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First-Principles Theory of Intermediate-Valence f -electron Systems

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We propose a first-principles based method for calculating the electronic structure and total energy of solids in an intermediate-valence configuration. The method takes into account correlation effects ($d - f$ Coulomb interaction) and many-body renormalization of the effective hybridization parameter of the f system. As an example, the formation of a pressure-induced intermediate-valence state in Yb is considered and its electronic structure and equation of state are calculated and compared to experimental data. The agreement is found to be excellent for both properties, and we argue that the developed method, which applies to any element or compound, provides for the first time a quantitative theoretical treatment of intermediate-valence materials.

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Intermediate-valence ($I\mathcal{V}$) systems form an interesting class of f -electron compounds with various anomalous electronic and lattice properties [1–4]. It is commonly accepted that a partial promotion of $4f$ electrons into the $5d$ band is the main physical origin of the $I\mathcal{V}$ phenomena in most rare-earth based compounds (however, for Ce the scenario of a Mott transition in the $4f$ band [5,6] seems to be more probable). The relevant interactions determining the intermediate-valence includes the $d - f$ hybridization as well as excitonic effects due to Coulomb attraction between the hole in the $4f$ shell and the promoted $5d$ electron [7,8]. The latter is usually referred to as “Falicov” interaction [9]; without this interaction it is impossible, for example, to explain the strong temperature dependence of the energy gap in the $I\mathcal{V}$ semiconductors [8]. Therefore, any quantitative theory of the $I\mathcal{V}$ should take into account some correlation effects. In particular, any first-principles approach to the electronic structure, based on the local density approximation (LDA) [10,11], must be modified.

By combining a model theory of $I\mathcal{V}$ phenomena developed in Ref. [8] and the approach for calculating valence stability, of Ref. [12], we propose here a novel first-principles scheme for the electronic structure calculations for the $I\mathcal{V}$ systems. As an example, the calculated volume versus pressure equation of state (EOS) of Yb is compared with diamond anvil cell measurements from Ref. [13]. We also compare the calculated electronic structure of Yb under pressure with recent x-ray absorption spectra measured in the Partial Fluorescence Yield mode and x-ray absorption spectroscopy (PFY-XAS) [14]. Excellent agreement is obtained for both properties.

Elemental Yb has received considerable attention in the past; the electronic properties have been measured at ambient pressure using photoelectron spectroscopy and

the magnetic properties show a temperature independent susceptibility [15], indicating that Yb at ambient conditions is divalent. However, the conclusion of the high pressure experiments of Ref. [16] was that Yb undergoes a pressure-induced transition to an $I\mathcal{V}$ state. These conclusions were only qualitative; the precise composition of the $I\mathcal{V}$ state in terms of contributions from Yb^{3+} and Yb^{2+} configurations were not determined, although at 100 GPa it was estimated that Yb has transformed completely to a trivalent state [13]. Unfortunately, it has been difficult in the past to obtain precise information for the degree of valency of $I\mathcal{V}$ systems in general, which calls for an accurate theoretical method. This is the main motivation of the present study.

The key problem is how to calculate the valence from first principles. One possible way has been proposed in Ref. [6] where an $I\mathcal{V}$ metal is considered as an alloy of, say, trivalent and divalent ions of the same element, the valence (that is, the concentration of the components) being found from the minimum of the total energy calculated in the coherent potential approximation (CPA). However, the last step makes the procedure computationally cumbersome. Also, the correlation effects are completely neglected in this procedure.

