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Method for analyzing the ground state of intermediate-valence systems: Application to metallic SmS

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We give a method of obtaining the electronic structure of the ground state of intermediate-valence systems by means of a nonlocal potential deduced by the variations of the total energy with the number of f electrons. In addition, we deduce this potential from the Green's function for interacting f systems and we calculate the band structure and the density of states of golden-phase SmS for several values of the energy U and lattice parameters.

I. INTRODUCTION

The band-structure scheme can be useful for explaining the properties of the ground state of some intermediate-valence (IV) and heavy-fermion (HF) systems.[1] In these systems, the f states are hybridized with other bandstates and this implies that the band effects can be larger than the disorder effects produced by the localization.[1,2] The main difficulty for obtaining the electronic structure of the IV and HF compounds is to find a potential for determining the dynamics of the heavy electrons.

SmS has two different phases[3-9] (black and golden) corresponding to semiconducting and metallic behaviors and the phase transition is produced by hydrostatic pressure. The SmS metallic phase is an IV compound which has been the subject of several investigations.[3-15] However, the theoretical density of states corresponding to the ground state is not well known. This IV material presents an experimental pseudogap δ similar to that of SmB$_6$) which splits off two 4f peaks in the density of states (DOS) and is located close to the Fermi energy.[3,13] The coherent f-d hybridization can be a cause for the appearance of these 4f peaks and then the consideration of these IV or HF materials as incoherent aggregation of f-electron atoms is dubious.[1-3,8,13] Therefore, the f electrons should be treated by means of one-body wave functions with all symmetries of the crystal spatial group.

In this paper, we give two procedures for determining the electronic structure of the IV or HF compounds and we calculate the band structure and the DOS for metallic SmS considering different values for the Coulomb correlation energy and lattice parameter (a). Our main objectives are the analysis of the f-d hybridization and the study of the conditions for an appearing pseudogap between two 4f peaks at the Fermi level. Both points, the f-d hybridization and the pseudogap, have been experimentally detected by low-energy spectroscopy and resistivity measurements.[3,13]

II. METHOD

The potential for obtaining the one-body spectrum of the IV or HF materials is obtained from the variations of the total energy when the f count in each lattice site varies, considering that all f-electron atoms are in the same charge state (see Refs. 2 and 4) (i.e., we consider a homogeneous mixed valence for this compound). The total energy for the IV or HF systems, calculated from the multiband Hubbard Hamiltonian in a first-order theory, reads[14,15]

$$\begin{aligned} E_T &= E_b + E_I + \Delta E \\ &= \int_{-\infty}^{E_F} \varepsilon N_0(\varepsilon)d\varepsilon + \tfrac{1}{2}\mathrm{N}\bar{n}(\bar{n}-1) \\ &\quad + \tfrac{1}{2}\mathrm{N}\sum_f \left[\langle n_f \rangle - \langle n_f \rangle^2 - \sum_{f\,(\neq f')} |\langle n_{ff'} \rangle|^2 \right] , \end{aligned} \tag{1}$$

where U stands for the Coulomb correlation energy which is considered as a fitting parameter; $\bar{n}$ represents the average number of f electrons per site; $\langle n_f \rangle$ is the average occupation number for each f orbital and is defined as

$$\langle n_f \rangle = N^{-1} \sum_{\mathbf{k},\alpha} |\langle \mathbf{k}\alpha | f \rangle|^2 n_{\mathbf{k}\alpha} \tag{2a}$$

and

$$\langle n_{ff'} \rangle = N^{-1} \sum_{\mathbf{k},\alpha} \langle \mathbf{k}\alpha | f \rangle \langle f' | \mathbf{k}\alpha \rangle n_{\mathbf{k}\alpha} ; \tag{2b}$$

the terms $\langle n_{ff'} \rangle$ with $f \neq f'$ become zero if the symmetries of the f orbitals are compatible with the point group of the crystal. $\bar{n}$ is equal to $\sum_f \langle n_f \rangle$. $N_0(\varepsilon)$ is the DOS curve arising from a spectrum ($\varepsilon^0_{\mathbf{k}\alpha}$) deduced from the equation:

$$[-\nabla^2 + V^n_{\mathrm{MT}}(\mathbf{I}-\mathbf{P}_f) + V^0_{\mathrm{MT}}\mathbf{P}_f] \, | \mathbf{k}\alpha \rangle = \varepsilon^0_{\mathbf{k}\alpha} \, | \mathbf{k}\alpha \rangle , \tag{3}$$

where V^0_{MT} is a potential which does not contain any f-f repulsive interaction in the local density potential and V^n_{MT} stands for the full muffin-tin potential deduced by means of the local density formalism. $\mathbf{P}_f(\mathbf{I})$ are the $l=3$ (unity) angular moment projection operators.

