Theory of pressure-induced magnetic and metal-insulator transitions

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A theory of pressure-induced simultaneous metal-insulator and magnetic phase transitions is presented. It is based on a model consisting of a periodic lattice with (1) an itinerant-electron band, (2) a narrow dispersionless band (localized states), (3) a hybridization term, (4) a very strong short-ranged repulsion between electrons of opposite spin in the localized states, and (5) a moderately strong short-ranged repulsion between electrons in the itinerant and localized bands. The problem is treated in the Hartree-Fock approximation, allowing spontaneous ferromagnetic broken symmetry. Pressure, which mainly changes the energy separation between the two bands, induces transitions from insulating, (ferro)magnetic states, to metallic states with no localized moments. The transition may be continuous or discontinuous, depending on the values of the interaction parameters. A richly structured phase diagram is obtained. For some values of the parameters the model reproduces in a reasonable fashion and for $T \rightarrow 0$ the complex transition recently found in NiI_2 at pressures of about 19 GPa.

I. INTRODUCTION

The metal-insulator transition is a phenomenon of great interest in solid-state physics.[1-3] It appears in a large variety of substances, including some elements, doped semiconductors, and transition-metal, rare-earth, and actinide compounds, and as a function of a variety of external parameters: pressure, temperature, and chemical composition. The conductivity transition can be discontinuous (first order) or continuous, and is many times associated with crystal structure modifications and/or drastic changes in the magnetic properties of the substance.

The diamond anvil cell,[4] with its great capabilities, has opened the exploration of new systems under pressure. In particular, a combination of techniques (diamond anvil cell, Mössbauer spectroscopy, conductivity, and x-ray structural measurements) has produced the discovery of a simultaneous metal-insulator and magnetic phase transition[5] in NiI_2, a layered transition-metal insulating compound at ordinary pressures. This compound consists of alternating hexagonal single-Ni and double-I atomic layers stacked along the c axis; it can be thought of, in the first approximation, as being made of face-centered-cubic I^- ions, intercalated every other layer by hexagonal monolayers of Ni^{2+}. The magnetic structure arises principally from the Ni^{2+} ions: each layer is *ferromagnetically* ordered, with successive layers being *antiferromagnetically* ordered with respect to each other.[6,7] At ordinary pressures the Néel temperature is approximately 80 K.

Under pressure the antiferromagnetic coupling becomes stronger, with the Néel temperature increasing by approximately a factor of 4 at pressures of about 19 GPa. At 19 GPa there is a phase transition with several well-defined characteristics: (1) the substance is no longer antiferromagnetic at any temperature, (2) it becomes metallic, and (3) there is no observable change either in the crystal structure, the atomic volume, or the lattice parameters.

Electronic band-structure calculations[8,9] of NiI_2 and the isostructural $NiBr_2$ and $NiCl_2$ yield metals for all three substances, with the Fermi level falling in the middle of the Ni $3d$ bands. The fact that all three are insulators indicates the failure of band theory, and the fact that correlation effects in the Ni $3d$ bands do produce a Mott insulator.[1,2] The application of pressure, similar to the substitution of a light halogen for a heavier one, reduces the energy difference between the halogen np and the Ni $3d$ states. The crystal Hamiltonian produces a hybridization between the various atomiclike orbitals, and favors the existence of itinerant electron states, i.e., metals. The effect of hybridization is paramount in states with the same or very close orbital energies. Therefore the application of pressure, by decreasing the energy difference between the Ni and the halogen orbital energies, might produce an insulator-to-metal transition, as it does in the specific case of NiI_2.

It is the purpose of this contribution to present a calculation in which these effects are explicitly modeled. The calculation is based on the Hartree-Fock approximation of a two-band Hamiltonian, which includes hybridization and short-range interactions: a strong one for electrons in the "localized" band, and a weaker one between electrons in the localized and the extended bands. The model has been called in the past the Falicov-Kimball model,[3,10] and can be considered a straightforward extension of the periodic Anderson model,[11,12] with an additional short-range interaction between electrons in the two different states. Various specific cases of the model have been studied but, as far as the authors are concerned, no self-consistent calculation has been performed, even for $T \rightarrow 0$ and in the Hartree-Fock approximation, for a system in which the magnetic moment (magnetization), the hybridization, and the orbital populations are included simul-

taneously as a function of the energy difference between the various levels (i.e., the applied pressure).

