

Theory of the nonmetal-metal transition in rare-earth compounds.

I. Electronic density of states

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A theory of the nonmetal-metal transition in rare-earth compounds which occurs with increasing temperature is presented. An essential feature of the transition is that a hybridization gap (an energy gap due to the hybridization between localized and conduction electrons) decreases continuously and vanishes at the transition temperature by virtue of the spin-field fluctuation that arises from the Coulomb repulsion between localized electrons. The transition is examined by the calculation of the electronic density of states for conduction and localized electrons in the periodic Anderson model. Its calculation is done by the functional-integral method using the static and single-site coherent-potential approximations. The one-particle Green's function at 0 K coincides with that obtained by the Hartree-Fock approximation, and there appears the hybridization gap. In the case of two electrons per site including spin degeneracy, the electronic state becomes insulating (or semiconducting). Temperature dependence of the electronic density of states is calculated in the paramagnetic state. With increasing temperature, the spin-field fluctuation grows in proportion to the square root of temperature at very low temperature compared with the width of the uncorrelated conduction band. The spin-field fluctuation makes the hybridization gap decrease continuously and vanish at the transition temperature. The insulating electronic state changes to a paramagnetic metal state.

I. INTRODUCTION

The present paper describes a theory of the nonmetal-metal transition with increasing temperature in the nondegenerate periodic Anderson model. The nonmetal-metal transition is observed in homogeneously mixed-valence materials, Sm compounds, especially SmB_6 and SmS under pressure.¹⁻⁶ Experiments of the electrical resistivity,⁷⁻¹² the dynamical conductivity,¹¹ the specific heat,^{12-14,9} and the Hall coefficient^{8-10,15} show that these materials are paramagnetic semiconductors with an energy gap at low temperatures and "poor metals" with no energy gap at high (room) temperatures. Especially the existence of the energy gap at low temperature is confirmed by recent tunneling experiments.^{11,16}

The electronic structure of the homogeneously mixed valence materials is characterized by the coexistence of the highly correlated atomiclike f levels and the wide sd bands near or at the chemical potential.^{4,17} The coexistence of two limiting states, i.e., atomic and itinerant states, provides a variety of unique electronic properties. At the same time, however, it makes the theoretical calculation very difficult. Whether the ground state of SmB_6 and SmS under pressure is metallic or nonmetallic has not yet been clarified theoretically based on energy-band calculations. This is contrasted to the case of LaB_6 ,¹⁸ where the chemical potential lies in the wide sd bands below f levels. The ground state of LaB_6 is confirmed to be metallic both in experiments and energy-band calculations.

Mott introduced an idea that the above Sm compounds are semiconductors with a very small energy gap due to the hybridization (a hybridization gap).¹⁹ A model that realizes the hybridization gap at the absolute zero tem-

perature is the periodic Anderson model^{20,21} that is an array of "Anderson impurities."²² In fact, in the case of two electrons per site, the existence of the hybridization gap at 0 K is shown theoretically on the basis of the Luttinger theorem²³ and the perturbation expansion theory.²⁴

Our interest lies in the finite temperature properties of the periodic Anderson model, i.e., whether the hybridization gap vanishes or survives at finite temperatures. Existing theories are grouped into two categories. One is the perturbation expansion theory that is justified when the Coulomb repulsion is much smaller than the hybridization. The lowest-order calculation is the Hartree-Fock approximation²¹ and its extension to dynamics (random-phase approximation).²⁵ Higher-order calculation up to fourth order is also done.²⁴ Another is appropriate to the opposite limit, i.e., decoupling approximation²⁰ based on a Hubbard-I type method,²⁶ coherent-potential approximation (CPA) (Hubbard-III type calculation²⁷) with replacement of the Coulomb interaction by random binary alloy potentials,^{28,23} and the Kondo lattice approximation.²⁹ In both of these categories, existing theories do not contain the vanishing of the hybridization gap at finite temperature, namely, they do not show the nonmetal-metal transition with increasing temperature.

In this paper we investigate the finite-temperature properties of the periodic Anderson model by use of the functional integral representation³⁰⁻³² that not only reproduces known results in both solvable limits of the vanishing hybridization and Coulomb repulsion, respectively, but also provides smooth interpolation between these limits. We find that the nonmetal-metal transition with increasing temperature occurs in the intermediate region where the hybridization and the Coulomb repulsion are of the

comparative order of magnitudes. With increasing temperature, the hybridization gap decreases continuously and vanishes at the transition temperature by the spin-field fluctuation that arises from the many-body effect of the Coulomb interaction.

The organization of the present paper is as follows. In Sec. II we shall present the model Hamiltonian, nondegenerate periodic Anderson model. In Sec. III we shall present the exact expression of the one-particle Green's function in the functional integral representation that is described in detail in Appendix A. In Sec. IV we describe methods of approximation, such as the static, single-site coherent potential, and further approximations needed for numerical calculation. In Sec. V we introduce a model band suitable for rare-earth compounds. In Sec. VI we show results of the numerical calculation.

II. FORMULATION OF THE PROBLEM

A. Model Hamiltonian

The electronic states of rare-earth compounds can be described by the nondegenerate periodic Anderson Hamiltonian^{20,21}

$$\hat{H} = \hat{H}_0 + \hat{H}_I, \quad (2.1)$$

$$\begin{aligned} \hat{H}_0 = & \sum_{i,j,\sigma} T_{ij}^\sigma c_{i\sigma}^\dagger c_{j\sigma} + \sum_{\substack{i,j,\sigma \\ i \neq j}} t_{ij} (c_{i\sigma}^\dagger f_{j\sigma} + f_{i\sigma}^\dagger c_{j\sigma}) \\ & + \sum_{i,j,\sigma} W_{ij}^\sigma f_{i\sigma}^\dagger f_{j\sigma} - \mu \hat{N}, \end{aligned} \quad (2.2)$$

$$\hat{H}_I = \sum_i U n_{fi} n_{fi}. \quad (2.3)$$

Here the model Hamiltonian \hat{H} consists of the unperturbed Hamiltonian \hat{H}_0 and the perturbation one \hat{H}_I . The first and third terms in Eq. (2.2) are, respectively, the uncorrelated, free hopping terms of s and f electrons. The operators $c_{i\sigma}$ and $f_{i\sigma}$ are the annihilation operators for electrons at site i with spin σ in the Wannier representation. They satisfy the ordinary anticommutation relations. The parameters T_{ij}^σ and W_{ij}^σ are the hopping integrals between i and j sites. The second term on the right-hand side of Eq. (2.2) is the hybridization between s and f electrons. The parameter t_{ij} is a transfer integral between different sites $i \neq j$. The last term in Eq. (2.2) is introduced to measure the energy with respect to the chemical potential μ that is determined later. The operator \hat{N} is the total-electron-number operator defined by

$$\hat{N} = \sum_{i,\sigma} (n_{ci\sigma} + n_{fi\sigma}), \quad (2.4)$$

where $n_{ci\sigma}$ and $n_{fi\sigma}$ are, respectively, the electron number operators of s and f electrons:

$$\begin{aligned} n_{ci\sigma} &= c_{i\sigma}^\dagger c_{i\sigma}, \\ n_{fi\sigma} &= f_{i\sigma}^\dagger f_{i\sigma}. \end{aligned} \quad (2.5)$$

The perturbation Hamiltonian \hat{H}_I is the repulsive Coulomb interaction between two f electrons with oppo-

site spin directions in the same f orbital at site i , and U is the Coulomb repulsion.

The parameters in this model Hamiltonian are the total number of electrons N_e , energy parameters T_{ij}^σ , W_{ij}^σ , t_{ij} , and U . Besides these, we have to add another parameter, temperature T or its inverse $\beta=1/T$ ($k_B=1$), to investigate the electronic states at finite temperatures.

