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Screening and correlation effects in CVV Auger spectra of transition metals

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Abstract. We develop a theory of the core–valence–valence Auger spectra from 3d transition metals including core-hole screening effects. First, we analyse the limiting case when the d electrons fully screen the core hole in the initial state. We employ the variational method including singly excited states to construct the ground state with a completely screened core hole and solve the resulting many-body problem for correlated valence electrons using the self-consistent version of the perturbation theory in powers of U/w (where U is Hubbard on-site interaction and w is the bandwidth) within the T-matrix approximation. The resulting lineshape has a contribution proportional to the one-particle density of valence states and, in addition, also the two-hole–one-electron contributions, but not the two-hole term that had been suggested in the literature. The latter arises only for filled bands. The comparison with experimental data is qualitatively good for early 3d metals, giving a natural explanation of the so-called 'negative-U' behaviour, but deteriorates with increasing atomic number. Next, we present a simple approximation to describe the effects of incomplete relaxation in the initial state. Contributions from the unrelaxed initial state are proportional to a two-hole density of states convolved with a suitable core lineshape. This removes the difficulties with the late transition metals. Our results indicate that the core-hole screening becomes progressively less complete towards the end of the 3d series. The theory then reduces to the standard one, based on two-hole propagators in the low-density approximation.

1. Introduction

The core–valence–valence (CVV) Auger spectra from late 3d transition metals (for example, Cu) are strongly influenced by electron–electron correlations responsible for their quasi-atomic character, as explained by the Cini–Sawatzky theory [1, 2]. The situation is still far from being understood in the middle or at the beginning of the 3d series. Indeed, the Cini–Sawatzky theory was formulated originally for completely occupied bands, where no core-hole screening is possible, and it is now well established [3] for such situations (Cu, Ag, Au [4]). It was then extended [5] to the case of a small hole concentration n_h (i.e. almost completely filled bands). One can prove rigorously that core-hole screening effects are $O(n_h)$, and thus the spectrum can be well approximated by the two-hole equilibrium density of states that can be calculated in the low-density approximation. Such a theory was successfully applied to Pd [6]. On the other hand, there is currently no correlated theory for large n_h, and tentative applications of the Cini–Sawatzky formulae to such situations gave surprising results. The Auger spectra from early transition metals (for example, Sc and Ti) and some of their compounds are shifted towards higher kinetic energies, which was initially interpreted [7] in terms of a negative value of the Hubbard interaction parameter U. While

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a negative U is perhaps not impossible in principle, it is generally believed that the evidence in this sense is weak. In a more recent paper, Hedegård and Hillebrecht [8] suggested that self-convolving the x-ray emission spectrum instead of the photoemission spectrum would lead to a shift in the correct direction. This approach lacks a clear theoretical foundation, but has the merit of suggesting that the screening electrons could play a role; no such effects can exist in the Cini–Sawatzky theory for completely occupied bands, while in the low-density expansions they are negligible. Recently, Sarma and co-workers [9] re-evaluated the experimental data and fitted the measured spectra as superpositions of the photoemission lineshape and its self-convolution. They also proposed a mechanism involving the electron cloud screening the core hole. The initial state of the Auger transition can be written as $\underline{c}3d^n\alpha$, where $\underline{c}$ denotes a hole in a core level, and α is the screening electron. This state can decay via two distinct Auger processes.

(i) The well known two-hole Auger transition or two-hole [2h] process

$$\underline{c}3d^n\alpha \rightarrow 3d^{n-2}\alpha'\beta' + e^- \tag{1}$$

in which the core hole is filled by a 3d electron, while a second 3d electron is ejected in the continuum. The two 3d holes in the final state are screened by the electrons α' and β'. They assume that this process contributes to the lineshape a term proportional to the 2h density of states.

(ii) The one-hole [1h] Auger process, proposed by Sarma and co-workers [9]

$$\underline{c}3d^n\alpha \rightarrow 3d^{n-1}\alpha' + e^- \tag{2}$$

in which the core hole is filled by the screening electron α and a 3d electron is ejected in the continuum, or conversely, the core hole is filled by a 3d electron, while the screening electron α is ejected. A single 3d hole in the final state is screened by one electron α'. Despite the success of Sarma and co-workers [9] in fitting, for example, the Ti lineshape, we remark that (2) does not explain the nature of the proposed 1h mechanism correctly. Nor is it at all clear why it should give a contribution proportional to the one-hole density of states. It is obvious that strictly 1h processes are impossible, since two electrons are involved in an Auger process in any case. Since the very nature of the mechanisms involved needs to be clarified, we propose a simple theory in order to explore the qualitative features. In section 2 we develop a variational approximation for the ground state, which is used in sections 3 and 4 to calculate the spectrum assuming that the Auger decay takes place in the fully relaxed initial state (two-step theory). In section 5 we include the main effects of incomplete relaxation. The complexity of the many-body calculation will be kept to a minimum, and we shall focus on the principles. Numerical examples are presented in section 6 and discussed in section 7, while the main findings are summarized in section 8. The results should pave the way to more realistic calculations that are currently under way.

