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Parametrization of the electronic structure of $Z+1$ impurities

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The local electronic structure of substitutional $Z+1$ impurities in metals is calculated self-consistently by means of the Korringa-Kohn-Rostoker Green's-function formalism, and parametrized in terms of a generalized Clogston-Wolff impurity model. The purpose of this approach is to investigate the core-hole effect, which is encountered in high-energy spectroscopies. The analysis is applied to simple metals as well as transition metals, including the complete 4*d* row. For the *d* states a clear renormalization of the impurity-host interaction is observed. We find general agreement between the values of the attractive potentials and the differences in effective levels obtained by first-principles calculations. Within the formalism of the Clogston-Wolff model the trend in the values of the attractive potentials for the 4*d* states can be explained by a local screening condition and the position of the Fermi level in the band. We comment on the transferability of the model parameters and investigate the screening of a $Z+1$ impurity in a metal. The effect of a locally overscreened or underscreened core hole is found to be related to the band filling and the character of the Friedel oscillations.

I. INTRODUCTION

To a good approximation, a deep core hole created by means of photon impact may be identified with an additional nuclear charge. A $Z+1$ (or equivalent core) approximation may therefore be considered as a reasonable starting point in the interpretation of experimental data obtained by high-energy spectroscopies like x-ray photoelectron spectroscopy (XPS) and x-ray-absorption spectroscopy (XAS).[1,2]

In a recent study we have reported that the local electronic structure of a substitutional $Z+1$ impurity, which is calculated by the Korringa-Kohn-Rostoker (KKR) Green's-function method, can be parametrized by an impurity Hamiltonian, which is based on a tight-binding description of the solid state.[3] The impurity scheme we employ is a generalized version of the Clogston-Wolff (CW) Hamiltonian,[4-6] which has been proposed in addition to the more established impurity models.[7-9] In particular, it has been shown that the local electronic structure of a $Z+1$ impurity is determined, for each symmetry-projected local density of states (LDOS) separately, by the unperturbed partial LDOS and two parameters Δ and α, describing an effective (attractive) potential and a renormalization of the impurity-host interaction. With this set of parameters we obtain excellent agreement between self-consistent and model calculations of the LDOS for transition-metal impurities as well as *sp* impurities.

The purpose of this approach is twofold. First, we aim to obtain a set of parameters that allows easy access to the calculation of the LDOS at a $Z+1$ impurity site and that, in addition, can be used as a basis for an estimation of the core-hole effect in high-energy spectroscopies like XAS and Auger electron spectroscopy (AES).[10-12] A $Z+1$ approximation has been chosen,[1] since we are not concerned at this stage with the exact identity of the core hole. An application to the interpretation of the Si *K* XAS spectra of transition-metal silicides is the subject of a parallel study.[13]

The second purpose is to analyze the processes which underly the screening of a core hole (see, e.g., Ref. 14, and references therein). Our starting point is that, because of the excellent performance of the generalized CW impurity model in reproducing the self-consistently obtained results, we may use this model also as a probe of the physical processes that govern the distribution of electronic states around a localized perturbation.

The relation between the model and the *ab initio* calculation has been discussed before.[3] In the present study we discuss the derivation of the parameters in more detail, and extend our earlier analysis to include in particular the full series of 4*d* transition metals. We comment on the transferability of the parameters from the pure metal to compounds, and investigate the screening process as it is dealt with according to the formalism of the CW model. In the following section we will first present the theoretical background to the parametrization, with special reference to the calculation of the screening charge and the treatment of the transferability of the parameters.

II. THE MODEL AND THE PARAMETRIZATION OF THE *ab initio* CALCULATION

The Hamiltonian of the generalized CW impurity model in its nonmagnetic single-band versions is expressed as

$$
\begin{aligned}
H &= H_0 + V \ , \\
H_0 &= \sum_{j,l} t_{jl} a_j^\dagger a_l \ , \\
V &= \Delta a_0^\dagger a_0 + \tau \sum_{j \neq 0} (t_{0j} a_0^\dagger a_j + t_{j0} a_j^\dagger a_0) \ .
\end{aligned}
\tag{1}
$$

Here H_0 represents the Hamiltonian of the unperturbed host system, and the perturbation at the impurity site, which is located at the origin, is given by V. In these expressions a_j is the annihilation operator for the local orbital j, 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 (attractive or repulsive) potential at the impurity site 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 impurity on-site Green's function is expressed as

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

where $z = \varepsilon + i0$, $\alpha = \tau + 1$, and $g_{00}(\varepsilon)$ is the host Green's function. From the local Green's function, the LDOS at the impurity site is derived as

$$
n(\varepsilon) = -\frac{1}{\pi} \mathrm{Im}[G_{00}(\varepsilon)] \ . \tag{3}
$$

The model also allows the calculation of the change in the *total* density of states of the alloy (impurity *and* host) as[6,15]

$$
\begin{aligned}
\delta n(\varepsilon) &= -\frac{1}{\pi} \mathrm{Im} \left[\sum_j [G_{jj}(\varepsilon) - g_{jj}(\varepsilon)] \right] \\
&= -\frac{1}{\pi} \mathrm{Im} \left[\frac{-(\alpha^2-1) g_{00}(\varepsilon) - [(\alpha^2-1)(z-\varepsilon_c)+\Delta] \partial g_{00}(\varepsilon)/\partial \varepsilon}{\alpha^2 - g_{00}(\varepsilon)[(\alpha^2-1)(z-\varepsilon_c)+\Delta]} \right] \ .
\end{aligned}
\tag{4}
$$

