Realistic treatment of the self-energy formalism in heavy-fermion metals: Application to superconducting phases of $CeRu_2$ and $CeOs_2$

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A self-energy approximation is applied for obtaining the electronic structure of these two super-conducting heavy-fermion systems and we explain some of their main experimental features by analyzing the calculated total and partial density of states. The superconducting mechanism is discussed and we determine relations between the density of states and the superconducting parameters.

I. INTRODUCTION

The one-body scheme deduced from the band-structure models can explain the properties of the heavy-fermion (HF) systems.[1,2] The main difficulty for obtaining the electronic structure of the HF compounds is to find a potential for determining the dynamics of the heavy electrons.[1] This potential should reconcile the strong correlation of the f electrons with the translational symmetry of their Bloch wave functions (i.e., we should consider that the HF systems are f lattices and not an incoherent aggregation of impurities). In this paper we analyze the electronic structure of two HF compounds ($CeRu_2$ and $CeOs_2$) determined by means of a self-energy procedure. These compounds have received a great deal of experimental attention.[3-9] However, the theoretical interpretation of these results is in controversy, perhaps due to the deficiency of a clear systematic procedure for knowing the electronic structure of the HF systems.[10] The main feature of the density of states (DOS) of these two materials is the existence of a pseudogap between two $4f$ peaks close to the Fermi level. This pseudogap has been experimentally detected by thermal, magnetic, and electric measurements[5,9] and electron spin resonance,[7] and it is related to the superconducting mechanism of these compounds. In the second part of this work we perform a study from a set of equations which relates the descriptive parameters of the density of states curve with the physical variables of the superconducting behavior.

$CeRu_2$ and $CeOs_2$ are two nonmagnetic and superconducting HF systems which present intermediate valence, the f-electron count being less than one. The mechanism of the attractive electron-electron interaction is an open question since there is not a clear reason for considering these compounds either as BCS or HF superconductors.[5,8] On the other hand, $CeRu_2$ and $CeOs_2$ are two similar compounds since their respective ligand atoms (Ru and Os) are isoelectronic ($4d^6 5s^2$ and $5d^2 6s^2$) and the interatomic f-d hybridization is the main cause for the

appearance of the coherence pseudogap. These two facts produce similar DOS in both compounds. However, some subtle differences in their respective DOS in the vicinity of E_F are the cause of the difference between the superconducting properties of these two Ce systems.

II. METHOD OF CALCULATION

We start from the multiband Hubbard Hamiltonian

$$H = \sum_{k,\alpha} \varepsilon^0_{k\alpha} c^\dagger_{k\alpha} c_{k\alpha} + \frac{U}{2} \sum_{i,f,f'} c^\dagger_{if} c^\dagger_{if'} c_{if'} c_{if} , \qquad (1)$$

where the energies $\varepsilon^0_{k\alpha}$ are obtained from the following equation:

$$[-\nabla^2 + V^n_{MT}(I - P_f) + V^0_{MT} P_f] \varphi_{k\alpha}(\mathbf{r}) = \varepsilon_{k\alpha} \varphi_{k\alpha}(\mathbf{r}) , \qquad (2)$$

where V^0_{MT} is a muffin-tin self-consistent potential which contains no f-f repulsive interaction in order to avoid repetitions when considering the f-f Coulomb correlation. V^n_{MT} is the full muffin-tin self-consistent potential. $P_f(I)$ stands for the orbital projection operator corresponding to $l = 3$ (unity) (i.e., $P_f = \sum_m |3m\rangle\langle 3m|$ and $I = \sum_{lm} |lm\rangle\langle lm|$). The operators $c^\dagger_{if}$ and c_{if} are defined as

$$c_{if} = N^{-1/2} \sum_{k,\alpha} \langle f | k\alpha \rangle e^{i\mathbf{k}\cdot\mathbf{R}_i} c_{k\alpha} ,$$
$$c^\dagger_{if} = N^{-1/2} \sum_{k,\alpha} \langle k\alpha | f \rangle e^{-i\mathbf{k}\cdot\mathbf{R}_i} c^\dagger_{k\alpha} , \qquad (3)$$

i.e., we assume that the f states are band states with more or less $E(\mathbf{k})$ dispersion and they can be more or less hybridized with s, p, and d states. $|f\rangle$ are f orbitals defined in all f electron atoms and whose symmetries are compatible with the crystal. The Hamiltonian (1) is similar to the periodic version of the Anderson Hamiltonian since the f-d hybridization terms of this Hamiltonian are included in the calculation of the $\varepsilon^0_{k\alpha}$ spectrum.

