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Coulomb gap in $4f$ systems: One-body treatment. Application to $4f^{13}$ and $4f^{1}$ configurations

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A potential depending on the f count is deduced from the Coulomb correlation energy. This is applied to two cases in order to describe the Coulomb gap effects within the $4f$ systems.

It is generally accepted (since the last two MV conferences[1,2]) that the f electrons at low temperatures behave as heavy quasiparticles with a definite k value. The intrasite e-e interaction and the hybridization play an important role in the $4f$ systems in such a way that the band models are able to explain the electronic structures whenever these effects were included in the one-body Hamiltonians. However, it is not well established which is the most appropriate potential. This potential has to take into account that the hybridization favors the hopping of f electrons which allows for nonintegral values of the n_f numbers. So the 14 f orbitals will suffer an energy shift proportional to the number of empty levels, at other sites, available for hopping.[1] The main aim of this paper is to give a band model, including U and V_{fk} effects, valid for all configurations [integral (n) and nonintegral (x) f counts]. Two specific cases illustrate this model: in the first one (Yb_2O_3) the U effects produce a metal semiconductor transition, keeping the configuration $n=13$; the second case ($CeAl_2$) corresponds to a metal with x close to 1(0.95).

The hopping processes imply atomic fluctuations of n_f and thus, the intrasite correlation can be defined as the square of the standard deviation around the average occupation numbers of electrons in the f orbitals[3,4]

$$\Delta E^{\mathrm{Cc}}=\tfrac{1}{2}NU\sum_{\nu}^{14}\Delta n_\nu^2,\quad \Delta n_\nu^2=\langle n_\nu^2\rangle-\langle n_\nu\rangle^2\ ,$$

where $n_\nu=N^{-1}\sum_{\vec{k}\alpha}|\langle\vec{k}\alpha|f_\nu\rangle|^2c^{\dagger}_{\vec{k}\alpha}c_{\vec{k}\alpha}$. Evaluating ΔE^{Cc} in a similar way as in recent papers,[3] one obtains $\Delta E^{\mathrm{Cc}}=\frac{1}{2}NU\sum_\nu\langle n_\nu\rangle(1-\langle n_\nu\rangle)$.

The fluctuations in n_ν produce a variational potential $\delta\Delta E^{\mathrm{Cc}}/\delta x=U\sum_\nu^{14}(\frac{1}{2}-\langle n_\nu\rangle)$ where x is equal to $\sum_\nu^{14}\langle n_\nu\rangle$. This potential, so defined, does not satisfy the condition previously mentioned at the beginning of the introduction since it shifts all f orbitals in a similar amount of energy. Therefore these orbitals could simultaneously cross E_F, violating the Luttinger theorem.[5-7] This is avoided by multiplying each factor $U(\frac{1}{2}-\langle n_\nu\rangle)$ by its corresponding spatial projection operator $|\beta_\nu\rangle\langle\beta_\nu|$ and thus the potential reads

$$U(\vec{r},x)=U\sum_{\nu}^{14}(\tfrac{1}{2}-\langle n_\nu\rangle)|\beta_\nu\rangle\langle\beta_\nu|\ ,\tag{1}$$

U being the Coulomb correlation energy.

The potential (1) is nonmuffin tin for compounds with an unfilled $4f$ shell. Then, we have considered the standard symmetrization of the non-muffin-tin effects, within the augmented plane wave (APW) methods[8,9] (the crystal structures analyzed below, advise the use of the SAPW method[10]). This symmetrization determines the linear combinations of $1=3$ orbitals (β_ν) and the self-consistent (SC) determination of the change density fixes the average occupation numbers $\langle n_\nu\rangle$. The potential $U(\vec{r},x)$ lowers the energy of the bands with $\langle n_\nu\rangle$ greater than $\frac{1}{2}$ and the opposite occurs for $\langle n_\nu\rangle$ less than $\frac{1}{2}$. Thus the half occupation ($\langle n_\nu\rangle=\frac{1}{2}$) becomes an unstable equilibrium point. Therefore $U(\vec{r},x)$ may modify the SC charge density of the occupied $4f$ orbitals and these possible variations could change the local density potential of the $H_{\mathrm{band}}[V_{\mathrm{MT}}(\rho_T(\vec{r}))]$ since this depends on the whole density charge. We have followed the standard construction of the MT potentials;[8] therefore, V_{MT} moves down (up) the energies of all atomic characters when x decreases (increases), compensating the variations of the f charge density due to the effects of $U(\vec{r},x)$.