Section II briefly describes the model. Section III contains the approximations and the method of solution. Section IV presents the results, the discussion, and conclusions.

II. THE MODEL

A model that describes the concurrent magnetic and metal-insulator phase transition in NiI_2 must contain the following basic ingredients.

(i) An electronic structure that contains extended, only weakly correlated band states. In case of NiI_2, the I^- $5p$ bands are of this kind. For simplicity, the present model takes only a single band, with dispersion ε_k, into consideration. The operators $c_{k\sigma}$ ($c^\dagger_{k\sigma}$) annihilate (create) particles in the extended band states with wave vector k, spin σ, and energy ε_k.

(ii) The most energetic electrons of the Ni^{2+} ions form a highly correlated, localized $(3d)^8$ configuration, i.e., each Ni^{2+} ion sustains two holes in the $3d$ shell, as opposed to a collective Ni $3d$ conduction band in which the number of electrons at each site fluctuates. For two holes the lowest-energy term corresponds to total spin $S=1$. The strong Coulomb repulsion between localized holes on the same site eliminates fluctuations between different configurations, and produces the Mott insulator, i.e., a nonconducting, localized picture for Ni^{2+} $3d$ states. In the model considered here, only one spin-degenerate localized orbital per unit cell is taken into account. This is a crude approximation, because it is only capable of describing spin magnetic moments, with no contribution arising from the orbital part and the degeneracy of the d band. The operators $d_{k\sigma}$ ($d^\dagger_{k\sigma}$) annihilate (create) particles in the localized states with wave vector k, spin σ, and energy E. This orbital has no dispersion.

(iii) Excess occupancy of the localized orbital is energetically unfavorable because of the strong intrasite Coulomb interaction. The model includes this property by a short-range repulsion term, of magnitude U, that describes the strong screened Coulomb interaction for two holes in the same site.

(iv) The periodic potential of the lattice is responsible for a hybridization term, of strength V, between the extended c and the localized d orbitals of the crystal.

(v) The experimental situation[5,13] clearly indicates that the magnetization changes discontinuously at the transition pressure. A first-order, discontinuous transition can only be obtained if a repulsion between particles in localized and extended states (of strength G) is included in the model.

In summary the Hamiltonian operator is

$$H=\sum_{k,\sigma}\varepsilon_k c^\dagger_{k\sigma}c_{k\sigma}+\sum_{k,\sigma}E d^\dagger_{k\sigma}d_{k\sigma}+V\sum_{k,\sigma}(d^\dagger_{k\sigma}c_{k\sigma}+c^\dagger_{k\sigma}d_{k\sigma})+\frac{U}{N}\sum_{k,k',q}d^\dagger_{k+q\uparrow}d^\dagger_{k'-q\downarrow}d_{k'\downarrow}d_{k\uparrow}+\frac{G}{N}\sum_{\sigma,\sigma'}\sum_{k,k',q}d^\dagger_{k+q\sigma}c^\dagger_{k'-q\sigma'}c_{k'\sigma'}d_{k\sigma}\ , \tag{1}$$

where N denotes the number of unit cells in the crystal.

The function ε_k and the four parameters E, V, U, and G depend directly on the volume of the unit cell and, through an equation of state, on the applied pessure. A direct study of the pressure dependence is not possible in the framework of this approach. It is therefore assumed that the main effect of an external pressure is a shift of the parameter E, i.e., a decrease in the difference between the average energy value of the extended and localized states, which leads to a significant band overlap and a growing importance of the hybridization. This assumption is supported by existing band-structure calculations,[8,9] and by the experimentally found increase of Néel temperature with pressure.[5]

The model introduced above and its numerous relatives have been studied for the past 30 years in the context of the intermediate-valence systems,[12] the Kondo problem,[14] and heavy-fermion systems.[15]

