

Calculations of the one-body electronic structure of the strongly correlated systems including self-energy effects

J. Costa-Quintana, M. M. Sánchez-López, and F. López-Aguilar

Grup d'Electromagnetisme, Edifici Cn, Universitat Autònoma de Barcelona 08193, Bellaterra, Barcelona, Spain

(Received 29 January 1996; revised manuscript received 3 June 1996)

We give a method to obtain the quasiparticle band structure and renormalized density of states by diagonalizing the interacting system Green function. This method operates for any self-energy approximation appropriated to strongly correlated systems. Application to CeSi₂ and YBa₂Cu₃O₇ is analyzed as a probe for this band calculation method. [S0163-1829(96)06036-5]

Since some years ago, there has been a tendency to attempt to describe the electronic structure of strongly correlated systems (SCS's) from a one body point of view¹⁻⁸ either including self-energy effects in the local- (spin-) density approximation [L(S)DA] Refs. 3-6 or by other methods.⁸ Some authors have considered that the reason for the fiasco of the standard LDA in the description of the electronic structure of the SCS's lies in the determination of the crystal potential, which does not include (and it should) the so-called self-interaction correction (SIC).¹ Other authors have added to the LDA potential a term which depends on the occupation of each strongly correlated orbital in such a way that it is able to reproduce the characteristic Hubbard-like splitting. This method is called LDA+*U*.² Both the SIC and the LDA+*U* methods can be considered mean-field approximations, since the corresponding added potentials are independent of the energy. Other authors include energy-dependent pseudopotentials derived from several self-energy approximations either inspired in the three-body Fadeev equations⁵ or based on the *GW* approximation (*GWA*) theory⁷ adapted to the SCS's.^{3,4} The aim of this paper is to give a system for obtaining the electronic structure of the SCS's valid for any pseudopotential (SIC, LDA+*U*, or any approximation to the self-energy).

The method we present here is based on the diagonalization in **k** space of the interacting Green function in which a self-energy is considered. Thus the matrix element of the interacting Green function is given by $G_{\alpha\beta}(\mathbf{k}, \omega)^{-1} = (\omega - \varepsilon_{\mathbf{k}\alpha}^0 \pm i\theta^+) \delta_{\alpha\beta} - M_{\alpha\beta}(\mathbf{k}, \omega)$, where $M_{\alpha\beta}(\mathbf{k}, \omega)$ is the self-energy matrix element calculated between two eigenstates $|\mathbf{k}\alpha\rangle$ and $|\mathbf{k}\beta\rangle$ of the noninteracting system's Hamiltonian (H_{LDA}) of eigenvalues $\varepsilon_{\mathbf{k}\alpha}^0$ and $\varepsilon_{\mathbf{k}\beta}^0$ respectively (α and β are band indexes). The interacting Hamiltonian of SCS's, considered here, has only terms between strongly correlated orbitals belonging to *f* or/and *d* atoms, therefore, the self-energy only affects the strongly correlated component of the band states. Then the Green functions can be written as

$$G_{\alpha\beta}(\mathbf{k}, \omega)^{-1} = (\omega - \varepsilon_{\mathbf{k}\alpha}^0 \pm i\theta^+) \delta_{\alpha\beta} - \sum_{mm'} \sum_{vv'} \langle \mathbf{k}\alpha | m v \rangle M_{mm'}^{vv'}(\mathbf{k}, \omega) \langle m' v' | \mathbf{k}\beta \rangle. \tag{1}$$

The matrix of the former equation must be constructed and diagonalized for each **k**. This requires a first band calculation in order to determine $\varepsilon_{\mathbf{k}\alpha}^0$ and $\langle \mathbf{k}\alpha | m v \rangle$. We have performed a LDA band structure calculation with a standard symmetrized augmented plane-wave method, and determined $\varepsilon_{\mathbf{k}\alpha}^0$ and $\langle m v | \mathbf{k}\alpha \rangle$, whose expression is

$$\begin{aligned} \langle m v | \mathbf{k}\alpha \rangle = & \frac{i4\pi g}{n_p} \sum_i \sum_R v(\mathbf{k}_i, \varepsilon_{\mathbf{k}\alpha}^0) [\Gamma_{11}^\alpha(R)]^* \\ & \times e^{iR\mathbf{k}_i \cdot \mathbf{r}_\nu} \frac{j_l(R\mathbf{k}_i, S_\nu)}{u_l(S_\nu, \varepsilon_{\mathbf{k}\alpha}^0)} \mathcal{Y}_p(\theta_i, \varphi_i) \\ & \times \sqrt{\int r^2 dr |u_l(|\mathbf{r} - \mathbf{r}_\nu|; \varepsilon_{\mathbf{k}\alpha}^0)|^2}. \end{aligned} \tag{2}$$