B. Unperturbed system

In order to study the unperturbed system, we transform the representation of wave functions from the Wannier to Bloch one. The corresponding transformation of the operator $a_{i\sigma}$ is given by

$$a_{i\sigma} = N^{-1/2} \sum_{\vec{k}} a_{\vec{k}\sigma} e^{i\vec{k} \cdot \vec{R}_i}, \quad (2.6)$$

where N is the total lattice site number. With this transformation, the unperturbed Hamiltonian reads

$$\begin{aligned} \hat{H}_0 = & \sum_{\vec{k},\sigma} \tilde{\epsilon}_{c\vec{k}\sigma} c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + \sum_{\vec{k},\sigma} (V_{\vec{k}} c_{\vec{k}\sigma}^\dagger f_{\vec{k}\sigma} + V_{\vec{k}}^* f_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma}) \\ & + \sum_{\vec{k},\sigma} \tilde{\epsilon}_{f\vec{k}\sigma} f_{\vec{k}\sigma}^\dagger f_{\vec{k}\sigma}, \end{aligned} \quad (2.7)$$

where

$$\tilde{\epsilon}_{a\vec{k}\sigma} = \epsilon_{a\vec{k}\sigma} - \mu, \quad (2.8)$$

$$\epsilon_{c\vec{k}\sigma} = \sum_i T_{ij}^\sigma e^{-i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)},$$

$$\epsilon_{f\vec{k}\sigma} = \sum_i W_{ij}^\sigma e^{-i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)}, \quad (2.9)$$

$$V_{\vec{k}} = \sum_{i(\neq j)} t_{ij} e^{-i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)}.$$

The unperturbed one-particle Green's functions in the Wannier and Bloch representations are defined, respectively, by³³

$$\begin{aligned} g_{ai,bj}^\sigma(\tau - \tau') \delta_{\sigma\sigma'} &= -\langle T_\tau a_{i\sigma}(\tau) b_{j\sigma'}^\dagger(\tau') \rangle, \\ g_{a,b}^\sigma(\vec{k}, \tau - \tau') \delta_{\vec{k}\vec{k}'} \delta_{\sigma\sigma'} &= -\langle T_\tau a_{\vec{k}\sigma}(\tau) b_{\vec{k}'\sigma'}^\dagger(\tau') \rangle, \end{aligned} \quad (2.10)$$

where the operators a and b represent c or f , and

$$a_{i\sigma}(\tau) = e^{\tau \hat{H}_0} a_{i\sigma} e^{-\tau \hat{H}_0}.$$

The notation T_τ is the "time" ordering operator, and $\langle \rangle$ denotes the grand canonical ensemble average with the unperturbed Hamiltonian defined by

$$\langle A \rangle = \text{Tr}(A e^{-\beta \hat{H}_0}) / \text{Tr} e^{-\beta \hat{H}_0}. \quad (2.11)$$

In Eq. (2.10), we have used the invariance of \hat{H}_0 for translations and spin rotations. The two Green's functions defined by Eq. (2.10) satisfy the relation

$$g_{ai,bj}^\sigma(\tau) = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} g_{a,b}^\sigma(\vec{k}, \tau). \quad (2.12)$$

The equation of motion method leads to the following

exact expressions for the unperturbed one-particle Green's functions:

$$g_{a,b}^{\sigma}(\vec{k}, \tau - \tau') = \frac{1}{\beta} \sum_n e^{-i\omega_n(\tau - \tau')} g_{a,b}^{\sigma}(\vec{k}, i\omega_n), \quad (2.13)$$

$$\omega_n = \frac{2n+1}{\beta} \pi, \quad n=0, \pm 1, \pm 2, \dots \quad (2.14)$$

$$g_{f,f}^{\sigma}(\vec{k}, i\omega_n) = \frac{i\omega_n - \tilde{\epsilon}_{c\vec{k}\sigma}}{(i\omega_n - \tilde{\epsilon}_{c\vec{k}\sigma})(i\omega_n - \tilde{\epsilon}_{f\vec{k}\sigma}) - |V_{\vec{k}}|^2},$$

$$g_{c,c}^{\sigma}(\vec{k}, i\omega_n) = \frac{i\omega_n - \tilde{\epsilon}_{f\vec{k}\sigma}}{(i\omega_n - \tilde{\epsilon}_{c\vec{k}\sigma})(i\omega_n - \tilde{\epsilon}_{f\vec{k}\sigma}) - |V_{\vec{k}}|^2}, \quad (2.15)$$

$$g_{c,f}^{\sigma}(\vec{k}, i\omega_n) = \frac{V_{\vec{k}}}{(i\omega_n - \tilde{\epsilon}_{c\vec{k}\sigma})(i\omega_n - \tilde{\epsilon}_{f\vec{k}\sigma}) - |V_{\vec{k}}|^2},$$

$$g_{f,c}^{\sigma}(\vec{k}, i\omega_n) = \frac{V_{\vec{k}}^*}{(i\omega_n - \tilde{\epsilon}_{c\vec{k}\sigma})(i\omega_n - \tilde{\epsilon}_{f\vec{k}\sigma}) - |V_{\vec{k}}|^2}.$$

We depict diagrams of these Green's functions in Fig. 1(a).

III. ONE-PARTICLE GREEN'S FUNCTION

A. Definition

An exact one-particle Green's function for the total Hamiltonian \hat{H} in the Heisenberg representation of the operators A and B is defined by³³

$$G_{Ai, Bj}^{\sigma}(\tau - \tau') \delta_{\sigma\sigma'} = - \langle \langle T_{\tau} A_{i\sigma}(\tau) B_{j\sigma'}^{\dagger}(\tau') \rangle \rangle, \quad (3.1)$$

where

$$A_{i\sigma}(\tau) = e^{\tau\hat{H}} a_{i\sigma} e^{-\tau\hat{H}},$$

and the notation $\langle \langle \rangle \rangle$ denotes the grand canonical ensemble average with the total Hamiltonian \hat{H} (Appendix A).

The chemical potential μ introduced in Eq. (2.2) should be determined by the self-consistent equation that the total number of electron N_e is equal to the grand canonical ensemble average of the total electron number operator

$$N_e = \langle \langle \hat{N} \rangle \rangle. \quad (3.2)$$

By definition (3.1), the average number of electrons $\langle \langle n_{Ai\sigma} \rangle \rangle$ is given by the one-particle Green's function,

$$\langle \langle n_{Ai\sigma} \rangle \rangle = G_{Ai, Ai}^{\sigma}(-0)$$

$$= \int_{-\infty}^{\infty} d\omega f(\omega) \rho_{Ai\sigma}(\omega), \quad (3.3)$$

where $f(\omega)$ and $\rho_{Ai\sigma}(\omega)$ are the Fermi-Dirac distribution function and the electronic density of states:

$$f(\omega) = (e^{\beta\omega} + 1)^{-1}, \quad (3.4)$$

$$\rho_{Ai\sigma}(\omega) = -\frac{1}{\pi} \text{Im} G_{Ai, Ai}^{R\sigma}(\omega). \quad (3.5)$$

$$g_{f,f}(\tau, \tau'); \text{ ---}$$

$$g_{c,c}(\tau, \tau'); \text{ - - -}$$

$$g_{c,f}(\tau, \tau'); \text{ ~~~~~}$$

$$g_{f,c}(\tau, \tau'); \text{ - - - -}$$

(a)

$$\langle S(\beta) \rangle; \text{ } \bigcirc + \bigcirc + \bigcirc + \bigcirc + \dots$$

(b)

$$G_{f,f}^v(\tau, \tau'); \text{ } \equiv \equiv \text{ ---} + \text{ ---} + \text{ ---} + \text{ ---} + \dots$$

$$G_{c,c}^v(\tau, \tau'); \text{ } \equiv \equiv \text{ ---} + \text{ ---} + \text{ ---} + \text{ ---} + \dots$$

$$G_{c,f}^v(\tau, \tau'); \text{ } \equiv \equiv \text{ ~~~~~} + \text{ ~~~~~} + \text{ ~~~~~} + \text{ ~~~~~} + \dots$$

$$G_{f,c}^v(\tau, \tau'); \text{ } \equiv \equiv \text{ - - - -} + \dots$$

(c)

FIG. 1. (a) Diagrams of the unperturbed Green's functions. (b) A diagram corresponding to $\langle S(\beta) \rangle$. Dotted lines denote the potential $v_{i\sigma}$. (c) Diagrams corresponding to $G_{a,b}^v(\tau, \tau')$.

Here $G_{Ai, Ai}^{R\sigma}(\omega)$ in Eq. (3.5) is the retarded Green's function that is obtained from the analytic continuation of the Fourier coefficient $G_{Ai, Ai}^{\sigma}(i\omega_n)$:

$$G_{Ai, Ai}^{R\sigma}(\omega) = G_{Ai, Ai}^{\sigma}(\omega + i0^+),$$

$$G_{Ai, Ai}^{\sigma}(\tau - \tau') = \frac{1}{\beta} \sum_n e^{-i\omega_n(\tau - \tau')} G_{Ai, Ai}^{\sigma}(i\omega_n).$$

B. One-particle Green's function in the functional integral method

By virtue of the functional integral formulation in Appendix A, the one-particle Green's function defined by Eq. (3.1) can be rewritten in the form [see Eq. (A15)]

$$G_{Ai, Bj}^{\sigma}(\tau - \tau') \delta_{\sigma\sigma'} = \langle G_{ai\sigma, bj\sigma'}^v(\tau, \tau') \rangle_{FA}, \quad (3.6)$$

$$G_{ai\sigma, bj\sigma'}^v(\tau, \tau') = - \frac{\langle T_{\tau} a_{i\sigma}(\tau) b_{j\sigma'}^{\dagger}(\tau') S(\beta) \rangle}{\langle S(\beta) \rangle}, \quad (3.7)$$

where the operators a and b are expressed in the interaction representation. Superscript v denotes the one-particle Green's function moving in the random one-body potential field defined by Eq. (A14). Subscript FA means the functional average with the distribution function of fictitious random fields [see Eqs. (A16)–(A19)].

