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# Thermodynamics of the metal-insulator transition: Discontinuous transitions in the paramagnetic phase

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We analyze the thermodynamic properties of the metal-insulator transitions at nonzero temperature in the paramagnetic phase, within a model proposed recently. The correlated motion of electrons is expressed through a band narrowing $\Phi$ which reflects a restricted hopping of electrons due to on-site Coulomb interaction $U$ between them. The factor $\Phi$ describes the portion of the total number of electrons which contribute to the band motion and is calculated self-consistently. We obtain discontinuous transitions from the metallic to the insulating phase above a critical value of $U/W=1.646$, where $W$ is the bare bandwidth. For $U/W<1.765$ this transition is followed by a second discontinuous transition back to the metallic phase at higher temperature. The entropy at both of these transitions is calculated. These features provide a semiquantitative theory of the experimentally observed behavior in pure and Cr-doped $V_2O_3$ in the paramagnetic phase.

## I. INTRODUCTION

The purpose of the present paper is to treat electron correlation effects in a narrow band at nonzero temperature ($T\neq 0$). The treatment given predicts the occurrence, under appropriate conditions, of one or more discontinuous metal-insulator transitions with rising temperature, which reproduce the principal qualitative features of experimental observations encountered in compounds such as $(V_{1-x}Cr_x)_2O_3$. Additionally, we show that for sufficiently strong correlations the system remains in the insulating state over the whole range of accessible temperatures; NiO may represent one example of such a system.

Considerable prior effort has been devoted to the electron correlation problem, but most of these studies have been restricted to the case of zero temperature where thermal entropy effects play no role. Intuitively, one then expects a changeover from metallic to insulating behavior when correlation effects due to Coulombic repulsion between electrons become comparable to the energies of electrons in band states. This point was first made by Mott[1] and was further developed and placed on a more formal footing by Hubbard,[2] Gutzwiller,[3] Kanamori,[4] and by Brinkman and Rice.[5] There also exist treatments of the correlation effect at nonzero temperatures by Cyrot[6] as well as by Moriya and Hasegawa[7] and by Chao and Berggren,[8] but most of the features described in the present article are missing in the studies by these authors.

In this paper we adopt a two-phase model composed of itinerant and localized particles, each with an appropriate weight calculated self-consistently. We then show that the main features of the phase diagram (indicating stability ranges of various metallic and insulating phases) under appropriate conditions lead to reentrant metallic properties. This requires the self-consistent calculation of a band-narrowing factor characteristic of correlated electron motion, which is the main conceptual principle employed in our analysis.

## II. FREE ENERGY FUNCTIONAL FOR THE TWO-PHASE MODEL: GENERAL FEATURES

The point of departure for the two-phase model is our earlier formulation[9] of the correlation effect (hereafter designated as I). The basic problem arises from the necessity of combining two disparate starting points for an adequate description of a state intermediate between the extended and localized electron configurations in a solid. For the former the reference state is an electron gas whose wave functions form modulated plane waves extending throughout the crystal. In the latter the electrons tend to be localized on atoms; for incompletely filled valence shells, and with electrons subject to Hund's rule, one encounters localized magnetic moments which are one manifestation of the so-called Mott-Hubbard insulating state. The question then arises as to how to describe an intermediate state in which the band and atomic portions of the total energy are comparable in magnitude. The method used in I was to subdivide the electron collection into two subsystems: a category of $\Phi N$ electrons in the itinerant state and a collection of $(1-\Phi)N$ electrons in the localized configuration. This corresponds to the circumstance that both band and localized states should be treated on an equal footing. Such a subdivision follows from the fact, elaborated in I, that $\Phi$ represents the probability of electron hopping between neighboring sites. The factor $\Phi$ was then determined self-consistently by introducing a variational parameter $\eta\equiv\langle n_{i\uparrow}n_{i\downarrow}\rangle$ describing the probability of encountering a doubly occupied atomic site. This parameter, which represents a two-particle correlation function for the ground state, was then used to minimize the free energy functional that involves $\eta$ explicitly as well as implicitly in $\Phi(\eta(T),T)$.

The fraction $\Phi$ of itinerant electrons is involved in the relation $E_B/N=\Phi\bar{\varepsilon}$, where $E_B/N$ is the average band energy per site and $\bar{\varepsilon}$ is the corresponding quantity in the bare (uncorrelated) band. $\Phi$ also appears in the expression $E_{\mathbf{k}}=\Phi\epsilon_{\mathbf{k}}$, where $\epsilon_{\mathbf{k}}$ is the bare-band energy of an electron in state $\mathbf{k}$, and $E_{\mathbf{k}}$ is the corresponding quantity for the correlated charge carriers (quasiparticles). Thus, $\Phi$ may also be considered as a band narrowing factor whereby the electron motion is impeded by the relatively strong on-site Coulomb repulsion $U$ when the latter becomes comparable to the bandwidth $W$.