The derivation of this expression is given in the Appendix. Note that in Ref. 6 a comparable expression was derived within the framework of a two-band Hamiltonian. The total screening charge is the excess charge introduced in the lattice by the substitutional impurity and is therefore given by

$$
\Delta Z = \int^{\varepsilon_F} \delta n(\varepsilon) d\varepsilon = -\frac{1}{\pi} \mathrm{Im}(\ln\{\alpha^2 - g_{00}(\varepsilon_F)[(\alpha^2-1)(\varepsilon_F - \varepsilon_c)+\Delta]\}) \ . \tag{5}
$$

This expression can also be written as

$$
\Delta Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l(\varepsilon_F) \ , \tag{6}
$$

where $\delta_l(\varepsilon_F)$ is the scattering phase shift at the Fermi level. The phase shift, associated with the orbital screening charge, is calculated from Eq. (5) as

$$
\delta_l(\varepsilon_F) = \mathrm{Im} \left[\ln \left[\frac{G_{00l}(\varepsilon_F)}{g_{00l}(\varepsilon_F)} \right] \right] \ . \tag{7}
$$

It can therefore be obtained directly from the self-consistently computed host and impurity on-site Green's functions. In the *ab initio* calculation the screening process is treated by taking into account the potential perturbation on a single shell of nearest neighbors. Free flow of charge is thus allowed within a cluster consisting of the impurity and its nearest neighbors (eight for bcc, 12 for fcc structures).

The parameters α and Δ associated with a $Z+1$ impurity are characteristic for each partial LDOS in the pure metal. It is therefore important to know if these parameters are transferable from the pure metal to an arbitrary chemical environment. Although the self-consistent calculation of the LDOS at an impurity site in an arbitrary compound does not as yet belong to the state-of-the-art first-principle methods, we can investigate the transferability of parameters within the KKR–Green's-function formalism in a relatively simple and effective way. To that purpose we consider here as compounds the dilute alloys. The local electronic structure of a substitutional impurity in a given host is thus compared with the electronic structure of the $Z+1$ impurity in the same host. This allows a variety of chemical environments to be tested in a straightforward way. From Eq. (2) it can be seen that the local Green's functions $G_{00}^A(\varepsilon)$ at the impurity site and at the $Z+1$ species, $G_{00}^B(\varepsilon)$, are related as

$$
G_{00}^B(\varepsilon) = \frac{G_{00}^A(\varepsilon)}{\beta^2 - G_{00}^A(\varepsilon)[(\beta^2-1)(z-\varepsilon_c-\Delta_A)+\Delta_B-\Delta_A]} \ , \tag{8}
$$

where $\beta = \alpha_B/\alpha_A$, and Δ_A and Δ_B are the CW potentials of the impurity and its $Z+1$ partner in the unperturbed material. Equation (8) thus shows that transferability can be investigated by considering the ratio of both α parameters and the difference of both impurity potentials.

III. RESULTS

A. General remarks on the parametrization

For an explanation of the performance of the model we refer to Fig. 1, which shows the effect of the parameters on a simplified DOS [Fig. 1(a)]. An attractive potential,

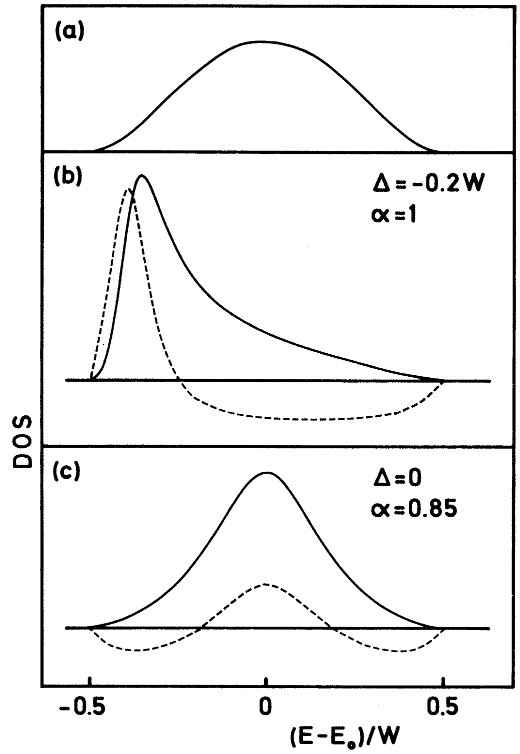

FIG. 1. Effect of both parameters of the generalized CW impurity model on the LDOS at the perturbed site (solid lines) and on the change in the total DOS $\delta n(\varepsilon)$ of the impurity system (dashed lines) for a simple host band. The band shape (a) is given by $n(\varepsilon)=[(\varepsilon-\varepsilon_c)^2-W^2/4]^2$, where W is the bandwidth.

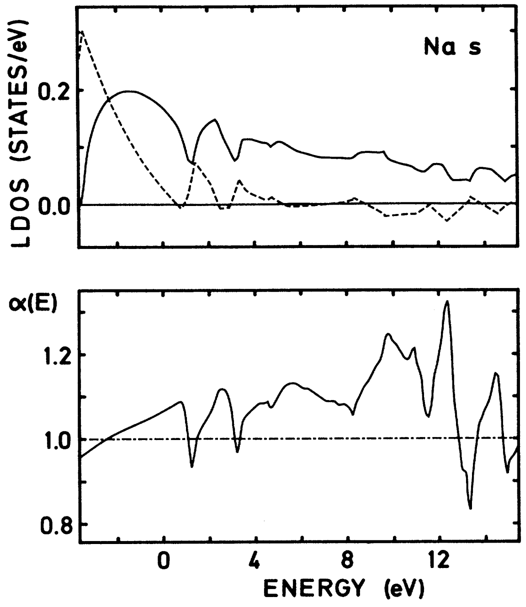

FIG. 2. Upper panel: the s partial DOS of metallic Na (solid line) and the real part of the Green's function (dashed line) as calculated self-consistently using the KKR–Green's-function formalism. Lower panel: energy fluctuations $\alpha(\varepsilon)$ in the renormalization of the impurity-host interaction for states of s symmetry in the case of a $Z+1$ impurity (Mg) in Na.

or energy shift Δ of the effective level of the impurity states with respect to the unperturbed state, results for the LDOS at the impurity site in a uniform redistribution of weight towards the bottom of the band [Fig. 1(b)]. The decrease in impurity-host interaction, as represented by the dimensionless parameter α, may indicate a spatial contraction of the wave function within the impurity Wigner-Seitz cell and leads to a partial decoupling of the impurity states from the host states. The effect of this decrease in orbital overlap on the LDOS is an increased localization of states and a narrowing of the band [Fig. 1(c)].