The philosophy of our calculation is to find a new spectrum $\varepsilon_{\mathbf{k}\alpha}$ such that the total energy of expression (1) can be given by

$$E_T = \sum_{\mathbf{k},\alpha} \varepsilon_{\mathbf{k}\alpha} n_{\mathbf{k}\alpha} = \int_{-\infty}^{E_F} \varepsilon N(\varepsilon) d\varepsilon , \tag{4}$$

where $N(\varepsilon)$ is the new DOS determined from the $\varepsilon_{\mathbf{k}\alpha}$ spectrum.

The total energy of expressions (1) and (4) can be obtained from an effective Hamiltonian:

$$H=\sum_{\mathbf{k},\alpha}\varepsilon^{0}_{\mathbf{k}\alpha}c^{\dagger}_{\mathbf{k}\alpha}c_{\mathbf{k}\alpha}+\sum_{\mathbf{k},\alpha,\mathbf{k}',\alpha'}\langle \mathbf{k}'\alpha'\,|\,V_{ff}\,|\,\mathbf{k}\alpha\rangle c^{\dagger}_{\mathbf{k}'\alpha'}c_{\mathbf{k}\alpha}\ , \tag{5}$$

where the expression for V_{ff} is

$$V_{ff}=N^{-1}\sum_{f}\left[\frac{\partial E_I}{\partial \bar{n}}+\frac{\partial \Delta E}{\partial\langle n_f\rangle}\right]|f\rangle\langle f|\ , \tag{6a}$$

$$V_{ff}=N^{-1}\sum_{f}U(\bar{n}-\langle n_f\rangle)\,|f\rangle\langle f|\ , \tag{6b}$$

then the spectrum $\varepsilon_{\mathbf{k}\alpha}$ is obtained [by diagonalizing the Hamiltonian (5)] from the following equation:

$$[-\nabla^2+V^{n}_{\mathrm{MT}}(\mathbf{I}-\mathbf{P}_f)+V^{0}_{\mathrm{MT}}\mathbf{P}_f]\varphi_{\mathbf{k}\alpha}(\mathbf{r})+\int d^3r'\,U\sum_{f}(\bar{n}-\langle n_f\rangle)f(\mathbf{r})f^{*}(\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}')=\varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r})\ ; \tag{7a}$$

this equation is equivalent to

$$[-\nabla^2+V^{n}_{\mathrm{MT}}(\mathbf{r})]\varphi_{\mathbf{k}\alpha}(\mathbf{r})+\int d^3r'\,\Sigma(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}')=\varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r})\ , \tag{7b}$$

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

$$\Sigma(\mathbf{r},\mathbf{r}')=\sum_{f}\{U(\bar{n}-\langle n_f\rangle)-[V^{n}_{\mathrm{MT}}(\mathbf{r})-V^{0}_{\mathrm{MT}}(\mathbf{r})]\}f(\mathbf{r})f^{*}(\mathbf{r}')\ . \tag{8}$$

The problem in IV or HF systems arises when an f orbital 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 (see, for instance, Ref. 16) and the bands arising from the totally unoccupied f orbitals are split by the U energy. In our model, the locations of the different f orbitals, with respect to the totally occupied f orbitals in the ground state, are obtained by the term

$$V'_{ff}=\sum_{f}U(1-\langle n_f\rangle)\,|f\rangle\langle f|\ , \tag{9a}$$

where V'_{ff} acts as

$$V'_{ff}\varphi_{\mathbf{k}\alpha}(\mathbf{r})=\int d^3r'[\Sigma(\mathbf{r},\mathbf{r}')-\Sigma^{\mathrm{occ}}(\mathbf{r},\mathbf{r}')]\varphi_{\mathbf{k}\alpha}(\mathbf{r}') \tag{9b}$$

with

$$\Sigma^{\mathrm{occ}}(\mathbf{r},\mathbf{r}')=\sum_{f}\{U(\bar{n}-1)-[V^{n}_{\mathrm{MT}}(\mathbf{r})-V^{0}_{\mathrm{MT}}(\mathbf{r})]\}f(\mathbf{r})f^{*}(\mathbf{r}')\ . \tag{10}$$

We formulate V'_{ff} depending implicitly on the energy since we calculate the radial wave functions of the orbitals $|f\rangle$ at the energies of the eigenvalues. This fact implies that V'_{ff} produces effects in each $\varphi_{\mathbf{k}\alpha}(\mathbf{r})$ state according to its spatial localization since the localizations of the f orbitals strongly depends on the energy. The radial part of these functions $f(\mathbf{r},\varepsilon_{\mathbf{k}\alpha})$ is obtained by means of the renormalized atom approach[17] and are truncated at the muffin-tin radii of the f-electron atoms. In addition, as we have written above,