In summary, we introduce a potential $U(\vec{r},x)$ which is summed to $V_{\mathrm{MT}}(\rho_T(\vec{r}))$ and whose final pattern consists in the splitting of the different spin bands according to the occupation of its corresponding β_ν orbitals. This picture can describe both the metal semiconductor (MS) transition and the mixed valence in either metallic or semiconducting phases. We have applied this model to Yb_2O_3 and $CeAl_2$ since these two cases are complementary in order to analyze the consequences of the Coulomb gap. A MS transition occurs in Yb_2O_3 and a metallic phase is the final state in $CeAl_2$. Moreover, the unoccupied β_ν orbital per rare-earth (RE) atom in the $4f^{13}$ configuration coincides with the occupied orbital for the other case ($CeAl_2$).

The $X\alpha$ exchange potential depending on the charge density and the spin polarization has been used for Yb_2O_3. The choice of the α parameters required a previous calculation. This was made, solving the radial Dirac equation within the MT spheres and fitting this potential so that our results coincided with the available experimental and theoretical data[11,12] [$E(4f_{7/2})-E(5p_{3/2})=1.05$ Ry, $E(5p_{3/2})-E(5s)=2.60$ Ry, $E(1s)=-39.36$ Ry, and our results with $\alpha_{\mathrm{O}}=1.00$ and $\alpha_{\mathrm{Yb}}=0.93$ are 1.03, 2.30, and -39.78 Ry, respectively].

Figures 1(a) and 1(b) show the metallic phase when one considers $U=0$ and this disappears when $U=0.48$ Ry, which is the value calculated in a previous paper[13] in agreement with the experimental measurements.[14] The SC calculation of the terms $|\langle\vec{k}\alpha|f_\nu\rangle|^2$ reveals that the average occupation number $\langle n_\nu\rangle$ for the orbital $XYZ(Y_2^3-Y_{-2}^3)$ is very close to zero. This fixes the potential $U(\vec{r},x)$ and the symmetries of the unoccupied f bands in the calculation corresponding to $U=0.48$ Ry [Fig. 1(c)]. The first band not including $U(\vec{r},x)(\Gamma_1^+\Lambda_1H_4^+)$ is almost parabolic, not showing any dominant 1 character. When $U(\vec{r},x)$ is in-