Figures 1(b) and 1(c) also show the total change in DOS $\delta n(\varepsilon)$, in accordance with Eq. (4). States redistribute within the system in such a way as to provide for the total screening charge. It is important to note that even a partial decoupling of the impurity states from the environment introduces a redistribution of states [see Fig. 1(c)], and accordingly a flow of screening charge, the direction of which depends on the position of the Fermi level.

An example of the derivation of the effective parameter α associated with a $Z+1$ impurity in a simple metal is shown in Fig. 2 for the Na s states. Presented are the self-consistently calculated real and imaginary parts (or LDOS) of the Green's function, which enter the calculation through the relation

$$\operatorname{Im}\left[\frac{1}{G_{00}(\varepsilon)}\right]=\alpha^2(\varepsilon)\operatorname{Im}\left[\frac{1}{g_{00}(\varepsilon)}\right], \tag{9}$$

as explained before.[3] Together with the local Green's function for the perturbed site, these quantities determine the fluctuations of the parameter α over the band. An effective value of α, which is needed because the parameter is defined as a constant in the CW model, is found by averaging these fluctuations over a certain energy range. Averaging from the bottom of the band over ranges varying from 2 to 12 eV yields for this specific case values of α between 0.98 and 1.05. On the other hand, extending the energy range results in effective values which progressively tend to 1.00. The example we show here is typical for the s and p states of the simple metals, and we conclude that this analysis does not provide us with a clear argument to assume an effective renormalization of the impurity-host hybridization matrix elements for the s and p states in the simple metals, at least not for a local perturbation that is caused by an extra nuclear charge.

For the d states in the transition metals a different picture is observed. Figure 3 shows the fluctuations found in the parameter α for the LDOS of e_g symmetry of a $Z+1$ impurity (Mo) in Nb as compared to a $Z-1$ impurity (Zr). Since we expect the parameter α to depend on the extent of the wave functions around the impurity, we assume that a comparison of $Z+1$ impurities with $Z-1$ impurities should be illuminating. The analysis shows that, over the energy range of the Nb d band, these fluctuations are considerably smaller than for states of s and p symmetry (cf. Fig. 2), and that the resulting

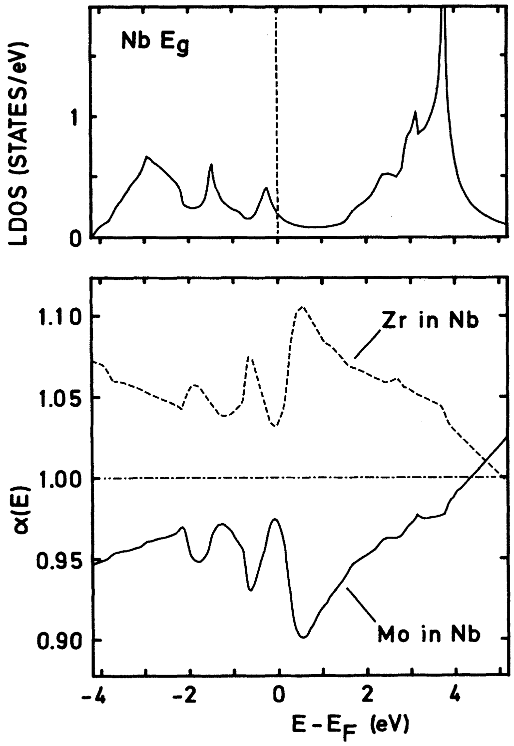

FIG. 3. Renormalization of the impurity-host interaction α as function of band energy for the d-e_g states of a $Z+1$ impurity (Mo) as compared to a $Z-1$ impurity (Zr) in Nb. The upper panel shows the Nb e_g partial DOS.

effective value of α is significantly larger than 1.0 for Zr in Nb, but smaller than 1.0 for Mo in Nb. Towards higher energy above the Fermi level, which means outside of the d band, we find the stronger fluctuations about $\alpha=1.0$, which are observed for the states of s and p symmetry in the simple metals. By averaging over the d band from the bottom of the band to 4.0 eV above the Fermi level by means of Eq. (9), we obtain the effective values $\alpha=0.95$ for Mo in Nb and $\alpha=1.06$ for Zr in Nb. The effective values mostly differ for states of e_g and t_{2g} symmetry, with the value for the t_{2g} states being in general somewhat larger (at most 2.5%). Since it is difficult to decide from our analysis to what extent these differences are systematic, we average both α values in order to obtain a single effective parameter α to be associated with the d states.

The values of Δ that we have derived for the s and p states of the simple metals are obtained by a least-squares fit to the self-consistently calculated LDOS using $\alpha=1.0$. Equally good fits can, however, be obtained using values between roughly 0.95 and 1.05, which results in attractive potentials differing as much as 0.5 eV. This leaves the fitting procedure for the s and p states somewhat ill-defined, and results in a relatively large margin of uncertainty in the value of Δ. By contrast, the fit results for the d states are more or less unambiguous. We have found no systematic differences in the Δ parameters of the e_g and t_{2g} states, and have accordingly interpreted the differences between both potentials as an uncertainty (of the order of ±50 meV) in the value of Δ associated with the d states.