The denominator of Eq. (3.7) is given by the grand canonical ensemble average of the series expansion (A13) with respect to the unperturbed Hamiltonian \hat{H}_0 . By using the Bloch–de Dominicis theorem and recollecting the series into exponential, we obtain^{31,32}

$$\langle S(\beta) \rangle = \exp \left[- \int_0^\beta d\tau_1 \text{Tr}[\underline{v}(\tau_1) \underline{g}_{ff}(-0)] - \frac{1}{2} \int \int_0^\beta d\tau_1 d\tau_2 \text{Tr}[\underline{v}(\tau_1) \underline{g}_{ff}(\tau_1 - \tau_2) \underline{v}(\tau_2) \underline{g}_{ff}(\tau_2 - \tau_1)] \right. \\ \left. - \frac{1}{3} \int \int \int_0^\beta d\tau_1 d\tau_2 d\tau_3 \text{Tr}[\underline{v}(\tau_1) \underline{g}_{ff}(\tau_1 - \tau_2) \underline{v}(\tau_2) \underline{g}_{ff}(\tau_2 - \tau_3) \underline{v}(\tau_3) \underline{g}_{ff}(\tau_3 - \tau_1)] - \cdots \right], \quad (3.8)$$

where we have used the matrix form for the Green's functions and random field,

$$\underline{g}_{ab}(\tau - \tau') = \{g_{ai, bj}^\sigma(\tau - \tau')\}, \quad (3.9)$$

$$\underline{v}(\tau) = \{v_{i\sigma}(\tau)\}, \quad (3.10)$$

and Tr means the trace with respect to both site and spin variables. A diagram corresponding to Eq. (3.8) is depicted in Fig. 1(b). In Fig. 1(b) dotted lines correspond to the interaction vertex $v_{i\sigma}(\tau)$. Here we would like to point out that (i) at the cross point of dotted and solid lines, summation with respect to both site and spin variables and integration with respect to τ should be taken, (ii) a factor of $1/n$ (where n is the number of vertices) should be included,

ed, and (iii) a factor (-1) should be attached to each closed loop of f electron lines. Equation (3.8) can be rewritten into another form. Introducing the dimensionless parameter λ , we obtain the formal expression^{31,32}

$$\langle S(\beta) \rangle = \exp \left[- \int_0^1 d\lambda \int_0^\beta d\tau \text{Tr}[\underline{v}(\tau) \underline{G}_{ff}^{\lambda v}(\tau, \tau + 0^+)] \right], \quad (3.11)$$

where $G^{\lambda v}$ is given by Eq. (3.7) with an alternation of v to λv .

The numerator of Eq. (3.7) can be calculated in a manner similar to that of Eq. (3.8). Then we obtain the perturbation series expansion of the one-particle Green's function under the random field^{31,32}

$$\underline{G}_{ab}^v(\tau, \tau') = \underline{g}_{ab}(\tau - \tau') + \int_0^\beta d\tau_1 \underline{g}_{af}(\tau - \tau_1) \underline{v}(\tau_1) \underline{g}_{fb}(\tau_1 - \tau') \\ + \int_0^\beta d\tau_1 \underline{g}_{af}(\tau - \tau_1) \underline{v}(\tau_1) \int_0^\beta d\tau_2 \underline{g}_{ff}(\tau_1 - \tau_2) \underline{v}(\tau_2) \underline{g}_{fb}(\tau_2 - \tau') + \cdots. \quad (3.12)$$

Diagrams corresponding to Eq. (3.12) are depicted in Fig. 1(c). We expand Eq. (3.12) into Fourier series with respect to τ . Introducing

$$\underline{G}_{ab}^v(\tau, \tau') = \frac{1}{\beta} \sum_n \sum_{n'} \underline{G}_{ab}^v(n, n') e^{-i\omega_n \tau + i\omega_{n'} \tau'}, \quad (3.13)$$

$$\underline{g}_{ab}(\tau - \tau') = \frac{1}{\beta} \sum_n \underline{g}_{ab}(i\omega_n) e^{-i\omega_n(\tau - \tau')}, \quad (3.14)$$

$$\underline{v}(\tau) = \sum_{\nu=-\infty}^{\infty} \underline{v}(\nu) e^{-i\omega_\nu \tau}, \quad (3.15)$$

$$\omega_\nu = \frac{2\pi\nu}{\beta}, \quad \nu = 0, \pm 1, \pm 2, \dots \quad (3.16)$$

we obtain

$$\underline{G}_{ab}^v(n, n') = \underline{g}_{ab}(n) \delta_{nn'} + \underline{g}_{af}(n) \underline{v}(n - n') \underline{g}_{fb}(n') + \underline{g}_{af}(n) \sum_m \underline{v}(n - m) \underline{g}_{ff}(m) \underline{v}(m - n') \underline{g}_{fb}(n') + \cdots. \quad (3.17)$$

The function $\underline{G}_{ab}^v(\tau, \tau')$ is not a function of the difference $\tau - \tau'$. It arises from the τ dependence of the random field and makes the calculation difficult. In order to avoid this difficulty we introduce approximations in the next section.

IV. APPROXIMATIONS

A. Static approximation

As described in Sec. III B, the τ dependence of the random field makes further calculation difficult. We make use of the static approximation that the τ dependence of the random field is neglected:

$$\underline{v}(\tau) = \underline{v} = \text{const}. \quad (4.1)$$

The static approximation provides the smooth interpolation between the weak coupling limit ($U \rightarrow 0$) and the strong coupling limit.^{31,32} In this approximation, the

functional integral reduces to the normal one. The one-particle Green's function given by Eq. (3.17) becomes diagonal with respect to n . We obtain

$$\underline{G}_{ab}^v(n, n') = \underline{G}_{ab}^v(n) \delta_{n, n'}, \quad (4.2)$$

$$\underline{G}_{ab}^v(n) = \underline{g}_{ab}(n) + \underline{g}_{af}(n) \underline{v} \underline{g}_{fb}(n) \\ + \underline{g}_{af}(n) \underline{v} \underline{g}_{ff}(n) \underline{v} \underline{g}_{fb}(n) + \cdots. \quad (4.3)$$

From the formal solution $\underline{G}_{ff}^v(n)$ and the transformation of variables

$$\xi_i = \left[\frac{\pi U}{\beta} \right]^{1/2} x_i, \quad \eta_i = \left[\frac{\pi U}{\beta} \right]^{1/2} y_i, \quad (4.4)$$

the average of the physical quantity with respect to the random field variables ξ_i and η_i , which is given by Eqs. (A14)–(A19) and (3.11), becomes the simplified form

$$\langle f(\xi_1, \xi_2, \dots; \eta_1, \eta_2, \dots) \rangle_{\text{FA}} = \frac{\int \prod_i d\xi_i d\eta_i e^{-\beta\Psi} f(\xi_1, \xi_2, \dots; \eta_1, \eta_2, \dots)}{\int \prod_i d\xi_i d\eta_i e^{-\beta\Psi}}, \quad (4.5)$$

$$\Psi = \Psi(\xi_1, \xi_2, \dots; \eta_1, \eta_2, \dots) = \Psi_0 + \Psi_1, \quad (4.6)$$

$$\Psi_0 = \frac{1}{U} \sum_i (\xi_i^2 + \eta_i^2), \quad (4.7)$$

$$\Psi_1 = -\frac{1}{\beta} \sum_n e^{i\omega_n 0^+} \text{Tr} \ln[\underline{1} - \underline{v} \underline{g}_{ff}(n)], \quad (4.8)$$

$$(\underline{v})_{i\sigma} = \sigma \xi_i + i \eta_i. \quad (4.9)$$

Equations (3.6), (4.2), and (4.5)–(4.9) show that the one-particle Green's function is given by the ensemble average of the one-particle Green's function under the random potential field, which is analogous to the theory of random alloys.³⁴ The distribution function of the random field $\exp(-\beta\Psi)$, however, is not a simple product of the distribution functions containing only variables referring to a single site, because the function Ψ_1 is not a simple sum of the function containing only variables referring to a single site, which can be seen from the Taylor-series expansion of the right-hand side of Eq. (4.8). The situation makes further calculation difficult, so we introduce approximations in the following sections.