The former equation, after the standard notation,⁶ defines the shape of the *m* strongly correlated orbitals $[\mathcal{Y}_m(\theta_i, \varphi_i) u_l(|\mathbf{r} - \mathbf{r}_\nu|; \varepsilon_{\mathbf{k}\alpha}^0)]$. The radial part of these orbitals (*u_l*), centered in the *ν* atoms, is calculated by means of the radial part of the Schrödinger equation for the energy of the crystal eigenstate (i.e., $E = \varepsilon_{\mathbf{k}\alpha}^0$) and the symmetries of the angular part of these orbitals $[\mathcal{Y}_p(\theta_i, \varphi_i)]$ are compatibilized with the crystal symmetry. Therefore, these orbitals are affected by both the crystal symmetry and solid-state effects via the dispersion energy of the eigenstates. The coefficients $v(\mathbf{k}_i, \varepsilon_{\mathbf{k}\alpha}^0)$ which also define the $|\mathbf{k}\alpha\rangle$ state are obtained in this first LDA calculation.

When a complex self-energy is considered, Eq. (1) becomes a complex ω -dependent non-Hermitical matrix whose eigenvalues $[E_{\mathbf{k}\alpha}(\omega)]$ can be written as $E_{\mathbf{k}\alpha}(\omega) = \varepsilon_{\mathbf{k}\alpha}(\omega) + i\gamma_{\mathbf{k}\alpha}(\omega)$. Then $G_{\alpha\beta}$ can be rewritten in the diagonalized form as $G_{\mathbf{k}\alpha}(\omega)^{-1} = \omega - \varepsilon_{\mathbf{k}\alpha}(\omega) - i\gamma_{\mathbf{k}\alpha}(\omega)$. The spectrum of the interacting system is given by the poles of the Green function; we find then quasiparticle states of energy $\omega_0 = \varepsilon_{\mathbf{k}\alpha}(\omega_0)$ and half-life $\tau_{\mathbf{k}\alpha} = \gamma_{\mathbf{k}\alpha}(\omega_0)^{-1}$. The density of states (DOS) is calculated from the spectral functions $[A_{\mathbf{k}\alpha}(\omega) = (1/\pi) |\text{Im}G_{\mathbf{k}\alpha}(\omega)|]$. Developing the function $\omega - \varepsilon_{\mathbf{k}\alpha}(\omega)$ in a Taylor series around the solution of $\omega_0 = \varepsilon_{\mathbf{k}\alpha}(\omega_0)$, the following spectral function is obtained:

$$A_{\mathbf{k}\alpha}(\omega) = \frac{1}{\pi} \frac{Z_{\mathbf{k}\alpha}^2(\omega_0) \gamma_{\mathbf{k}\alpha}(\omega_0)}{[\omega - \varepsilon_{\mathbf{k}\alpha}(\omega_0)]^2 + [Z_{\mathbf{k}\alpha}(\omega_0) \gamma_{\mathbf{k}\alpha}(\omega_0)]^2}, \tag{3}$$

where the renormalization factor $Z_{\mathbf{k}\alpha}(\omega_0)$ corresponding to the quasiparticle state of energy $\varepsilon_{\mathbf{k}\alpha}(\omega_0)$ is given by $Z_{\mathbf{k}\alpha}^{-1}(\omega_0) = |1 - (\partial\varepsilon_{\mathbf{k}\alpha}/\partial\omega)|_{\omega=\omega_0}$. The band calculation method explained above presents obvious advantages in comparison with our previous method,⁶ since it provides an exact evaluation of the half-life of the quasiparticles as well as of the renormalization factor within the self-energy approximation, while in our previous method⁶ these two variables were calculated up to the first order of approximation. On the other hand, it makes it possible to consider matricial self-energies $M_{mm'}^{vv'}$, which arise, for example, from regarding a $U_{mm'}^{vv'}$ matrix for the bare interaction between electrons in strongly correlated orbitals of different atoms. This method is also more advantageous than those of Refs. 1 and 2, since it admits any pseudopotential (including of course those of Refs. 1 and 2), and furthermore it can consider any dynamical effects corresponding to any Dyson solution for effective interactions between quasiparticles. Moreover, the method presented here constitutes a completely general system, valid for any approximation to the self-energy. In this paper, though, our attention is not centered in the self-energy analysis, therefore, an expression for the self-energy which has yielded results⁶ in reasonable good agreement with the experimental data, will be used to test this method with respect to that of previous papers.⁶ The self-energy expression used in the examples of the electronic structures given in the present paper is