III. THE HARTREE-FOCK APPROXIMATION

A Hartree-Fock approximation $H_{\rm HF}$ to the many-body Hamiltonian (1) is given by

$$H_{\rm HF}=\sum_{k,\sigma}\tilde{\varepsilon}_k c^\dagger_{k\sigma}c_{k\sigma}+\sum_{k\sigma}\tilde{U}_\sigma d^\dagger_{k\sigma}d_{k\sigma}+\sum_{k\sigma}\tilde{V}_\sigma(d^\dagger_{k\sigma}c_{k\sigma}+c^\dagger_{k\sigma}d_{k\sigma})-NU\Delta_\uparrow\Delta_\downarrow-NG\Lambda(\Delta_\uparrow+\Delta_\downarrow)+NG(|\Gamma_\uparrow|^2+|\Gamma_\downarrow|^2)\ , \tag{2}$$

where the new mean-field, one-particle parameters $\tilde{\varepsilon}_k$, $\tilde{U}_\sigma$, and $\tilde{V}_\sigma$ are defined by

$$\tilde{\varepsilon}_k\equiv\varepsilon_k+G(\Delta_\uparrow+\Delta_\downarrow)\ , \tag{3a}$$

$$\tilde{U}_\sigma\equiv E+U\Delta_{-\sigma}+G\Lambda\ , \tag{3b}$$

$$\tilde{V}_\sigma\equiv V-G\Gamma_\sigma\ . \tag{3c}$$

They depend on the expectation values

$$\Lambda\equiv\Lambda_\uparrow+\Lambda_\downarrow\ , \tag{4a}$$

$$\Lambda_\sigma\equiv\frac{1}{N}\sum_k\langle c^\dagger_{k\sigma}c_{k\sigma}\rangle\ , \tag{4b}$$

$$\Delta\equiv\Delta_\uparrow+\Delta_\downarrow\ , \tag{4c}$$

$$\Delta_\sigma\equiv\frac{1}{N}\sum_k\langle d^\dagger_{k\sigma}d_{k\sigma}\rangle\ , \tag{4d}$$

and

$$\Gamma_\sigma\equiv\frac{1}{N}\sum_k\langle d^\dagger_{k\sigma}c_{k\sigma}\rangle\ . \tag{4e}$$

All Hartree-Fock states are assumed to conserve translational symmetry, an approximation that is valid for paramagnetic and ferromagnetic states, but not for antiferromagnets, ferrimagnets, and charge- and spin-density waves. Although NiI_2 is an antiferromagnet, each Ni plane is *ferromagnetic*, with alternating planes arranged antiferromagnetically with respect to each other. In the

present contribution the detailed antiferromagnetic correlation between Ni planes is neglected (it is a smaller effect, arising from Anderson superexchange[7]), and the magnetization m discussed below refers exclusively to the single-Ni-plane magnetization.[6]

The physical interpretation of the expectation values (4a)–(4e) is obvious: The quantity Δ in (4c) measures the total density of electrons in localized orbitals. Because of the repulsion between band and localized states [G term in (1)], the shift (3a) in band energy from ε_k to $\tilde{\varepsilon}_k$ is proportional to this density multiplied by the coupling constant G. Similarly, Λ measures the total density of band electrons. The effective field resulting from the G term shifts the energy of the localized orbitals, as given in (3b) by a term $G\Lambda$. These energies are also shifted by the repulsion between electrons in the same localized orbital with different spin by the $U\Delta$ term in (3b). The exchange in the G term leads to an extra spin-dependent contribution to the hybridization V, as seen in (3c).

Diagonalization of $H_{\rm HF}$ is straightforward. The quasiparticle excitation spectrum is given by

$$E_{\pm,k\sigma}=\tfrac{1}{2}(\tilde{\varepsilon}_k+\tilde{U}_\sigma)\pm[\tfrac{1}{4}(\tilde{\varepsilon}_k-\tilde{U}_\sigma)^2+\tilde{V}_\sigma^2]^{1/2}\ , \tag{5}$$

and the excitation spectrum $E_{\pm,k\sigma}$ develops the familiar hybridization gap for nonvanishing $\tilde{V}_\sigma$.