Substitution of (3) into (1) leads to

$$H = H_0 + V = \sum_{k,\alpha} \varepsilon^0_{k\alpha} c^\dagger_{k\alpha} c_{k\alpha} + \frac{U}{2N} \sum_{f,f'} \sum_{k,k',q} \sum_{\alpha,\beta,\gamma,\delta} \langle k\alpha | f \rangle \langle k'\beta | f' \rangle \langle f' | (k'+q)\gamma \rangle$$
$$\times \langle f | (k-q)\delta \rangle c^\dagger_{k\alpha} c^\dagger_{k'\beta} c_{(k'+q)\gamma} c_{(k-q)\delta} . \qquad (4)$$

$\alpha, \beta, \gamma, \delta$ are the band indices. The interaction line is defined as

$$\langle \mathbf{k}\alpha, \mathbf{k}'\beta \mid V \mid (\mathbf{k}-\mathbf{q})\delta, (\mathbf{k}'+\mathbf{q})\gamma \rangle = U \sum_{f,f'} \langle \mathbf{k}\alpha \mid f \rangle \langle \mathbf{k}'\beta \mid f' \rangle \langle f' \mid (\mathbf{k}'+\mathbf{q})\gamma \rangle \langle f \mid (\mathbf{k}-\mathbf{q})\delta \rangle . \tag{5}$$

The U parameter of this equation stands for the totally screened Coulomb correlation energy. Several procedures for obtaining the U energy can be drawn from the literature.[11-13] All of them determine U by calculating the difference between the total energies of the crystal with two different configurations, i.e.,

$$U = N^{-1}\{[E(4f^{n+1}) - E(4f^n)]$$
$$- [E(4f^n) - E(4f^{n-1})]\} , \tag{6}$$

where $E(4f^{n+1}) + E(4f^{n-1})$ is the total energy of the crystal when considering an electronic transference of one f electron between two f electron atoms in each unit cell, and $E(4f^n)$ is the same energy before the electronic transference. Then, the Coulomb correlation energy has the meaning of the effective interaction between the localized $4f$ electrons. Therefore, this definition of U can justify the consideration of a first-order approximation for the self-energy.

This self-energy in this one-line approximation becomes

$$M_{\alpha\gamma}(\mathbf{k}) = \langle \mathbf{k}\alpha \left[U \sum_{f,f'} (\langle n_{f'} \rangle \mid f \rangle \langle f \mid \right.$$
$$\left. - \langle n_{ff'} \rangle \mid f \rangle \langle f' \mid) \right] \mid \mathbf{k}\gamma \rangle , \tag{7}$$

where

$$\langle n_{ff'} \rangle = -iN^{-1} \sum_{\mathbf{q},\lambda,\mu} \langle f \mid \mathbf{q}\lambda \rangle \langle \mathbf{q}\mu \mid f' \rangle G_{\lambda\mu}(\mathbf{q},0^-) ,$$

$$\langle n_f \rangle = \langle n_{ff} \rangle , \tag{8}$$

$$G_{\lambda\mu}(\mathbf{q},0^-) = i \langle c^\dagger_{\mathbf{q}\mu} c_{\mathbf{q}\lambda} \rangle .$$

The terms $\langle n_{ff'} \rangle = 0$ if $f \neq f'$ because of the compatibility of the $\mid f \rangle$ orbitals with the crystal symmetry.

The Green function is a matrix whose dimension is the number of bands with states containing $l = 3$ component. This matrix can be obtained from the equation

$$\mathbf{G}(\mathbf{k},\omega) = [\mathbf{I} - \mathbf{G}_0(\mathbf{k},\omega)\mathbf{M}(\mathbf{k})]^{-1}\mathbf{G}_0(\mathbf{k},\omega) , \tag{9}$$

$$[\mathbf{G}_0(\mathbf{k},\omega)]_{\alpha\beta} = \left[\frac{n_{\mathbf{k}\alpha}}{\omega - \varepsilon^0_{\mathbf{k}\alpha} - i\delta} + \frac{1 - n_{\mathbf{k}\alpha}}{\omega - \varepsilon^0_{\mathbf{k}\alpha} + i\delta} \right] \delta_{\alpha\beta} ,$$

$\varepsilon^0_{\mathbf{k}\alpha}$ is the energy spectrum of the noninteracting system. The poles of the function $\det \mathbf{G}(\mathbf{k},\omega)$ are the new spectrum $(\varepsilon_{\mathbf{k}\alpha})$ of the interacting system. The new electron wave functions are obtained by means of the following Schrödinger-like equation:

$$h_0(\mathbf{r})\varphi_{\mathbf{k}\alpha}(\mathbf{r}) + \int M(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}')d^3r' = \varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \tag{10}$$

where $h_0(\mathbf{r})$ is the band Hamiltonian corresponding to $\varepsilon^0_{\mathbf{k}\alpha}$ [i.e., Eq. (2)]; and $M(\mathbf{r},\mathbf{r}')$ is the real space representation of $M(\mathbf{k})$. This potential $M(\mathbf{r},\mathbf{r}')$ is given by