$$M_{mm'}^{vv'}(\omega) = \delta_{mm'}\delta_{vv'}U_m^v(\frac{1}{2} - n_m^v) + \delta_{mm'}\delta_{vv'}U_m^v \frac{\Omega_{mv}^2 - y_{mv}^2}{2\Omega_{mv}} \times \left(\int_{-\infty}^{E_F} \frac{N_m^v(x)dx}{\omega + \Omega_{mv} - x - i\theta^+} + \int_{E_F}^{\infty} \frac{N_m^v(x)dx}{\omega - \Omega_{mv} - x + i\theta^+} \right) \quad (4)$$

(the meaning of the variables appearing in the above equation are given in Ref. 6). The term $U(\frac{1}{2} - n_m^v)$ yields the Hubbard splitting in the unrestricted Hartree-Fock approximation, and the two terms depending on ω arise from the extended random-phase-approximation (ERPA).⁶ The Ω_{mv} and y_{mv} parameters depend on the U_m^v energy and on the noninteracting density of states (which is modeled by means of Lorentzian-like curves), in such a way that the ω -dependent terms of the self-energy tend to zero when the bandwidths of the noninteracting system increase, and/or the strongly correlated orbital is either totally occupied or unoccupied. For each m strongly correlated symmetry of each v atom, the self-energy of Eq. (4) has two energy-dependent terms with two maxima at energies next to $\omega = \pm\Omega_{mv}$. These maxima would be divergences if the imaginary part of the self-energy had the shape of $\delta(\omega - \Omega_{mv})$ functions. But this is not the case here, since for Lorentzian-like noninteracting DOS's the imaginary part of the self-energy of Eq. (4) is also constituted by Lorentzian-like curves, and thus the self-energy presents, instead of divergences, maxima and minima more or less pronounced depending on the larger or smaller narrowness of the bandwidths (see Ref. 6). The self-

energy described above can be compared to other approximations to the self-energy, as, for example, those calculated from a one-band Hubbard Hamiltonian by Calandra and Manghi⁵ or from a multiorbital Hubbard Hamiltonian by Manghi, Calandra, and Ossini.⁵ In this work of Calandra and Manghi,⁵ the calculated hole and particle self-energies present a discontinuity at the Fermi level (E_F) which, as stressed by the authors, is responsible for the metal-insulator transition when increasing the ratio U/W (correlation-bandwidth). Except for this jump, the self-energy of Eq. (4) shows similar characteristics (see Ref. 6) to that of Calandra and Manghi's work. In fact, the agreement is excellent when the self-energy obtained by Calandra and Manghi is continuous at E_F [i.e. for $\Sigma_1^{(\pm)}(\omega) = 0$]. In this case the straight lines ($\omega - \varepsilon_{\mathbf{k}\alpha}$) cut off the real part of the self-energy, yielding poles of the Green function in the energy region near E_F , and therefore metallic behavior can arise. Obviously, this last case should be considered when analyzing the electronic structure of metallic CeSi_2 and $\text{YBa}_2\text{Cu}_3\text{O}_7$, which are the compounds studied in this work. This agreement can seem surprising, since the self-energy of Eq. (4) is obtained by summation of the ERPA,⁶ while Calandra and Manghi's calculations are performed considering three-body Fadeev equations. However, it must be remembered that the vertex effects vanish for sufficiently large bandwidths and, on the other hand, for these bandwidths and large number of particles (cases close to the half-filling condition) the bubble diagrams of the ERPA yield basically all characteristic features of the electronic structure of these systems.