The quantities of physical interest here are the total magnetization m,

$$m=|(\Lambda_\uparrow+\Delta_\uparrow)-(\Lambda_\downarrow+\Delta_\downarrow)|\ , \tag{6}$$

and the concentration (4a) of particles in the extended states Λ as a function of the various parameters, E in particular. The calculation (a nonlinear problem) requires self-consistency. It is equivalent to finding roots of five transcendental equations[16] that depend on the five variables E_F (Fermi energy), Δ, $\eta\equiv\Delta_\uparrow-\Delta_\downarrow$, $\Gamma_\uparrow$, and $\Gamma_\downarrow$. The solution for the first two variables, E_F and Δ, as a function of the latter three is always unique, whereas η, $\Gamma_\uparrow$, and $\Gamma_\downarrow$ may have multiple solutions. Results are presented in the following section.

In order to understand the structure and physical content of the resulting Hartree-Fock ground state, the quasiparticle density of states

$$\rho_\sigma(\omega)\equiv\frac{1}{N}\sum_k[\delta(E_{+,k\sigma}-\omega)+\delta(E_{-,k\sigma}-\omega)] \tag{7}$$

is very useful. Some examples are also given in the following section.

IV. RESULTS AND DISCUSSION

Results for particular values of the parameters are shown in Figs. 1–3. In these figures the total number of electrons in the system is one per formula unit; the density of itinerant states (per spin, per formula unit) was assumed to take the (semicircular) form

$$\rho_0(\varepsilon)\equiv\frac{8}{\pi W^2}[\varepsilon(W-\varepsilon)]^{1/2}\ , \tag{8}$$

where W, the bandwidth [directly related to the band energies ε_k of (1)], is taken to be the energy unit of the problem. The value of W should be interpreted, rather than the actual bandwidth of the problem, as the value of the energy interval that contains one electron per spin per formula unit in the density of states.[17]

The other parameters were taken to be $U=5W$ and $V=0.1W$, a somewhat arbitrary but reasonable choice.

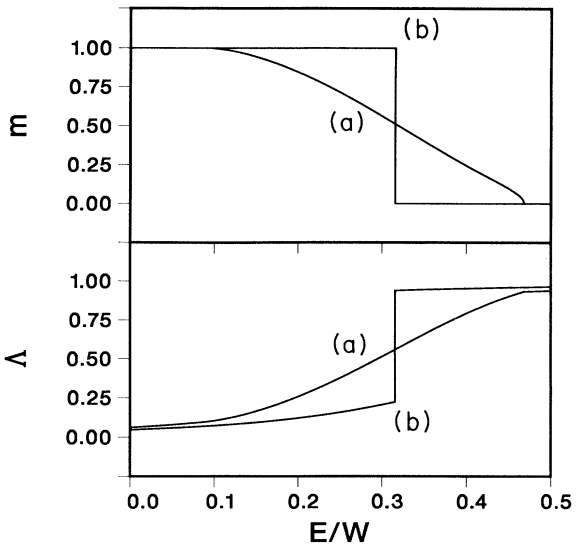

FIG. 1. The magnetization m (upper graph) and the extended-band occupation number Λ (lower graph) for $U=5W$ and $V=0.1W$, as functions of E: (a) $G=0.1W$; (b) $G=0.5W$. Case (a) exhibits two second-order transitions. Case (b) shows only a discontinuous transition.