B. Simple metals

Table I lists the attractive potentials and in addition the local charge transfer ΔQ into the impurity Wigner-Seitz cell for $Z+1$ impurities in the simple metals Na, Mg, and K. The magnitude of the charge transfer ΔQ shows that the s and p states are the main screening channels in the simple metals, although the contribution of the d channel is considerable in the heavier element K.

Since the potential in the CW model reflects the difference in the effective levels of the unperturbed and perturbed states, we have also listed in Table I for a few cases the differences in atomic orbital energies that result from Hartree-Fock calculations of the neutral atom.[16] Comparison with the potentials found by applying the CW impurity scheme indicate that the order of magnitude is predicted reasonably well.

C. The 4d transition-metal row

The CW parameters α and Δ for the 4d states are listed in Table II. The values of the parameter α, which for states of d symmetry in general prove to be smaller than 1.0, reflect the change in hybridization between impurity and host states. Exceptions to this rule do occur at the beginning (for Y in Sr) and at the end of the series (for Ag in Pd). The attractive potentials are also shown in Fig. 4. One observes a smooth trend in the middle of the 4d series and a rather strong increase of the attractive potential at both ends. Table II lists in addition the local charge transfer ΔQ at the impurity site, which indicates that the d states are, because of their localized character, the main screening channels for $Z+1$ impurities in the transition metals. It is observed here that the local charge transfer is approximately equal to one unit charge, except at the beginning (for Y in Sr) and at the end of the series (for Ag in Pd), where the local charge transfer is

TABLE I. Parameters of the s, p, and d states for a $Z+1$ impurity in the simple metals Na, Mg, and K. Listed are the local charge transfer ΔQ into the impurity Wigner-Seitz cell, the attractive potential Δ, and for some instances the differences in orbital energies Δ_R from atomic calculations (Ref. 16). For the hybridization scaling factor we assume $\alpha=1$.

		ΔQ	Δ (eV)	Δ_R (eV)
Na	s	0.585	−1.9	−1.93
	p	0.343	−1.9	
	d	0.006	−1.6	
Mg (fcc)	s	0.441	−2.8	−3.82
	p	0.565	−2.6	−1.95
	d	0.023	−1.9	
K	s	0.461	−1.4	−1.31
	p	0.273	−1.5	
	d	0.171	−2.6	

TABLE II. The effective parameters α and Δ for the d states of the $Z+1$ impurities in the $4d$ transition metals. Also listed are the occupancy in the unperturbed state N_d, the local charge transfer ΔQ, and for a few cases the differences in the positions of the resonances of the unperturbed and the perturbed d states Δ_R.

	N_d	ΔQ_d	α	Δ (eV)	Δ_R (eV)
Sr	0.671	0.819	1.00	-1.58	
Y (fcc)	1.740	0.985	0.98	-1.16	
Zr (fcc)	2.705	1.060	0.97	-1.09	
Nb	3.665	1.041	0.97	-1.03	-1.14
Mo	4.520	1.054	0.97	-0.99	-0.98
Tc (fcc)	5.541	1.127	0.96	-0.81	
Ru (fcc)	6.542	1.080	0.97	-0.86	
Rh	7.601	1.039	0.97	-0.92	
Pd	8.738	0.808	1.02	-1.95	-1.73

somewhat smaller than 1.0. This reflects the basic difference between the simple and transition 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, which we leave out of consideration in the present analysis.

For some metals we have computed the position of the resonance of the d states in the perturbed and the unperturbed systems. The differences of these values, Δ_R in Table II, are related to the differences in effective levels associated with the d states, and should thus be compared with the values of the attractive potentials that result from the parametrization by means of the CW impurity scheme. The agreement we find is good.

D. The 3*d* states

Table III lists the parameters of the d states for the $Z+1$ impurities Cr in V and Mn in Cr. The local charge and screening mechanism are comparable to those associated with $4d$ bcc metals Nb and Mo at corresponding positions in the Periodic Table. The effective parameters α and Δ, however, turn out to be smaller than for the $4d$ metals. The agreement with the calculated resonance differences, again, is very good.

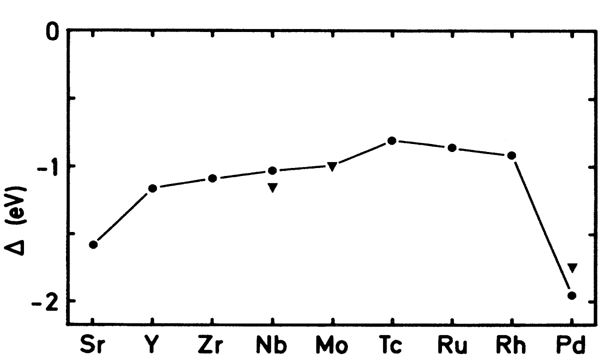

FIG. 4. The attractive CW potentials Δ for the d states of $Z+1$ impurities over the $4d$ transition-metal row (dots) as listed in Table II. The differences in the calculated positions of the host and impurity d resonance (triangles) are shown for Nb, Mo, and Pd.

E. The screening mechanism

Although the values of the local charge transfer ΔQ as listed in Tables I–III provide a clear estimate of the importance of the different orbital screening channels, ΔQ is not a proper parameter to characterize the screening process. A concept of local (on-site) screening applies only approximately, and an exact measure can in principle only be given by considering the sum of the contributions of each orbital channel to the total screening charge ΔZ in accordance with the Friedel sum rule

