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Electronic structure of $Z+1$ impurities in metals

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We present a theoretical analysis of the electronic structure of substitutional $Z+1$ impurities in simple and transition metals. Self-consistent calculations for Mg in Na and Tc in Mo have been performed using the Korringa-Kohn-Rostoker Green's-function formalism, and have been analyzed in terms of a simplified impurity model. At the impurity site a strong redistribution of states for both the occupied and unoccupied levels, in particular for the *s* and *p* states in the case of the simple metals and for the *d* states in the case of the transition metals, is observed. We show that the local electronic structure at the impurity site can be interpreted in terms of the electronic structure of the unperturbed host and two sets of parameters representing the attractive potential and a change in the orbital hybridization.

I. INTRODUCTION

The electronic structure of a substitutional impurity with an extra nuclear charge ($Z+1$ or equivalent core approximation) can be considered as a basis to describe the redistribution of states produced in the course of a deep core-level excitation by, e.g., electron or photon impact. The analysis of such data is important for a large variety of spectroscopic techniques like electron-loss spectroscopy (ELS), x-ray-photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), or x-ray-absorption spectroscopy (XAS). Here we present calculations of the electronic structure for substitutional $Z+1$ impurities in metals, and it is our aim to interpret the results in terms of the underlying physical processes.

The theoretical analysis, i.e., the calculation of the response of the system to the introduction of a localized perturbation, is complicated due to the break in the translational symmetry. With the advent of modern band-structure schemes, it is currently possible to calculate the electronic structure at the impurity site and in its solid environment in a fully-self-consistent manner. This applies to metals (see, e.g., Ref. 1) and semiconductors[2] as well as to compounds (see, e.g., Refs. 3 and 4). However, the results of a band-structure calculation are not readily transparent to the way in which governing physical factors lead to the calculated distribution of states. In this context it is useful to employ impurity models which have been proposed in the early 1960s.[5-7] Based on a tight-binding description of the solid state, these models allow a separation of the various physical processes in terms of effective parameters.[4]

We have performed self-consistent *ab initio* electronic-structure calculations, based on the Korringa-Kohn-Rostoker (KKR) Green's-function formalism[1,8,9] for $Z+1$ impurities in a series of simple and transition metals. In this paper we show that the results can be interpreted by means of an impurity model. We are able to demonstrate that for each symmetry-projected density of states (DOS) separately the electronic structure around a $Z+1$ impurity is determined by the following:

(a) The corresponding partial DOS of the unperturbed host, and two parameters Δ and α, which describe, respectively, the following two cases:

(b) An effective shift of the valence-band energy levels, caused by the attractive Coulomb potential of the extra nuclear charge on the impurity atom, and

(c) a change in the spatial extension of the impurity wave functions and its influence on the impurity-host interaction.

In the following we present the results of our analysis for Mg in Na and Tc in Mo. We first describe the impurity Hamiltonian and give details of the computational scheme used to obtain the effective parameters. We then interpret our calculated DOS in terms of the underlying physics.

II. THE MODEL AND ITS RELATION TO THE BAND-STRUCTURE CALCULATION

The model we use is a generalized version of an impurity model, referred to in the literature as the Clogston-Wolff (CW) model,[7,10-12] where the single-band (nondegenerate) Hamiltonian is given in the form

$$H=\sum_{j,l} t_{jl}a_j^\dagger a_l+\Delta a_0^\dagger a_0+\tau\sum_{j\neq 0}(t_{0j}a_0^\dagger a_j+t_{j0}a_j^\dagger a_0)\ . \tag{1}$$

Here $a_j^\dagger$ and a_j are the creation and annihilation operators for electrons in the band, t_{jl} ($j\neq l$) is the transfer integral between sites j and l, and $t_{jj}=\varepsilon_c$ is the effective energy level of the unperturbed host states. The impurity atom is located at the origin and its (attractive or repulsive) potential is represented by the energy shift Δ. The proportionality factor τ allows for a renormalization of the impurity-host interaction with respect to the host-host interaction. The parameter $\alpha=\tau+1$ ($\alpha\geq 0$) may therefore be interpreted as a scaling factor, expressing the relative strength of the impurity-host as compared to the host-host hybridization matrix elements. The impurity on-site Green's function is derived as[10,13]

$$G_{00}(z)=\frac{g_{00}(z)}{\alpha^2-g_{00}(z)[(\alpha^2-1)(z-\varepsilon_c)+\Delta]}\ , \tag{2}$$

where $z=\varepsilon+i0$ and $g_{00}(z)$ is the corresponding host Green's function. The original CW model follows for $\alpha=1$, assuming that the impurity-host transfer integrals are not altered by the presence of the impurity.[7] For α close to zero a localized Lorentzian-like local density of states (LDOS) is found, more in line with a treatment according to the Anderson model.[6] In this case the impurity states are largely decoupled from the host states.