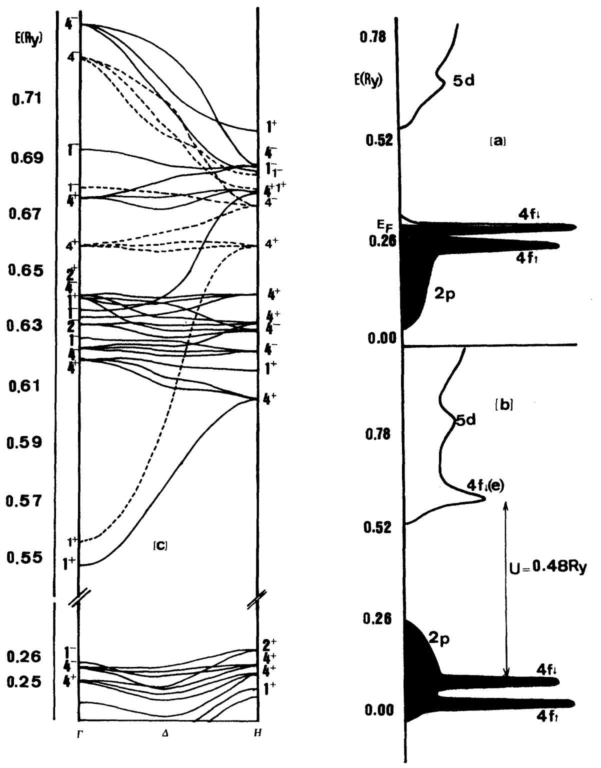

FIG. 1. (a) Schematic densities of states (DOS) without the potential $U(\vec{r},x)$. (b) DOS with $U(\vec{r},x)$. (c) —— denoted spin-down band structure (symmetry line 100) with $U(\vec{r},x)$ potential. – – – denotes spin-down conduction band without $U(\vec{r},x)$. The spin-up conduction band without $U(\vec{r},x)$ is similar to the spin-down one although slightly shifted (-0.1 eV) and the spin-up band structure with $U(\vec{r},x)$ is equal to that with spin up without $U(\vec{r},x)$; therefore, these bands have been omitted in the drawing. The crystalline structure, lattice parameters, etc., have been taken from Gschneidner and Eyring (Ref. 15). The energies of the figures are relative to the average potential of the interstitial region: -1.55 Ry in Yb_2O_3 and -1.22 Ry in $CeAl_2$.

cluded, this band is hybridized with the unoccupied $4f$ states obtaining two $\Gamma_1^+\Delta_1H_4^+$ bands and 15 narrow bands slightly hybridized with the d orbital (Yb_2O_3 has 16 Yb atoms per primitive cell[15]). This picture is consistent with the criticism of Andersson[1] to Mott's hybridization model, with Martin's model in other Coulomb-gap processes,[5,6] and with some x-ray experiences.[16] The group of the five bands [without $U(\vec{r},x)$] located between 0.66 and 0.68 Ry has the $5d$ character. This character is substituted in these bands by the $4f$ one (if $U=0.48$ Ry) producing an energy shift of the bands with $5d$ predominance, being located around 0.83 Ry. The $2p$-$5d$ gaps are ~ 6 eV in Fig. 1(a) (when $U=0$ Ry) and 7.6 eV in Fig. 1(b); this last value is close to the L_{III} experimental results of the Refs. 17 and 18 (7.8 eV). The dispersion of the $4f$ charge by the hybridizations implies a broadening (~ 2.5 eV) of the unoccupied $4f$ band. For instance, the band $\Gamma_1^-\Delta_2H_4^-$ at 0.69 Ry presents the following characteristics: $n_f=0.15$ and the charge outside the muffin tin spheres is 64%. This broadening is in agreement with the model of the screened orbitals induced by the photoelectron spectroscopy of Fuggle *et al.*[19]

The exchange and correlation potential used for the calculation of the electronic structure of $CeAl_2$ is the Gunnarsson-Lunqvist[20] potential with spin polarization. We have followed a calculation procedure similar to that of Hasegawa and Yanase for $LaAl_2$.[21] The spin down band structure of $CeAl_2$ [see Fig. 2(a)] corresponds strictly to the $4f^{0\downarrow}$ configuration which is equal to the $LaAl_2$ band structure and is in good concordance with the calculation of Hasegawa and Yanase. The occupied f orbital in the atoms of Ce is the XYZ, the same as the unoccupied one for Yb_2O_3. This consideration affects the construction of the $U(\vec{r},x)$ potential and the symmetries of the occupied bands. For the $4f^{1\uparrow}$ configuration, $U(\vec{r},x)$ establishes a relation among the parameters n_f, U, and E_f (binding energy of the $4f$ band center respect to the E_F) through the equation $n_f \cong \frac{1}{2} - E_F/U$ which is reasonably satisfied experimentally.[22-24] Figure 2(b) shows the final form of the ↑ band structure of $CeAl_2$. The bands $\Gamma'_{25}\Delta'_2X_1$, $\Gamma'_{12}\Delta'_2X_1$, and $\Gamma_{15}\Delta_1X_1$ located at 0.40 Ry have $\sim 62\%$, $\sim 34\%$, and $\sim 94\%$, respectively, of their charge in the XYZ orbital, within the MT sphere of Ce. The calculation of the E_F has been made by means of the single histogram procedure, resulting n_f equal to ~ 0.95 and the binding energy E_f is around -2.75 eV. This value is similar to the results of the measurement of Croft *et al.*[23] ($E_F=-2.55$ eV) and Allen *et al.*[22] ($E_f=-2.80$ eV). At the same time, the $4f$ count (x) lies in the interval of the experimental data given by Fuggle *et al.*[24] (from 0.8 up to 1.1). The hybridization of the XYZ orbital with other extended orbitals [fundamentally p(Al) and d(Ce)] appears from 0.37 up to 0.65 Ry. For instance, the state Δ'_2 of the band $\Gamma'_2\Delta'_2X_1$ located at 0.48 Ry is composed by $n_f=0.10$, $n_{3p}=0.23$, and $n_{5d}=0.20$. If we