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

where $\Delta V_{\mathrm{ex},c}(\mathbf{r})$ is a correction to the local exchange and correlation potential $V_{\mathrm{ex},c}(\mathbf{r})$. $\Delta V_{\mathrm{ex},c}(\mathbf{r})$ and $V_{\mathrm{ex},c}(\mathbf{r})$ are included within $V^{n}_{\mathrm{MT}}(\mathbf{r})$, therefore, Eqs. (7a) and (7b) can also be written as

$$[-\nabla^2+V^{n}_{\mathrm{MT}}(\mathbf{r})]\varphi_{\mathbf{k}\alpha}(\mathbf{r})+\int d^3r'\,U\sum_{f}(1-\langle n_f\rangle)f(\mathbf{r},\varepsilon_{\mathbf{k}\alpha})f^{*}(\mathbf{r}',\varepsilon_{\mathbf{k}\alpha})\varphi_{\mathbf{k}\alpha}(\mathbf{r}')=\varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r})\ . \tag{11}$$

The potential V'_{ff} locates each f orbital at an energy $\varepsilon_f=\varepsilon_0+U(1-\langle n_f\rangle)$, ε_0 being the gravity center of the $4f$ band determined with the V^{n}_{MT} potential. For $U=0$, (11) represents a standard local density equation, therefore, the strong correlation effects are included by means of the nonlocal correction of this equation. The potential V'_{ff} commutes with all symmetry operations of the point group if and only if the terms $\langle n_f\rangle$ are equal for all bases of each subspace of the decomposition $D_7(2l+1)=\Gamma'_2\oplus\Gamma_{15}\oplus\Gamma_{25}$ (this decomposition corresponds to the group O_h). The values of $\langle n_f\rangle$ for each subspace can be different and therefore the potential (9a) can produce different $4f$ peaks (three peaks). In addition, the f-d hybridization can induce a gap or pseudogap which splits off two $4f$ structures.

The self-consistent procedure for determining V^{n}_{MT} and V'_{ff} has been given in Ref. 6 and can be summarized as follows. For the zero iteration, the f level is considered as an atomic resonance with n electrons ($4f^{n}$ is the integral configuration of the ground state). For successive

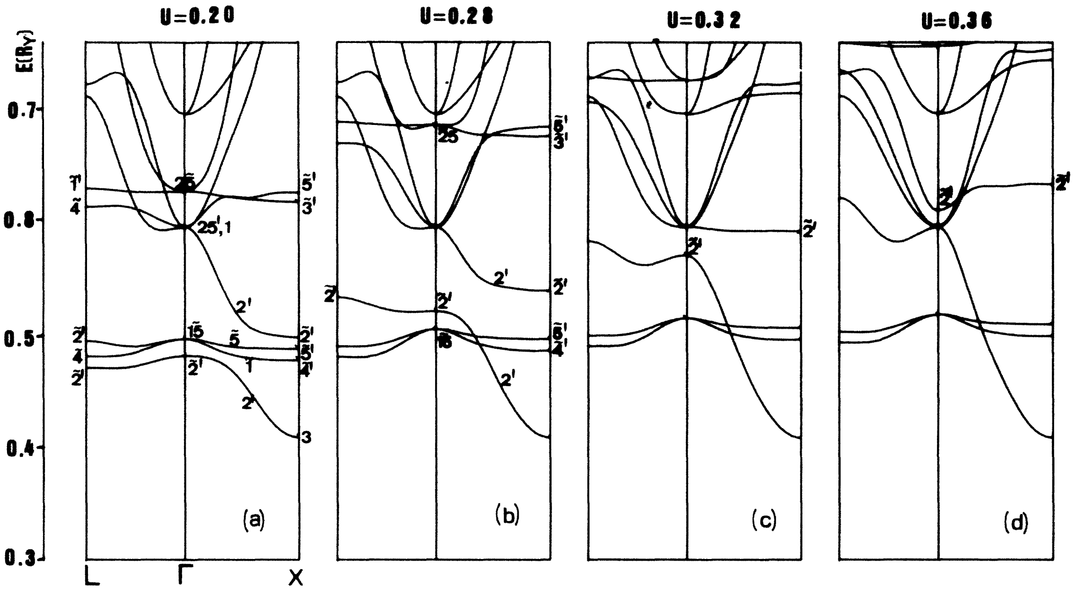

FIG. 1. Different band structures in the directions (100) and (111) for the golden SmS with a crystal volume $0.85V_0$ and several values for the U energy: (a) $U=0.20$ Ry, (b) $U=0.28$ Ry, (c) $U=0.32$ Ry, and (d) $U=0.36$ Ry. The states marked with ~ are pure $4f$ states, i.e., they have $\sum_f |\langle \mathbf{k}\alpha | f \rangle|^2 \geq 0.9$.