In order to make a connection of this single-band impurity Hamiltonian with the more realistic KKR Green's-function calculation we make use of the fact that the on-site impurity Green's function in the latter case can be written as

$$G_{00}(z)=\frac{\tilde{g}_{00}(z)}{1-\tilde{g}_{00}(z)\Delta t_0(z)}\ . \tag{3}$$

Here $\Delta t_0(z)$ is the difference of the impurity t matrix with respect to the reference system which contains all perturbations from the host except for the on-site impurity perturbations. Therefore, $\tilde{g}_{00}(z)$ differs from the ideal host Green's function $g_{00}(z)$ mainly due to potential perturbations on the neighboring atoms. Equation (3) is a matrix equation in angular momentum; in the case of cubic symmetry and for $l \leq 2$, it is diagonal and can be compared with Eq. (2) separately for s, p, $d-e_g$, and $d-t_{2g}$ symmetry. The constant parameters α and Δ in Eq. (2) approximately represent the effect of $\Delta t_0(z)$ and the change from $g_{00}(z)$ to $\tilde{g}_{00}(z)$.

The effective parameters α and Δ are derived in the following way. From Eq. (2) follows

$$\mathrm{Im}[1/G_{00}(z)]=\alpha^2\mathrm{Im}[1/g_{00}(z)]\ . \tag{4}$$

Here we use the host and impurity Green's functions from the *ab initio* calculation, and this relation provides us with an estimate of the energy dependence of the factor α. We find that over the band α tends to fluctuate about an average value, which defines its effective value.[14]

The parameter Δ is determined by fitting the model LDOS to the self-consistently calculated LDOS, using Eq. (2) and for the parameter α, the value derived from Eq. (4). Note that the impurity Hamiltonian [Eq. (1)] applies to a limited band with a well-defined effective level. The parameter Δ, which represents the difference in the effective levels of the perturbed and the unperturbed LDOS, therefore cannot be estimated using the real part of the self-consistently calculated Green's function. The latter results from a treatment of the potential over an in principle infinite energy range,[9] which is inconsistent with the model Hamiltonian. Instead we have recalculated the real part directly from the LDOS using the Kramers-Kronig relation and choosing the position of the cutoff energy such that the integrated number of states in the band agrees with the orbital degeneracy (e.g., 2 for states of s symmetry, etc.).

III. RESULTS

A. Simple metals

In Fig. 1 we present the results for the LDOS of our self-consistent electronic-structure calculations for Na as a host and Mg as a substitutional impurity. The electronic structure of Mg in Na has been calculated before by other computational schemes, employing the "spherical solid" model,[15] or the linear-muffin-tin-orbital (LMTO) method.[16] The partial occupancies, as shown in Table I, are in close agreement with these earlier results.[16] The LDOS on the impurity site is strongly distorted with respect to the DOS in the unperturbed host system. In particular, a dramatic enhancement at the bottom of the band occurs. As is clear from Fig. 1, mainly the redistribution of states of s symmetry gives rise to the major increase of intensity at the bottom of the band. The calculated distortion of the valence band has been observed experimentally in XES (Ref. 17) and has been related to the attractive force of the extra nuclear charge on the impurity site which pulls states down to the bottom of the band (see, e.g., Refs. 15, 17, and 18). It is this attractive poten-