B. CPA

1. An approximation to the distribution function of the random variables

In order to apply the single-site CPA,³⁴ we assume that the distribution function $\exp(-\beta\Psi)$ can be approximated to the simple product of the exponentials of the single-site function $\psi_i(\xi_i, \eta_i)$ that depends only on ξ_i and η_i :

$$\exp[-\beta\Psi(\xi_1, \xi_2, \dots; \eta_1, \eta_2, \dots)] \simeq \exp\left[-\beta \sum_i \psi_i(\xi_i, \eta_i)\right]. \quad (4.10)$$

The function ψ_i is determined by the following two steps. First, we maximize $\ln\langle U(\beta) \rangle$ [$U(\beta)$ is given by Eq. (A12)] with respect to ψ_i . Then the function ψ_i should satisfy the self-consistent equation³⁵

$$\psi_i(\xi, \eta) = \int \prod_{j(\neq i)} d\xi_j d\eta_j \phi_j(\xi_j, \eta_j) \times \Psi(\xi_1, \xi_2, \dots; \eta_1, \eta_2, \dots) \Big|_{\xi_i = \xi, \eta_i = \eta}, \quad (4.11)$$

$$\phi_j(\xi, \eta) = e^{-\beta\psi_j(\xi, \eta)} / \int d\xi' d\eta' e^{-\beta\psi_j(\xi', \eta')}.$$

Here the right-hand side of Eq. (4.11) means the average of Ψ over the fields at sites other than the i th site with the distribution function ϕ_j . Second, we apply the single-site CPA to Eq. (4.11). Then the function ψ_i is given by^{35,36}

$$\psi_i(\xi, \eta) = \psi_0(\xi, \eta) + \psi_1(\xi, \eta), \quad (4.12)$$

$$\psi_0(\xi, \eta) = \frac{1}{U} (\xi^2 + \eta^2), \quad (4.13)$$

$$\psi_1(\xi, \eta) = -\frac{1}{\beta} \sum_n e^{i\omega_n 0^+} \times \sum_\sigma \ln\{1 - G_{fi,fi}^\sigma(i\omega_n)[v_\sigma - \Sigma_\sigma(i\omega_n)]\}, \quad (4.14)$$

$$v_\sigma = \sigma \xi + i \eta, \quad (4.15)$$

where $G_{fi,fi}^\sigma(z)$ and $\Sigma_\sigma(z)$ are, respectively, the diagonal element of the one-particle Green's function and the self-energy of the f electron shown in the next section.

2. One-particle Green's function and self-energy

The one-particle Green's function under the static approximation and the single-site CPA can be calculated in a manner similar to that described in Ref. 34. We obtain

$$G_{Ai,Bj}^\sigma(\tau - \tau') = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} \times \frac{1}{\beta} \sum_n e^{-i\omega_n(\tau - \tau')} G_{AB}^\sigma(\vec{k}, i\omega_n), \quad (4.16)$$

$$G_{ff}^\sigma(\vec{k}, z) = \frac{z - \tilde{\epsilon}_{c\vec{k}\sigma}}{(z - \tilde{\epsilon}_{c\vec{k}\sigma})[z - \tilde{\epsilon}_{f\vec{k}\sigma} - \Sigma_\sigma(z)] - |V_{\vec{k}}|^2},$$

$$G_{cc}^\sigma(\vec{k}, z) = \frac{z - \tilde{\epsilon}_{f\vec{k}\sigma} - \Sigma_\sigma(z)}{(z - \tilde{\epsilon}_{c\vec{k}\sigma})[z - \tilde{\epsilon}_{f\vec{k}\sigma} - \Sigma_\sigma(z)] - |V_{\vec{k}}|^2}, \quad (4.17)$$

$$G_{cf}^\sigma(\vec{k}, z) = \frac{V_{\vec{k}}}{(z - \tilde{\epsilon}_{c\vec{k}\sigma})[z - \tilde{\epsilon}_{f\vec{k}\sigma} - \Sigma_\sigma(z)] - |V_{\vec{k}}|^2},$$

$$G_{fc}^\sigma(\vec{k}, z) = \frac{V_{\vec{k}}^*}{(z - \tilde{\epsilon}_{c\vec{k}\sigma})[z - \tilde{\epsilon}_{f\vec{k}\sigma} - \Sigma_\sigma(z)] - |V_{\vec{k}}|^2}.$$

The above result shows that the one-particle Green's functions of the perturbed system are given by an alternation of $\epsilon_{f\vec{k}\sigma}$ to $\epsilon_{f\vec{k}\sigma} + \Sigma_\sigma(z)$ in each expression of the unperturbed Green's functions. It is a natural result because the

Coulomb repulsion only applies to f electrons. We notice that the self-energy $\Sigma_\sigma(z)$ does not depend on \vec{k} in the single-site CPA.³⁴

The self-consistent equation for the self-energy is obtained from the CPA condition that the average of the scattering matrix is zero^{35,36}

$$\Sigma_\sigma(z) = \left\langle \frac{v_\sigma}{1 - G_{fi,fi}^\sigma(z)[v_\sigma - \Sigma_\sigma(z)]} \right\rangle_{\text{FA}} \quad (4.18)$$

or

$$G_{fi,fi}^\sigma(z) = \left\langle \frac{1}{[G_{fi,fi}^\sigma(z)]^{-1} - v_\sigma + \Sigma_\sigma(z)} \right\rangle_{\text{FA}}, \quad (4.19)$$

where $\langle \rangle_{\text{FA}}$ denotes the average with respect to the variables referring to a single site:

$$\langle f(\xi, \eta) \rangle_{\text{FA}} = \frac{\int d\xi d\eta e^{-\beta\psi_i(\xi, \eta)} f(\xi, \eta)}{\int d\xi d\eta e^{-\beta\psi_i(\xi, \eta)}}. \quad (4.20)$$

Now we can solve a set of the self-consistent equations that consist of the electron-number conservation, the Green's function, and the definition of the ensemble average with respect to the random field variables. With suitable assumptions on the band parameters $\epsilon_{c\vec{k}\sigma}$, $\epsilon_{f\vec{k}\sigma}$, $V_{\vec{k}}$, and U , the total number of electrons N_e , and temperature T , we can obtain the chemical potential μ , the Green's function $G(z)$, the self-energy $\Sigma_\sigma(z)$, and the single-site function $\psi_i(\xi, \eta)$.

3. Absolute-zero temperature

At 0 K, $\beta \rightarrow \infty$, the average value in Eq. (4.20) is calculated with the steepest-descent method. Then Eq. (4.18) reduces to

$$\Sigma_\sigma(z, T=0) = v_{\sigma, \text{ex}}^0,$$

where $v_{\sigma, \text{ex}}^0$ is the solution of the self-consistent equation

$$\partial\psi_i/\partial\xi=0, \quad \partial\psi_i/\partial\eta=0,$$

evaluated under the condition $\beta \rightarrow \infty$. From the above equations, we obtain

$$\Sigma_\sigma(z, T=0) = UN_{fi, -\sigma}. \quad (4.21)$$

It is nothing but the Hartree-Fock approximation (HFA).²¹ The self-energy at 0 K is a real constant.

The electron numbers $N_{fi\sigma}$ and $N_{ci\sigma}$ are determined by the self-consistent equation (3.2). The solution $N_{fi\sigma}$ has either one real root or many real roots. In the case of one real root, either the paramagnetic or the ferromagnetic state is stable. In the case of many real roots, the paramagnetic state may be unstable and a spin-ordered state can appear. Which case appears depends on the band parameters and is classified from the distribution function of the random field. In the paramagnetic state, the minimum of the single-site function ψ_i with respect to ξ is at zero, namely

$$\xi_{\text{ex}}^0 = 0 \quad \text{and} \quad (\partial^2\psi_i/\partial\xi^2)_{\xi=0} > 0. \quad (4.22)$$

The condition of the formation of the local moment is

given by

$$\xi_{\text{ex}}^0 = 0 \quad \text{and} \quad (\partial^2\psi_i/\partial\xi^2)_{\xi=0} = 0 \quad (4.23)$$

or

$$\xi_{\text{ex}}^0 \neq 0, \quad (4.24)$$

because the minimum of ψ_i is not at zero. Which case appears depends on the band parameters.³⁶

The self-energy at 0 K reduces to that of HFA. At finite temperature, however, the self-energy deviates considerably from that of HFA. It is shown in the following sections.

C. Approximations for numerical calculation at finite temperature

1. Reduction of random field variables

We reduce two random field variables (ξ, η) into one (ξ) as follows. First, the integral with respect to η field is done by the steepest-descent³² with each configuration ξ . The field strength at the steepest descent path is given by $\partial\psi_i/\partial\eta=0$. The steepest-descent approximation breaks spin rotational invariance, but the discrepancies of numerical results between the full two-field calculation and the steepest-descent approximation are small within the static approximation.³⁷ Second, we assume that the ξ dependence of the η field is weak. Then we use $\eta(\xi)$ at ξ_{ex} which yields an extremal value of ψ_i : $\partial\psi_i/\partial\xi=0$.³⁶ Then ξ_{ex} and $\eta(\xi_{\text{ex}})$ are given by the solution of the self-consistent equations

$$\xi_{\text{ex}} = -\frac{U}{2} \sum_{\sigma} \sigma R_{\sigma},$$

$$i\eta_{\text{ex}} = \frac{U}{2} \sum_{\sigma} R_{\sigma},$$

$$R_{\sigma} = \frac{1}{\beta} \sum_n \frac{G_{fi,fi}^\sigma(i\omega_n)}{1 - G_{fi,fi}^\sigma(i\omega_n)[v'_\sigma - \Sigma_\sigma(i\omega_n)]},$$