The entropy of the system is similarly decomposed into a contribution arising from localized and from itinerant carriers, each with an appropriate weight that is determined self-consistently.

We summarize here the main features of the model formulated in I and correct several typographical errors in the original presentation. In the model discussed earlier the free energy functional is given by

$$\frac{F}{N}=\frac{1}{N}\sum_{\mathbf{k},\sigma}E_{\mathbf{k}}f(E_{\mathbf{k}})+U\eta+\Phi\frac{k_BT}{N}\sum_{\mathbf{k},\sigma}\{f(E_{\mathbf{k}})\ln f(E_{\mathbf{k}})+[1-f(E_{\mathbf{k}})]\ln[1-f(E_{\mathbf{k}})]\}$$
$$+k_BT(1-\Phi)[\eta\ln\eta+\nu(\ln\nu-\ln2)+(1+\eta-n)\ln(1+\eta-n)]\;, \tag{2.1}$$

where $f(E_{\mathbf{k}})$ is the Fermi-Dirac function for quasiparticles of energy $E_{\mathbf{k}}$, $n$ is the number of electrons per site (the degree of band filling), $T$ is the absolute temperature, $k_B$ is Boltzmann's constant, and $\nu\equiv n-2\eta$ is the probability for single-particle occupancy on a given site.

In this and the next sections we consider the special case of a half-filled band, $n=1$, which permits us to set the chemical potential $\mu=0$ at all temperatures, so long as the assumed density of states (DOS) for the bare band is symmetric with respect to its midpoint.

On adopting a rectangular density-of-states function, Eq. (2.1) may be rewritten as

$$F/WN=-(2k_BT/W)(1-\Phi)\ln\cosh(W\Phi/4k_BT)-(2k_BT/W)\Phi\ln2$$
$$-(2k_BT/W)[(2\Phi-1)J(\Phi)]+(U/W)\eta-k_BT(1-\Phi)\{(1-2\eta)\ln[2/(1-2\eta)]-2\eta\ln\eta\}\;, \tag{2.2}$$

where

$$J(\Phi)=\int_0^1 dx\,\ln\cosh(W\Phi x/4k_BT)\;, \tag{2.3}$$

and

$$\Phi(\eta)=8\eta(1-2\eta)\;. \tag{2.4}$$

The above expressions represent the free energy functional which must be minimized with respect to the variational parameter $\eta$.

From the requirement $(\partial F/\partial\eta)_T=0$, Eq. (2.3), and Eq. (2.4) one obtains the following condition on $\eta$:

$$(2k_BT/W)(\Phi'/\Phi)(1-\Phi)\ln\cosh(W\Phi/4k_BT)-[(1-\Phi)\Phi'/2]\tanh(W\Phi/4k_BT)-(2k_BT\Phi'/W)\ln2$$
$$-(2k_BT/W)(\Phi'/\Phi)J(\Phi)+(k_BT\Phi'/W)\{(1-2\eta)\ln[2/(1-2\eta)]-2\eta\ln\eta\}$$
$$+[2k_BT(1-\Phi)/W]\ln[2\eta/(1-2\eta)]+U/W=0\;, \tag{2.5}$$

wherein

$$\Phi'\equiv d\Phi/d\eta=8(1-4\eta)\;. \tag{2.6}$$

The above equation specifies the local extremum $\eta=\eta(k_BT/W,U/W)$ of the free energy $F=F(\eta(T),T)$. In general, for a given $\eta$, several solutions are found from which one must select the one with the lowest $F$. The crossing of two $F(\eta)$ curves at a particular $\eta$ signals the occurrence of a first-order transition at that point, unless the tangents coincide. It may be shown without difficulty that in the limit $T\rightarrow0$, the above analysis correctly reduces to the results cited in I for $\eta_0$ and $E_G$, respectively.

In what follows we will numerically evaluate the following quantities:

(i) The fraction of doubly occupied sites when the system is in equilibrium, $\eta=\eta(k_BT/W,U/W)$. The calculations are based on Eq. (2.5), using (2.3), (2.4), and (2.6). Since on the average there is one electron per site ($n=1$), $\eta$ is a measure of the equilibrium density of charge carriers per site in the system. It is therefore a parameter of fundamental importance in determining whether a given system in the ground state is an insulator or a metal.

(ii) The reduced free energy per site, according to Eqs. (2.2), (2.3), and (2.4).

(iii) The total reduced entropy per site $S/k_BN$ as obtained from the relation $S=-\partial F(\eta(T),T)/\partial T$.

## III. METAL-INSULATOR TRANSITION AND THE INSULATING PHASE AT $T \neq 0$

In what follows we shall briefly summarize the thermodynamic properties of correlated electron systems for the case $n=1$ and for a rectangular DOS in the context of three physically distinct regimes.