$$M(\mathbf{r},\mathbf{r}') = U \sum_f (n - \langle n_f \rangle)\varphi_f(\mathbf{r})\varphi_f^*(\mathbf{r}') , \tag{11}$$

where $n = \sum_f \langle n_f \rangle$. Equation (10) can also be written as

$$[-\nabla^2 + V^n_{MT}(\mathbf{r})]\varphi_{\mathbf{k}\alpha}(\mathbf{r}) + \int d^3r' V(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}')$$
$$= \varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \tag{12}$$

where $V(\mathbf{r},\mathbf{r}')$ takes the form

$$V(\mathbf{r},\mathbf{r}') = \sum_f \{ U(n - \langle n_f \rangle)$$
$$- [V^n_{MT}(\mathbf{r}) - V^0_{MT}(\mathbf{r})]\}\varphi_f(\mathbf{r})\varphi_f^*(\mathbf{r}') . \tag{13}$$

When $V = 0$ the resulting equation is the standard local density (LD) band Hamiltonian.

The problem in HF systems raises when an orbital f is partially occupied in all f electron atoms of the crystal. Since the f bands arising from the totally occupied orbitals can be treated by means of the local density formalism.[14,15] $V(\mathbf{r},\mathbf{r}')$ can be also written as

$$V(\mathbf{r},\mathbf{r}') = V_{occ}(\mathbf{r},\mathbf{r}') + \Sigma(\mathbf{r},\mathbf{r}') , \tag{14}$$

where

$$\Sigma(\mathbf{r},\mathbf{r}') = \sum_f U(1 - \langle n_f \rangle)\varphi_f(\mathbf{r})\varphi_f^*(\mathbf{r}') , \tag{15}$$

and

$$V_{occ}(\mathbf{r},\mathbf{r}') = \sum_f \{ U(n - 1)$$
$$- [V^n_{MT}(\mathbf{r}) - V^0_{MT}(\mathbf{r})]\}\varphi_f(\mathbf{r})\varphi_f^*(\mathbf{r}') . \tag{16}$$

The difference between $V^n_{MT}(\mathbf{r})$ and $V^0_{MT}(\mathbf{r})$ gives the local Coulomb repulsion potential for an f electron produced by the other $n - 1$ electrons. Therefore, this difference should be equal to $U(n - 1)$ according to the definition of U. This is not exact because the ways for obtaining the muffin-tin potentials and U are not equal. In addition, as we say above,

$$\int d^3r' V_{occ}(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}') = \Delta V_{ex,c}(\mathbf{r})\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \tag{17}$$

where $\Delta V_{ex,c}(\mathbf{r})$ is a correction to the local exchange and correlation potential $V_{ex,c}(\mathbf{r})$. $\Delta V_{ex,c}(\mathbf{r})$ and $V_{ex,c}(\mathbf{r})$ are included within $V^n_{MT}(\mathbf{r})$ and $\Delta V_{ex,c}(\mathbf{r})$ can be arbitrarily small if one conveniently determines the potential $V^n_{MT}(\mathbf{r})$.

In our method, we calculate the radial wave functions of the orbitals $\varphi_f(\mathbf{r})$ at the energies of the eigenvalues. This fact implies that Σ produces effects in each $\varphi_{\mathbf{k}\alpha}(\mathbf{r})$ state according to its spatial localization since the localization of the f orbitals strongly depends on the energy. The radial part of these functions $\varphi_f(\mathbf{r}, \varepsilon_{\mathbf{k}\alpha})$ are obtained by means of the renormalized atom approach[11-13] and are truncated at the muffin-tin radii of the f-electron atoms. Therefore, Eq. (12) can also be written as

$$[-\nabla^2 + V_{MT}^n(\mathbf{r})]\varphi_{\mathbf{k}\alpha}(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha})\varphi_{\mathbf{k}\alpha}(\mathbf{r}')$$

$$= \varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \quad (18)$$

with

$$\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha}) = U \sum_f (1 - \langle n_f \rangle)\varphi_f(\mathbf{r},\varepsilon_{\mathbf{k}\alpha})\varphi_f^*(\mathbf{r}',\varepsilon_{\mathbf{k}\alpha}) . \quad (19)$$

An equivalent equation to (9) has to be developed to introduce the potential $\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha})$ instead of $M(\mathbf{r},\mathbf{r}')$. Then Eq. (9) will read

$$G(\mathbf{k},\omega) = [I - G_0(\mathbf{k},\omega)\Sigma(\mathbf{k},\omega)]^{-1}G_0(\mathbf{k},\omega) , \quad (20)$$

where G_0 is the Green function corresponding to a spectrum deduced from the standard LD potential (i.e., with $\Sigma = 0$). The potential Σ commutes with all crystal symmetries of the point group if the terms $\langle n_f \rangle$ are equal for all bases of each f subspace of the decomposition $D_7(2l+1) = \Gamma_2' \oplus \Gamma_{15} \oplus \Gamma_{25}$ (this decomposition corresponds to the groups O_h). Moreover, Σ is compatible with the translational crystal symmetries because $\langle n_f \rangle$ is equal for all f-electron atoms.