iterations, the $E(\mathbf{k})$ dispersion implies different self-consistent occupation ($\langle n_f \rangle$) for the several f symmetries. Then, the nonlocal terms of Eq. (11) cause the splitting of the f symmetries and the convergency of the process, if any, coincides with the stability of the $4f^{\bar{n}}$ configuration. The technical details of the band calculation method are given in Refs. 6 and 7.

A. The energy spectrum with $U \neq 0$

The main advantage of this band method is that one can determine simultaneously both the occupied and the unoccupied $4f$ bands. The occupied $4f$ bands arise from f orbitals such that $0 < \langle n_f \rangle < 1$ (in our work, the Γ_{15} and Γ_2' subspaces, see Figs. 1 and 2). The actual cases al-

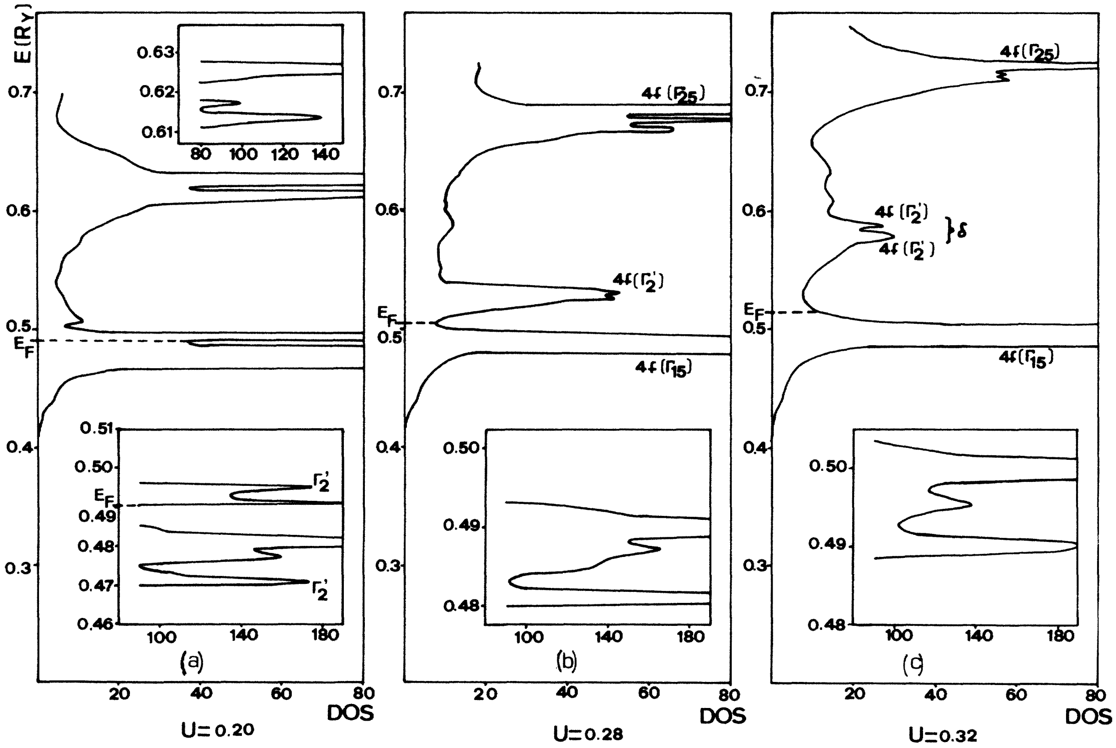

FIG. 2. Density of states per spin direction corresponding to the band structures of Figs. 1(a), 1(b), and 1(c), respectively.