Regime I. $U/W<1.646$; the system is a correlated metal.

Regime II. $1.646<U/W<2.0$; with rising $k_BT/W$ the system changes from a correlated metal to a paramagnetic insulator and back to a correlated metal via two sharp phase transitions, as long as $1.646<U/W<1.765$; only one sharp correlated metal to paramagnetic insulator transition is found for $1.765<U/W<2.0$.

Regime III. $U/W>2.0$; the system remains in the Mott-Hubbard insulating state.

*Regime I.* The changes of $\eta$ with temperature in regime I are displayed as the upper curves of the $\log_{10}\eta$ versus $k_BT/W$ plot in Fig. 1 for $U/W=0$, 1.0, 1.5, and 1.64. No discontinuities are encountered in this range of $U/W$. The band-narrowing factor $\Phi$ diminishes from $\Phi=1$ (for $U/W=0$) to $\Phi \simeq 0.33$ (for $U/W=1.64$). Thus, an appreciable fraction of charge carriers remains itinerant, which is why this state has been identified as a correlated metallic phase. The corresponding free energy curve for $U/W=1.5$ is shown in Fig. 3 as a plot of $F/WN$ versus $k_BT/W$; it diminishes approximately as $T^2$ with increasing reduced temperature.

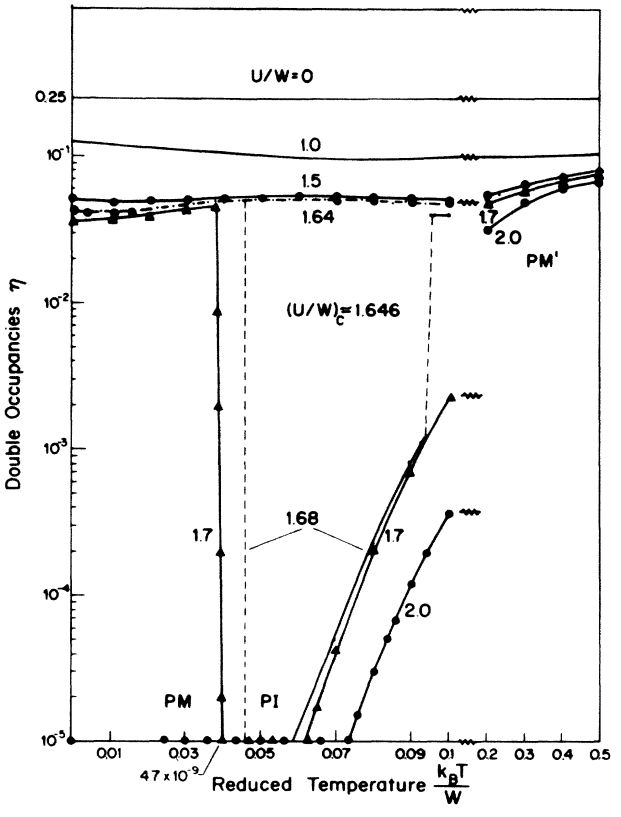

FIG. 1. Temperature dependence of double occupancy $\eta$ for various values of $U/W$. Note the logarithmic scale on $y$ axis and the change of abscissa scale for $k_BT/W>0.1$.

*Regime II.* The variation of $\log_{10}\eta$ with $k_BT/W$ for regime II is shown in the lower set of curves in Fig. 1 for $U/W=1.68$, 1.7, and 2.0. In contrast to regime I, one now encounters two first-order transitions whose locations on the reduced-temperature scale vary with $U/W$. The lower transition occurs in the range $0<k_BT/W<0.07$, wherein $\eta$ changes by 4 to 22 orders of magnitude at the transition. This is interpreted as reflecting a changeover from a lower-temperature, quasimetallic state (PM; $\eta \sim 5\times10^{-2}$, $\Phi \simeq 0.32$ for $U/W=1.66$) to a paramagnetic insulator configuration (PI; $\eta \simeq 10^{-5}$ to $10^{-24}$, $\Phi \ll 10^{-2}$). The upper transition occurs in the range $0.07<k_BT/W<0.11$, depending on the value of $U/W$. This represents a transformation from the PI configuration back to a paramagnetic metallic state (PM'; $\eta \sim 9\times10^{-2}$, $\Phi \simeq 0.3$ for $U/W=1.66$), very similar to the low-temperature metallic state. In this latter transition the discontinuity in $\eta$ amounts to 1.5 to 2 orders of magnitude.