$$v'_\sigma = \sigma\xi_{\text{ex}} + i\eta_{\text{ex}}.$$

The average with respect to the random field ξ is given by

$$\langle f(\xi) \rangle_{\text{FA}} = \frac{\int d\xi e^{-\beta\psi(\xi)} f(\xi)}{\int d\xi e^{-\beta\psi(\xi)}}, \quad (4.25)$$

$$\psi(\xi) = \frac{1}{U} \xi^2 - \frac{1}{\beta} \sum_n e^{i\omega_n 0^+} \sum_{\sigma} \ln \{ 1 - G_{fi,fi}^\sigma(i\omega_n) \times [v_\sigma - \Sigma_\sigma(i\omega_n)] \}, \quad (4.26)$$

$$v_\sigma = \sigma\xi + i\eta_{\text{ex}}. \quad (4.27)$$

The Taylor-series expansion of Eq. (4.26) around ξ_{ex} , which is useful at low temperature, is given by

$$\psi(\xi) = \text{const} + \sum_{m=2}^{\infty} A_m (\xi - \xi_{\text{ex}})^m, \quad (4.28)$$

$$A_m = \frac{1}{U} \delta_{m,2} + \frac{1}{m} \sum_{\sigma} \sigma^m \frac{1}{\beta} \sum_n e^{i\omega_n 0^+} \left[\frac{G_{fi,fi}^{\sigma}(i\omega_n)}{1 - G_{fi,fi}^{\sigma}(i\omega_n)[v_{\sigma} - \Sigma_{\sigma}(i\omega_n)]} \right]^m \Big|_{\xi=\xi_{\text{ex}}}$$

2. A fluctuating field approximation

The CPA condition given by Eq. (4.18) or (4.19) is a nonlinear integral equation, so the numerical calculation is laborious. We introduce an approximation that the fluctuation of the random field is assumed to be small and moments higher than third order are assumed to be decomposed into the products of moments lower than second order.³⁸ We expand the right-hand side of Eq. (4.19) in powers of

$$v_{\sigma} \{ [G_{fi,fi}^{\sigma}(z)]^{-1} + \Sigma_{\sigma}(z) \}^{-1},$$

and assume

$$\langle v_{\sigma}^{2m} \rangle_{\text{FA}} \simeq \{ \langle v_{\sigma}^2 \rangle_{\text{FA}} \}^m, \quad (4.29)$$

$$\langle v_{\sigma}^{2m+1} \rangle_{\text{FA}} \simeq \{ \langle v_{\sigma}^2 \rangle_{\text{FA}} \}^m \langle v_{\sigma} \rangle_{\text{FA}}.$$

Recollecting the expansion, we obtain

$$G_{fi,fi}^{\sigma}(z) = \left[1 + \frac{\langle v_{\sigma} \rangle_{\text{FA}}}{[G_{fi,fi}^{\sigma}(z)]^{-1} + \Sigma_{\sigma}(z)} \right] H_{\sigma}(z), \quad (4.30)$$

$$H_{\sigma}(z) = \frac{1}{2} \sum_{\sigma} \frac{1}{[G_{fi,fi}^{\sigma}(z)]^{-1} + \Sigma_{\sigma}(z) + \sigma(\langle v_{\sigma}^2 \rangle_{\text{FA}})^{1/2}}. \quad (4.31)$$

In this approximation, the square root of the second moment, in other words, the fluctuation $(\langle v_{\sigma}^2 \rangle_{\text{FA}})^{1/2}$ plays an important role, so we may call the approximation a "fluctuating field approximation." Equations (4.30) and (4.31) can be written into another form³⁶:

$$\Sigma_{\sigma}(Z) = \langle v_{\sigma} \rangle_{\text{FA}} + \{ \langle v_{\sigma}^2 \rangle_{\text{FA}} - [\Sigma_{\sigma}(z)]^2 \} G_{fi,fi}^{\sigma}(z). \quad (4.32)$$

Considering $\langle v_{\sigma} \rangle_{\text{FA}}$ and $\langle v_{\sigma}^2 \rangle_{\text{FA}}$ as parameters, we can calculate the Green's function and the self-energy from Eqs. (4.30)–(4.32). The relation of parameters $\langle v_{\sigma} \rangle_{\text{FA}}$ and $\langle v_{\sigma}^2 \rangle_{\text{FA}}$ to temperature is given by the self-consistent equation (4.25).

3. Lowest-order approximations in a paramagnetic state

In the paramagnetic state, the Green's functions and the self-energies with up and down spins are the same,

$$G_{ab} \equiv G_{ai,bi}^{\dagger} = G_{ai,bi}^{\dagger},$$

$$\Sigma \equiv \Sigma_{\uparrow} = \Sigma_{\downarrow},$$

and ξ_{ex} is zero. Odd-order terms in the expansion of ψ , Eq. (4.28), are identically zero because of $\sum_{\sigma} \sigma^m$. And the first-order moment of the random field identically vanishes: $\langle \xi \rangle_{\text{FA}} = 0$. The relation between the second moment of the random field and temperature is given by

$$\langle \xi^2 \rangle_{\text{FA}} = \frac{\int d\xi e^{-\beta\psi(\xi)} \xi^2}{\int d\xi e^{-\beta\psi(\xi)}}.$$

We introduce approximations that hold at sufficiently low temperatures. At very low temperatures (high β), the main contribution to the integration is the small region around zero. Then we have to leave only lower-order terms in the expansion of ψ . In the paramagnetic state ($A_2 > 0$), it is sufficient to leave a second-order term. We obtain

$$\langle \xi^2 \rangle_{\text{FA}} = (2\beta A_2)^{-1},$$

where A_2 is given by Eq. (4.28). Next we assume that the temperature dependence of A_2 is weak at very low temperatures and can be replaced by the value at 0 K:

$$\langle \xi^2 \rangle_{\text{FA}} = T / [2A_2(T=0)], \quad (4.33)$$

$$A_2(T=0) = \frac{1}{U} + \int_{-\infty}^{\mu} d\omega \left[-\frac{1}{\pi} \right] \times \text{Im}[G_{ff}(\omega + i0^+)]^2. \quad (4.34)$$

The physical meanings of Eqs. (4.33) and (4.34) are as follows. From Eq. (4.33), A_2 should be positive in the paramagnetic state. The spin-field fluctuation $(\langle \xi^2 \rangle_{\text{FA}})^{1/2}$ increases in proportion to the square root of temperature. And the growing rate of the fluctuation becomes larger as A_2 becomes smaller. This means that if A_2 is small, the spin-field fluctuation grows rapidly even with the slight increase of temperature. On the other hand, the relation between A_2 and U is given by Eq. (4.34). The second term of the right-hand side depends strongly on the band parameters. In the case of electron-hole symmetry as described in Sec. VI, the second term does not depend on U . So A_2 becomes small with increasing U . Thus, even in the paramagnetic state, the spin-field fluctuation is very effective to the physical quantities with suitable choice of the band parameters.

V. A MODEL BAND

A. Model band parameters

In this section we assume the band parameters $\epsilon_{\sigma \vec{k} \sigma}$, $\epsilon_{f \vec{k} \sigma}$, and $V_{\vec{k}}$ suitable to rare-earth compounds. In rare-earth compounds the $4f$ electron is localized in one atomic site. Then we neglect the \vec{k} dependence of the uncorrelated f electron band

$$\epsilon_{f \vec{k} \sigma} = \epsilon_{f \sigma} \text{ for all } \vec{k}. \quad (5.1)$$

And we also neglect the \vec{k} dependence of the hybridization

$$V_{\vec{k}} = V \text{ for all } \vec{k}. \quad (5.2)$$

Under these assumptions the diagonal element of the Green's function with respect to the site variables is given by [see Eq. (4.16)]

$$G_{Ai,Bi}^\sigma(i\omega_n) = \int d\epsilon \rho_{c\sigma}^0(\epsilon) G_{AB}^\sigma(\epsilon, i\omega_n), \quad (5.3)$$

$$\rho_{c\sigma}^0(\epsilon) = \frac{1}{N} \sum_{\vec{k}} \delta(\epsilon - \epsilon_{\vec{k}\sigma}). \quad (5.4)$$

Here $\rho_{c\sigma}^0(\epsilon)$ is the density of states of the uncorrelated s electron, and its detailed form is given by the energy-band calculation. A typical model density of states is given in the next section.