ways are $\langle n_f \rangle < 1$ due to the f-d hybridization and the delocalization produced by the pressure effects. Then, V'_{ff} causes a tendency to the unoccupancy of the corresponding f symmetry. However, a decrease of $\langle n_f \rangle$ implies the decrease of the f-f repulsive interaction in V^{n}_{MT} and thus a shift down of ε_0. Therefore, V^{n}_{MT} and V_{ff} produce competitive effects which can cause instabilities in the total f count $\bar{n}$ when $\langle n_f \rangle$ is different from 1 or 0. For $\langle n_f \rangle \sim 1$ (the Γ_{15} subspace in our case, see Figs. 1 and 2), the f symmetry is stable and the corresponding f bands are similar to the so-called lower Hubbard bands. For $\langle n_f \rangle \simeq 0$, the corresponding $4f$ bands are totally empty in the ground state (Γ_{25} subspace in our calculation, see Figures). These unoccupied $4f$ bands represent the different ways to occupy the $4f^{\bar{n}+1}$ configuration in a crystal where all electronic conduction states are described, even the $4f$ ones, by means of Bloch functions and whose ground-state configuration is $4f^{\bar{n}}$. These bands are the upper Hubbard bands and can also be defined as the motion of an extra electron placed in the rare-earth atoms so that the $4f^{\bar{n}+1}$ configurations are moved through the lattice with a definite quasimomentum for the wave functions.[18]

Another point is the conservation of the Luttinger theorem in our calculations. This theorem implies that the $\mathbf{k}$-space volume occupied by the states below E_F is independent of the value of the U energy. In our results the f count is quasiconstant for different U values and this implies the verification of this theorem, since we consider the homogenity of the charge state in all f-electron atoms. The light modifications of the f count versus the U energy are produced by the dependence of the hybridizations on U.

III. ANOTHER VERSION OF THIS METHOD

In order to understand the contents of the method described in Sec. II we have deduced the main equations [i.e., potential (6b) and Eqs. (7a) and (7b)] from an approximation of the Green function for interacting f systems. The multiband Hubbard Hamiltonian reads

$$H = \sum_{\mathbf{k},\alpha} \varepsilon^{0}_{\mathbf{k}\alpha} c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha} + \frac{U}{2} \sum_{i,f,f'} c^{\dagger}_{if} c^{\dagger}_{if'} c_{if'} c_{if} \ , \tag{12}$$

where the energies $\varepsilon^{0}_{\mathbf{k}\alpha}$ were obtained by means of a self-consistent potential which does not contain any f-f repulsive interaction in order to avoid repetitions when considering the f-f Coulomb correlation, i.e., $\varepsilon^{0}_{\mathbf{k}\alpha}$ arises from an identical equation to (3). The operators $c^{\dagger}_{if}$ and c_{if} are defined as

$$\begin{aligned} c_{if} &= N^{-1/2} \sum_{\mathbf{k}\alpha} \langle f \mid \mathbf{k}\alpha \rangle e^{i\mathbf{k}\cdot\mathbf{R}_i} c_{\mathbf{k}\alpha} \ , \\ c^{\dagger}_{if} &= N^{-1/2} \sum_{\mathbf{k},\alpha} \langle \mathbf{k}\alpha \mid f \rangle e^{-i\mathbf{k}\cdot\mathbf{R}_i} c^{\dagger}_{\mathbf{k}\alpha} \ , \end{aligned} \tag{13}$$

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 *spd* hybridized. The Hamiltonian (12) 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 $\varepsilon^{0}_{\mathbf{k}\alpha}$ spectrum.

Substitution of (13) into (12) leads to

$$\begin{aligned} H = H_0 + V = \sum_{\mathbf{k},\alpha} \varepsilon^{0}_{\mathbf{k}\alpha} c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha} + \frac{U}{2N} \sum_{f,f'} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \sum_{\alpha,\beta,\gamma,\delta} & \langle \mathbf{k}\alpha \mid f \rangle \langle \mathbf{k}'\beta \mid f' \rangle \langle f' \mid (\mathbf{k}+\mathbf{q})\gamma \rangle \\ & \times \langle f \mid (\mathbf{k}'-\mathbf{q})\delta \rangle c^{\dagger}_{\mathbf{k}\alpha} c^{\dagger}_{\mathbf{k}'\beta} c_{(\mathbf{k}+\mathbf{q})\gamma} c_{(\mathbf{k}'-\mathbf{q})\delta} \ , \end{aligned} \tag{14}$$

where α, β, γ, and δ are the band indices. The Green's function is defined as

$$G_{\alpha\beta}(\mathbf{k},t) = -i \langle T[c_{\mathbf{k}\alpha}(t) c^{\dagger}_{\mathbf{k}\beta}] \rangle \ , \tag{15}$$

and its temporal evolution implies that

$$\frac{\partial G_{\alpha\beta}(\mathbf{k},t)}{\partial t} = -i\delta_{\alpha\beta}\delta(t) - i\varepsilon^{0}_{\mathbf{k}\alpha} G_{\alpha\beta}(\mathbf{k},t) - i \sum_{\gamma} M_{\alpha\gamma}(\mathbf{k}) G_{\gamma\beta}(\mathbf{k},t) \ . \tag{16}$$