Another perspective on the succession of phase changes is provided in Fig. 2, where $\log_{10}\eta$ is plotted against the reciprocal reduced temperature $W/k_BT$ for $U/W=1.64$, 1.65, 1.66, and 1.68, close to the lower critical $U/W=1.646$ ratio which separates regions I and II. The reentrant nature of the metallic phase is immediately apparent; for the intervening insulator $\eta$ varies exponentially with temperature. One should note the progressive reduction in the stability range of PM phase as one proceeds from the upper initial value of $U/W=2.0$ (the limiting value which separates regime II and III) toward $U/W=1.646$ (the limiting value which separates regions I and II and where the intervening PI phase is eliminated). The sharpness of delineation of these regions is characteristic of phase changes governed by electron correlation effects.

That these transitions are of first order is documented by free energy calculations. In regime II one obtains three

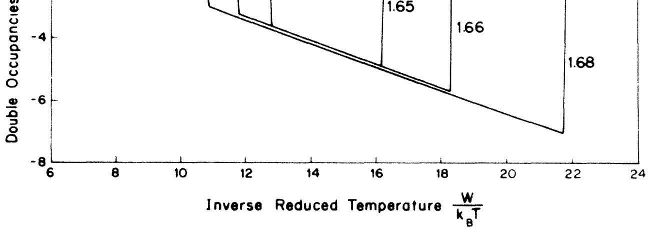

FIG. 2. $\log_{10}\eta$ as a function of inverse temperature $W/k_BT$ for $U/W=1.64$, 1.65, 1.66, and 1.68. Note the semiconducting character of the PI phase. The inset shows the inverse temperature dependence of conductivity for $(V_{1-x}Cr_x)_2O_3$ with $x=0.01$ (lower curve) and $x=0.006$ (from Ref. 12).

sets of $F/WN$ curves of which the lower two, corresponding to metallic and insulating states, are plotted in Fig. 3 as a function of $k_BT/W$ for $U/W=1.68$. Two intersections are clearly evident which occur at the two $k_BT/W$ values where $\eta$ suffers the discontinuities discussed earlier.

The phase transitions are also mirrored by the variation of entropy with temperature. Within any one of the phases PM, PI, or PM′ the entropy changes continuously as shown by the slopes of the free energy curves (see Fig. 3), whereas a discontinuity occurs at the phase boundaries. Plots of the entropy changes $\Delta S/k_BN$ versus $U/W$ at the transitions PM→PI and PI→PM′ are exhibited in Figs. 4(a) and 4(b). In the range where the PM phase is stable, $S/k_BN$ rises nearly linearly with $k_BT/W$ until the PM-PI phase boundary is reached. At that point there is a sudden jump in reduced entropy to the value ln2 characteristic of localized carriers with spin $\frac{1}{2}$, which value is closely maintained until the high-temperature PI→PM transition is reached. At that point the reduced entropy again increases discontinuously [cf. Fig. 4(b)]; in the high-temperature region $S/k_BN$ ultimately reaches the value of 2ln2 characteristic of free fermions in the high-temperature limit. It should be emphasized that all of the above phase changes occur solely as a function of $T$, for fixed $U/W$. Although the fraction of doubly occupied sites is extremely small in the PI phase, it suffices to account for the observed conductivities of the $(V_{1-x}Cr_x)_2O_3$ system on the assumption that the excited carriers are delocalized.

*Regime III.* In this regime all plots of $\ln\eta$ versus $1/T$ are found to be essentially linear, with an Arrhenius-type activation energy $\epsilon_a=U/2$. The reduced free energy in the range $U/W>2.0$ is given in first approximation by $F/WN=-(k_BT/W)\ln 2$. It follows that the entropy in this regime is approximately $S/k_BN=\ln 2$. All of these findings are consistent with the extremely low $\eta$ values encountered in this regime ($\eta<10^{-8}$ for $W/k_BT>10$) which also renders $\Phi$ extremely small ($\Phi<10^{-7}$ in the same range). Thus, one deals with an exceedingly small concentration of available carriers: the free energies and entropies are governed by electrons of spin $\frac{1}{2}$ located at singly occupied sites. These results are in agreement with an intuitive notion of the Mott insulator which is represented by a Heisenberg magnet.

