag{13}$$

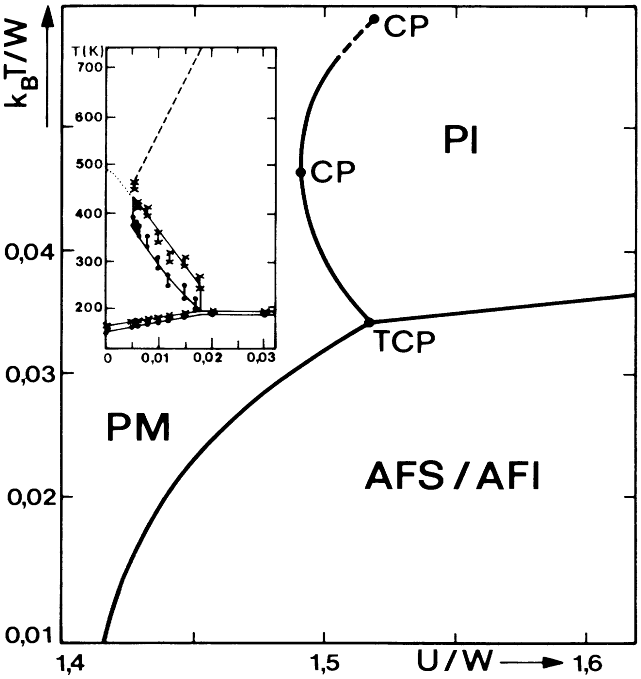

FIG. 1. Phase diagram on the plane T-U/W of possible metal-insulator transitions. CP denotes critical points and TCP tricritical point. Note reentrant metallic phases: one sandwiching AFS and PI phases, and one at high temperatures. Inset: Experimental transitions in the T-x plane for $(V_{1-x}Cr_x)_2O_3$.

This expression is based on the number of distinct configurations for a system of $N_e \equiv nN$ particles distributed among N sites with double occupancies excluded ($\eta = 0$) which is $2^{N_e}[N!/N_e!(N-N_e)!]$. Equation (13) reduces to ln2 for $n \rightarrow 1$. Taking into account that $F_m = \bar{\epsilon}(1-n)/(1-\frac{1}{2}n) - TS_m$, one can write as the coexistence condition of PM and PLM phases the expression $F_m = F$. This leads to the transition temperatures

$$k_B T_\pm = [3\Phi_0/2\pi^2\rho_0(\mu_0)][n\ln(2/n) - (1-n)\ln(1-n) \pm \sqrt{\Delta}], \tag{14}$$

with

$$\Delta = \left[n\ln\frac{2}{n} - (1-n)\ln(1-n) \right]^2 + \frac{4\pi^2}{3}\rho_0(\mu_0)\frac{U\eta + [\Phi - (1-n)/(1-\frac{1}{2}n)]}{\Phi_0}. \tag{15}$$

Note that now Φ_0 is given by $\Phi_0 = f_0 + f_1\eta_0 + f_2\eta_0^2$, where the coefficients f_i are specified in I, and $\eta_0 = (n^2/4)(1 - U/U_c)$. For $n \rightarrow 1$, Eq. (14) reduces to Eq. (5). The transition lines $T_\pm$ terminate from the low correlation side at a critical point (U_{lc}, T_c). In the strongly correlated limit $U > U_c = 2W$ only the PLM phase is stable at all T. The important point is that for $n \rightarrow 1$ the effective mass both in the PM phase and in the PLM phase is then large, since then $m^*/m_0 = 1/\Phi_0 = (1 - \frac{1}{2}n)(1-n) \gg 1$. The difference between the PLM and the PM phases is that for $n \rightarrow 1$ at high temperatures the molar entropy of the PLM phase approaches $R\ln2$ while in the latter case it approaches $2R\ln2$, where R is the gas constant. For $n < 1$, Eq. (13) yields an entropy of the PLM phase intermediate between these two values, depending on the deviation $\delta = 1 - n$ in any given system. This circumstance offers a resolution of the mutually exclusive conclusions reached concerning the asymptotic value of the entropy in Ref. 6 and Mayer *et al.*[15] for the heavy-fermion system UBe_{13}.

In summary, we have calculated the boundary between the Fermi-liquid and the local-moment phases. Further work is needed in order to unify the present approach with the phenomenological two-fluid models of MIT's[1] and of liquid ^{3}He in the normal phase.[16]

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