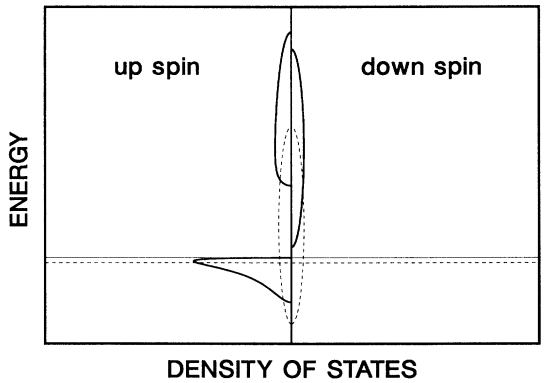

FIG. 2. Schematic representation of the density of quasiparticle states for the case $U=5W$, $V=0.1W$, $G=0.5W$, and $E=0.31W$. The horizontal thin solid line indicates the energy of the last occupied state. The dashed lines represent the densities of spin states in the absence of interactions and hybridization (the dashed straight lines are the localized states). Note that the system is fully magnetized (no down-spin states occupied) and is an insulator, with an energy gap between the last occupied (up-spin) states and the first empty (down-spin) states. There are additional localized down-spin states at higher energies, not included in the graph.

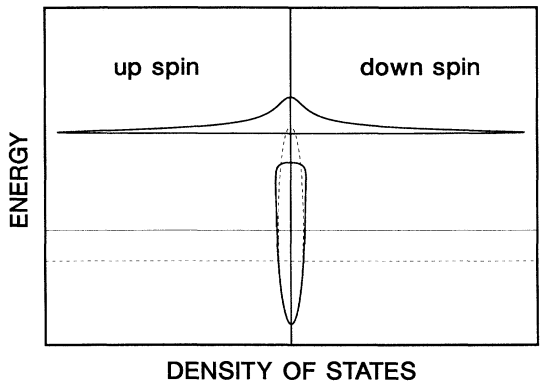

FIG. 3. Schematic representation of the density of quasiparticle states for the case $U=5W$, $V=0.1W$, $G=0.5W$, and $E=0.32W$. The horizontal thin solid line indicates the energy of the last occupied state. The dashed lines represent the densities of spin states in the absence of interactions and hybridization (the dashed straight lines are the localized states). Note that the system is not magnetic, with identical bands and identical occupation of both spins. It is also metallic, since the Fermi level falls in the middle of the lower band. There is considerable hybridization, and no clear distinction can be made between localized and extended states.

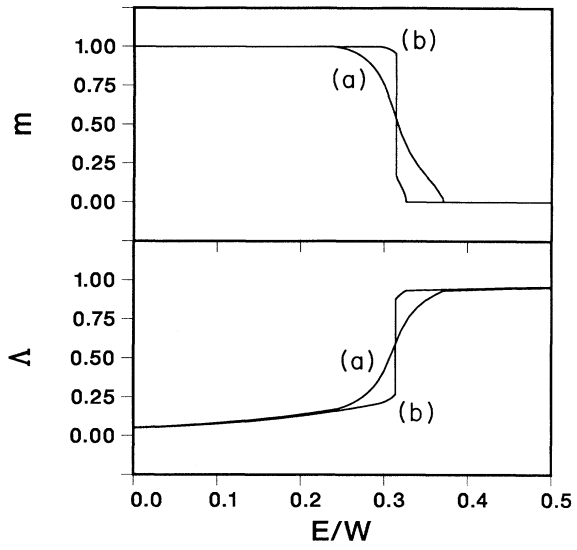

FIG. 4. The magnetization m (upper graph) and the extended-band occupation number Λ (lower graph) for $U=5W$ and $V=0.1W$, as functions of E: (a) $G=0.3W$; (b) $G=0.4W$. Case (a) exhibits two second-order transitions. Case (b) shows three singularities: two second-order transitions and, at an intermediate value of E, a discontinuous change.

Figure 1 shows the values of m and Λ for the cases of $G=0.1W$ and $G=0.5W$, as functions of the increasing values of E, i.e., increasing overlap between itinerant and localized states, i.e., increasing pressure. The $G=0.1W$ case exhibits a smooth increase in Λ and a continuous decrease in m. In particular, m is equal to 1 for values of E smaller than $E=0.093\,79W$, and equal to 0 for values of E greater than $E=0.468\,14W$. These two values of E can be considered those corresponding to pressures at which there are, at $T=0$, second-order phase transitions.[18] The $G=0.5W$ case exhibits a $T=0$ discontinuous (first-order) transition from $m=1$ to 0 for $E=0.315\,49W$; there is also a corresponding discontinuity in Λ. Figures 2 and 3 show the densities of quasiparticle states for two particular situations close to the transition: $G=0.5W$ and $E=0.31W$ and $G=0.5W$ and $E=0.32W$. It can be seen that the former corresponds to a fully magnetized insulator, whereas the latter is an unmagnetized metal. Hybridization plays a crucial role in all cases.