$$\Delta Z = \frac{2}{\pi} \sum_l (2l+1)\delta_l(\varepsilon_F) . \tag{10}$$

In the following we will discuss in more detail how the CW-model approach deals with the screening process. To offer a clearer picture of the orbital contributions to the screening process, we compare in Table IV the values of the local charge transfer ΔQ with the values of the screening charge ΔZ calculated by two different methods. Within the framework of the KKR–Green's-function method, the partial screening charges are computed from the generalized phase shifts using Lloyd's relation.[17–19] These screening contributions are listed as ΔZ_{sc} in Table IV. For Na and Mg, the values are comparable to previous results using an atom-in-jellium model[20] or the linear-muffin-tin-orbital method.[21] As appears from Table IV, agreement with the Friedel sum rule ($\Delta Z = 1.0$) is reasonable for the simple metals. For Na and Mg, the screening charges of the s states seem to agree with the intuitive notion that the screening contribution diminishes with increasing band filling. Agreement with the Friedel sum rule is, however, poor for the transition metals, in which case the total displaced charge seems either too small, as for Tc in Mo, or far too large, as for Ag in Pd. The cause of this is mainly the limited number of nearest neighbors that are allowed to participate in the screening process. Satisfactory agreement with Freidel's sum rule can in principle be obtained in a quite elaborate self-consistent computation involving a cluster of at least five shells of neighboring host atoms.[22] Although, notably for Tc in Mo, the s and p states contribute to the screening of the perturbation, it seems reasonable to conclude that the disagreement with

TABLE III. Parameters for the *d* states of $Z+1$ impurities in the bcc 3*d* transition metals V and Cr. The symbols have the same meaning as in Table II.

	N_d	ΔQ_d	α	Δ (eV)	Δ_R (eV)
V	3.639	1.060	0.94	−0.82	−0.80
Cr	4.542	0.995	0.95	−0.69	−0.70

Friedel's sum rule follows mainly from the calculated screening properties of the *d* channel. We note, furthermore, that states of *f* and *g* symmetry have been included in the *ab initio* calculations, but that their contribution to the total displaced charge is insignificant.

Within the scheme of the generalized CW impurity model, the contribution of the different screening channels to the screening charge has been calculated from the phase-shift analysis using Eq. (7). These values are listed as ΔZ_m in Table IV. We note that the values for the main screening channels (*s* and *p* for the simple metals; *d* for the transition metals) are in general smaller than the screening charges from the *ab initio* formalism, but that relative magnitudes are reproduced well. Similarly, agreement with the Friedel sum rule is not observed.

F. Transferability

Results of our analysis for the transferability of the parameters by means of Eq. (8) are given in Table V. We show here results for three impurity systems, which may be considered as representative of the kind of effects we can expect. In the case of the system Cr in Pd, for example, we compare the unperturbed system (Cr in Pd) with the perturbed system (Mn in Pd). Although it is difficult to judge the effect on the parameter α from the limited number of examples, it is certainly clear from comparison with the results for Cr, Zr, and Pd given in Tables II and III that the parameter Δ is not transferable from the pure metal to an arbitrary system. In particular, for the dilute system Cr in Pd, as compared to metallic Cr, we observe a strong weakening of the attractive potential.

IV. DISCUSSION

Before discussing the results of our analysis, we will comment on the approximations inherent in the formalism of the impurity model. The generalized CW model is a single-band model, i.e., the joint interactions of the impurity states with the environment are represented by the interaction with a lattice consisting of an infinite number of sites having states of equal symmetry. The hybridization matrix elements which determine the interaction of a local state with the different partial states at the surrounding sites are in general energy dependent (see, e.g., Refs. 23 and 24). It is therefore not trivial to assume that the renormalization of the impurity-host interaction α is constant, i.e., not energy dependent. The intermixing (rehybridization) of states of different symmetry due to interactions with and perturbations of the neighboring host states enters as an additional renormalization of the parameters that result from our analysis.

The parameter α, therefore, in a single constant, expresses the renormalization of the orbital overlap of the

TABLE IV. Local charge transfer ΔQ for *s*, *p*, and *d* states as compared to the partial screening charge, calculated within the KKR-Green's-function formalism ($\Delta Z_{\rm sc}$) or using the generalized CW impurity scheme (ΔZ_m). The occupancy *N* in the unperturbed state is also listed. Further explanation is in the text.

		N	ΔQ	$\Delta Z_{\rm sc}$	ΔZ_m
Na	*s*	0.595	0.585	0.441	0.38
	p	0.353	0.343	0.540	0.45
	d	0.046	0.006	−0.036	0.02
	tot.	0.994	0.934	0.945	0.85
Mg	*s*	0.872	0.441	0.367	0.26
	p	0.925	0.565	0.623	0.44
	d	0.185	0.023	0.050	0.05
	tot.	1.982	1.029	1.040	0.75
Mo	*s*	0.575	0.040	0.011	−0.07
	p	0.705	0.072	0.118	−0.08
	d	4.520	1.054	0.708	0.58
	tot.	5.800	1.166	0.837	0.43
Pd	*s*	0.547	0.067	0.027	−0.01
	p	0.561	0.062	−0.005	−0.04
	d	8.738	0.808	1.608	1.64
	tot.	9.846	0.937	1.630	1.59

TABLE V. Parameters of the *d* states for $Z+1$ impurities in the impurity systems Cr in Pd (nonmagnetic), Zr in Nb, and Pd in Ag. The symbols have the same meaning as in Table II.

	N_d	ΔQ_d	α	Δ (eV)
Cr in Pd	4.488	1.056	0.95	−0.20
Zr in Nb	2.679	0.987	0.96	−1.27
Pd in Ag	8.969	0.658	0.98	−2.81

impurity wave functions centered on the surrounding sites, and consists of contributions of all states that by symmetry are allowed to interact with the states at the impurity site. It is therefore important to note that, although effects due to, for example, the *d*-*d* interaction are incorporated in the decrease of α (see Tables II and III), the magnitude of this parameter by itself cannot be considered as a direct measure of the contraction of the *d* orbitals in the spirit of a muffin-tin-orbital formalism.[24,25] A further analysis of this point is required.