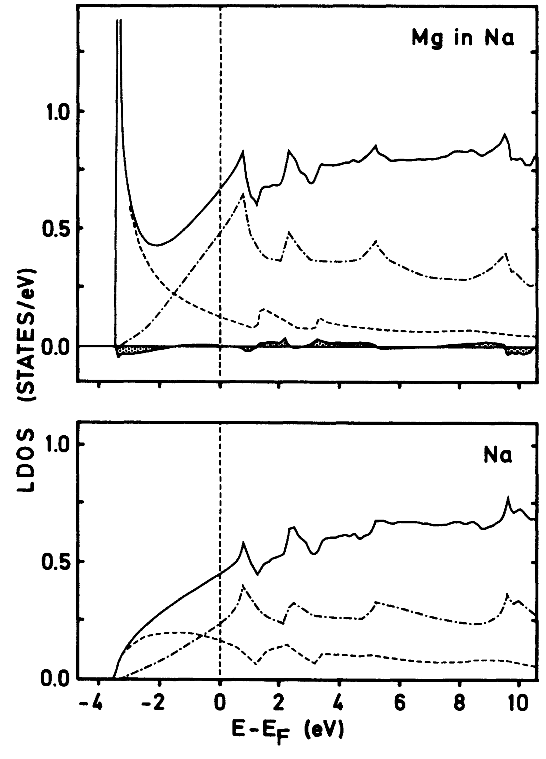

FIG. 1. Self-consistently calculated total (solid line) and partial DOS (dashed line, s projected; dashed-dotted line, p projected) for Na (lower panel) and for a Mg impurity in a Na host (upper panel). Indicated in addition (shaded area) is the difference between the *ab initio* total impurity LDOS and the LDOS calculated using the generalized CW impurity model and the parameters (α and Δ) listed in Table I.

TABLE I. Partial occupancies (N_H, host; N_I, impurity), and generalized CW impurity model parameters (the change in hybridization α and the attractive potential Δ) for Na and Mg in Na. Listed, in addition, is the charge transfer $Q=N_I-N_H$ into the impurity Wigner-Seitz cell.

	s	p	e_g	t_{2g}
N_H	0.595	0.353	0.020	0.026
N_I	1.180	0.696	0.023	0.029
Q	0.585	0.343	0.003	0.003
α	1.00	1.00	1.00	1.00
Δ	-1.9	-1.9	-1.7	-1.4

tial which we determine by our impurity model and which we represent by a parameter Δ, shifting the effective level of impurity states to lower energies. Values for the various parameters are given in Table I. These numbers show that the effective attractive potential varies for states of different symmetry. From the charge transfer Q into the impurity Wigner-Seitz cell one sees that, as expected, the s and p states are the main screening channels in the simple metals. However, it is important to notice that the distribution of the electronic states of *all* symmetries, including the d orbitals, is affected by the attractive potential on the impurity site and that the redistribution is not only restricted to the bottom of the band, but continues throughout the whole energy range of occupied and unoccupied energy levels. Our analysis, moreover, confirms that for the extended s and p states the impurity-host interaction does not change ($\alpha=1$).

We also indicate in Fig. 1 the agreement between the calculated DOS using the parameters α and Δ from Table I and the exact result from the self-consistent calculation. The minor differences we find result from the intrinsic approximations in the model Hamiltonian, like the choice of an essentially constant parameter α, and from the neglect of the intermixing (rehybridization) of states of different symmetry due to the perturbations on the neighboring host atoms.

B. Transition metals

For the transition metals, the d states around the Fermi level are expected to influence the electronic structure of a $Z+1$ impurity in a different way as compared to the simple metals.[19] As can be seen from Fig. 2, which shows the partial d LDOS for Mo and for Tc in Mo, the impurity causes a distinct redistribution of the d states, but does not produce the same dramatic enhancement at the bottom of the valence band which is characteristic for the simple metals. Instead the changes mainly occur within the d band, in particular an increase in intensity for the occupied states and a decrease for the unoccupied states. Further, one observes a major shift of the unoccupied d states toward the Fermi level. This results in an apparent narrowing of the d band on the impurity site as compared to the original width of the d band in the unperturbed host. Since in the bcc crystal structure the lower and upper d states can be directly related to the bonding and antibonding states, the observed reduction in energy separation immediately reflects the change in orbital hybridization between the impurity and the host. This is also confirmed by the values of the parameter α (listed in Table II), which for the states of $d-e_g$ and $d-t_{2g}$ symmetry are significantly smaller than for the s and p states.