The main effect of this Σ correction is to split the different f symmetries according to their occupation number $\langle n_f \rangle$ producing a multiple Hubbard splitting whose average interband separation is $\sim U(\langle n_{f'} \rangle - \langle n_f \rangle)$. This splitting rises because the nonlocal term depends on $\langle n_f \rangle$. On the other hand, the appearance of the $\langle n_f \rangle$'s in the self-energy is due to the exchange diagrams which only produce nonvanishing effects in the case of the degenerated f symmetries. Equations (8), (18), (19), and (20) are solved self-consistently. For the zero iteration, we obtain the parameters $\langle n_f \rangle$ from Eq. (8) considering G_0 instead of G. So, we determine Σ and G for the following iteration. For successive iterations the $\langle n_f \rangle$'s are self-consistently obtained. The technical details of the band-calculation method for solving similar equations to (18) are given in Refs. 15–17.

An important point is the conservation of the Luttinger theorem in our calculations. This theorem implies that the k-space volume occupied by the f states (or $f + d$ states if there is fd hybridization) below E_F is independent of the value of the U energy. In our results the f-electron count is conserved for $U \neq 0$ with respect to the case $U = 0$ and this implies the verification of this theorem, since we consider the homogeneity of the charge state in all f-electron atoms. The small variations of the f-electron count versus the U energy are produced by the dependence of the hybridizations on U. The model described in this section is similar to that given in Ref. 18 and the self-energy functional of (19) accomplishes the two conditions required in Ref. 19; i.e., $H_0 + \Sigma$ is Hermitical and Σ conserves the f-electron count n.

III. ELECTRONIC STRUCTURE

We analyze the electronic structure of CeRu$_2$ and CeOs$_2$ from $\varepsilon_{\mathbf{k}\alpha}$ deduced from Eq. (18) and the DOS and partial f-electron DOS determined by means of the tetrahedron division method.[20] The band structures of CeOs$_2$ and CeRu$_2$ are two clear and similar examples of

fd bands with strong interatomic hybridization (see Figs. 1 and 2). In both figures, the bands from the conduction bandbottom up to 0.7 Ry arise from $5d$ orbitals of Os and Ru, respectively, which gradually become hybridized with the f orbitals of Ce which are located just above E_F in CeOs$_2$ and at E_F in CeRu$_2$. As a consequence, the f count is smaller than the unity in CeOs$_2$ (~ 0.38 evenly divided per spin direction) and more close to 1 for CeRu$_2$ (~ 0.72 also evenly divided per spin direction).

Figures 3(a) and 3(b) and 4(a) and 4(b) show the DOS and the f-electron DOS of CeRu$_2$ (CeOs$_2$), respectively. The splitting between the occupied and unoccupied f symmetries produced by the potential Σ yields different f peaks in the DOS and f-electron DOS. There is a clear similarity in both DOS; however, the location of E_F is different. In CeRu$_2$, E_F lies at the minimum of the DOS between two f structures arising from the hybridization of the f orbital $R_3(|\mathbf{r}|)xyz/r^3$ and the d orbitals of Ru [see Figs. 5(a) and 6(a)]. In CeOs$_2$, E_F is just below the first peak of the double f structure arising from the same fd hybridization [see Figs. 5(b) and 6(b)].

The DOS obtained for CeRu$_2$ is in agreement with the available experimental data. Actually, the XPS results given by Allen et al.[3] and Gunnarsson et al.[4] present an f structure close to (and below) E_F and a value of $n \sim 0.8$ which is in agreement with our results. Moreover, the specific heat determined by Sereni[21] and Hiebl et al.[5] implies a DOS at the Fermi level of around 28.02 states/[(Ry)(cell)(spin direction)] which also agrees with our results ~ 31 states/[(Ry)(cell)(spin direction)]. In addition, the pattern of a pseudogap for the DOS where E_F is located [see Figs. 5(a) and 6(a)] reconciles the small value of specific heat of CeRu$_2$ with the presence of an f structure close to E_F.