The values of the attractive potentials which result from our model approach agree approximately with the differences in effective levels, which can be derived from atomic calculations (for *s* and *p* states) or from the positions of the resonances (for *d* states). On the other hand, these parameters, together with the symmetry-projected host DOS, should, within the formalism of the generalized CW model, form the basis for an interpretation of the screening process induced in a metallic solid by the introduction of an extra nuclear charge. That this model only includes a perturbation which is localized at the impurity site and, contrary to a self-consistent KKR–Green's-function calculation, does not allow for a perturbation of neighboring potentials, should not seriously hamper this interpretation. The screening process in the metal is completely and accurately described by the Friedel oscillations. These oscillations are long ranged, but are small in amplitude. The KKR–Green's-function calculations show that the extension of the self-consistency to a further shell of neighboring atoms hardly affects the charge, potential, and LDOS at the atoms in the inner shells. We therefore expect that the CW model, although it only considers the perturbation at the impurity site, should work well for the metal.

In the following we will deal with the results for the *d* states in more detail and we will attempt to obtain more insight in the trend observed for the values of the attractive potentials in the 4*d* row (Fig. 4). One would, for the transition metals, expect the value of the potential to agree with the condition that approximately a single *d* electron screens the extra nuclear charge (leaving the small screening contributions of the *s* and *p* states here out of consideration). This condition can, however, not be used, since we have from the results of the phase shift analysis in Table V concluded that, mainly due to the contribution of the *d* states, the Friedel sum rule is not obeyed. We will, however, argue here that the trend in the values of the attractive potentials for $Z+1$ impurities in the 4*d* row can be explained by means of a local screening condition. We start from our finding, derived from Tables II and III, that the extra nuclear charge is in general locally screened by approximately one unit charge ($\Delta Q \approx 1.0$).

We will therefore assume that the attractive potential is determined by the condition that one additional *d* electron is placed at the impurity site. This trend is illustrated in Fig. 5, where in the lower panel the Nb *d* partial DOS is presented as a typical example of a bcc type *d* band. The situation can be translated to the conditions for the other bcc transition metals (see the arrows in Fig. 5) by an appropriate renormalization of the energy scale. The lower panel in addition shows the potential Δ necessary to locally transfer 1.0 unit charge into the impurity site, where we assume $\alpha = 0.97$ (in accordance with the results listed in Table II). The figure demonstrates first of all that the potential necessary to screen the perturbation remains fairly constant in the middle of the band (between −2 and 4 eV), with slow fluctuations that appear to depend on the DOS at the Fermi level. Only at the bottom or the top of the band do we observe a strong increase of the attractive potential. Note that, near the top of the band, the required potential becomes infinite, because a nearly filled band sets a limit to the total amount of charge that can be locally transferred. Apparently this trend is the main cause of the variation in the size of the

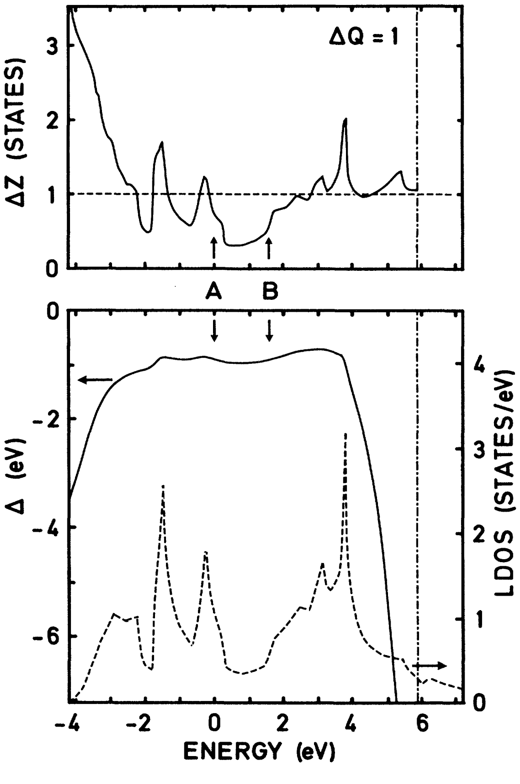

FIG. 5. The attractive potential Δ (lower panel, solid line) needed to locally screen one extra positive charge ($\Delta Q = 1$) (upper panel, dashed line) as a function of the position of the Fermi level for the typical bcc *d* band of Nb metal (lower panel, dashed line). In the upper panel is shown the screening charge ΔZ (solid line) as compared to ΔQ.

attractive potential over the 4*d* series, as illustrated in Fig. 4. Note also that at the beginning and the end of the series, where the potentials are relatively large, i.e., for Sr and Pd, the total *d* charge transferred locally is typically less than one unit charge, implying that the local perturbation (on the *d* states) is not strong enough to cause the required flow of charge.

In addition, we observe a trend of decreasing attractive potential in the series from Y to Rh. Although this trend could still be caused by the kind of variations in attractive potential observed in Fig. 5, it should be mentioned that also the gradual decrease in *d* bandwidth over the 4*d* series, from approximately 9 eV for Y to 7 eV for Rh, is a factor determining the size of the attractive potential. This can be understood in a simple way by noting that a renormalization of the energy scale, i.e., bandwidth, under condition of equal local charge transfer and (dimensionless) α parameter, will result in an equally renormalized attractive potential. This is evident from a comparison of the attractive potentials for the 4*d* bcc metals Nb and Mo with the potentials for the corresponding 3*d* bcc metals V and Cr.

It is now also clear why the transferability of the parameter Δ does not work. This is explained from the local screening condition, which is related to the phenomenon that the local *d* charge at a transition-metal site in a metallic compound depends only slightly on the chemical environment.[26] Together with the local *d* count, the local screening condition in the metallic environment is therefore also fixed. The attractive potential for the *d* states of the $Z+1$ impurity is therefore in general determined by the condition that $\Delta Q \approx 1.0$. The width of the *d* level for (paramagnetic) Cr in Pd, for example, is only about 0.5 eV,[27] which favors far more the occurrence of a relatively small attractive potential than the *d* bandwidth (about 7.0 eV) for pure Cr.[28] Therefore, the appropriate potential is easily calculated from the local screening condition, although the potential itself is not transferable.