Figure 4 shows two other cases, intermediate between those depicted in Fig. 1. They correspond to $G=0.3W$ and $G=0.4W$. Whereas the former still exhibits the two second-order transitions characteristic of small G values, the latter presents a different situation. There are in this

TABLE I. The self-consistent hybridization parameters for the examples of Figs. 1 and 4. In all cases $U=5W$ and $V=0.1W$. All energies are in units of W.

G/W	E/W	m	$\tilde{V}_\uparrow/W$	$\tilde{V}_\downarrow/W$
0.1	0.090 00	1.000 00	0.125 83	0.100 00
	0.320 00	0.497 21	0.131 35	0.101 11
	0.468 14	0.000 00	0.112 04	0.112 04
0.3	0.237 04	1.000 00	0.202 15	0.100 00
	0.320 00	0.438 56	0.199 04	0.104 71
	0.370 75	0.000 00	0.136 59	0.136 59
0.4	0.293 50	1.000 00	0.251 40	0.100 00
	0.313 93	0.954 43	0.257 94	0.100 24
	0.313 93	0.168 43	0.189 06	0.121 00
	0.326 10	0.000 00	0.148 85	0.148 85
0.5	0.315 48	1.000 00	0.297 16	0.100 00
	0.315 50	0.000 00	0.158 43	0.158 43

case, as E (or equivalently the pressure) increases, *three* $T=0$ phase transitions: a second-order one, where m departs from the $m=1$ value; a discontinuous one, where m jumps between two intermediate values; and another second-order transition, where m finally attains the $m=0$ value. The variety in the transitions is caused by a delicate interplay of the following basic processes.

(i) The d-band Coulomb repulsion U is responsible for the splitting of the two spin d bands and the related occurrence of local magnetic moments.[19]

(ii) The itinerant c bands and the localized d bands repel each other with a strength that is a function of the size of the parameter G. Depending on the position E of the d levels relative to the c band, the d bands push the itinerant states either to higher or to lower energies. If G is not too large, the lower d spin band and one c band (with opposite spin) may overlap, leading to a magnetization $m<1$. It is clear from this argument that it is not possible to obtain a discontinuous transition without an interaction G between localized and itinerant states.

(iii) It should be mentioned that the terminology "c or d band" is no longer applicable in a rigorous sense, because of the hybridization. However, if V is small, it is justified to think about "d-dominated and c-dominated c-d hybrids." There is always a hybridization gap between c- and d-dominated hybrids within one spin direction, therefore only c-and d-band overlap between opposite spin orientations may occur.

(iv) If E is sufficiently (positive) large, the system minimizes its energy by occupying only the itinerant states. Because of the G interaction, the localized states are pushed above the Fermi level and are no longer occupied (Fig. 3). Since the localized states are no longer occupied, and the electron repulsion only involves the d states, no local magnetic moment is formed. It depends on the magnitude of G whether the transition is continuous or discontinuous with E. The "critical" value G_c of G at which transition changes character is (as it is reasonable to expect) much smaller than U, but larger than V.

The influence of the interaction G, the self-consistency, and the relative overlap of the bands is most notable in the effective hybridization parameters of $\tilde{V}_\sigma$ of (3c). This is shown in Table I for the cases illustrated in Figs. 1 and 4.

It is instructive to plot the contours of constant m in the G-E plane (see Fig. 5). This plot divides the G-E plane into three regions: $m=1$, the first high-symmetry region; $m=0$, the second high-symmetry region; and intermediate values of m, the low-symmetry region. There are in this plane three lines of singularities, and three singular points. A second-order line separates regions of $m=0$ and nonzero m values, in which m varies continuously. Another second-order line divides regions of $m=1$ and $m<1$ values, in which m also varies continuously. There is a third line along which m has jump discontinuities; these can be between $m=1$ and 0, between intermediate values of m and $m=0$, or between two intermediate values of m. The separation of these three regimes is given by singular points where the second-order lines meet the line of discontinuities. Finally the line of discontinuities, where it separates two regions of low and identical symmetry, terminates at a *classical* critical point.