We do not dispose of XPS of CeOs$_2$ to be compared with our DOS results. However, Schlott et al.[7] suggested from electron spin resonance (ESR) measurements that the location of E_F just below an f structure is the main cause for the nonlinear behavior of the ESR linewidth versus the temperature which is in qualitative agreement with results of Figs. 5(b) and 6(b). On the oth-
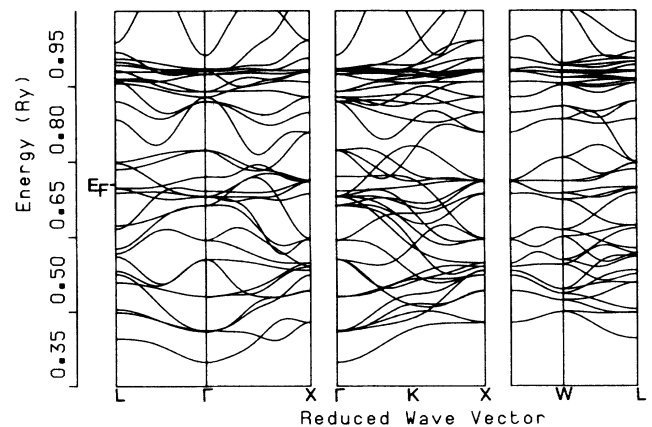

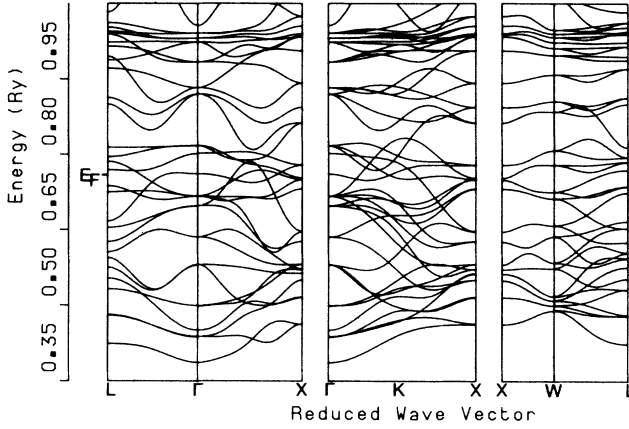FIG. 1. Band structure of CeRu$_2$ performed with $U = 0.53$ Ry.

FIG. 2. Band structure of $CeOs_2$ performed with $U = 0.55$ Ry.

er hand, the value of the f-electron count (0.19 per spin direction) and the corresponding Ce valence (3.6) is in agreement with the magnetic susceptibility and specific-heat measurement given by Hiebl et al.[5]

IV. STONER INSTABILITY

The Stoner enhancement factor (F_S) corresponding to the paramagnon effect has great relevance in the specific heat, magnetic behavior, and the superconducting mechanism of the HF compounds.[22] This factor is given by

$$F_S = [1 - IN(E_F)]^{-1} ,$$

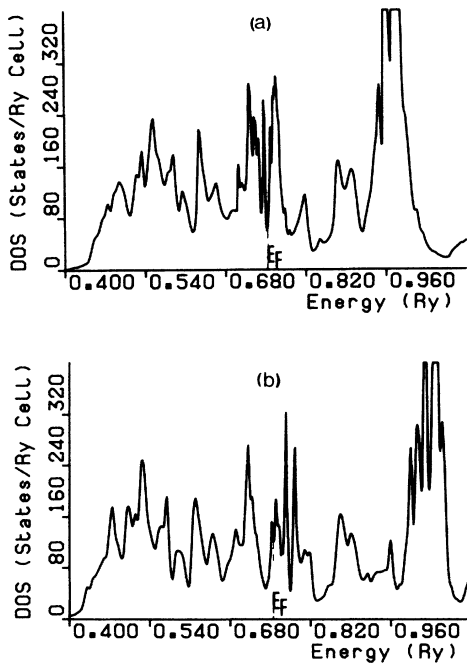where $N(E_F)$ is the DOS at E_F, and I corresponds to the repulsive interaction between those electrons located near
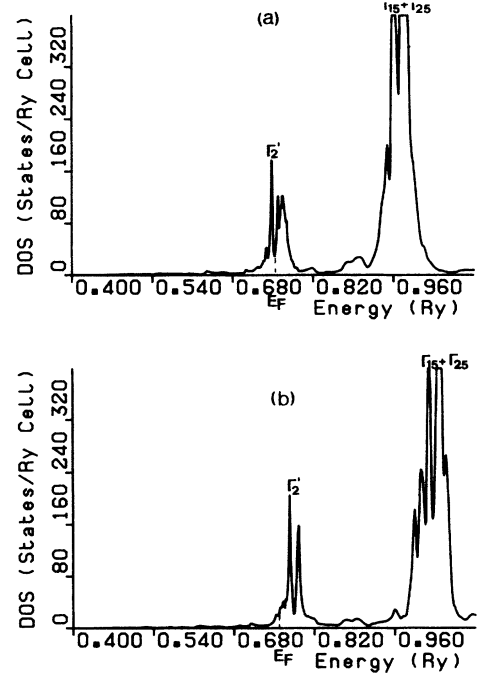

FIG. 4. (a) f-electron DOS of $CeRu_2$. (b) f-electron DOS of $CeOs_2$.