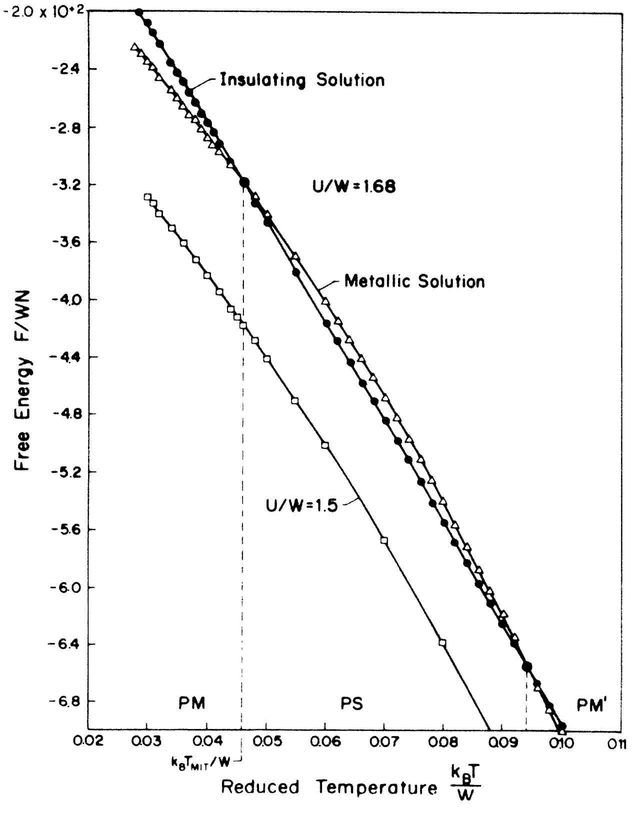

FIG. 3. Temperature dependence of the free energy for both insulating and metallic solutions when $U/W=1.68$. The crossing points mark the PM→PI and PI→PM′ transitions, respectively. The curve for $U/W=1.5$ was drawn for comparison.

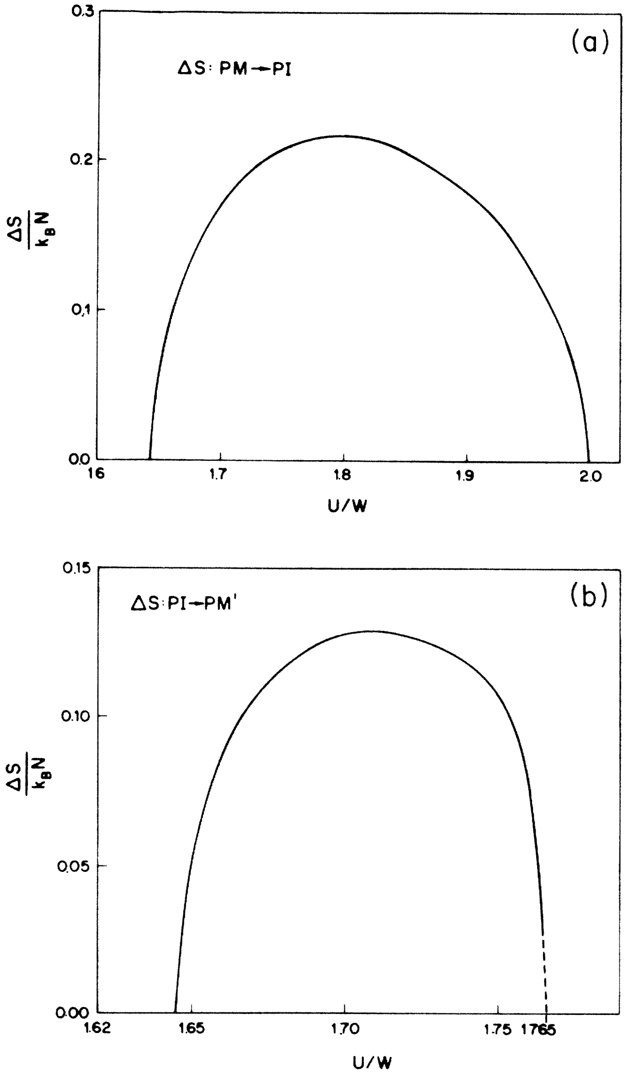

FIG. 4. (a) Entropy change $\Delta S=S_I-S_M$ of the PM→PI transition as a function of $U/W$. (b) The same for the PI→PM′ transition.

## IV. PHASE DIAGRAM

The phase diagram which may be constructed from the above data is displayed in Fig. 5 in the $(k_BT/W)$-$(U/W)$ plane. One should note several items.

(i) There exist three distinct phases already described earlier, two quasimetallic regimes PM and PM', separated from a paramagnetic insulating region by first-order transition curves, except at the critical point (0.07, 1.646). The insulating state at $T=0$ and $U>U_c=2W$ may be called the Mott-Hubbard insulator. The phase between two metallic states, encountered for $1.646<U/W<1.765$, we propose to call the Mott-Hubbard semiconductor since the temperature dependence of carrier concentration is an exponential function, with a temperature-independent activation energy.

(ii) A second critical point is encountered at $k_BT/W=0$, $U/W=2.0$.

(iii) The point $k_BT/W=0.1125$, $U/W=1.765$ terminates the boundary line PI-PM'. This means that for increasing temperatures and with fixed $U/W$ in the range $1.765<U/W<2.0$ one encounters only one first-order PM$\rightarrow$PI phase transformation at low $k_BT/W$ and supercritical behavior for $k_BT/W>0.1125$. Unfortunately, the numerical accuracy is not sufficient to establish whether the point (0.1125, 1.765) is a critical point. One should also note that we distinguish between PM and PM' phases because they are separated by the critical point (0.07, 1.646).