For s and f electrons, Eq. (5.3) yields

$$G_{ci,ci}^\sigma(z) = \int d\epsilon \frac{\rho_{c\sigma}^0(\epsilon)}{F_\sigma(z) - \tilde{\epsilon}}, \quad (5.5)$$

$$G_{fi,fi}^\sigma(z) = \frac{n_{c\sigma}^0}{z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z)} + \frac{|V|^2}{[z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z)]^2} G_{ci,ci}^\sigma(z), \quad (5.6)$$

$$F_\sigma(z) = z - \frac{|V|^2}{z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z)}, \quad (5.7)$$

$$n_{c\sigma}^0 = \int d\epsilon \rho_{c\sigma}^0(\epsilon). \quad (5.8)$$

We notice here that Eqs. (5.5) and (5.6) are analytic at the zero points of the equation $z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z) = 0$, provided V is finite. Analyticity of Eq. (5.5) is seen from the Taylor-series expansion

$$[F_\sigma(z) - \tilde{\epsilon}]^{-1} = \sum_{n=0}^{\infty} \{\epsilon/[F_\sigma(z) + \mu]\}^n,$$

$$a_1 + a_2 \Sigma + a_3 \Sigma^2 + a_4 \Sigma^3 = 0,$$

$$a_1 = \{\langle \xi^2 \rangle_{\text{FA}}\}^2 [-\tilde{\epsilon}_{f\sigma} + (1 + \alpha^2 V^2)z],$$

$$a_2 = -\{\langle \xi^2 \rangle_{\text{FA}}\}^2 \{2\tilde{\epsilon}_{f\sigma}^2 + \langle \xi^2 \rangle_{\text{FA}} - \alpha^2 V^4\} + \langle \xi^2 \rangle_{\text{FA}} \tilde{\epsilon}_{f\sigma} (4 + \alpha^2 V^2)z - \langle \xi^2 \rangle_{\text{FA}} (2 + \alpha^2 V^2)z^2, \quad (5.12)$$

$$a_3 = -\tilde{\epsilon}_{f\sigma} \{\tilde{\epsilon}_{f\sigma}^2 + 2\langle \xi^2 \rangle_{\text{FA}}\} + \{3\tilde{\epsilon}_{f\sigma}^2 + \langle \xi^2 \rangle_{\text{FA}} (2 - \alpha^2 V^2)\}z - 3\tilde{\epsilon}_{f\sigma} z^2 + z^3,$$

$$a_4 = -(\tilde{\epsilon}_{f\sigma}^2 + \alpha^2 V^4) + \tilde{\epsilon}_{f\sigma} (2 - \alpha^2 V^2)z + (-1 + \alpha^2 V^2)z^2,$$

$$\alpha = 2/D.$$

With given parameters D , $\epsilon_{f\sigma}$, V , and z , the coefficients of the cubic equation are calculated. The cubic equation has either three real roots or one real and two complex roots. The CPA condition (4.32) with $\langle v_\sigma \rangle_{\text{FA}} = 0$ indicates the equivalence of the nonzero imaginary part of the Green's function and that of the self-energy. Then the band edge is given by the condition that the discriminant of the cubic equation for the self-energy (5.12) is equal to zero. The resulting equation is, in general, a tenth-order algebraic equation for z . We can also obtain the cubic

with an assumption that moment of the model density of states is finite, say,

$$\left| \int d\epsilon \epsilon^n \rho_{c\sigma}^0(\epsilon) \right| < \infty.$$

Singular terms on the right-hand side of Eq. (5.6) cancel out at the zero points of $z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z) = 0$. The analytic properties mean absence of poles in $G_{ci,ci}^\sigma(z)$ and $G_{fi,fi}^\sigma(z)$ at the zero points of $z - \tilde{\epsilon}_{f\sigma} - \Sigma_\sigma(z) = 0$ and assure existence of the hybridization gap around $z = \tilde{\epsilon}_{f\sigma} + UN_{fi,-\sigma}$ at absolute zero temperature.

B. A model density of states

The model density of states we discuss here is the elliptic model density of states:

$$\rho_{c\sigma}^0(\epsilon) = \begin{cases} (2/\pi D)[1 - (\epsilon/D)^2]^{1/2}, & -D \leq \epsilon \leq D \\ 0, & \text{otherwise} \end{cases} \quad (5.9)$$

where D is the halfwidth of the uncorrelated s electron band. The total density of states is normalized to unity

$$\int_{-\infty}^{\infty} d\epsilon \rho_{c\sigma}^0(\epsilon) = 1. \quad (5.10)$$

Substituting Eq. (5.9) into Eq. (5.5), we obtain

$$G_{ci,ci}^\sigma(z) = \frac{2}{D} \left\{ \frac{F_\sigma(z)}{D} - \left[\left(\frac{F_\sigma(z)}{D} \right)^2 - 1 \right]^{1/2} \right\}. \quad (5.11)$$

Here the square root is two-valued. The sign should be taken such that density of states is non-negative, namely, the imaginary part of the Green's function is negative in the upper half-plane of the complex z plane.

The Green's function and the self-energy are given by Eqs. (4.32) with $\langle v_\sigma \rangle_{\text{FA}} = 0$, (5.11), and (5.6). We obtain cubic equations for the self-energy and Green's function after elementary but tedious calculations. The cubic equation for the self-energy is given by

equation for the Green's function of f electron, but the detailed expression is not written here.

VI. NUMERICAL CALCULATION

Essential parameters to describe the electronic states are D , N_e , $\epsilon_{f\sigma}$, V , U , and β . In order to clarify the physical meanings of the calculation, we decrease the number of parameters. First, we take the energy unit to half bandwidth D . Second, the electron number per site is 2 includ-

ing the spin degeneracy²³

$$N_e/N = 2. \quad (6.1)$$

In this case, the electronic state at 0 K is insulating, namely, the lower band below the hybridization gap around $z = \bar{\epsilon}_{f\sigma} + UN_{fi,-\sigma}$ is fully occupied and the upper band is empty, because the total number of electrons (the s and f electrons) in the lower band at 0 K is 2, irrespective of the other parameters. Third, without loss of generality, we assume electron-hole symmetry

$$\epsilon_{f\sigma} = -U/2. \quad (6.2)$$

In this case the real part of the Green's function is an odd function of the energy with respect to $\omega = \mu$, and the imaginary one is an even function. From the assumptions (6.1) and (6.2) and the electron-number conservation (3.2), the chemical potential does not depend on temperature. Then we move the origin of the energy so that the chemical potential is set equal to zero,

$$\mu = 0. \quad (6.3)$$

From the above assumptions, the parameters left are V , U , and β .

The phase diagram at 0 K is depicted in Fig. 2. The boundary of the formation of the local moment is drawn from Eq. (4.23). In the lower region of the boundary where the Coulomb repulsion is small and the hybridization is large, a paramagnetic insulating (PI) phase is stable. In this case, the single-site function $\psi(\xi)$ has a single minimum and is symmetric with respect to $\xi=0$. In the upper region of the boundary where the Coulomb repulsion is large and the hybridization is small, the paramagnetic state may be unstable and an ordered state of spin can appear. It may probably be the antiferromagnetic in-

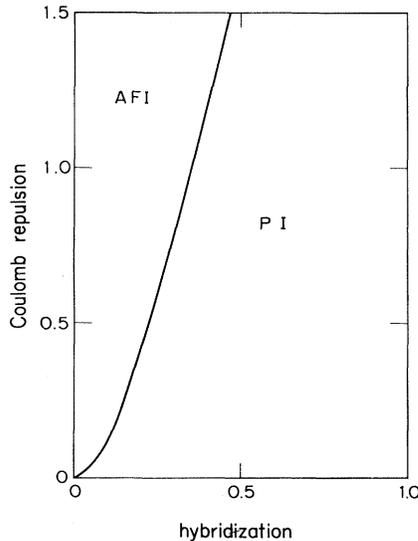


FIG. 2. Phase diagram at 0 K in the electron-hole symmetric case, showing the paramagnetic insulating (PI) phase and the antiferromagnetic insulating (AFI) phase. Energies are measured in units of the halfwidth of the uncorrelated s electron band.

ulating (AFI) state, which is consistent with other theoretical investigations within the Hartree-Fock approximation.^{21,25} The single-site function has a double-minimum structure (local moment case³⁶) and is symmetric with respect to $\xi=0$.

In the following we investigate the paramagnetic phase. The solution of Eq. (5.12) shows that when the spin-field fluctuation is small, the paramagnetic insulating phase with the hybridization gap appears. But with increasing fluctuation, the paramagnetic metal phase without the hybridization gap appears. In Fig. 3 we show the phase diagram of the paramagnetic insulator and metal (PM) in the $\langle \xi^2 \rangle_{FA} - V$ plane. (In Figs. 3–6, the subscript FA is omitted for brevity.) The boundary line is a monotonically increasing function of V . So, with increasing V , the large fluctuation is necessary for the nonmetal-metal transition, because the hybridization gap at 0 K increases.