E_F. One can consider the HF system constituted by a mixing of two Fermi liquids, one of them corresponding to the f electrons and the other, to the nonlocalized electrons. Then, it is necessary to differentiate the HF electrons at E_F $[N_f(E_F)]$ from those non-HF electrons $[N(E_F) - N_f(E_F)]$. In the HF liquid, the f states are hybridized with other extended bandstates, then their Bloch
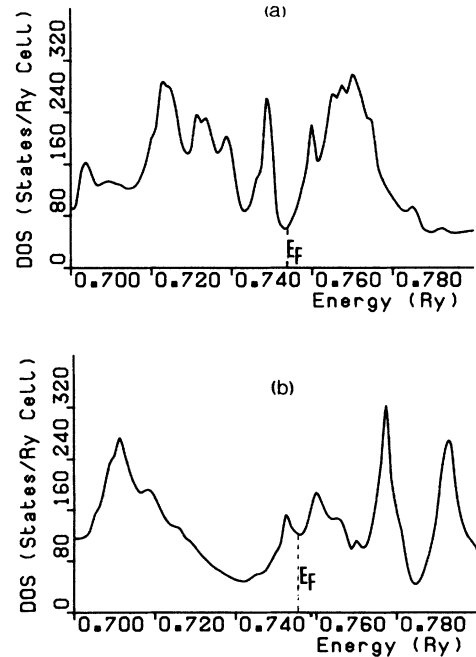

FIG. 3. (a) Total DOS of $CeRu_2$. (b) Total DOS of $CeOs_2$.

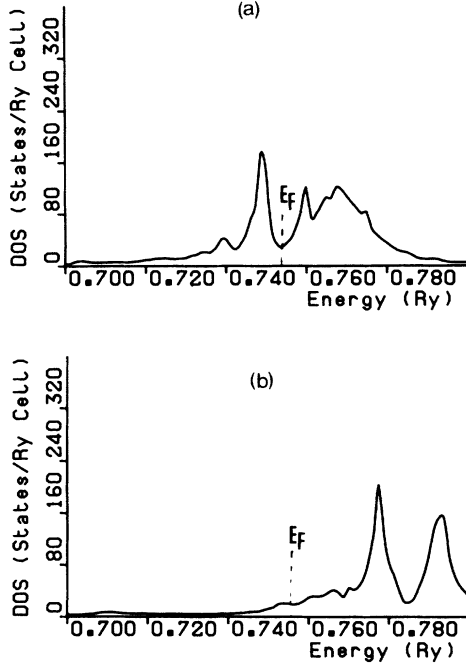FIG. 5. (a) Detailed DOS of $CeRu_2$ close to E_F. (b) Detailed DOS of $CeOs_2$ close to E_F

FIG. 6. (a) Detailed f-electron DOS of $CeRu_2$ close to E_F. (b) Detailed f-electron DOS of $CeOs_2$ close to E_F.

wave functions $| k\alpha \rangle$ can be considered as

$$| k\alpha \rangle = \sqrt{n} \, | kf \rangle + \sqrt{1-n} \, | kc \rangle \ , \tag{21a}$$

where $| kf \rangle$ is a state belonging to a pure f band and $| kc \rangle$ is an extended conduction bandstate. So,

$$I = \langle k\alpha k'\alpha' \, | \, V \, | \, k\alpha k'\alpha' \rangle \simeq Un^2 \ , \tag{21b}$$

U being the Coulomb correlation energy, and n being the f count per spin direction in each f-electron atom for a nonmagnetic HF system. Therefore, F_S for the HF liquid can be written as

$$F_S = [1 - Un^2 N_f(E_F)]^{-1} \ . \tag{22}$$

In the two cases analyzed in this paper, the values of U, n, $N_f(E_F)$, and E_F are given in Table I, and the values of F_S for $CeRu_2$ and $CeOs_2$ are 13.4 and 1.2, respectively. This means that $CeRu_2$ is closer to the magnetic transition than $CeOs_2$. Actually, for $Un^2N_f(E_F)=1$, F_S diverges and then a spontaneous magnetic transition occurs, since the electronic susceptibility takes the form $X=X_0F_S$, X_0 being the electronic susceptibility of the noninteracting systems. It is remarkable that the sign of

TABLE I. Different numerical results concerning the DOS of $CeRu_2$ and $CeOs_2$. Energies of E_F are given in Ry. The parameter n stands for the f-electron count.

	E_F	$N(E_F)$	n	$N_f(E_F)$	U
$CeRu_2$	0.7540	31.39	0.719	14.218	0.53
$CeOs_2$	0.7572	64.04	0.376	9.607	0.55

F_S is positive in both $CeRu_2$ and $CeOs_2$, and this implies that the HF superconductivity is possible in both cases. Under hydrostatic pressure, U remains almost constant but n and $N_f(E_F)$ become substantially modified. Therefore, the formation of localized magnetic moments can occur in $CeRu_2$ and $CeOs_2$ when applying the external stress.