This equation is obtained by considering a decoupling relation as

$$\sum_{\mathbf{q},l,l'} (\cdots) \langle c^{\dagger}_{\mathbf{k}\alpha} c^{\dagger}_{\mathbf{q}\mu}(t) c_{l\gamma}(t) c_{l'\lambda}(t) \rangle \approx \sum_{\mathbf{q},l,l'} (\cdots) [\langle c^{\dagger}_{\mathbf{k}\alpha} c_{l'\lambda}(t) \rangle \langle c^{\dagger}_{\mathbf{q}\mu}(t) c_{l\gamma}(t) \rangle - \langle c^{\dagger}_{\mathbf{q}\mu}(t) c_{l'\lambda}(t) \rangle \langle c^{\dagger}_{\mathbf{k}\alpha} c_{l\gamma}(t) \rangle] \ , \tag{17}$$

and we have defined

$$M_{\alpha\gamma}(\mathbf{k}) = \left\langle \mathbf{k}\alpha \middle| \left[U \sum_{f,f'} (\langle n_{f'} \rangle \mid f \rangle \langle f \mid - \langle n_{ff'} \rangle \mid f \rangle \langle f' \mid) \right] \middle| \mathbf{k}\gamma \right\rangle \ , \tag{18}$$

where

$$\langle n_{ff'} \rangle = -iN^{-1} \sum_{\mathbf{q},\lambda,\mu} \langle f \mid \mathbf{q}\lambda \rangle \langle \mathbf{q}\mu \mid f' \rangle G_{\lambda\mu}(\mathbf{q},0^-) ,$$
$$\langle n_f \rangle = \langle n_{ff} \rangle , \tag{19}$$
$$G_{\lambda\mu}(\mathbf{q},0^-) = i \langle c^\dagger_{\mathbf{q}\mu} c_{\mathbf{q}\lambda} \rangle ,$$

if we choose a basis for the f orbital space compatible with the crystal symmetry, all $\langle n_{ff'} \rangle$ are zero for $f \neq f'$.

The Green function is a matrix whose dimension is the number of bands with states containing $l=3$ component in their charge density. This matrix can be obtained from a Dyson-like equation

$$\mathbf{G}(\mathbf{k},\omega) = [\mathbf{I} - \mathbf{G}_0(\mathbf{k},\omega)\mathbf{M}(\mathbf{k})]^{-1}\mathbf{G}_0(\mathbf{k},\omega) ,$$
$$[\mathbf{G}_0(\mathbf{k},\omega)]_{\alpha\beta} = \left[\frac{n_{\mathbf{k}\alpha}}{\omega - \varepsilon^0_{\mathbf{k}\alpha} - i\delta} + \frac{1 - n_{\mathbf{k}\alpha}}{\omega - \varepsilon^0_{\mathbf{k}\alpha} + i\delta} \right] \delta_{\alpha\beta} , \tag{20}$$

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

$$[-\nabla^2 + V^n_{\mathrm{MT}}(\mathbf{I} - \mathbf{P}_f) + V^0_{\mathrm{MT}}\mathbf{P}_f]\varphi_{\mathbf{k}\alpha}(\mathbf{r}) + \int d^3r' M(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}\alpha}(\mathbf{r}') = \varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \tag{21}$$

where $M(\mathbf{r},\mathbf{r}')$ is the real-space representation of $M(\mathbf{k})$. $M(\mathbf{r},\mathbf{r}')$ is given by

$$M(\mathbf{r},\mathbf{r}') = U \sum_f (\bar{n} - \langle n_f \rangle) f(\mathbf{r}) f^*(\mathbf{r}') , \tag{22}$$

where $\bar{n} = \sum_f \langle n_f \rangle$ and $f(\mathbf{r})$ are f orbitals whose radial part is calculated to the energy of the corresponding eigenvalue of Eq. (21) (as in Sec. II) and the angular part have symmetries compatible with the crystal. Equation (21) can also be written as

$$[-\nabla^2 + V^n_{\mathrm{MT}}(\mathbf{r})]\varphi_{\mathbf{k}\alpha}(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha})\varphi_{\mathbf{k}\alpha}(\mathbf{r}') = \varepsilon_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}(\mathbf{r}) , \tag{23}$$

where $\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha})$ takes the form

$$\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{\mathbf{k}\alpha}) = \sum_f \{ U(\bar{n} - \langle n_f \rangle) - [V^n_{\mathrm{MT}}(\mathbf{r}) - V^0_{\mathrm{MT}}(\mathbf{r})] \} \times f(\mathbf{r},\varepsilon_{\mathbf{k}\alpha}) f^*(\mathbf{r}',\varepsilon_{\mathbf{k}\alpha}) . \tag{24}$$

When $\Sigma = 0$, the resulting equation is the standard local density band Hamiltonian.