We show the density of states for $V=0.3$ in Fig. 4. Before explaining the figure we notice the selected parameter. We restrict our calculation in the paramagnetic ground state. From Fig. 2 the large hybridization is favorable to the paramagnetic phase. From Fig. 3 the small hybridization is favorable to the nonmetal-metal transition with the small fluctuation. So we choose the typical value of V to 0.3. Figure 4(c) shows the density of states in the insulating phase. At 0 K, $\langle \xi^2 \rangle_{FA} = 0$; the hybridization gap appears around zero energy. Both the s and f electron density of states increase abruptly near the hybridization gap. The density of states for the f electron has sharp peaks and decreases with the factor $1/\omega^2$. In the case of two electrons per site, the lower bands for the s and f electrons are fully occupied and the upper bands are empty. The chemical potential lies in the center of the hybridization gap. With increasing the fluctuation, the bandwidth of s and f electrons increases and the hybridization gap decreases. The distance between peak positions of the f electron increases, which is consistent with the fluctuating field approximation. In Figs. 4(b) and 4(a) we show the density of states in the metallic phase. With increasing fluctuation, the hybridization gap disappears and

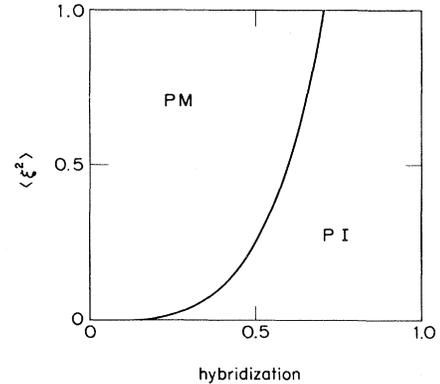


FIG. 3. Phase diagram at finite temperature in the paramagnetic phase in Fig. 2, showing the insulating (PI) phase and the metallic (PM) phase. The ordinate is the square of the spin-field fluctuation.

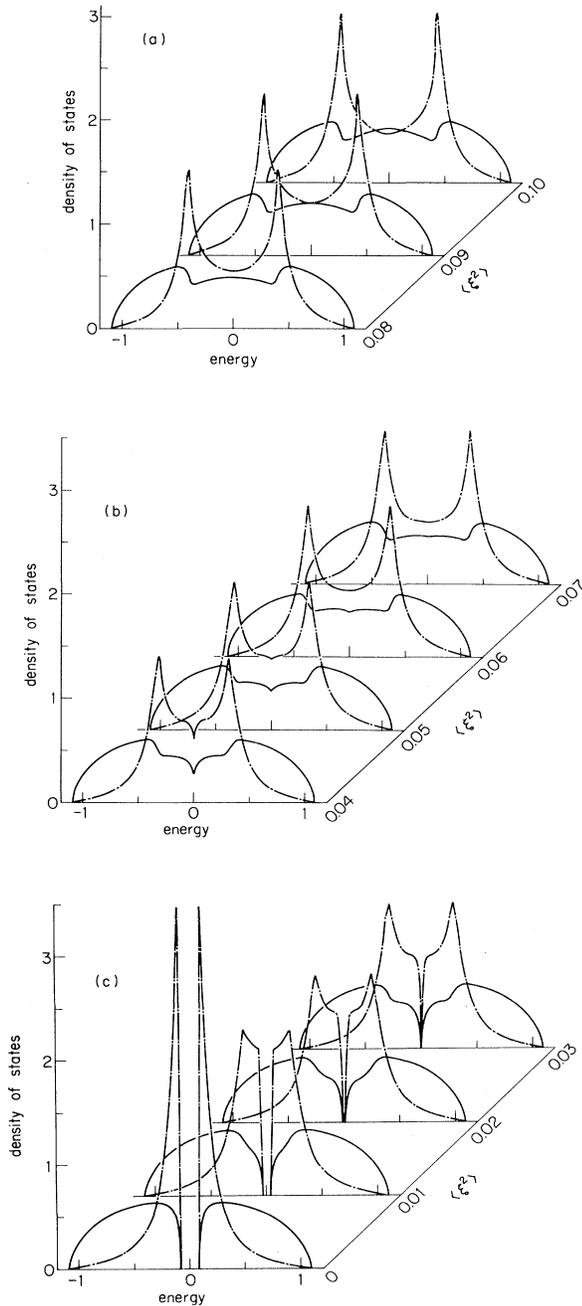


FIG. 4. Density of states in the paramagnetic phase with increasing spin-field fluctuation. Solid line denotes the density of states for the s electron and dot-dashed line denotes that for the f electron. (a) and (b) Metallic phase. (c) Insulating phase.

two bands merge into one band. This is the nonmetal-metal transition.

In Fig. 5 we show the hybridization gap and the density of states at the chemical potential as a function of the square of the fluctuation. The hybridization gap decreases with increasing $\langle \xi^2 \rangle_{FA}$. Above the transition point, the density of states of the s electron at the chemical potential

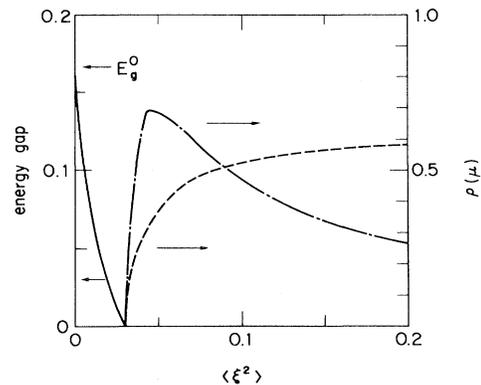


FIG. 5. Energy gap and density of states at the chemical potential as a function of the square of the spin-field fluctuation. Solid curve is energy gap, broken curve is density of states at the chemical potential for the s electron, and dot-dashed curve is that of the f electron.

rises abruptly, then increases slowly, while that of the f electron first rises, and then declines.

In Fig. 6 we show the relation between the square of the fluctuation and temperature at $V=0.3$ drawn from Eqs. (4.33) and (4.34). The fluctuation increases rapidly as a function of temperature with increasing U in the paramagnetic phase. The broken line in Fig. 6 is the square of the fluctuation where the hybridization gap disappears. From the cross points of broken and solid lines, we can obtain the transition temperature T_c where the hybridization gap disappears. With increasing U , the transition temperature is lowered in comparison with the bandwidth D . This is depicted in Fig. 7. We draw the transition temperature as a function of U with fixed V . We can see that for fixed V , the transition temperature is lowered with increasing U , which shows the importance of careful treatments of the electronic correlations. And for fixed U , the transition temperature is lowered with decreasing V , because the hybridization gap decreases. The parameters of U and V with zero T_c give the phase boundary line in Fig. 2.

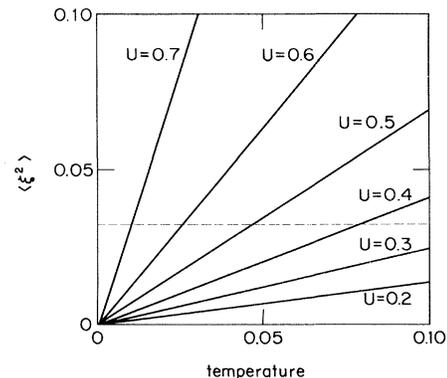


FIG. 6. Square of the spin-field fluctuation as a function of temperature. With increasing U , the gradient becomes abrupt.

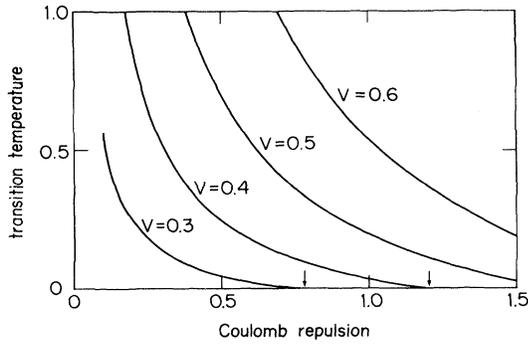


FIG. 7. Transition temperature as a function of the Coulomb repulsion.

In conclusion we summarize the numerical result. At 0 K, the paramagnetic insulator phase is stable in the U - V plane in Fig. 2. With increasing spin-field fluctuation, the hybridization gap decreases, and the electronic state changes its phase to the paramagnetic metal state. The square of the spin-field fluctuation increases in proportion to temperature. The spin-field fluctuation grows rapidly both with increasing temperature and with increasing U in the paramagnetic region.

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APPENDIX A: A GENERAL THEORY OF THE FUNCTIONAL INTEGRAL METHOD

In this appendix we describe a general formulation of the functional integral method, by which we can calculate the grand canonical ensemble average of any physical

$$\langle\langle T_{\tau} F\{A(\tau_1)A(\tau_2)\cdots A^{\dagger}(\tau_{n+1})A^{\dagger}(\tau_{n+2})\cdots\}\rangle\rangle = \frac{\langle T_{\tau} F\{a(\tau_1)a(\tau_2)\cdots a^{\dagger}(\tau_{n+1})a^{\dagger}(\tau_{n+2})\cdots\}U(\beta)\rangle}{\langle U(\beta)\rangle}. \quad (\text{A7})$$

Here the operators on the right-hand side are given by the interaction representation

$$a(\tau) = e^{\tau\hat{H}_0} a e^{-\tau\hat{H}_0}, \quad a^{\dagger}(\tau) = e^{\tau\hat{H}_0} a^{\dagger} e^{-\tau\hat{H}_0}, \quad (\text{A8})$$

and $\langle \rangle$ is the grand canonical ensemble average with the unperturbed Hamiltonian.