Our method can be also compared to those arising from the GWA, where a dynamical screened interaction is considered to obtain the self-energy by means of the well-known Hedin-Lundqvist⁷ theory. Some authors³ have recently attempted to apply this GWA theory to strongly correlated systems. The self-energy (4) of our calculation could be classified within the GWA models, and two main differences can nevertheless be established between our method and that of Ref. 3. The first one concerns the self-energy used, and concretely the number of cuts between its real part and the straight line $\omega - \varepsilon_d$, i.e., it concerns the number of solutions of the equation $\omega - \varepsilon_d - \Sigma_1(\omega) = 0$. While according to what appears in Ref. 3 there seems to be only one solution, placed next to E_F , in our case there are at least three solutions for each energy of the noninteracting system. Therefore, the resulting electronic structure of Ref. 3 corresponds to an interacting Fermi liquid and, due to the existence of only the one solution of the above equation, the satellite states of NiO do not appear. In our results a multipeak structure arises (see for instance Fig. 1 of the present work) and, as commented upon in Ref. 6, when increasing the bandwidth the self-energy (4) tends to have only one cut, and therefore the Hubbard Hamiltonian yields a classical interacting Fermi liquid. The second difference mentioned above corresponds to the procedure for integrating the Schrödinger-like equation when considering the self-energy operators. In Ref. 3, the self-energy operator is applied to the orbitals, and the effect over the crystal electronic states is obtained from their linear muffin-tin orbital structures, that are linear combinations of orbitals, some of which are affected by the self-energy. This method presents some difficulties when the real part of the self-energy and the

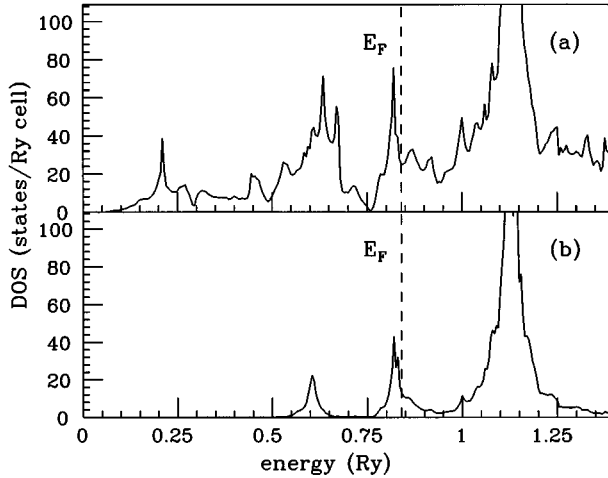


FIG. 1. (a) DOS of CeSi_2 deduced from the self-energy of Eq. (4). (b) Partial f -DOS of CeSi_2 .

straight line $\omega - \varepsilon_d$ had several cuts, since for each orbital of the noninteracting system there would be as many strongly correlated orbitals as the number of these cuts. As a result, the dimension of the Hilbert space would be modified, and the analyticity of the perturbation theory could be affected. This difficulty is not present in the method described in Eqs. (1)–(3), because the interacting Green function is diagonalized in \mathbf{k} space and therefore the self-energy operators are applied to the Bloch states and not to the d or f orbitals.

The most conspicuous feature of the electronic structure yielded by the self-energy (4) is the multipeak character that the electronic structure arising from each $m\nu$ orbital can present (according to the bandwidth of the noninteracting system), where the position of the peaks depends on the occupation of every $m\nu$ symmetry, and their intensity depends on the weight of the states over every $m\nu$ orbital⁶ (this characteristic is present in other self-energy approximations, such as that of Unger and Fulde in Ref. 8).

The band calculation method described in this paper is applied to analyze the electronic structure of the f system CeSi_2 and the d/p system $\text{YBa}_2\text{Cu}_3\text{O}_7$, since both are well-known strongly correlated materials. CeSi_2 is a nonmagnetic material in which the f occupation per cerium atom is ≈ 0.96 ; therefore one can consider only one occupied f symmetry. The characteristics of the noninteracting system are such that the self-energy (4) depends on ω . The multipeak structure of this compound can be seen in Figs. 1(a) and 1(b), which show the renormalized total and partial f DOS's, respectively, with $U = 5.7$ eV. They display the following resonances: the one located at ≈ 3 eV below E_F corresponds to the $4f^0$ final state in a photoemission process and can be attributed to the lower Hubbard band (LHB); the structure at ≈ 4 eV above E_F corresponding to the $4f^2$ final state in the bremsstrahlung spectroscopy [the upper Hubbard band (UHB)]; and a central peak next to E_F which arises from the spectral transference between the LHB and UHB. The middle energy resonances (MER's) practically join the $4f^0$ with the $4f^2$ final states, yielding an almost continuous f band whose total bandwidth is clearly stretched, this being a main feature which has been experimentally detected.^{9,10} This MER has a first structure at ≈ -110 meV, a second one