2. Screening of the core hole

The core hole in transition metals does not produce the impurity bound state and it is screened predominantly by the d-electrons, while the contribution of the s and p electrons is

small [10]. We may thus expect that most of the physics can be captured by a simple model for the valence electrons described by the d-times degenerate Hamiltonian of Hubbard type

$$H = H_0 + H_{ee} + H_{ch} \tag{3}$$

where

$$H_0 = \sum_{k\alpha} E(k) n_{k\alpha} \tag{4}$$

is the band term,

$$H_{ee} = U \sum_i {\sum_{\alpha\beta}}' n_{i\alpha} n_{i\beta} \tag{5}$$

is the interaction term, and

$$H_{ch} = -W \sum_\alpha n_{0\alpha} \tag{6}$$

describes the coupling of valence electrons to the core hole at the origin. The indices α and β denote degenerate spin-orbitals ($\alpha, \beta = 1, .., d$), and $n_{k\alpha} = a^+_{k\alpha} a_{k\alpha}$ and $n_{i\alpha} = a^+_{i\alpha} a_{i\alpha}$ are number operators in the Bloch and site representations, respectively. They are defined via annihilation and creation operators $a_{k\alpha}$, $a_{i\alpha}$, etc. In the case of the d states, the degeneracy $d = 10$. The average electron concentration per site and per spin-orbital will be denoted as n, $(0 \leqslant n \leqslant 1)$.

Let $|\Psi\rangle$ be the (normalized) ground state of the Hamiltonian (3) without the core hole ($W = 0$):

$$(H_0 + H_{ee})|\Psi\rangle = E_0|\Psi\rangle \qquad \langle\Psi|\Psi\rangle = 1. \tag{7}$$

The ground state $|\Phi\rangle$ of non-interacting electrons ($U = 0$), or interacting electrons ($U > 0$) treated within the Hartree–Fock approximation, in the presence of the core hole ($W > 0$) is given just by a single Slater determinant built up from the occupied one-electron eigenstates $|p\alpha\rangle$ of a single impurity Hamiltonian:

$$|\Phi\rangle = \prod_{p\alpha}^{occ} a^+_{p\alpha} |\text{vac}\rangle. \tag{8}$$

The ground state $|\Psi\rangle$ without the core hole ($W = 0$) has the same form, but the states $|p\alpha\rangle$ are replaced by the Bloch states $|k\alpha\rangle$. The state $|\Phi\rangle$ can be obtained from $|\Psi\rangle$ by creating an infinite number of electron–hole pairs [11], and it is orthogonal to $|\Psi\rangle$, $\langle\Psi|\Phi\rangle = 0$ (the so-called Anderson orthogonality catastrophe). On the other hand, the photoemission and Auger spectra can be calculated with high accuracy, if one includes only the one and two electron–hole excitations [12]. We will thus analyse a simple class of trial states

$$|\Phi\rangle = \left(a + \sum_{q\alpha} b_{q\alpha} a^+_{0\alpha} a_{q\alpha}\right)|\Psi\rangle \qquad \langle\Psi|\Phi\rangle = 0 \qquad \langle\Phi|\Phi\rangle = 1. \tag{9}$$

The variational parameters $b_{q\alpha}$ should be determined so that $\overline{E} = \langle\Phi|H_0 + H_{ch}|\Phi\rangle$ attains its minimum. They are non-zero only for occupied states $|q\alpha\rangle$, and due to the equivalence of spin-orbitals α, $b_{q\alpha} = b_q$ for all α. The variational procedure is complicated by the presence of a sharp Fermi surface, and if we equate the first variation to zero using as usual Lagrange multipliers, we find a relative minimum that is not physically relevant. In the appendix, we outline the derivation of the ground state within the Hartree–Fock approximation and show that a slightly modified orthogonality theorem holds in the present model. The analysis is greatly simplified by assuming that the b_q depend only on the energy $E(q)$, but not on the direction of the vector q:

$$b_q = \frac{1}{\sqrt{N}}\beta(E(q)) \tag{10}$$

which is a reasonable approximation for isotropic solids. As a result, we get a simple form of the ground state $|\Phi\rangle$ with a completely screened core hole ($W > 0$):

$$|\Phi\rangle = \frac{1}{\sqrt{(1-n)d}}\sum_{\alpha} a_{0\alpha}^{+}a_{F\alpha}|\Psi\rangle. \tag{11}$$

As explained in the appendix, the states $|F\alpha\rangle$ from which the screening electrons are removed belong to the Fermi surface, as one would intuitively expect [10, 13], because this yields the lowest possible energy for the screening state. This simple model describes the essential features of core-hole screening, although it neglects some of its details, as the modification of the atomic wavefunctions by the core-hole potential and the Friedel oscillations.

3. Description of the Auger process: fully relaxed initial state

In this section we employ the approximations currently used in the literature. We use (i) the two-step approximation, i.e. we assume that formation of the core hole and the Auger process are independent, (ii) neglect competition with other decay processes, (iii) use the Golden Rule of quantum mechanics to calculate the transition rate, (iv) assume a sharp core level, (v) assume that the Auger electron does not interact with the solid left behind, (vi) assume that the Auger process is localized on one atom, (vii) assume constant (energy-independent) transition matrix elements, and (viii) neglect all surface-related effects. On the other hand, we assume that the core hole is completely screened by valence electrons. The Auger intensity is then given by

$$I_{rel}(E) = -\frac{1}{\pi}\mathrm{Im}\left(\int_0^{+\infty} \mathrm{e}^{-\mathrm{i}(E-\mathrm{i}0)t}(-\mathrm{i})\langle\Phi|H_A\mathrm{e}^{-\mathrm{i}Ht}H_A|\Phi\rangle\mathrm{d}t\right) \tag{12}$$

where $|\Phi\rangle$ is the ground state of the electronic system with a completely screened core hole, approximately given by (11), E is the kinetic energy of the Auger electron, H is the Hamiltonian of the valence electrons (3), and