We propose a simple and efficient algorithm to find the valence. To be specific, let us start with a divalent rare-earth element corresponding to an f -shell configuration f^{n+1} . For a given volume, we can calculate the total energy difference, Δ_0 , between the trivalent (f^n configuration) and the divalent state using the method of Ref. [12]. A straightforward application of this method cannot account for an $I\mathcal{V}$ state; it simply concludes that if $\Delta_0 > 0$ then the divalent state is stable. We are interested in the $I\mathcal{V}$ case, and the relevant case is when $\Delta_0 \leq 0$. As a first step, let us neglect the correlation effects as well as the

finite width of the f -level. Then the valence $z = 2 + x$ is determined by the energy balance between the difference of the f^{n+1} and f^n configurations and the variation of the band energy when promoting x electrons:

$$x = \int_{E_F}^{E_F + |\Delta(x)|} dEN(E), \quad (1)$$

where E_F is the Fermi energy for the divalent state, $N(E)$ is the density of states of itinerant electrons (for Yb metal it is dominated by the $5d$ states), and $\Delta(x)$ is a renormalized promotion energy which will be defined in the next paragraph. It should be noted that Eq. (1) originates from a model Hamiltonian treatment, therefore it does not contain a double counting term as is usual in density functional theory.

In Ref. [8], a BCS-like theory of the $I\mathcal{V}$ systems, with a $d-f$ excitonic pairing instead of the usual Cooper pairing, has been proposed. From that model treatment it follows that the main correlation effect on the valence is just the Hartree-Fock renormalization of Δ_0 , i.e.,

$$\Delta(x) = \Delta_0 + Gx, \quad (2)$$

where G is the Falicov interaction parameter. All other effects are connected with the renormalization of the hybridization and will be considered below; one can neglect their influence on the valence provided that the effective hybridization is much smaller than the $5d$ bandwidth, which is always true with a very high accuracy. One then obtains the valence by solving Eqs. (1) and (2) iteratively. We neglect here any dependence of the correlation energy on the valence. Our results show that this simplified approach works surprisingly well for Yb metal.

The parameter G can be determined as the derivative of the center of the $5d$ band with respect to the number of $4f$ electrons, or, equivalently (apart from a change of sign), with respect to x . For Yb metal, as shown in Fig. 1, G has

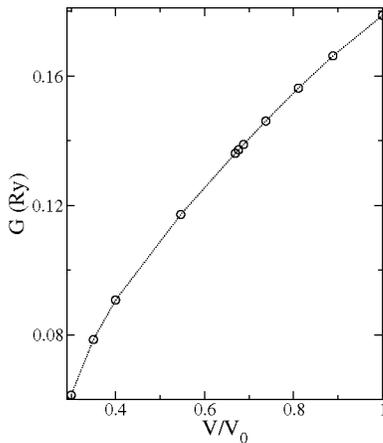


FIG. 1. Calculated G parameter for Yb as a function of the reduced volume V/V_0 . Circles indicate calculated values while the dotted line is a guide for the eye.

an almost linear behavior as a function of the reduced volume V/V_0 and it decreases from an initial value of 0.18 Ry at ambient conditions to a value of 0.06 Ry at $V = 0.25V_0$ (corresponding to a pressure of about 100 GPa [13]). All band structure calculations were made in the generalized gradient approximation (GGA) [17] using the electronic structure method described in Ref. [18]. Also, the $4f$ -electrons are treated as core states.

The effective hybridization v_{eff} between d and f states with the many-body renormalization can be calculated using the electronic structure expression from Ref. [8]

$$v_{eff} \left[1 - G \int \frac{dEN(E)}{\sqrt{(E-Y)^2 + 4v_{eff}^2}} \right] = v, \quad (3)$$

where $Y = E_F + |\Delta(x)|$ is the renormalized Fermi energy and v is the bare hybridization parameter calculated from first principles as suggested in Ref. [19].