V. SUPERCONDUCTING PROPERTIES

The superconductivity in the Ce systems is an open question. This question is more intriguing in $CeRu_2$ and $CeOs_2$ than other Ce compounds since the optical spectroscopies detect the f structures close to E_F, which could imply an HF superconductivity, and, however, the tunnel spectrum ensures a superconducting gap around 1.6 meV for $CeRu_2$ which points out a tendency towards the BCS superconductivity. Our results do not clarify this dilemma *a priori* since close to E_F there is a similar number of f states and other extended states, and this induces a supplementary difficulty for discerning the superconducting mechanism.

The governing parameters in the superconductivity are Δ and T_C and the relation between them in $CeRu_2$ is $2\Delta \simeq 7k_B T_C$ (Ref. 5) which is double that foreseen by all BCS theories. Therefore, it is logical to look for other explanations for the electrical behavior of these two compounds.

In this section we shall discuss, for the electronic structure, the possible mechanism for the superconductivity of $CeRu_2$ and $CeOs_2$. We start from the superconductivity gap equations and the formulation of the attractive e-e interaction according to the Anderson-Brinkmann theory:[22]

$$\Delta_k(0) = - \sum_{k'} V_{k'-k} \langle c_{-k'} c_{k'} \rangle_0 \ , \tag{23}$$

$$\Delta_k(T) = - \sum_{k'} V_{k'-k} \langle c_{-k'} c_{k'} \rangle_T \ , \tag{24}$$

$$V_{k'-k} = \frac{-1}{2} Un^2 [1 - Un^2 X(k'-k)]^{-1} \ , \tag{25}$$

where $\langle \ \rangle_0 (\langle \ \rangle_T)$ stands for the expected value for a zero (T) temperature; X is the magnetic susceptibility corresponding to the $\varepsilon_{k\alpha}$ spectrum deduced with the method of the former section.

The evidence of a gap in the I-V curves of the tunnel current in the SM devices of $CeRu_2$ (Ref. 8) leads to conclusions in the reasonable validity of the isotropic conditions for the pair potential. Therefore, we assume that $\Delta_k \simeq \Delta$ and $V_k \simeq V_0$, where Δ is the experimental value which we consider as an average value of Δ_k, and V_0 is the pair potential in the Brillouin-zone center (Γ). Equations (23), (24), and (25) can be written as

$$-1 = \frac{V_0}{2} \int_{-\hbar\omega}^{\hbar\omega} N_f(\epsilon) \frac{d\epsilon}{(\epsilon^2 + \Delta^2)^{1/2}} \ , \tag{26}$$

$$-1 = \frac{V_0}{2} \int_{-\hbar\omega}^{\hbar\omega} N_f(\epsilon) \tanh \left[\frac{\epsilon}{2kT_C} \right] \frac{d\epsilon}{\epsilon} \ , \tag{27}$$

$$V_0 = \frac{-1}{2} \frac{Un^2}{[1 - Un^2 N_f(E_F)]} \ . \tag{28}$$

$\hbar\omega$ is the bandwidth around E_F where the pair potential is nonvanishing and $N_f(\epsilon)$ is the partial f-electron DOS previously calculated. We determine V_0 by means of Eq. (28) and according to this expression both CeOs$_2$ and CeRu$_2$ can be superconductors since $Un^2N_f(E_F)$ is less than unity in both cases. $|V_0|$ is larger for CeRu$_2$ than for CeOs$_2$ (0.22 Ry for CeRu$_2$ and 0.012 Ry for CeOs$_2$) due to the different values of n and $N_f(E_F)$. The experimental values for Δ and T_C for CeRu$_2$ are 1.6 meV and 7 K, respectively, and the value of $\hbar\omega$ can be calculated either by Eq. (26) or (27). Then, the simultaneous verification of (26) and (27) implies that the value for the pair potential V_0 can be correct. The differences between Eqs. (26), (27), and (28) from the corresponding BCS equations are the consideration of $N_f(\epsilon)$ within the integrand instead of $N(\epsilon)-N_f(\epsilon)$ and the way for obtaining the pair potential. Besides, the large gradients, versus the energy, in the f-electron DOS hinders consideration of the $N_f(\epsilon)$ constant in the integration interval, as it is considered in the standard BCS model.