$$H_A = \sum_{\alpha,\beta} M_{\alpha\beta}a_{0\alpha}a_{0\beta} \tag{13}$$

is the Hamiltonian of the Auger transition. According to assumption (vii), the transition matrix elements $M_{\alpha\beta}$ are constants independent of energy, and the summation runs over the spin-orbitals α and β on the site at the origin. Within the degenerate band model, $M_{\alpha\beta} = -M_{\beta\alpha}$, and $|M_{\alpha\beta}| = M = \text{constant}$. Employing (11) and (13), the Auger intensity can be expressed as

$$I_{\text{rel}}(E) = -\frac{1}{\pi}\,\frac{2|M|^2}{(1-n)d}\,\text{Im}\left(\int_0^{+\infty} \mathrm{e}^{-\mathrm{i}(E-\mathrm{i}0)t} \sum_{\alpha\beta\gamma} G_c^{(\text{hhe})}(\alpha\beta\gamma, t)\,\mathrm{d}t\right) \tag{14}$$

in terms of the three-particle causal Green function, which has already been used in this context [5]:

$$G_c^{(\text{hhe})}(\alpha\beta\gamma, t) = (-\mathrm{i})^3\langle\Psi|T\{a_{0\gamma}(t)a_{0\beta}^+(t)a_{0\alpha}^+(t)a_{0\alpha}a_{0\beta}a_{0\gamma}^+\}|\Psi\rangle. \tag{15}$$

In (14), we have omitted the exponential factor $\exp[-\mathrm{i}(E_0 - E_F)t]$, where E_0 is the energy of the ground state $|\Psi\rangle$. This is equivalent to choosing a new origin on the energy scale. The superscripts (hhe) denote that this Green function describes the propagation of two holes and one electron.

4. Approximate solution of the many-body problem

In order to calculate the three-particle Green function $G_c^{(\text{hhe})}(\alpha\beta\gamma, t)$, equation (15), which is a very difficult problem, we develop an approximate method based on the usual many-body perturbation theory in powers of U/w, where w is the bandwidth. We shall neglect all the terms corresponding to the genuine three-particle correlations, i.e. those containing simultaneously the interactions between two or three different pairs of particles, for example α–β and α–γ. On the other hand, we shall retain the terms that include interactions between particles belonging to one pair, say α–β, but no interactions with the third particle γ. The three-particle Green function is then expressed via the two-particle and one-particle ones. Using obvious notation:

$$\begin{aligned} G_c^{(\text{hhe})}(\alpha\beta\gamma, t) = {} & G_c^{(\text{hh})}(\alpha\beta, t)G_c^{\text{e}}(\gamma, t) + G_c^{(\text{he})}(\alpha\gamma, t)G_c^{\text{h}}(\beta, t) + G_c^{(\text{he})}(\beta\gamma, t)G_c^{\text{h}}(\alpha, t) \\ & - 2G_c^{(\text{h})}(\alpha, t)G_c^{(\text{h})}(\beta, t)G_c^{(\text{e})}(\gamma, t) \end{aligned} \tag{16}$$

if $\alpha \neq \beta$, $\alpha \neq \gamma$ and $\beta \neq \gamma$. If, however, two indices are equal, the non-zero average values of the number operators have to be taken into account and we find

$$\begin{aligned} G_c^{(\text{hhe})}(\alpha\gamma\gamma, t) = {} & (1-n)^2 G_c^{(\text{h})}(\alpha, t) + G_c^{(\text{hh})}(\alpha\gamma, t)G_c^{\text{e}}(\gamma, t) + G_c^{(\text{he})}(\alpha\gamma, t)G_c^{\text{h}}(\gamma, t) \\ & - G_c^{(\text{h})}(\alpha, t)G_c^{(\text{h})}(\gamma, t)G_c^{(\text{e})}(\gamma, t) \end{aligned} \tag{17}$$

for $\beta = \gamma$, and a similar expression for $\alpha = \gamma$. The last term in (16) and (17) has to be subtracted in order to avoid double counting.

The expression for the Auger intensity is found by inserting (16) and (17) into (14):

$$I_{\text{rel}}(E) = -\frac{1}{\pi}\,\text{Im}A(E)\Theta(E_F - E) \tag{18}$$

where

$$A(E) = (1-n)^2 G_c^{(h)}(E) + (d-1)\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i}\left(\Delta G_c^{(he)}(E-\omega)G_c^{(h)}(\omega)\right)$$

$$+ \tfrac{1}{2}d\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i}\, G_c^{(hh)}(E-\omega)G_c^{(e)}(\omega). \tag{19}$$

We have omitted the constant prefactors and performed the Fourier transformation in (14) from the time representation of the Green functions to the energy representation. The two-particle functions correspond to different spin-orbital indices, which can be suppressed for the degenerate model, and

$$\Delta G_c^{(he)}(E) = G_c^{(he)}(E) - \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i}\, G_c^{(e)}(E-\omega)G_c^{(h)}(\omega) \tag{20}$$

is the interaction part of the electron–hole two-particle Green function. Thus, the 'totally relaxed' spectrum is generally a superposition of 1h and 2h1e contributions. When n approaches unity, the relaxed ground state remains orthogonal to $|\Psi\rangle$, but the spectrum approaches the Cini–Sawatzky lineshape. At $n = 1$, the relaxed ground state coincides with $|\Psi\rangle$ and the usual closed-band theory is recovered.