In Table I, the calculated valence of fcc Yb, obtained from Eqs. (1) and (2), is listed for different considered volumes. Only one iteration was used to obtain the valence since further iterations would correct z only to the third decimal figure. The second (third) column shows the value z_0 (z) calculated if the Falicov interaction G is neglected (taken into account). The valence z_0 increases in a monotonic way when pressure increases while the corrected valence, z , changes less rapidly due to the Coulomb attraction of the promoted charge from the f hole. The mechanism behind this is simple: with an increased value for the promoted charge follows a larger Coulomb attraction back into the localized f shell. Hence, the window of pressures for the total delocalization of one f electron from the initially filled f shell to the f^{13} configuration becomes larger. Note that experimentally [13], Yb undergoes various structural phase transitions in the investigated region. However, the energy differences between different structures are very small (0.5–1 mRy/atom [20]) and therefore unimportant for the determination of the valence. Hence, we have for simplicity assumed an fcc structure for this part of our calculation. The smoothness of the experimental equation of state reported in Fig. 2 is consistent with the fact that structural changes are not relevant.

TABLE I. Calculated valence for fcc Yb as a function of the reduced volume V/V_0 . z_0 indicates the valence calculated without taking into account the Coulomb attraction of the promoted electronic charge from the resulting hole in the f shell; z is the valence when this last correction is not neglected.

V/V_0	z_0	z
1	2	...
.67	2.50	2.37
.55	2.82	2.57
.40	2.90	2.72

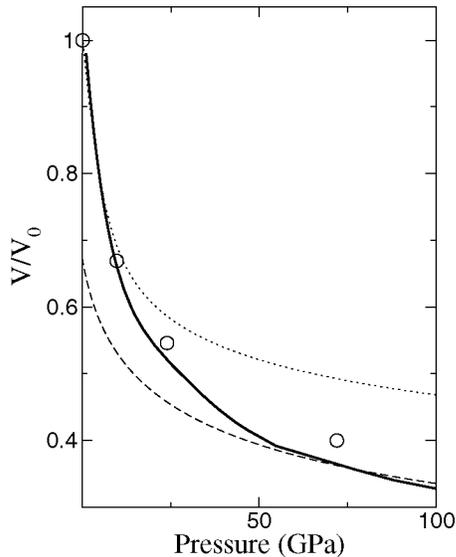


FIG. 2. Calculated equation of state for fcc Yb (open circles) compared to experiment (full line) taken from Ref. [13]. The two broken lines are isothermal equation of states for divalent (upper dotted line) and trivalent (lower dashed line) fcc Yb.

To gain insight about the order of magnitude of the correlation effects on the $d-f$ hybridization parameter we have calculated the bare hybridization parameter, ν , and the effective hybridization parameter, ν_{eff} , as defined in Eq. (3) for Yb at a pressure of 20 GPa. We obtain a value of 5.96 mRy for the effective hybridization parameter starting from a bare ν of 5.40 mRy. A correction of the order of 10%, due to correlation, is reasonable.

Using our calculated values for the valence z we have then performed CPA calculations [21] in order to evaluate the equation of state of Yb. For each considered volume the fraction of Yb^{3+} and Yb^{2+} was calculated using the model described above (i.e., the Yb^{3+} concentration equals $z-2$), after which a regular CPA calculation was made considering an alloy of Yb^{3+} and Yb^{2+} atoms. For each valence and volume, we have calculated the pressure from these CPA calculations. In practice this was done from a numerical derivation of the energy fitting with a Birch-Murnaghan equation of state [22].

We plot in Fig. 2 the calculated EOS (open circles) together with the experimental data (full curve) of Ref. [13]. For comparison, the equation of state for divalent and trivalent Yb is also shown in the figure. The agreement between experiment and the theory that includes correlations effects is good, whereas the trivalent and divalent EOS curves do not capture the behavior of the experimental data.