The sequence of phases PM, PI, and PM' may be understood using the following argument that is supported by detailed numerical analysis. For $1.645<U/W<2.0$ the band energy $E_B$ slightly outbalances the correlation energy $U$. However, at nonzero but low temperature the contribution to the entropy of itinerant electrons ($\sim T$) is small compared to that associated with electrons in the insulating phase ($k_B\ln 2$). Therefore, the insulating state may have a lower free energy than the metallic state above a temperature $T$ for which $k_BT\ln 2>|E_B/N+U\eta|$. On the other hand, at sufficiently high temperature, the entropy of the itinerant state approaches the limit $2k_B\ln 2$ and hence, eventually overcomes the entropy of the insulating phase. Thus, under appropriate conditions, the high-temperature phase may again become metallic.

## V. DISCUSSION AND OVERVIEW OF THE PRESENT APPROACH

Historically, electron correlation effects were first considered by Mott[1] who essentially approached the problem in the spirit of the Fermi-Thomas model. The electron interactions in the metallic phase were handled in terms of the mutual screening of charge carriers in the metallic phase. The degree of screening diminishes with charge carrier density. At a critical electron density, $n^{1/3}=0.26/a_0$, where $a_0$ is the Bohr radius of the 1s state in the solid, the system changes discontinuously into an insulating ground state in which every electron is localized on an atom. In the Hubbard treatment[2] of the problem the ratio $U/W$ was used as the relevant variable; the correlation effects were studied for the case $T=0$ via operator algebra involving the Green function technique. For a semielliptic DOS the critical $U/W$ ratio, close to 0.83, was the end point for a continuous transition from metallic to insulating behavior as $U/W$ increases. Brinkman and Rice[5] found explicit solutions that characterized the metal-insulator transition at $T=0$ within the Gutzwiller[3] approach. Their results for $T=0$ are equivalent to the critical ratio $(U/W)_{\rm cr}=2$ for a rectangular DOS. The changeover from metallic to insulating state was found to be mirrored in a continuous drop of $\eta$ to zero at the transition. These authors also obtained an enhancement in the paramagnetic susceptibility in the above scheme. Chao and Berggren[8] generalized this approach to nonzero temperatures and specifically introduced a band-narrowing factor as a means of handling electron interactions at $T>0$. While the authors considered the electron correlation problem in terms of the two-phase model considered in Secs. II and III, they did not explicitly adopt such a scheme in their treatment. Cyrot,[6] as well as Moriya and Hasegawa[7] examined the Hubbard model in the coherent potential approximation at $T>0$ within the functional-integral scheme. In their approximation the metal-insulator transition is once again continuous both as a function of $U/W$ and as a function of $T$. No reentrant metallic behavior was reported for any of the above treatments.

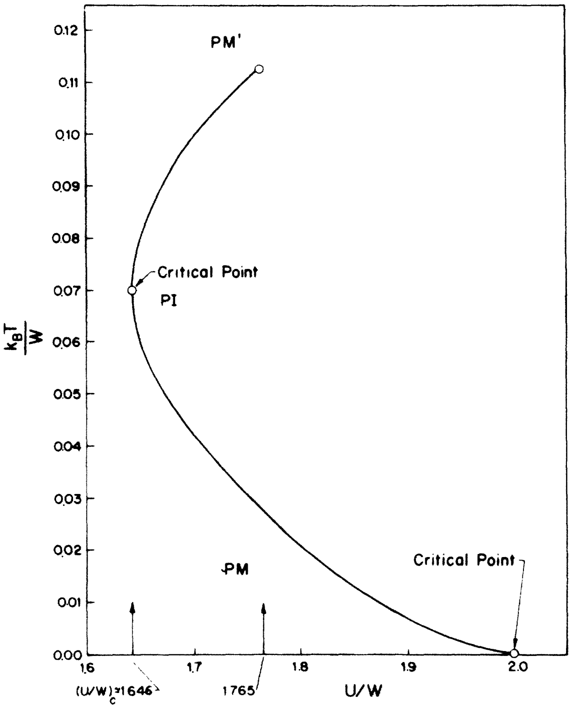

FIG. 5. Phase diagram on the plane $k_BT/W-U/W$ with border lines separating the paramagnetic metallic (PM,PM') and insulating (PI) phases. Note the two critical points with coordinates (0.07, 1.646) and (0, 2.0), respectively. The limiting point (0.1125, 1.765) terminates the first-order transition boundary, separating reentrant metallic behavior from a supercritical behavior.