We have calculated the one-particle and two-particle Green functions within the T-matrix approximation. This approximation is exact in the limit of a low concentration of particles, either electrons or holes, and it yields a reasonable interpolation between these two limiting cases. Moreover, it is a conserving approximation in Baym and Kadanoff sense [14], it has correct symmetry with respect to the electron–hole transformation and it obeys the Luttinger theorem [15]. For simplicity, we have considered only the non-magnetic solution, although it is incorrect in the case of Fe, Co and Ni. The two-hole Green functions contain the two-hole T-matrix (ladder), and the electron–hole Green functions are constructed from the electron–hole T-matrix. We have employed the so-called local approximation, which consists in keeping only the terms diagonal in the site representation in all equations for Green functions. The causal Green functions are replaced by the retarded ones. The details, particularly the derivation of the set of the integral equations that should be solved self-consistently, can be found in [16, 17]. Concerning the above treatment of correlation effects, we wish to stress that the many-body problem is very involved. However, at the beginning of the 3d series, the correlation effects are evidently moderate and any many-body scheme will produce essentially the same results. Near the end of the series, where correlations are large and produce quasi-atomic resonances with their multiplet splittings, we are favoured by the fact that such effects are now well understood [18, 19] and the ladder approximation becomes exact in the limit of closed bands. To this level of sophistication, we may think that each multiplet component can be dealt with independently and our treatment describes each multiplet component in turn, with its effective U. Thus we have good reason to believe that the present simplified analysis will turn out to be adequate to give a first insight into the problem.

5. Incomplete relaxation effects

For n close to unity, we are free to assume complete relaxation (as in the last two sections) or even a complete lack of relaxation: the theory predicts the same lineshape in both cases. Except for this limiting case, which is well understood, the problem is very difficult: the predictions of the two approaches differ vastly, and none of them is justified, since we must include the possibility that the system fails to relax completely around the core hole before the Auger decay takes place. Here, we wish to propose a simple approximation that should include the main effects of partial relaxation provided that we are ready to ignore plasmon and other shake-up satellites.

We introduce the inverse δ of the hole lifetime and the inverse Γ of the relaxation time needed to screen the core hole. We assume that both are small, compared to the other relevant energies. We use the one-step description [20] of the Auger process, but assume that the most important intermediate states are the orthogonal states $|\Phi\rangle$ and $|\Psi\rangle$; in other terms, our approximation for the spectrum is

$$I_{\mathrm{tot}}(E) = \int_0^{+\infty} \mathrm{d}t \int_0^{+\infty} \mathrm{d}t' f(t,t') \mathrm{e}^{\mathrm{i}E(t-t')} \tag{21}$$

where

$$f(t,t') = \sum_{m,m'=\Phi,\Psi} \langle \Psi | a_{\mathrm{c}}^{+} \mathrm{e}^{\mathrm{i}[H(0)+\mathrm{i}\Gamma_{\mathrm{op}}]t'} a_{\mathrm{c}} | m \rangle \langle m | H_{\mathrm{A}}^{+} \mathrm{e}^{\mathrm{i}H(1)(t-t')} H_{\mathrm{A}} | m' \rangle \times \langle m' | a_{\mathrm{c}}^{+} \mathrm{e}^{-\mathrm{i}[H(0)-\mathrm{i}\Gamma_{\mathrm{op}}]t} a_{\mathrm{c}} | \Psi \rangle. \tag{22}$$

In this equation, $H(\nu)$ is the Hamiltonian with ν core electrons, Γ_{op} is a complicated operator describing virtual Auger transitions and the various relaxation processes that eventually take $|\Psi\rangle$ into $|\Phi\rangle$. One of the ingredients of (22) is just the Green function of the core hole:

$$g_{\mathrm{c}}(t) = -\mathrm{i}\langle \Psi | a_{\mathrm{c}}^{+} \mathrm{e}^{\mathrm{i}[H(0)+\mathrm{i}\Gamma_{\mathrm{op}}]t} a_{\mathrm{c}} | \Psi \rangle. \tag{23}$$

When our assumptions apply, in (21) we may replace $g_{\mathrm{c}}(t)$ by its long-time expansion. Neglecting fine details like the infrared catastrophe and all other shake-up effects, we can model it as follows:

$$g_{\mathrm{c}}(t) = -\mathrm{i}\mathrm{e}^{-\mathrm{i}\varepsilon_{\mathrm{c}}t-(\Gamma+\delta)t}. \tag{24}$$

The density of states that is associated with this quantity is the same as that observed in photoemission. In this approximation, it is a Lorentzian and both lifetime and relaxation effects contribute to its width. This is correct, although in a more precise description the relaxation broadening should be asymmetric.

The terms with $m = |\Psi\rangle$ and $m' = |\Phi\rangle$ or $m = |\Phi\rangle$ and $m' = |\Psi\rangle$ in (22) vanish because $H(1)$ cannot evolve a 3h1e state into a 2h state. Thus, to obtain a sensible approximation, we need the long-time behaviour of

$$\beta_{\mathrm{c}}(t) = -\mathrm{i}\langle \Phi | a_{\mathrm{c}}^{+} \mathrm{e}^{\mathrm{i}[H(0)+\mathrm{i}\Gamma_{\mathrm{op}}]t} a_{\mathrm{c}} | \Psi \rangle. \tag{25}$$

The unrelaxed ground state evolves into $|t\rangle = e^{i[H(0)+i\Gamma_{op}]t}a_c|\Psi\rangle$, and for long times t, this should be proportional to $|\Phi\rangle$. Since the hole decays, the normalization condition is

$$|g_c(t)|^2 + |\beta_c(t)|^2 = e^{-2\delta t} \tag{26}$$

and asymptotically

$$\beta_c(t) = \beta(\infty)e^{-i\varepsilon_\beta t-\delta t} \tag{27}$$

where $\varepsilon_\beta = \varepsilon_c + E_{gs}$, and E_{gs} is the relaxed ground-state energy; $\beta(\infty)$ is a constant phase factor of modulus unity, that we do not need to calculate. Thus

$$I_{tot}(E) = I_{\phi\phi}(E) + I_{\psi\psi}(E) \tag{28}$$

should be the sum of two terms. The first one is

$$I_{\phi\phi}(E) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{I_{rel}(E-\omega)}{(\omega-\epsilon)^2+\delta^2}. \tag{29}$$