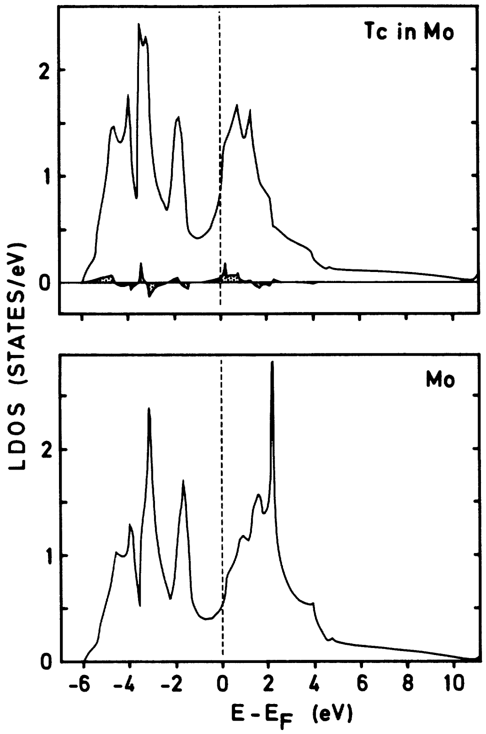

FIG. 2. Self-consistently calculated d partial DOS for Mo and for Tc in Mo. Also shown, as in Fig. 1, is the difference between the *ab initio* result and the impurity-model fit using for states of e_g and t_{2g} symmetry the parameters listed in Table II.

Again, the full impurity calculation is modeled remarkably well (see Fig. 2) by our parametrized impurity scheme with values for the different orbital contributions as given in Table II. These numbers, in particular the charge transfer Q, reflect the basic difference between the transition and simple metals, i.e., the dominating contribution of the d states to the screening process and a minor role for the transition metal s and p states.

IV. INTERPRETATION AND DISCUSSION

The parametrization of the self-consistent electronic-structure calculation for the $Z+1$ impurity by means of

TABLE II. Partial occupancies and generalized CW impurity model parameters for Mo and Tc in Mo. The symbols have the same meaning as in Table I.

	s	p	e_g	t_{2g}
N_H	0.575	0.705	1.583	2.937
N_I	0.615	0.777	2.014	3.560
Q	0.040	0.072	0.431	0.623
α	1.00	1.00	0.96	0.97
Δ	-0.5[a]	-0.5[b]	-1.0	-0.9

[a] Over 1.3 states in the band.

[b] Over 2.4 states in the band.

a generalized CW impurity model works for both the extended *s* and *p* states in simple metals as well as for the narrow *d* bands in transition metals. By our analysis we have reduced the full electronic-structure problem to a simplified impurity scheme, characterized by a set of parameters, two for each partial LDOS, and by the unperturbed DOS of the host. This limits the relevant physical factors to essentially local parameters which are related to the attractive Coulomb potential on the impurity site and to the change in impurity-host interaction.

The *attractive potential* results in a shift of the effective atomic levels and causes a redistribution in intensity throughout the whole band. This works as a driving force to localize weight on the impurity site for the states below the Fermi level and in this way accumulates screening charge from the surrounding solid state. The differences in size for the shift of the *s*, *p*, and *d* states are related to the differences in response of these orbitals in order to screen the local perturbation. However, the size of the shift of the effective level is not related in a simple way to the size of the charge transfer, but depends on the overall distribution of states within the bands.

The decrease in *impurity-host interaction,* as represented by the parameter α, indicates an actual spatial contraction of the wave function within the impurity Wigner-Seitz cell and leads to a partial decoupling from the extended states of the host. The effect of a decrease in the orbital overlap on the local DOS leads to a narrowing of the whole band and to a reduced separation of bonding and antibonding states for the transition metals (see Fig. 2). It is this relative shift of peaks in the LDOS, which in general is an indication of a changed impurity-host transfer integral. The observed reduction in α for the *d* states can already be expected from the change in bandwidth observed within the transition-metal row.[20] Note that a change in the orbital transfer integrals alone introduces a redistribution of states through the Fermi level and accordingly leads to a change in the occupancy.