The upper panel in Fig. 5, furthermore, shows the screening charge ΔZ associated with the calculated potential and obtained from Eq. (5). We will first discuss the trend for the approximately constant potential Δ, i.e., from -2 to 4 eV. We observe here that the magnitude of the screening charge follows the DOS at the Fermi level. This can be understood by means of Eq. (5), which in first-order approximation can be reformulated as

$$\Delta Z = n(\varepsilon_F)\Delta \ . \tag{11}$$

The screening contribution due exclusively to the contraction of the wave function is neglected here, because α is close to 1. Although the local screening condition is kept unchanged, it is thus observed that strong fluctuations in the size of the screening charge over the band occur, which are caused by the variation in the DOS (and not in the parameter Δ). Only at the bottom of the band is an increase of screening charge observed, which is directly related to the increase of the potential.

Since the Friedel sum rule, even in the self-consistent calculation from which the model parameters have been derived, is only approximately obeyed, we cannot at this stage specify how accurate our description of the screening process by means of the generalized CW impurity scheme can possibly be. The general performance of this model in reproducing the LDOS at the impurity site, however, certainly justifies some more than merely qualitative considerations. Our argument is based on the observation (see Table IV) that for Tc in Mo the screening charge ΔZ associated with the *d* channel is smaller than the local charge transfer ΔQ, while for Ag in Pd the screening charge is larger. Note that the validity of this statement does not depend on the method we used to calculate the screening charge. We find, therefore, that in Mo the *d* channel locally overscreens the perturbation, while in Pd underscreening occurs, which implies that part of the screening is done by *d* states having host character.

The relative sizes of the local charge transfer ΔQ and the screening charge ΔZ correspond to a general trend as to which the screening properties of a given orbital channel are related to the position of the Fermi level in the band. This behavior can be fully understood within the scheme of the CW impurity model, and is explained in more detail in Fig. 6 on the basis of a simple two-state model. This figure compares, as a function of the position of the Fermi level, the local charge transfer ΔQ with the screening charge ΔZ corresponding to the situation described in Fig. 1(b). According to the two-state model, a shift in energy of the effective (atomic) levels causes a redistribution of bonding and antibonding states, and although the bonding states have mainly impurity character, host character always mixes in. The total increase in charge ΔZ is therefore always larger than the local increase in charge ΔQ when the Fermi level is positioned near the bottom of the band. Also, if the Fermi level is located near the top of the band, one finds $\Delta Z > \Delta Q$, since here the highest antibonding states for the unperturbed system, having host *and* impurity character, determine the charge redistribution. Of course, $\Delta Z = \Delta Q = 0$ in case the Fermi level is located at the bottom or the top of the band, because no effective redistribution of charge can take place within an empty or a

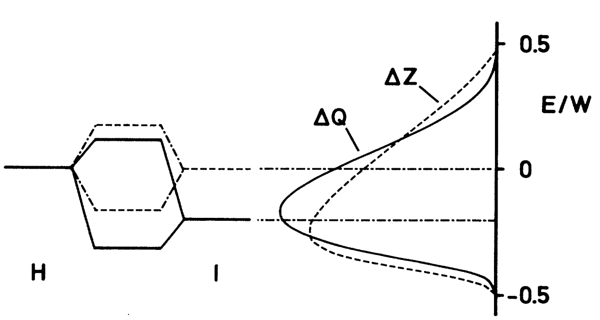

FIG. 6. The total screening charge ΔZ and the local screening charge ΔQ as a function of the Fermi level for the DOS of Fig. 1 using the model parameters $\Delta = -0.2W$, $\alpha = 1.0$. The relative magnitude of ΔZ and ΔQ is explained from a comparison with a two-state model representing the interaction between the host (H) and the impurity (I), which is characterized by the attractive potential.

filled band. Note that we do not consider the case of split-off states here. The position of the Fermi level is thus crucial for the screening response of a given channel to the local perturbation, and determines whether local overscreening ($\Delta Q > \Delta Z$) or underscreening ($\Delta Q < \Delta Z$) occurs. The mechanism of the screening process that we observed for Tc in Mo as opposed to Ag in Pd thus corresponds to the contrasting situations where the Fermi level is located in the middle or at the top of the *d* band. Note that the general trend is also recognized in Fig. 5, where in the middle of the band ΔQ is in general larger than ΔZ, while near the band edges the opposite situation tends to occur. Moreover, we believe that this mechanism lies at the root of the relative magnitudes of the local and total displaced charges for impurities in Cu and Ag.[17,18]

The dependence of the screening mechanism on the band filling is related to a tight-binding theorem, according to which physical quantities which are expressible in terms of Green's functions oscillate in sign as the Fermi level moves through the band.[29,30] According to this corollary, a quantity like the local charge transfer *j* hops (or sites) away from the impurity atom has at least $2j$ zeros as a function of the Fermi level, apart from both zeros at the bottom and top of the band. This is illustrated in Fig. 7, which pictures the situation described in Fig. 6 from a different viewpoint. We compare here the excess charge ΔQ at the impurity site plotted as a function of the Fermi level with the estimated excess charge at nearest-neighbor sites. Although the CW model only allows the calculation of the redistribution of states at the impurity site itself and within the total impurity system, we can estimate the excess charge on nearest-neighbor sites by assuming that the perturbation on other than nearest neighbors is sufficiently small.[25] A reasonable estimate of the excess charge on the nearest neighbors is therefore obtained from the approximation

$$\int^{\varepsilon_F} \mathrm{Im}\left[\sum_{j}^{N} [G_{jj}(\varepsilon)-g_{jj}(\varepsilon)]\right] d\varepsilon \approx \Delta Z - \Delta Q \ , \qquad (12)$$