We now write

$$|M|^2 = \frac{|M_0|^2\delta}{\pi} \tag{30}$$

where M_0 is a new constant, in order to acknowledge that $|M|^2$ is proportional to the decay rate and hence to the core-hole inverse lifetime. Thus, we see that the totally relaxed lineshape is convolved with a suitable Lorentzian to account for the hole decay. The second term is

$$I_{\psi\psi}(E) = |M|^2 \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{D(E-\omega)}{(\omega-\varepsilon_c)^2+\Gamma^2} \tag{31}$$

where D is the 2h density of states; it is convolved with a Lorentzian of width Γ and centred at energy ε_c. The ratio of the areas δ/Γ is a measure of the degree of relaxation of the initial state of the Auger transition. Thus, (28) interpolates smoothly between two opposite situations. When metallic screening prevails, and core holes are long lived, δ/Γ will be small and the Auger spectrum will be well approximated by the fully relaxed theory. For closed or nearly closed bands, the degrees of freedom responsible for core-hole screening are slow, and core-hole decay can be neglected: this is the established theory. It is for small n that we expect the spectrum to be a linear combination of two widely different ones, originating from relaxed and unrelaxed initial states.

However, what we propose is not just interpolation, because δ and Γ can be measured and calculated independently. For instance, the lifetime is known from Auger matrix element

calculations, and core photoemission allows an empirical determination of Γ. Auger-photoelectron coincidence spectroscopy (APECS) provides a further experimental test of the validity of our model. If (22) holds, both spin–orbit split components of the core L photoemission lines should consist of a main peak and a shake-up satellite, separated from it by the relaxation energy E_{gs}. The satellite intensity may vanish, in which case the Auger lineshape should be the one of section 4. Otherwise, APECS should allow the observation of the lineshapes originating from both; they should turn out to be rather different at the beginning of the series, and while the spectrum in coincidence with the main peak should be the one of section 4, the shape of the one deriving from the satellite should reflect the 2h density of states.

6. Numerical results

The calculations were done for all transition 3d metals using a simple model given by the semi-elliptic density of states with the bandwidth $w = 2$. We have employed the strengths of the pair interaction as given in [21], corrected with respect to the actual d-band filling $n_d = nd$. The values of n_d were taken from [22]. These input parameters are summarized in table 1.

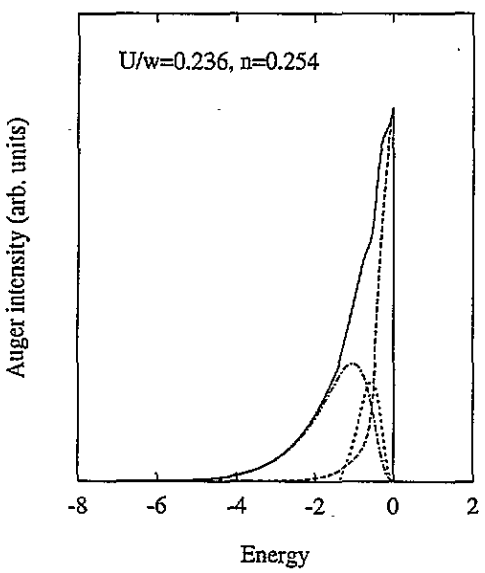

Figure 1. Computed Auger spectrum assuming perfect screening of the core hole (section 4). The parameters $U/w = 0.236$ and $n = 0.254$ correspond to Ti. The contributions from the one-hole process (broken curve), the electron–hole bound state convoluted with the one-hole propagator (dotted curve) and from the two-hole process convoluted with the one-electron propagator (chain curve) are shown together with the total Auger intensity (full curve). The origin of the energy axis is shifted to E_F. The energy is measured in relative units such that the unperturbed bandwidth $w = 2$.

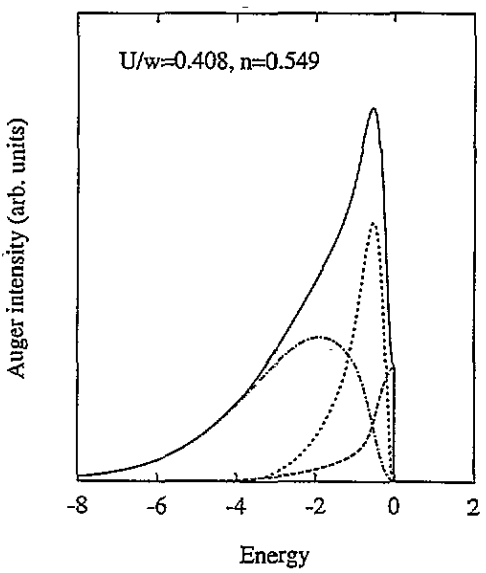

Figure 2. The same as in figure 1, but for the parameters $U/w = 0.408$ and $n = 0.549$ corresponding to Mn.

Table 1. The parameters used to calculate Auger spectra of 3d metals: occupancy of the d-band n_d, Hubbard U, and the bandwidth w, together with the weights of various Auger processes determined by the present theory.

	n_d^a	U^b	w^a	U/w	W_{1h}^c	W_{ch*h}^c	W_{hh*c}^c
Sc	1.54	1.263	6.80	0.186	0.566	0.058	0.376
Ti	2.54	1.684	7.14	0.236	0.379	0.137	0.484
V	3.61	1.938	7.48	0.259	0.245	0.198	0.557
Cr	4.52	2.302	7.14	0.322	0.165	0.259	0.576
Mn	5.49	2.638	6.46	0.408	0.107	0.310	0.583
Fe	6.53	2.818	5.44	0.518	0.067	0.342	0.591
Co	7.53	3.062	5.10	0.600	0.043	0.328	0.629
Ni	8.55	3.284	4.08	0.805	0.023	0.303	0.674
Cu	9.51	3.561	3.06	1.163	0.009	0.113	0.878

[a] Ref. [22].
[b] Ref. [21].
[c] This work.