The discussion shows that the parameters Δ and α depend critically on the elements studied, and we argue that these values lead to a charge transfer which is related in a rather complex way to the details of the host band structure, the position of the Fermi level, and the atomic properties of the impurity in question. Furthermore, these parameters have been derived for each partial DOS separately, but are clearly not independent from each other. The relative numbers are governed by the different contributions to the total screeing charge in accordance with the Friedel sum rule.[5] The actual size is given by various contributions like the attractive Coulomb potential of the extra nuclear charge, the electron-electron repulsion, and the structure of the unperturbed DOS. These are complicated factors, which, however, are—at least within the limits of the local-density approximation—exactly calculated in our *ab initio* electronic-structure formalism. In principle, the effective parameters can be derived directly from the *ab initio* calculation, as has been recently performed by Gunnarsson *et al.*[4]

V. CONCLUSION

The fact that the generalized CW impurity model constitutes an excellent description of the distribution of electronic states around a $Z+1$ impurity in a metallic host is an important result. It means that knowledge of the set of effective parameters (α and Δ) and the unperturbed DOS is sufficient to describe the LDOS at the impurity site within a solid-state environment. The CW Hamiltonian may thus in principle serve as a basis to describe the LDOS from the *atomic* properties of the impurity and the band structure of the host alone without the necessity to incorporate a cumbersome electronic-structure calculation for impurity atoms.

Future applications of our approach which we have in mind are a straightforward physical interpretation of the screening processes in the solid-state environment and the provision of effective parameters in order to estimate AES and XAS spectra from a given ground-state DOS. A crucial factor to be determined is then, of course, the transferability of the model parameters from the pure metal to an arbitrary solid-state environment. In a forthcoming paper these matters will be discussed.[14]

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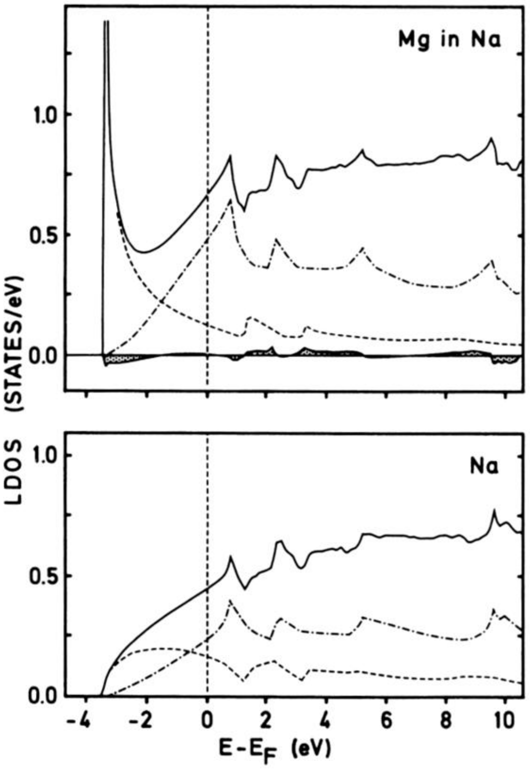

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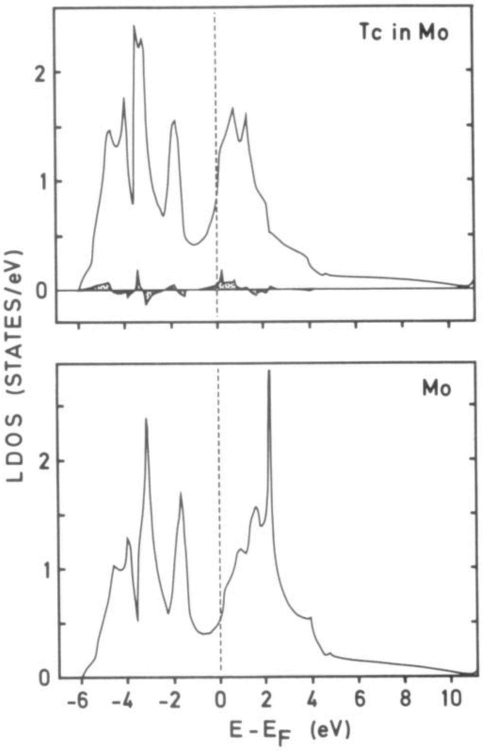

FIG. 2. Self-consistently calculated *d* partial DOS for Mo and for Tc in Mo. Also shown, as in Fig. 1, is the difference between the *ab initio* result and the impurity-model fit using for states of e_g and t_{2g} symmetry the parameters listed in Table II.