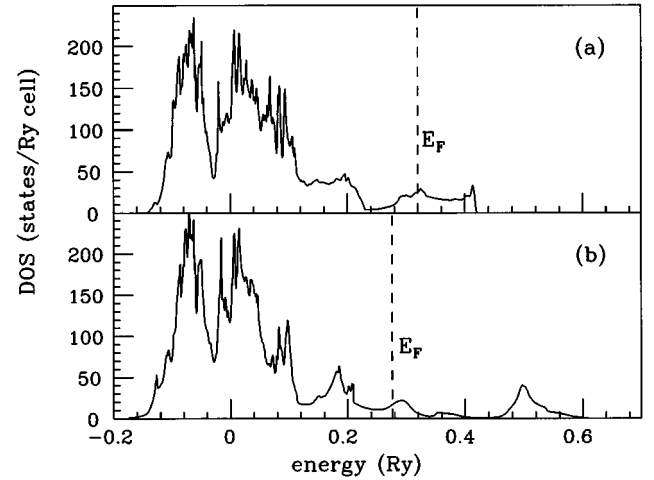


FIG. 2. (a) DOS of $\text{YBa}_2\text{Cu}_3\text{O}_7$ deduced from a constant self-energy with $U_d = 0.26$ Ry and $U_p = 0.22$ Ry; (b) DOS of $\text{YBa}_2\text{Cu}_3\text{O}_7$ calculated from an ω -dependent self-energy like that of Eq. (4).

at ≈ -30 meV, and a shoulder just above E_F centered at ≈ 40 meV. The location of the two structures just below and above E_F (those at ≈ -30 and ≈ 40 meV) present an excellent agreement with the experimental data of the Los Alamos's group of Ref. 10. However, there is a discrepancy about the first peak in the near-Fermi region, since it lies at ≈ -300 meV in the photoemission spectra,¹⁰ while in our results it is located at ≈ -110 meV. This discrepancy can be justified by the absence of a spin-orbital correction in our LDA Hamiltonian, which is estimated to be around 0.2 eV. Therefore, the results shown in Fig. 1 are in good agreement, both quantitatively and qualitatively, with the experimental data.^{9,10} We wish to emphasize the impossibility of obtaining the central peaks that correspond to the f symmetry from non-energy-dependent self-energy approximations, such as those given in the SIC and LDA+ U approximations.

We have performed two calculations of the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$. One of them considers only the constant (not depending on ω) part of the self-energy (4), while in the other the full expression (4) is taken into account. The orbitals Cu(1) $3d_{x^2-z^2}$, O(1) $2p_y$, O(4) $2p_z$, Cu(2) $3d_{x^2-y^2}$, O(2) $2p_x$, and O(3) $2p_y$ (after the atomic notation of Ref. 11) are partially occupied and therefore the strong correlation plays a role in these orbitals. Figure 2(a) shows the DOS of $\text{YBa}_2\text{Cu}_3\text{O}_7$ deduced from a constant self-energy with $U_d = 3.5$ eV and $U_p = 2.9$ eV. These results are in a reasonable agreement with other mean-field calculations.¹² In Fig. 2(b) the energy-dependent term of the self-energy expression (4) has also been taken into account, i.e., the fluctuation effects yielded by the self-energy are included. These fluctuations give rise to a transference of the spectral functions between the LHB and UHB for each strongly correlated orbital, and therefore we obtain a different pattern in both figures. The states at E_F in Fig. 2(b) have almost exclusively O(4) character, while those of Fig. 2(a) are mostly Cu(2), O(2), and O(3) states, having a negligible O(4) weight. The peak located at ≈ 3 eV above E_F in Fig. 2(b) corresponds to the UHB; it has Cu(2) character and shows a small tail due to Cu(1) states. The intermediate

states between E_F and the UHB have mainly Cu(1), O(1), and O(4) weights. $\text{YBa}_2\text{Cu}_3\text{O}_7$ presents a p -type electronic structure, as shown by several measurements (Hall effect, x-ray spectroscopy, and electron-energy-loss spectroscopy),¹¹ with holes both in the CuO_2 planes and the CuO_3 chains. The hole distribution on the different oxygen and copper sites that correspond to Fig. 2(b) are as follows: 0.33 holes on O(1), 0.14 on O(2) and O(3), 0.78 on O(4), 0.86 on Cu(1), and 1.12 on Cu(2). By comparing them to the ones obtained by Nücker *et al.* and Krol *et al.*,¹¹ we find a reasonable agreement except in the case of O(4), for which

there is a considerable difference of ≈ 0.6 . Although Fig. 2(b) shows a better description of the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ than Fig. 2(a) (where the constant versus ω self-energy is considered), we believe that a more accurate description of the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be obtained by means of other approximations to the self-energy, and will be the aim of further work.