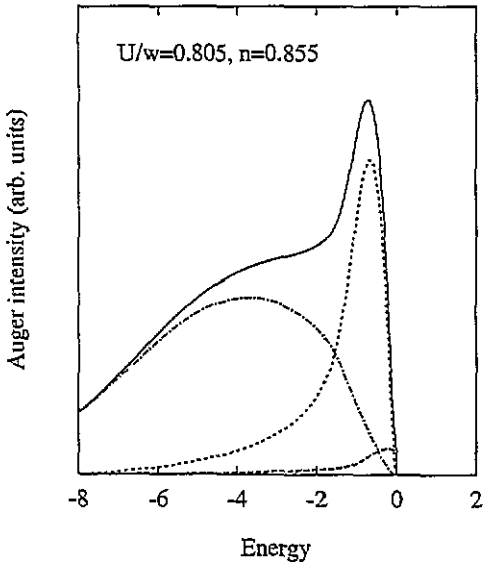

Figure 3. The same as in figure 1, but for the parameters $U/w = 0.805$ and $n = 0.855$ corresponding to Ni.

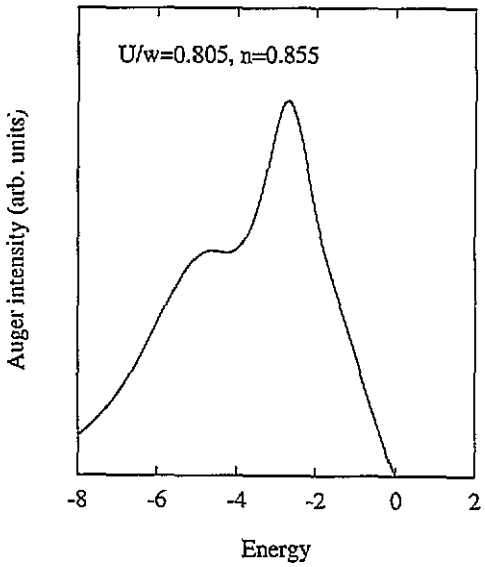

Figure 4. The Auger spectrum without core-hole screening calculated according to the Cini–Sawatzky theory. The parameters $U/w = 0.805$ and $n = 0.855$ correspond to Ni. The origin of the energy axis is shifted to $2E_F$. The energy is measured in relative units such that the unperturbed bandwidth $w = 2$.

The calculated Auger spectra for Ti, Mn and Ni are shown in figures 1–3, and the Auger spectrum of Ni without the core-hole screening is shown in figure 4. The relative weights of the three contributions to the total spectrum (19) are given in table 1. In figure 5, we compare the present theory including the core-hole screening and the Cini–Sawatzky theory without screening directly with the experimental data for Ti taken from [8]. In figure 6, we make a similar comparison for Ni with experimental data taken from [23].

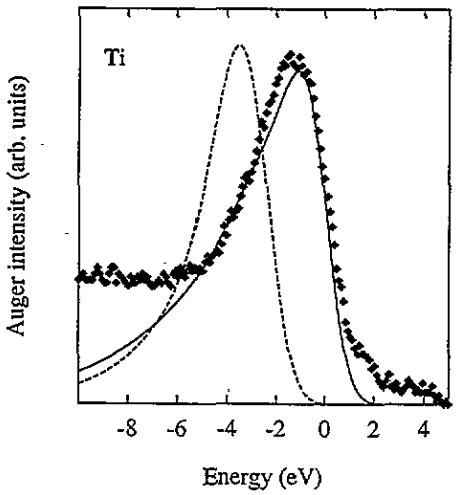

Figure 5. Experimental Ti $L_2 - M_{45}M_{45}$ spectrum (black points) taken from [8] compared with the theoretical curve calculated according to the present theory assuming complete screening of the core hole (full curve) and according to the Cini–Sawatzky theory (broken curve) for the parameters $U = 1.684\,\text{eV}$, $w = 7.14\,\text{eV}$ and $n = 0.254$ corresponding to Ti. The theoretical curves were broadened by a Gaussian with $\sigma = 0.7\,\text{eV}$.

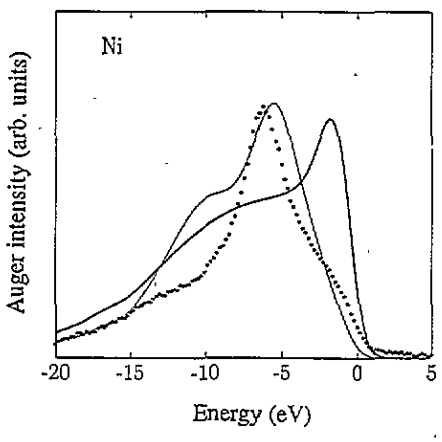

Figure 6. Experimental Ni $L_3 - M_{45}M_{45}$ spectrum (black points) taken from figure 2 of [23] compared with the theoretical curve calculated according to the present theory assuming complete screening of the core hole (thick full curve) and according to the Cini–Sawatzky theory (thin full curve) for the parameters $U = 3.284\,\text{eV}$, $w = 4.08\,\text{eV}$ and $n = 0.855$ corresponding to Ni. The theoretical curves were broadened by a Gaussian with $\sigma = 0.7\,\text{eV}$.