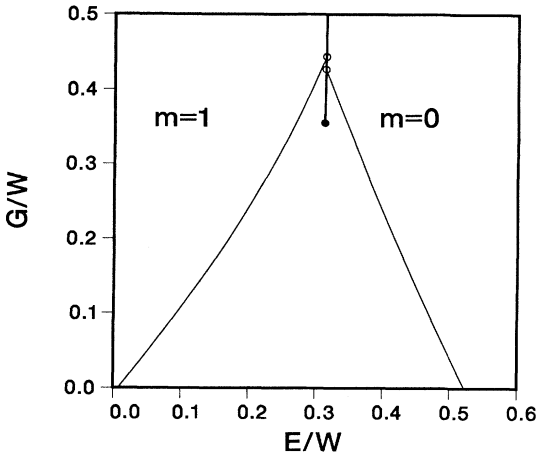

FIG. 5. The regions in the G-E plane where, for $U=5W$ and $V=0.1W$, m takes specific values: $m=1$, the first high-symmetry region; $m=0$, the second high-symmetry region; and intermediate values of m, the low-symmetry region. Thin lines indicate second-order transitions, where m departs from one of the high-symmetry values and varies continuously. The thick line indicates discontinuous changes in the values of m. The open circles show the intersection of the line of discontinuities with the second-order-transition lines, and separate regions where m jumps from 1 to 0, from an intermdiate value to zero, and between two intermediate values. The black dot indicates the "classical" critical point, where the line of discontinuities stops, i.e., the discontinuities vanish.

Even though only a few cases have been explored in detail, it is evident that the model described by Eq. (1) exhibits a great richness of structure and possibilities. The examples studied here, in any case, encompass that which motivated this study: The simultaneous magnetic and insulator-metal transition in NiI_2. The graph of Fig. 4, case (b), seems to reproduce fairly well the behavior of the hyperfine field, i.e., the Ni-plane magnetization, as determined by Mössbauer spectroscopy, and reported in Ref. 5. The densities of quasiparticle states shown in Figs. 2 and 3, when account is taken for the difference in band structure between the present model and the Ni halogenides, describe qualitatively the electronic changes expected in these transitions.

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[13]The experiment shows, as a function of increasing pressure and at low temperatures, a small decrease in the sublattice magnetization, followed by a discontinuous change at 19 GPa, from a large to a small value, followed by a gradual decrease to zero. The discontinuous change cannot be explained without the G interaction; the continuous changes preceding and following the discontinuity require, on the other hand, a sizable hybridization, the V term.

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[16]In the self-consistency problem, only Λ, as given by (4a), rather than the individual spin components Λ_σ, given by (4b), appear. In addition, the self-consistent equation for Λ is automatically satisfied with the determination of the Fermi level E_F and Δ, because $(\Lambda+\Delta)$ equals the total number of particles per site.

[17]It should be emphasized that even though the present formulation treats itinerant and localized *electrons,* the actual case of NiI_2 corresponds to itinerant *holes* derived from the $5p$ electrons of I, and localized *holes* in the $(3d)^8$ configuration of NiI^{2+}. The transformation from electrons to holes is elementary; the multiplicity of states on the localized $(3d)^8$ configuration, caused by the orbital angular momentum, is not included in the present model. For the particular case of NiI_2, where the conduction band is derived from the $5p$ electrons of I and there are two I per formula unit, the value of W should be approximately one-sixth of the total $5p$-band width, or probably smaller, given the accumulation of states at the top of the $5p$ band.

[18]Second-order phase transitions, as used here, are in the sense defined by Landau [see, for instance, L.D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1958), Chap. XIV]. The order parameter in this case is the magnetization, with the values of $m=0$ and 1 constituting two distinct high-symmetry phases, and intermediate values of m being the low-symmetry phase.

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