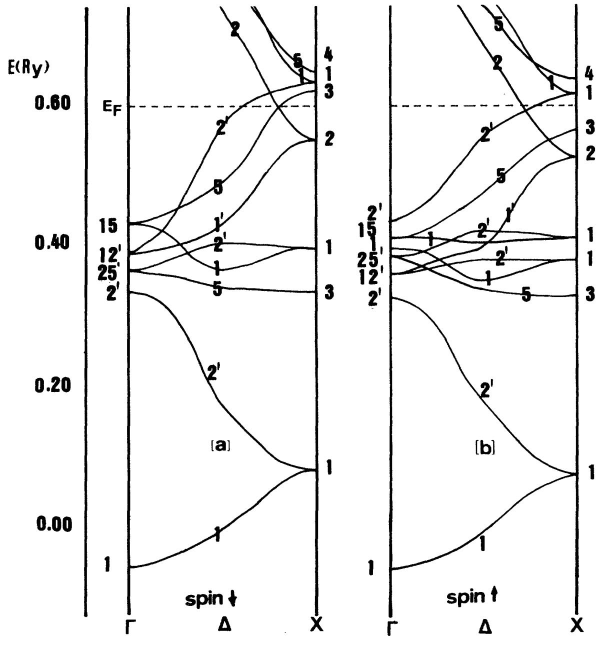

FIG. 2. (a) Spin-down band structure of $CeAl_2$, made with $U(\vec{r},x)$. (b) Spin-up band structure corresponding to the $4f^1$ configuration [with $U(\vec{r},x)$]. The value of the energy U for this compound has been given by Fuggle *et al.* (Ref. 24) and its value is 6.4 eV. The crystalline structure and the lattice parameters are in Ref. 15 (see Buschow). The energies of the figures are relative to the average potential of the interstitial region: -1.55 Ry in Yb_2O_3 and -1.22 Ry in $CeAl_2$.

define the f width as the energy interval including states with $n_f \geqslant 0.1$, then δ_f becomes approximately 1.5 eV which is close to the 1.3 eV given by Allen *et al.*[22]

We have dealt with some aspects of the Coulomb-gap effects through these two band structures, allowing several conclusions about the f delocalization in strong correlated systems to be drawn. Firstly, each f state coherently mixes with one and only one $\vec{k}$ (s, p, or d) band state and, at the same time, not all of these orbitals f hybridize in the same way. Secondly, our potential model is consistent with the picture of different shifts for each orbital according to its occupation suggested previously.[1,3,4] In addition, the final pattern provided by $U(\vec{r},x)$ agrees with the so-called "three or four peaks" model (see Ref. 6) for metallic compounds with more than one f electron per RE atom. Evidently, for f counts greater than 2 and mixed valence situations, the totally occupied f_ν orbitals will suffer, with respect to the noninteracting system [without $U(\vec{r},x)$], an energy shift of $-U/2$. The energy shift of the totally empty f_ν orbitals will be $+U/2$ and $U(r,x)$ potential yields an energy change proportional to $(\frac{1}{2}-\langle n_\nu \rangle)$ for average occupation numbers $\langle n_\nu \rangle$ between 0 and 1 (i.e., $0<\langle n_\nu \rangle<1$), making possible the appearance of the three or four peaks predicted by Martin.

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