7. Discussion

Let us first consider the Auger CVV spectra calculated under the assumption of complete screening of the core hole. They are given, according to (19), by a sum of three contributions.

(i) The one-particle density of valence states. This arises from pinning the energy of one of the two holes at the Fermi level due to the screening effects. Its threshold is, in fact, the same as for the usual self-convolution of the one-particle density of states. It corresponds to the one-hole process proposed by Sarma and co-workers [9].

(ii) The three-particle density of states corresponding to the bound (excitonic-like) state of one electron–hole pair convoluted with the one-hole propagator.

(iii) The three-particle density of states which comes from the usual two-hole process, but, in addition, it is convolved with the one-electron propagator.

There are important differences between the theory of sections 3 and 4 and the approach proposed by Sarma and co-workers [9]. Our theory describes the Auger spectrum in terms of the three-particle Green function which may be contracted into the one-particle GF, if two spin-orbitals coincide leading thus to the 1h process. On the other hand, Sarma and co-workers [9] from the beginning postulate the 1h and 2h processes. Their description of the 2h process is conceptually incorrect, because they neglect the dynamics of the screening electrons. This dynamics is simply but consistently included in the present theory via three-particle Green functions. The good quality of the fit of experimental data presented in [9] can be explained as follows. The 2h density of states is constructed as a self-convolution of the photoemission spectral densities, which are, in fact, one-particle densities of states broadened by the lifetime and measuring device functions. Such a quantity can successfully

mimic the contribution from the three-particle GF, which is a correct quantity yielding the Auger spectrum in the fully screened case.

Taking into account the L_2VV spectrum, the results show quite good agreement with experimental data in the case of early 3d metals (see figure 1 and particularly figure 5). The process (ii) in these early metals gives the contribution which can mimic, to some extent, the shape and position of the one-hole process (i). The applicability of the 'completely relaxed' theories to these metals confirms the conclusions from electron energy loss experiments by Fink and co-workers [24]. It was concluded from a comparison of such experiments with earlier photoemission data [25] that lifetime broadening gives only a small contribution to the 2p level width, and according to section 5 the Auger decay must predominantly occur in a relaxed ground state.

Not unexpectedly, the agreement of the relaxed theory with experiment deteriorates in the middle of the 3d series (figure 2) and the calculated weights of the processes (i)–(iii) differ more significantly from the results of the analysis of experimental data.

The trend continues in the late 3d metals, and figure 3 reports the results of a calculation which assumes a relaxed initial state in the Ni case. The weight of the one-hole process is low, but the process (ii) gives a strong contribution situated very close to E_F. Moreover, the contribution from the process (iii), which would correspond to the usual two-hole transition, is significantly broadened by the convolution with the density of the almost occupied one-electron valence band. The resulting spectrum clearly differs from that measured experimentally. In figure 6 we compare the experimentally measured spectrum [23] of Ni with that predicted by the present theory including the core-hole screening and by the Cini–Sawatzky theory without screening. The Cini–Sawatzky theory agrees much better with experimental data.

Here, the theory of section 5 is particularly needed. According to it, incomplete relaxation becomes important. This is physically reasonable, because for small n_h there is little phase space left for the screening electrons, the screening degrees of freedom must become slow, and the lifetime contribution to the photoemission core level width is therefore important. The absence of evident core-hole screening effects in the case of Ni and other late 3d metals is due to the fact that little screening actually takes place during the core-hole lifetime. In fact, it has been known for a long time [5,26] that a low hole density expansion is adequate for Ni. Even the usual two-hole density of states (figure 4) that follows from the Cini–Sawatzky theory [1,2] does much better than the 'fully relaxed theory', in describing the measured spectrum. The theory of section 5 aims to provide the principle for describing the whole 3d series. The above numerical results show that, at least, we achieved an explanation of the 'negative-U' behaviour of early transition metals and a reasonable interpolation between the two ends of the series.

8. Conclusions

We have developed a simple theory describing the Auger electron spectra from open-band systems. The main issue is that of properly describing the effects of core-hole screening, which do not arise in closed-band systems and are therefore ignored in the Cini–Sawatzky theory and its extensions.

An extreme point of view would lead one to assume that core-hole screening is perfect (sections 2–4). We developed this case using a simple form of the screened ground state, and omitting the genuine three-particle correlations in the evaluation of the three-particle Green function. Both these approximations can somewhat affect the final form of the theoretically

calculated Auger lineshape. However, the simplified ground state fulfills the Anderson orthogonality theorem.

We have found that assuming a complete screening of the core hole is far better than neglecting screening effects near the beginning of the series, but is worse near the end, where the previous theory is much preferable. In fact, near the beginning of the series, we explain the main features of the spectra without assuming a 'negative U'. However, in order to describe correctly the evolution of the CVV Auger spectra within the whole transition metal series it is essential to use a dynamical theory taking properly into account the time dependence of the core-hole screening by the valence electrons. A more complete theory was therefore proposed in section 5. As shown there, we believe that the intermediate transition metals are particularly promising samples for future APECS experiments. Auger spectra from main and satellite core lines are predicted by sections 4 and 5, respectively, and may well be very different. The theory of section 5 also recovers the results of the low-density approximation near the end of the series, where the effects of core-hole screening on Auger lineshapes are small.

Thus, we obtained a coherent picture that accounts for the main experimental features throughout the 3d series, at least qualitatively. The known results for the late transition metals are included and reconciled with a fair understanding of the so-called 'negative-U' behaviour at the beginning of the series. A more quantitative understanding of the behaviour in the middle of the series requires further work, including multiplet effects and a proper account of ferromagnetism; such work is under way.