Within our approximation scheme we obtain the following new features which may be compared with experiment: a reentrant metallic phase, a phase diagram with several critical points, entropies of transition in their dependence on $U/W$, and discontinuous phase transitions across phase boundaries.

## VI. COMPARISON WITH EXPERIMENT: $(V_{1-x}Cr_x)_2O_3$

So far the theoretical analysis has been based on the use of $U/W$ as the independent parameter. However, this quantity is not directly accessible to experiment; instead, it is the chromium mole fraction $x$ (or, equivalently,[10] the effective pressure $p$) that is subject to direct experimental control. Thus, it is necessary to establish a relation between $U/W$ and $x$ before a comparison between theory and experiment can be undertaken.

There are two distinct mechanisms by which the Cr substitution for V affects $U/W$. The first involves the direct influence of Cr content on electron interactions. In the virtual crystal approximation the Hubbard parameter $U$ is replaced by an effective parameter,

$$\bar{U}=U_{\text{V}}(1-x)+U_{\text{Cr}}x\ , \tag{6.1}$$

where an obvious notation has been adopted. For the corresponding effective bandwidth we assume the elementary proportionality $W\sim t_{ij}\sim\exp(-\lambda R_{ij})$ between $W$ and the transfer integral $t_{ij}$ that involves nearest-neighbor centers $i$ and $j$, as well as their separation distance $R_{ij}$. Next, set $R_{ij}=R_{ij}+\Delta R_{ij}$, where $R_{ij}$ is a standard separation distance and $\Delta R_{ij}$ is the deviation from this value. The first-order term in the Taylor's series expansion may be replaced by the corresponding change of volume $(\Delta V/V_0)^{1/3}x$; at very dilute concentrations of Cr in the $V_2O_3$ host lattice one may introduce Vegard's law which involves a linear scaling of distances with the concentration of diluent. In the above $\Delta V$ is the change in volume $V_0$ of the unit cell for the $V_2O_3$ host per unit replacement of V by Cr. Under this set of assumptions

$$t_{ij}\sim[\exp(-\lambda R_{ij})][1+x(\Delta V/V_0)^{1/3}]\ ,$$

where

$$\bar{W}=W[1+(\Delta V/V_0)^{1/3}x]\equiv W_{\text{V}}+(W_{\text{Cr}}-W_{\text{V}})x\ .$$

On combining the above contributions one obtains

$$\left[\frac{\bar{U}}{\bar{W}}\right]=\frac{U_{\text{V}}+(U_{\text{Cr}}-U_{\text{V}})x}{W_{\text{V}}+(W_{\text{Cr}}-W_{\text{V}})x}\approx\frac{U_{\text{V}}}{W_{\text{V}}}\left[1+\left[\frac{U_{\text{Cr}}-U_{\text{V}}}{U_{\text{V}}}+\frac{W_{\text{V}}-W_{\text{Cr}}}{W_{\text{V}}}\right]x\right]\ . \tag{6.2}$$

A second change of $U/W$ with $x$ arises from the effect of the atomic potential fluctuations. The substitution of Cr for V produces deeper potential wells that are randomly distributed among the vanadium potentials. Let $\Delta\epsilon\equiv\epsilon_{\text{Cr}}-\epsilon_{\text{V}}<0$ be the difference in energy of an electron localized at a Cr and at a V atom. The energy value of the localized electrons is given by $\sum_{(i\sigma)}E_i\langle n_{i\sigma}\rangle$, wherein $E_i$ assumes the value $\epsilon_{\text{Cr}}$ or $\epsilon_{\text{V}}$. This expectation value is represented by $(1-\Phi)x\Delta\epsilon$; the first factor specifies the probability of finding an electron in a localized state and the second factor $x$, the probability of encountering a Cr site. In other words, we explicitly take into account that the inhomogeneity of the system enhances the localization as expressed through the factor $(1-\Phi)$. This correction must be added to $-(W/4)\Phi$ of Eq. (2.9) which specifies the total band energy.

One then obtains the effective band energy,

$$\bar{E}_B=x\,\Delta\epsilon-\frac{W}{4}\left[1+\left[\frac{4\Delta\epsilon}{W}\right]x\right]\Phi\ . \tag{6.3}$$

Since $\Delta\epsilon<0$, the term $[1-(4|\Delta\epsilon|/W)x]$ represents an additional band-narrowing factor associated with lattice disorder induced by the random distribution of Cr atoms. In the limit of strong disordering one encounters Anderson localization which is not treated here, since we assume that the principal source of localization are electron-electron interactions.