The potential (22) is identical to (6b) and the nonlocal terms of Eqs. (21) and (7b) are also identical. In addition, Eqs. (11) and (23) yield similar results if the calculations are performed self-consistently.

An equivalent equation to (20) 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. (20) will read

$$\mathbf{G}(\mathbf{k},\omega) = [\mathbf{I} - \mathbf{G}_0(\mathbf{k},\omega)\Sigma(\mathbf{k},\omega)]^{-1}\mathbf{G}_0(\mathbf{k},\omega) , \tag{25}$$

now $\mathbf{G}_0$ is the Green function corresponding to a spectrum deduced from the standard local density (LD) potential (i.e., with $\Sigma = 0$). The potential Σ is the key of this method for obtaining the HF electronic structure. The main effect of this Σ correction is the splitting of the different f symmetries according to their average 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 is also obtained by means of the procedure in Sec. II, since this splitting rises by the dependence of the nonlocal term on $\langle n_f \rangle$. On the other hand, the appearance of the $\langle n_f \rangle$'s in the self-energy deduced in this section is due to the exchange term of the decoupling equation (17) which only produces nonvanishing effects in the case of the degenerated f symmetries.

The model described in these two sections is similar to that given in Ref. 19, and the self-energy functionals of (11) and (23) accomplish the two conditions required in Ref. 20, i.e., $H_0 + \Sigma$ is Hermitical and Σ conserves the f count $\bar{n}$.

IV. COMMENTS ON THE RESULTS

The second part of this work describes the results of the electronic structure of the metallic phase of SmS performed with the first version of this method (i.e., Sec. II). This phase is obtained by mixing the $4f$ band with the conduction band due the hydrostatic pressure. Another consequence of the pressure is a larger delocalization of the radial wave functions in the golden phase than in the black phase. This implies a larger f-d hybridization and an increase of the f-band widths, and therefore the U energy decreases for this golden phase of SmS.

We show in Fig. 1 the band calculation performed for a crystal volume $0.85V_0$ (V_0 being the crystal volume at room pressure) and for different values of the U energy. The f-d hybridization is clear in the bands $\Gamma'_{25}\Delta'_2X'_2$ and $\Gamma'_2\Delta'_2X_3$ since their states share the f and d orbitals. The electronic structure of Fig. 1 presents the f-d hybridization feature of the IV and HF compounds described in recent papers.[21,22]

The first electronic structure [$U = 0.20$ Ry, Figs. 1(a) and 2(a)] shows the existence of five maxima in the DOS curve close to E_F [Fig. 2(a)]. The f-d hybridization produces two maxima (Δ'_2 bands), being the other three are generated by the Γ_{15} bands. The Fermi level lies on a relative minimum [see Fig. 2(a)] and the pseudogap between the third and fourth maximum is not a hybridization pseudogap because these two maxima arise from the degenerate Γ_{15} subspace. Therefore, this pseudogap is due to the crystal symmetry effects.

For $U > 0.22$ Ry, E_F is above the Γ_{15} bands and cuts off the band $\Gamma'_2\Delta'_2X_3$. This implies that the Fermi energy is close to the absolute minimum of the DOS curve and lies between the peaks Γ'_2 and Γ_{15} (see Figs. 1 and 2). Therefore, the pseudogap located at E_F is raised by the different Coulomb correlation effects for each f subspace and is not a proper hybridization pseudogap (δ). The splitting between the Γ'_2 and Γ_{15} peaks increases when the U value increases. For values close to $U = 0.26$, our DOS curve presents a similar structure to that given by Travaglini and Watcher in Ref. 3. For $U > 0.26$ Ry an actual δ can appear [see Fig. 2(c)] due to the f-d hybridization in the Δ_2' bands. Figures 1(c) and 2(c) show a clear δ and a clear splitting between the several $4f$ bands. For $U > 0.36$ Ry [Fig. 1(d)], the location of the Fermi energy is also in agreement with the experimental results, however the Γ_2'-Γ_{15} splitting is too large.

For values of $U \geq 0.15$ Ry, the bands coming from the Γ_{25} orbitals are located above E_F. These Γ_{25} orbitals are empty in the ground state. Therefore these $4f$ bands can be assimilated to the upper Hubbard bands whose locations are detected by bremsstrahlung isochromat spectroscopy (BIS) measurements. For instance, Oh and Allen[9] determine this $4f$ peak to be around 4 eV above the Fermi energy which is close to the splitting displayed by the results of Figs. 1 and 2.