where N indicates the number of nearest neighbors. The quantity $\Delta Z - \Delta Q$ is shown in Fig. 7 as a function of the position of the Fermi level. Interpreted as the excess charge on the nearest neighbors, it shows the (minimum) expected number of two zeros when the Fermi level moves through the band. The more strongly oscillating character of the excess charge on the second nearest neighbors is indicated approximately by means of equally spaced zeros. Figure 7 thus illustrates the origin of the Friedel oscillations, which constitute the spatial redistribution of charge density within the host material as a consequence of the localized perturbation. The position of the Fermi level, moreover, determines the behavior of these oscillations, which are slow at the top and the bottom of the band (for impurities in Pd), but rapid in the middle of the band (for impurities in Mo). The screening mechanisms of overscreening and underscreening that follow from an analysis of the CW impurity formalism are therefore directly related to the Friedel oscillations that are generated by the perturbation. Note, furthermore, that the Friedel oscillations have been derived on the basis of a general tight-binding principle, without residing in the usual description in terms of *k* vectors. Application of the above theorem to an interpretation of the screening mechanism in the simple metals seems inappropriate, since a finite band is presupposed.[29]

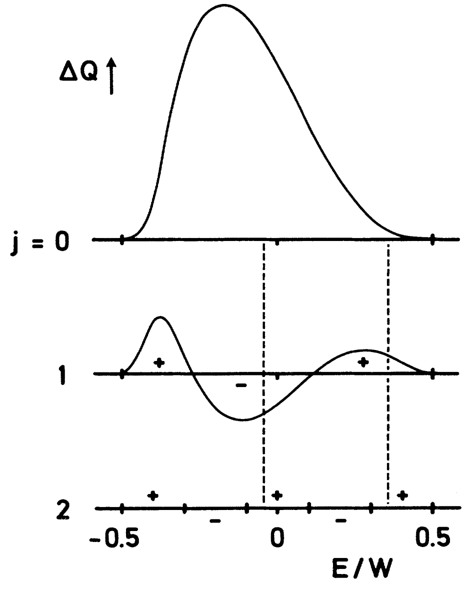

FIG. 7. The excess charge ΔQ as a function of the Fermi level at the impurity site ($j = 0$) and the (estimated) excess charge at neighboring sites one or two hops away from the impurity atom. Since the excess charge at the second-nearest neighbors is considered vanishingly small, only its oscillation as a function of energy is indicated. The dashed lines illustrate the behavior of the Friedel oscillations for a half-filled as compared to a nearly filled band. Adapted from Heine and Samson (Ref. 29).

V. CONCLUSION

We have shown how the LDOS at a $Z+1$ impurity site, calculated by an *ab initio* formalism, can be parametrized in detail by a generalized CW impurity model. This parametrization has provided a set of parameters that may serve as a starting point for an estimation of the core-hole effect in relation to notably high-energy spectroscopies like XAS and AES by relatively simple means. Note that this treatment allows incorporation of the full chemical environment of the perturbation. Our findings indicate that for a correct description of the transition-metal *d* states, a renormalization of the impurity-host interaction is needed. Sufficiently accurate values of the attractive potentials may, for example, be derived from atomic calculations or by means of a local screening condition.

Moreover, we have discussed the physical background of the $Z+1$ parametrization on the basis of the CW impurity Hamiltonian. The parameter α may indicate a contraction of a *d* wave function around the $Z+1$ site, but further analysis is needed to elucidate its precise physical meaning. The bandwidth as well as the position of the Fermi level to a high degree determine the value of the attractive potential for the d states. Finally, the generalized CW model has allowed a qualitative interpretation of the screening mechanism around a $Z+1$ impurity. We have, in particular in relation to the d states, demonstrated the mechanisms of overscreening and underscreening that follow directly from the position of the Fermi level in the band and are related to the behavior of the Friedel oscillations.

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APPENDIX

The single-particle Hamiltonian given in Eq. (1) can be solved by means of the matrix relation

$$G=g+gVG\ , \tag{A1}$$

which is a Dyson equation for the Green's functions $g=(\varepsilon I-H_0)^{-1}$ and $G=(\varepsilon I-H)^{-1}$ corresponding to the unperturbed host and the impurity system, respectively. The explicit expression for this Dyson equation is

$$\begin{aligned} G_{jl}=g_{jl}+g_{j0}\Delta G_{0l}+\tau g_{j0}\sum_{k\neq 0} t_{0k}G_{kl} \\ +\tau\left[\sum_{k\neq 0} g_{jk}t_{k0}\right]G_{0l}\ . \end{aligned} \tag{A2}$$

Using the definition of the Green's function, one obtains

$$\sum_{k\neq 0} t_{k0}g_{jk}=(z-\varepsilon)g_{j0}-\delta_{j0} \tag{A3}$$

and

$$\sum_{k\neq 0} t_{0k}G_{kj}=\left[\frac{1}{\tau+1}\right][(z-\varepsilon_c-\Delta)G_{0j}-\delta_{0j}]\ , \tag{A4}$$

from which

$$\begin{aligned} G_{jl}=g_{jl}+\frac{1}{\alpha}g_{j0}G_{0l}[(\alpha^2-1)(z-\varepsilon_c)+\Delta] \\ -\frac{\alpha-1}{\alpha}g_{j0}\delta_{0l}-(\alpha-1)G_{0l}\delta_{j0}\ . \end{aligned} \tag{A5}$$

The on-site impurity Green's function, given by Eq. (2), follows directly from Eq. (A5) by setting $j=l=0$. Using the property

$$\sum_j g_{0j}g_{j0}=\frac{\partial g_{00}}{\partial\varepsilon}\ , \tag{A6}$$

the total change in the DOS of the impurity system, Eq. (4), can now also be obtained by simple algebra.

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