Acknowledgments

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Appendix. Ground state with the core hole

We find

$$\overline{E} = E_0[|a+bd|^2 + d(1-n)S] + (1-n)(FS-M)\dot{d} - W[|a+bd|^2 - (1-n)|a+b(d-1)|^2 + (1-n)S + n(1-n)S(d-1)] \tag{A1}$$

where

$$E_0 = d\sum_q^{\text{occ}} E(q) \qquad b = \frac{1}{\sqrt{N}}\sum_q^{\text{occ}} b_q \qquad S = \sum_q^{\text{occ}} |b_q|^2$$
$$F = \frac{1}{1-n}\frac{1}{N}\sum_q^{\text{unocc}} E(q) \qquad M = \sum_q^{\text{occ}} E(q)|b_q|^2. \tag{A2}$$

The normalization and orthogonality constraints are

$$\langle\Phi|\Phi\rangle = |a+bd|^2 + (1-n)Sd = 1 \qquad \langle\Psi|\Phi\rangle = a+bd = 0. \tag{A3}$$

The orthogonality is being assumed for the moment, but will be discussed below. The average energy is then simplified:

$$\overline{E} = E_0 + F - W[1 + n(d-1)] + (1-n)[W|b|^2 - M]d. \tag{A4}$$

Because only the fourth term on the right-hand side of (A4) depends on b_q, we need to minimize the quadratic form

$$Q = W|b|^2 - M = W\left|\frac{1}{\sqrt{N}}\sum_q b_q\right|^2 - \sum_q E(q)|b_q|^2 \tag{A5}$$

under the normalization constraint

$$S = \sum_q^{\text{occ}} |b_q|^2 = \frac{1}{(1-n)d}\,. \tag{A6}$$

This can be achieved by finding the eigenvector belonging to the smallest eigenvalue of the matrix associated with the quadratic form (A5). The same result can be easily found by a different approach. With the assumption of (10), equation (A5) can be written as

$$Q = W\left|\int_{-\infty}^{E_F} \rho(\varepsilon)\beta(\varepsilon)\mathrm{d}\varepsilon\right|^2 - \int_{-\infty}^{E_F} \varepsilon\rho(\varepsilon)|\beta(\varepsilon)|^2\mathrm{d}\varepsilon \tag{A7}$$

and the normalization constraint (A6) as

$$\int_{-\infty}^{E_F} \rho(\varepsilon)|\beta(\varepsilon)|^2\mathrm{d}\varepsilon = \frac{1}{(1-n)d} \tag{A8}$$

where $\rho(\varepsilon)$ is the density of states corresponding to the dispersion law $E(q)$, and E_F is the Fermi energy. The second term in (A7) will achieve its minimum under the normalization constraint (A8) if all the weight of $|\beta(\varepsilon)|^2$ is concentrated at E_F: $|\beta(\varepsilon)|^2 \propto \delta(E - E_F)$. The function $\beta(\varepsilon)$ would then be given by a square root of the Dirac distribution, which is not a well defined quantity. We thus employ the representation

$$\beta(h, \varepsilon) = \mathrm{e}^{\mathrm{i}\phi(h,\varepsilon)}[(1-n)\rho(E_F)hd]^{1/2}\ \Theta(E_F - \varepsilon)\Theta(\varepsilon - E_F + h) \tag{A9}$$

where $\phi(h, \varepsilon)$ is the phase angle and Θ denotes the Heaviside function. At the end of the calculations, we take the limit $h \to 0$. Without loss of generality, we can set $\phi(0, E_F) = 0$. The first term of (A7), which is always non-negative, then also reaches its minimum (= 0). The one-particle states $|F\alpha\rangle$, from which the screening electrons are removed, are defined as

$$|F\alpha\rangle = \sqrt{(1-n)d}\lim_{h\to 0}\frac{1}{\sqrt{N}}\sum_q \beta(h, E(q))|q\alpha\rangle. \tag{A10}$$

They are normalized to unity, mutually orthogonal, $\langle F\alpha|F\beta\rangle = \delta_{\alpha\beta}$, and orthogonal to Wannier states: $\langle i\beta|F\alpha\rangle = 0$ for all i, α, and β. We find $b = 0$, and thus $a = 0$. The ground state $|\Phi\rangle$ is then given by (11).

Let us now deal with the orthogonality issue. The vanishing of b can be understood from general principles. Indeed, we are free to choose the phases of each b_q arbitrarily; hence, the phase of b can be changed at will without changing the physics. Since the energy of (32) depends on b, the ground state must correspond to $b = 0$. Inserting this and the normalization condition into (32), we get

$$\overline{E} = E_0 - nW + d(1-n)S\{F - W[1 + (d-2)n]\} - d(1-n)M. \qquad \text{(A11)}$$

The optimum for a fixed S is obtained for

$$|\beta(\varepsilon)|^2 = \frac{S}{\rho(E_F)}\delta(\epsilon - E_F) \qquad \text{(A12)}$$

yielding $M = SE_F$. Next, we minimize with respect to S as well, keeping in mind the normalization condition. If W is so small that

$$F - E_F > W[1 + (d-2)n] \qquad \text{(A13)}$$

then the optimum is $S = 0$ and $|\Phi\rangle = |\Psi\rangle$. In this model a fixed energy $F - E_F$ is needed to localize the screening electron, and there is an unphysical threshold for W, below which the system remains in the unperturbed ground state. Above threshold, however, the system will polarize, and the optimal value of S corresponds to the maximum; then $a + db = 0$ and $\langle\Phi|\Psi\rangle = 0$. This is the orthogonality theorem for the present model.

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