In our calculations, the number of states at the Fermi level decreases when U increases in such a way that for $U > 0.25$ Ry, E_F is located in the absolute minimum and this is in agreement with the electrical resistivity measurements.[3,13] The value of the DOS in this minimum (seven states per Ry and primitive cell) is 2 orders of magnitude less than the value in the f maximum (596 states/[Ry/(primitive cell)]) (this relation between the maximum and minimum of the DOS is also estimated by Travaglini and Watcher[3]).

The results of the band structure and DOS curve for $U = 0$ (i.e., results from the standard local density formalism) are given in Fig. 3. These results are in good agreement with former calculations performed with similar procedures.[4,5] The lack of the splitting of the different f symmetries implies that the $4f$ bands arising from the Γ_{25} space fall in the energy interval where the possible hybridization pseudogap appears. Therefore, none of the experimental features of the density of states mentioned above are present in these results. Actually, the hybridization exists but the pseudogap does not appear because the Γ_{25} peaks lie on the same energy interval. The Fermi level is not located in a minimum of the DOS curve since this lies close to a giant f maximum (~ 1600 states/[Ry/(primitive cell)], see Fig. 3). The position of E_F with respect to the conduction-band bottom (~ 0.1 eV) presents lesser agreement with the experimental data (1 eV) than the results obtained with $U \neq 0$ (see Fig. 2). Moreover, the splitting between occupied and unoccupied $4f$ bands is not given when one considers $U = 0$.

In our results, $N_0(E_F) \gg N(E_F)$, however, the number of f electrons in all Sm atoms varies from slightly versus U ($\bar{n}$ is between 5.7 and 5.4 for U values between 0 and 0.36 Ry). The differences of $\bar{n}$ are compensated with the light increase of the d count in the f-electron atoms. This implies that the number of $f + d$ states below E_F is conserved when considering U different from 0 and this is in agreement with the Luttinger theorem (see Ref. 19).

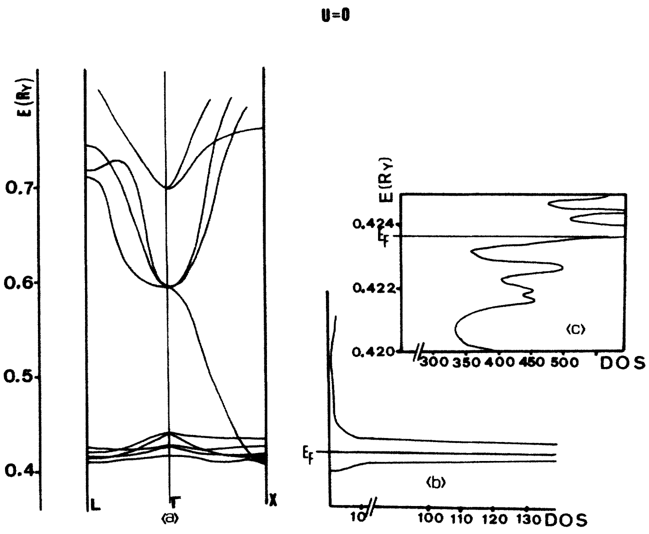

FIG. 3. Band structure and density of states per spin direction calculated with $U = 0$ (i.e., calculated with the standard local density formalism). (a) band structure for $U = 0$; (b) density of states corresponding to $4f$ bands; (c) detailed DOS curve corresponding at energies close to E_F.

We have performed other band-structure calculations for this compound (which we do not give in the figures) with different lattice parameters and the tendency of the electronic structure is similar to that obtained in the former calculations. However, the values of U should be increased, when the lattice parameter increases, for obtaining similar $4f$ structures to those given in Figs. 1 and 2.

In conclusion, the f-d hybridization scheme is clear in the symmetry line (100) for U values between 0.20 and 0.36 Ry. The f-d hybridization is caused by the coherent mixing of the orbital XYZ with the different d orbitals and thus a small δ can appear. The splitting between the Γ_2' and Γ_{15} peaks increases for increasing U values and the value of the Γ_2' maximum in the DOS (Fig. 2) decreases when U increases. Therefore, for values of the U energy between 0.24 and 0.28 Ry, our results present the best agreement with the experimental data. For $U = 0$, our results show the nonappearance of any pseudogap close to E_F. Therefore, the existence of this pseudogap is justified in our calculations by the influence of two different effects which act together, the f-d hybridization and the different Coulomb correlation effects for each subspace.

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