The total variation of $U/W$ with $x$ is then given by

$$\frac{\bar{U}}{\bar{W}}=\frac{U_{\text{V}}}{W_{\text{V}}}\left[1+\left[\frac{4|\Delta\epsilon|}{W}+\frac{U_{\text{Cr}}-U_{\text{V}}}{U_{\text{V}}}+\frac{W_{\text{V}}-W_{\text{Cr}}}{W_{\text{V}}}\right]x\right]. \tag{6.4}$$

In summary, for dilute dispersions of Cr among V sites, the effective Hubbard parameter $U/W$ varies linearly with $x$ as specified by Eq. (6.4). This permits a direct comparison to be made between the specification of various thermodynamic quantities (including phase diagrams) in terms of $U/W$ and their correspondence to the experimentally accessible composition variable $x$. As determined empirically,[10] $x$ in turn is proportional to an applied hydrostatic pressure. The change of $U/W$ with $x$ reflects both the lattice disorder and additional electron correlations introduced by formation of the $(V_{1-x}Cr_x)_2O_3$ alloys.

One should finally note that the above treatment involves a subdivision of charge carriers into localized and itinerant groups. It should be noted that the two-phase model leads to a residual entropy of $S_0=k_BN(U/2W)^2\ln2$ for the correlated metallic phase and to a value $S_0=k_BN\ln2$ for the Hubbard-Mott insulating state. This nonzero value of $S_0$ was also encountered in prior treatments[6,7] of the correlated problem. The nonzero value of $S_0$ can be ascribed to the disorder present in any mixed system.

The various features described above have their experimental counterpart in the $(V_{1-x}M_x)_2O_3$ system, where $M=$ Cr, Al, Ti, or □ (cation vacancy); an extensive literature concerning the physical properties of this alloy system has accumulated over several decades. Some representative papers are listed in Refs. 10 and 11. For certain concentration ranges $x$ the $(\text{V-Cr})_2O_3$ and $(\text{V-Al})_2O_3$ alloy systems display reentrant metallic properties in the range 180—900 K although the PI→PM′ transformation at higher temperatures is spread over roughly 50 K instead of being sharp, as predicted by the present theory. (Compare Fig. 2 and the inset.) The calculated $\Delta S_{\text{PI-PM}}$ values of the sharp PM-PI insulating transition in the range 180—300 K for the various alloys matches the observed values[10] within a factor of 2. The above indicates that correlation phenomena do play an important role in accounting for the physical characteristics of the $V_2O_3$ system. On the other hand, there are unmistakable signs that the lattice also is of importance in determining the properties of the system at temperatures above 200 K, whereas magnetic ordering effects dominate the low-temperature regime. These features must be built into the present theory before any quantitative comparison between theory and experiment can be attempted. Nevertheless, the various physical characteristics of the $V_2O_3$ system can be reasonably matched by the present theory on adopting the linear dependence of $U/W$ on $x$.

The present model contains two characteristic features: it takes into account the correlation phenomena stressed by McWhan and collaborators[11] in their interpretation of the metal-insulator transition. Also, it enables the Mott-Hubbard insulating phase to be described in terms of two-band semiconductor as proposed by Kuwamoto, Honig, and Appel.[10] In this sense the theory mediates between the two previous formulations. The two-fluid model proposed here thus permits one to interpret measurements such as magnetic susceptibility in terms of localized carriers. By contrast, measurements such as conductivity in the semiconducting phase reflect the properties of thermally activated itinerant carriers present in a narrow lower Hubbard subband and in a wider upper Hubbard subband, which play the role of valence and conduction bands, respectively.

The present theory allows also for identification of NiO as a Mott insulator, with $U > 2W$. Namely, in this case $\epsilon_a = U/2$; one can estimate[12] that then $U \sim 4$ eV $\gg W \lesssim 1$ eV.

## VII. CONCLUSIONS

In this paper we have provided a detailed discussion of metal to insulator transitions at nonzero temperatures. The theory was developed in the spirit of Landau's approach by introducing the extra variable $\eta$ into the free energy. The coefficients of the expansion are determined by comparing the results with known limiting cases of the microscopic theory for narrow-band electrons (cf. I for details).

The cardinal feature in the present analysis in Secs. II and III is the ansatz that on a macroscopic level electrons may be divided into two groups: a portion $(1-\Phi)$ representing the local moments and a portion $\Phi$ representing a Fermi fluid. The weight $\Phi$ is calculated self-consistently.

The theory depends parametrically on the ratio $U/W$. It was shown that for *fixed* $U/W$ the system as a function of temperature can undergo zero, one, or two metal-insulator transitions (and exhibit reentrant metallic behavior in the latter case) depending on the chosen value of $U/W$. The conditions leading to these various transitions are summarized in Fig. 5. The specific formulation here deals with the case of a half-filled band ($n=1$) and a rectangular DOS; also, lattice effects and magnetic ordering at low temperature must still be introduced. Additionally, we disregard in our analysis in Secs. II and III the explicit dependence of the band-narrowing factor $\Phi$ on $T$. Work designed to eliminate some of these restrictions is currently under way.

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