We acknowledge financial support from DGICYT from Spain, Project No. PB93-1249, and from CIRIT from Catalonia (Spain), Grant No. 1995SGR 00039.

-
- ¹A. Svane and O. Gunnarsson, *Europhys. Lett.* **7**, 171 (1988); *Phys. Rev. B* **37**, 9919 (1988); *Phys. Rev. Lett.* **65**, 1148 (1990); A. Svane, *ibid.* **68**, 1900 (1992); W. M. Temmerman, Z. Szotek, and H. Winter, *Phys. Rev. B* **47**, 11 533 (1993).
- ²V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Phys. Rev. B* **44**, 943 (1991); V. I. Anisimov, M. A. Korotin, J. Zaanen, and O. K. Andersen, *Phys. Rev. Lett.* **68**, 345 (1992).
- ³F. Aryasetiawan and O. Gunnarsson, *Phys. Rev. Lett.* **74**, 3221 (1995).
- ⁴Arno Schinlmayr and R. W. Godby, *Phys. Rev. B* **51**, 10 427 (1995).
- ⁵T.C. Hsu and B. Douçot, *Phys. Rev. B* **48**, 2131 (1993); C.Chen, *Phys. Rev. Lett.* **73**, 1982 (1994); J. Igarashi, P. Unger, K. Hirai, and P. Fulde, *Phys. Rev. B* **49**, 16 181 (1994); C. Calandra and F. Manghi, *ibid.* **50**, 2061 (1994); F. Manghi, C. Calandra, and O. Ossini, *Phys. Rev. Lett.* **73**, 3129 (1994).
- ⁶F. López-Aguilar, J. Costa-Quintana, and L. Puig-Puig, *Phys. Rev. B* **48**, 1128 (1993); **48**, 1139 (1993); M. M. Sánchez-López, J. Costa-Quintana, and F. López-Aguilar, *Europhys. Lett.* **27**, 235 (1994); J. Costa-Quintana, E. González-León, F. López-Aguilar, L. Puig-Puig, and M. M. Sánchez-López, *Physica B* **206&207**, 186 (1995).
- ⁷L.Hedin and S. Lundqvist, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1969), p. 1; M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- ⁸H. Eskes, M. B. J. Meinders, and G. A. Sawatzky, *Phys. Rev. Lett.* **67**, 1035 (1991); M. B. J. Meinders, H. Eskes, and G. A. Sawatzky, *Phys. Rev. B* **48**, 3916 (1993); P. Unger and P. Fulde, *ibid.* **51**, 9245 (1995); P. Unger, J. Igarashi and P. Fulde, *ibid.* **50**, 10 485 (1994).
- ⁹R. M. Wentzocovitch, W. W. Schultz, and P. B. Allen, *Phys. Rev. Lett.* **72**, 3389 (1994); M. M. Steiner, R. C. Albers, and L. J. Sham, *ibid.* **72**, 2923 (1994); P. Weibel, M. Grioni, D. Malterre, B. Dardel, and Y. Baer, *ibid.* **72**, 1252 (1994); E. K. R. Runge, R. C. Albers, N. E. Christensen, and G. E. Zwicknagl, *Phys. Rev. B* **51**, 10 375 (1995).
- ¹⁰J. J. Joyce, A. J. Arko, J. Lawrence, P. C. Canfield, Z. Fisk, R. J. Barlett, and J. D. Thompson, *Phys. Rev. Lett.* **68**, 236 (1992); F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, *ibid.* **58**, 2810 (1987); D. Malterre, M. Grioni, P. Weibel, B. Dardel, and Y. Baer, *Europhys. Lett.* **20**, 445 (1992).
- ¹¹N. Nücker *et al.*, *Phys. Rev. B* **51**, 8529 (1995); A. Krol *et al.*, *ibid.* **45**, 2581 (1992).
- ¹²H. Kim and J. Ihm, *Phys. Rev. B* **51**, 3886 (1995).