We have obtained $\hbar\omega$ (0.6 meV in CeRu$_2$) from Eq. (26) considering the experimental value for Δ and the V_0 deduced from (28). We wish to remark that $\hbar\omega$ is so small because V_0 is very large. Taking into account this $\hbar\omega$ in (27), we obtain a T_C of around 9 K which is 30% larger than the experimental value. If we determine $\hbar\omega$ from (27) considering the experimental value for T_C and the above-mentioned V_0, we obtain $\Delta \simeq 1.2$ meV which is 25% less than the experimental data. The differences between calculated and experimental values for Δ and T_C can be attributed to anisotropy in the pair potential which is neglected in these calculations. The same analysis for CeOs$_2$ seems to exclude the superconducting behavior for the cubic Laves phase of this alloy since we have not found any T_C for which these equations were compatible. Some authors have also stated the inexistence of a T_C from resistivity measurements in this compound.[9]

From the former discussion, we conclude that CeRu$_2$ can be a HF superconductor. Besides, the pseudogap at E_F in the f-electron DOS is an important feature for finding the attractive pair interaction. Actually, if E_F is located in the f peaks, as it is in the DOS determined by local-density formalisms, $N_f(E_F)$ is much larger than the value that produces the Stoner instability [i.e., $1 = Un^2N_f(E_F)$]. Finally, we have to recognize that the extreme sensitivity of the F_S factor before variations of the f-electron count and $N_f(E_F)$ requires a great prudence in the quantitative conclusions.

VI. FLUCTUATION OF THE f COUNT

In this section we analyze the relation between the properties of the charge-density fluctuation (CDF) and the superconducting instability of the HF systems. The CDF becomes defined by the fluctuation of the f-electron count (Δn). This is a parameter with a crucial influence in both the magnetic order and the appearance of the superconducting transition in the HF systems. Δn can be

determined by means of the indetermination of the operator $n = \sum_f c_f^\dagger c_f$ and this is given by[23,24]

$$(\Delta n)^2 = \langle n \rangle^2 - \langle n^2 \rangle = \sum_f (\langle n_f \rangle - \langle n_f \rangle^2)$$

$$= n - \sum_f \langle n_f \rangle^2 . \qquad (29)$$

The quantum indetermination Δn implies a supplementary Coulomb correlation energy for each f site defined as

$$\Delta E_c = \tfrac{1}{2} U (\Delta n)^2 . \qquad (30)$$

The tendency of the f systems is towards the minimum indetermination, i.e., $\Delta n \to 0$. This implies that the f orbitals tend either to the total occupation or total unoccupation; however, this tendency is compensated for by the variation of the V_{MT}^n before the changes in the f count produced by the minimization of the term ΔE_c. For the cases with $\Delta n \neq 0$, different instabilities such as Kondo, magnetic and superconducting transitions can appear.

In the Ce systems crystallizing in cubic symmetry and with a $4f^n$ configuration between 1 and 0, the f electrons are localized in the f orbital XYZ because of the nonlocal effects defined in Eq. (19). This occurs in the two cases studied in this paper since $\langle n_{XYZ\sigma} \rangle = \langle n_{XYZ-\sigma} \rangle = 0.19$ (0.36) for CeOs$_2$ (CeRu$_2$) (it must be remembered that both alloys are nonmagnetic at room pressure). This implies that both CeRu$_2$ and CeOs$_2$ are two charge-density fluctuators whose indetermination in the f count is

$$\Delta n = \left[\sum_\sigma (\langle n_{XYZ\sigma} \rangle - \langle n_{XYZ\sigma} \rangle^2 \right]^{1/2} = 0.66 \text{ and } 0.56 ,$$

respectively [the values for $\langle n_{XYZ\sigma} \rangle$ are determined by expression (8)]. The maximum value of Δn for a nonmagnetic Ce systems is 0.71 which corresponds to the case of $\langle n_{XYZ\sigma} \rangle = 0.5$. Therefore, the valence fluctuation for these two compounds is close to the maximum and larger in CeRu$_2$ than in CeOs$_2$.

There is an intriguing correspondence between the indetermination of n and the appearance of the HF superconductivity. When $\Delta n = 0$, the f count tends either to 1 or 0. For the cases with $n \simeq 1$, $\langle n_{XYZ\sigma} \rangle \to 1$ and $\langle n_{XYZ-\sigma} \rangle \to 0$ since this is the only case for which $\Delta n = 0$. This fact implies a magnetic order and the bands are spinbands occupied by one electron. In this situation, the Σ potential shifts down (up) the spinbands arising from the orbital $XYZ\sigma$ ($XYZ - \sigma$) and then $N_f(E_F) \to 0$, hindering the appearance of the HF superconductivity (all these facts occur in γ-CeAl$_2$).[25] On the other hand, the shift down suffered by the occupied spinbands leads to an increase of the f localization and a decrease of the fd hybridization which is also coherent with the interdition of the HF superconducting state.[6] Moreover, $N_f(E_F) = 0$ implies that F_S is close to unity so that the Stoner transition is forbidden. When $\Delta n \neq 0$, E_F is located near the f structures of the DOS, the magnetic order usually disappears and the f-electron DOS can be such that Eqs. (26), (27), and (28) are compatible for a finite value of T_C as it occurs in CeRu$_2$.

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