In the usual Feynman diagram method, $U(\beta)$ in Eq. (A6) is directly expanded in the power series of \hat{H}_I , and the series is substituted into Eq. (A7). The grand canonical ensemble average of the product of the operators is factorized by use of the Bloch-de Dominicis theorem. After resummation of the series, the numerator of Eq. (A7) is factorized into the sum of linked graphs and $\langle U(\beta)\rangle$. Then Eq. (A7) becomes a linked cluster expansion:

$$\langle\langle T_{\tau} F\{A(\tau_1)A(\tau_2)\cdots A^{\dagger}(\tau_{n+1})A^{\dagger}(\tau_{n+2})\cdots\}\rangle\rangle = \langle T_{\tau} F\{a(\tau_1)a(\tau_2)\cdots a^{\dagger}(\tau_{n+1})a^{\dagger}(\tau_{n+2})\cdots\}U(\beta)\rangle_{\text{linked}}. \quad (\text{A9})$$

In this method higher-order calculations are difficult, because the number of diagrams shows a catastrophic increase with increasing order of the expansion. Here we describe the functional integral method which allows us another approximation based on physical intuition.

An essential point of the functional integral method is

quantity in a physical system where the Coulomb interaction is introduced to the unperturbed system. The formulas described below are the natural generalization of the functional integral method for the free-energy calculation^{31,32} to that of any physical quantity.

Consider the grand canonical ensemble average of arbitrary function that consists of the product of the creation and annihilation operators in the Heisenberg representation. The average is taken with the total Hamiltonian:

$$\langle\langle T_{\tau} F\{A(\tau_1)A(\tau_2)\cdots A^{\dagger}(\tau_{n+1})A^{\dagger}(\tau_{n+2})\cdots\}\rangle\rangle. \quad (\text{A1})$$

Here $\langle\langle \rangle\rangle$ denotes the grand canonical ensemble average with the total Hamiltonian \hat{H} of the system, and is defined by

$$\langle\langle F\rangle\rangle = \text{Tr}(F e^{-\beta\hat{H}}) / \text{Tr} e^{-\beta\hat{H}}, \quad (\text{A2})$$

where $A(\tau)$ and $A^{\dagger}(\tau)$ are the operators in the Heisenberg representation

$$A(\tau) = e^{\tau\hat{H}} a e^{-\tau\hat{H}}, \quad (\text{A3})$$

$$A^{\dagger}(\tau) = e^{\tau\hat{H}} a^{\dagger} e^{-\tau\hat{H}}.$$

In order to calculate (A1), we introduce the interaction representation.³³ We decompose the total Hamiltonian into the unperturbed and perturbation parts

$$\hat{H} = \hat{H}_0 + \hat{H}_I. \quad (\text{A4})$$

Corresponding to this decomposition, we formally decompose the exponential function of \hat{H} into the exponential function of \hat{H}_0 and the other parts:

$$e^{-\beta\hat{H}} = e^{-\beta\hat{H}_0} U(\beta, 0). \quad (\text{A5})$$

The formal solution of $U(\beta, 0)$ is given by

$$U(\beta) \equiv U(\beta, 0) = T_{\tau} \exp \left[-\int_0^{\beta} d\tau \hat{H}_I(\tau) \right]. \quad (\text{A6})$$

Then the quantity defined by (A1) becomes

to rewrite $U(\beta)$, given by Eq. (A6), by use of (i) transformation of the interaction term to a quadratic form and (ii) an operator identity

$$e^{A^2} = \int_{-\infty}^{\infty} dx e^{-\pi x^2 \pm 2\sqrt{\pi} Ax}. \quad (\text{A10})$$

Here, the transformation of the Coulomb interaction

term to a quadratic form is not unique and leads to controversies as reviewed in the literature.^{31,32,35-41} If the physical quantity is calculated exactly, the final result is independent of the transformation for the interacting term. When an approximation is made, the final result may be different depending on the choice of the transformation. The choice of the transformation and approximation depends on the physical situation of the problem. The first controversy is the one-field (a spin-field) scheme³¹ versus the two-field (spin- and charge-field) scheme.³² The diagram analysis shows that the one-field scheme with use of a fermion operator identity $n_{fi\sigma}^2 = n_{fi\sigma}$ leads to unphysical contributions resulting from spurious interaction of equal spins.^{39,40} The two-field scheme we use here is free from the spurious contributions. The second controversy is concerned with rotational invariance of the spin-field term. There are two types of transformation for the interacting term: Ising-type^{32,36,37} and Heisenberg-type transformations.^{35,41} The most simple transformation of Ising type is given by

$$\hat{H}_I = \sum_i \left[-\frac{U}{4}(n_{fi\uparrow} - n_{fi\downarrow})^2 + \frac{U}{4}(n_{fi\uparrow} + n_{fi\downarrow})^2 \right]. \quad (\text{A11})$$

The Ising-type transformation itself preserves spin rotational invariance of the original Hamiltonian if both the spin and charge fields are treated on the same basis.³⁷ The spin-field term alone, however, does not have rotational invariance, which leads to the concept of the Heisenberg-type transformation. Examples of the Heisenberg-type transformation are given in the literature.^{35,41} The transformation of Heisenberg type preserves rotational invariance with respect to both the spin and charge fields, respectively.⁴¹ Also, the use of the vector spin field allows us the general description of the spin-field structure, the variation in magnitude as well as the direction of the spin field.³⁵ In the following we use the Ising-type transformation because of its simplicity.^{32,36,37}

From Eqs. (A10) and (A11) Eq. (A6) is rewritten as^{31,32,37}

$$U(\beta) = \int \prod_i \delta x_i(\tau) \delta y_i(\tau) \exp \left[-\int_0^\beta d\tau \sum_i \frac{\pi}{\beta} \{ [x_i(\tau)]^2 + [y_i(\tau)]^2 \} \right] S(\beta), \quad (\text{A12})$$

where

$$S(\beta) = T_\tau \exp \left[-\int_0^\beta d\tau \sum_{i,\sigma} v_{i\sigma}(\tau) n_{fi\sigma}(\tau) \right] \\ = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta \cdots \int_0^\beta d\tau_1 \cdots d\tau_n T_\tau \left[\sum_{i,\sigma} v_{i\sigma}(\tau_1) n_{fi\sigma}(\tau_1) \cdots \sum_{j,\sigma'} v_{j\sigma'}(\tau_n) n_{fj\sigma'}(\tau_n) \right], \quad (\text{A13})$$

$$v_{i\sigma}(\tau) = \left[\frac{\pi U}{\beta} \right]^{1/2} \sigma x_i(\tau) + i \left[\frac{\pi U}{\beta} \right]^{1/2} y_i(\tau). \quad (\text{A14})$$

Inserting Eqs. (A12)–(A14) to Eq. (A7), we obtain the final result

$$\langle\langle T_\tau F \{ A(\tau_1) A(\tau_2) \cdots A^\dagger(\tau_{n+1}) A^\dagger(\tau_{n+2}) \cdots \} \rangle\rangle = \left\langle \frac{\langle T_\tau F \{ a(\tau_1) a(\tau_2) \cdots a^\dagger(\tau_{n+1}) a^\dagger(\tau_{n+2}) \cdots \} S(\beta) \rangle}{\langle S(\beta) \rangle} \right\rangle_{\text{FA}}, \quad (\text{A15})$$

$$\langle f[x_1, x_2, \dots; y_1, y_2, \dots] \rangle_{\text{FA}} = \frac{\int \prod_i \delta x_i(\tau) \delta y_i(\tau) e^{-\beta\Psi} f[x_1, x_2, \dots; y_1, y_2, \dots]}{\int \prod_i \delta x_i(\tau) \delta y_i(\tau) e^{-\beta\Psi}}, \quad (\text{A16})$$

$$\Psi = \Psi[x_1, x_2, \dots; y_1, y_2, \dots] = \Psi_0 + \Psi_1, \quad (\text{A17})$$

$$\Psi_0 = \frac{\pi}{\beta^2} \int_0^\beta d\tau \sum_i \{ [x_i(\tau)]^2 + [y_i(\tau)]^2 \}, \quad (\text{A18})$$

$$\Psi_1 = -\beta^{-1} \ln \langle S(\beta) \rangle. \quad (\text{A19})$$

Equations (A15)–(A19) and (A13) and (A14) are the general and exact expressions.

The above formulas show that the average of any physical quantity is calculated by two steps in the functional integral method. The first step is to calculate the interior of $\langle \rangle_{\text{FA}}$ in Eq. (A15). It can be calculated by the usual diagram method. Its calculation is easier than that of Eq. (A9), because the exponential of $S(\beta)$ in Eq. (A13) contains only one-body potentials. The random one-body po-

tential contains a factor \sqrt{UT} , which means that the random field is effective with large U or high T .

The second step is to calculate the average by the functional integral with the weight $\exp(-\beta\Psi)$. The second step is much more difficult than the first one, because in Ψ , $2N_e$ variables get intertwined in a complex manner. We can do this complex calculation with an introduction of approximations based on physical pictures.

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