Next, we address the recently measured PFY-XAS of Yb [14], where the unoccupied states were measured as a function of pressure. The experiments probed the L -edge by detecting the Partial Fluorescence from the $3d-2p$ decay. This means that the unoccupied $5d$ -density of

states (DOS) was mapped with the reduced lifetime broadening of the $3d$ core-hole and the spectral features could be observed with higher contrast with respect to traditional L -edge XAS [23]. The experimental spectrum, taken at a pressure of 20 GPa [24], is shown in Fig. 3 (upper curve) and, when a comparison to a $5d$ -projected DOS of the divalent state is made (lower curve of Fig. 3), a rather large disagreement with experimental data is observed. It may be observed that although the two peaks at lower energies are reproduced with some accuracy from this calculation, there is a substantial part of the experimental spectrum, at 10 eV and above, that is not present at all in the calculated DOS of the purely divalent configuration. A comparison of the DOS of a purely trivalent configuration with the PFY-XAS data in Fig. 3 gives an equally poor agreement (data not shown). The large deviation from a divalent configuration at elevated pressures is a finding that is consistent with the EOS analysis described in the first part of this Letter. In fact, the calculation that corresponds to an $I\mathcal{V}$ regime gives a spectrum that agrees much better with experiment. This is shown in Fig. 3 (middle curve) where one can see that the three main peaks of the experiment are better reproduced, both in terms of their positions as well as in their intensity. The calculated spectrum shown in Fig. 3 is a superposition of contributions to the spectrum both from divalent Yb atoms and from trivalent Yb atoms as calculated in the CPA potential of their alloy. There is a chemical shift of the core states between these two

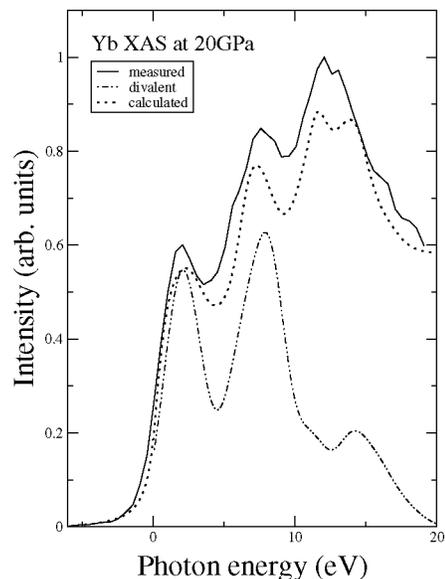


FIG. 3. Measured and calculated x-ray absorption spectrum of elemental bcc Yb at a pressure of 20 GPa. The full line represents experimental PFY-XAS data, the dotted line (middle curve) shows the calculated spectrum of the $I\mathcal{V}$ state, whereas the dot-broken line (lower curve) is the spectrum obtained for a divalent configuration. The first peak is aligned and the zero of the photon energy scale is arbitrarily chosen.

atom types, a shift we calculate to be of 7 eV. This shift must be considered in order to calculate the XAS spectrum, and is the main reason for the spectrum calculated from a mixed valence system being broader than the one of the divalent system. In the theoretical spectrum in Fig. 3 (middle curve) the shift applied is of 5.7 eV [25]. In this case the calculations are made for bcc Yb. The reason for this is that while the change in the valence between bcc and fcc is negligible, the DOS reflects unforgivably any structural change.

In conclusion, we have shown that a first principles based method that takes into account correlation effects, i.e., $d-f$ Coulomb interaction and many-body renormalization of the effective hybridization parameter of the f -system, reproduces both the measured electronic structure (as given by PFY-XAS) as well as the equation of state of elemental Yb. Quantitative information about the concentration of di- and trivalent Yb atoms has been calculated for each pressure, providing detailed information about the intermediate-valence state. One may observe that it is by no means clear that the electronic structure of a first-principles based method should reproduce the details of an x-ray absorption spectrum since it has been observed that Kohn-Sham eigenvalues may not necessarily be compared to excited state properties of materials [26,27]. In addition, it has been shown that for the x-ray absorption process one should consider the final state electronic structure [28]. These issues are clearly important also for Yb metal, but we argue that for a d -band metal with a large bandwidth it is, from experience [29], better to compare the x-ray data with the initial state electronic structure. Finally, we note that the developed method should be applicable to any element or compound.

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