Spin-polarization in ccv Auger electron spectroscopy for transition metals

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Abstract

The contributions of core states and the valence band to spin-resolved ccv Auger electron spectra (AES) are discussed in terms of a relativistic, spin-polarized theory. The influence of the core-state spin polarization and of selecting particular valence bands via cross sections is shown for the surface layer of BCC Fe(100) as calculated by means of the Screened KKR ab-initio electronic structure method. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Auger electron spectroscopy; Spin polarization; Transition metal – surfaces; Screened KKR; relativistic

In a relativistic multiple scattering theory [1–3], Auger electron spectroscopy (AES) can be formulated in a spin-polarized manner that permits simultaneously to calculate transition matrix elements and the DOS. A similar approach was presented for the core–valence–valence (ccv) case [4]; however, if one is interested in the valence band properties it seems to be more convenient to analyze two core states, i.e., ccv AES, instead of convoluting the valence bands.

For a ccv AES process, we have to describe the electronic transitions from initial states \(c_2\) — the upper core states and \(v\) — the valence states, and from the final states \(c_1\) — the lower core states and \(A\) — the outgoing ‘Auger’ electron. Obviously, there are two possible transition processes: the direct (D) process \(c_2 \rightarrow c_1\) and \(v \rightarrow A\) and the exchange (E) process \(c_2 \rightarrow A\) and \(v \rightarrow c_1\). Thus, the emission intensity as given by

\[
I(e) = \delta(e_2 - e)|D - E|^2 = I^{ccv}(e; s, \hat{p}),
\]

can be determined as spin (\(s\)) and angle (\(\hat{p}\)) resolved. Inserting the actual involved states and the electronic interaction as a static Coulomb interaction into the direct and exchange integrals the transition intensity can, as usual, be decomposed into a matrix of cross sections \(\sigma_Q^{ccv}(e; s, \hat{p})\) and the DOS defined in multiple scattering theory by the imaginary part of the scattering path operator \(\text{Im} \tau_Q(e)\)

\[
I^{ccv}(e; s, \hat{p}) = -\frac{1}{\pi} \sum_Q \sigma_Q^{ccv}(e; s, \hat{p}) \text{Im} \tau_Q(e),
\]

that includes a sum over all valence states \(Q_v = (\kappa \mu)\) .

In a spin-polarized relativistic treatment, all involved states are sums of the coupled solutions \(Q\) of the following form

\[
\psi_Q(r) = \sum_{\tilde{\gamma}} \left( \begin{array}{c} g_{\tilde{\gamma}Q}(r) \chi_{\tilde{\gamma}}(\hat{r}) \\ \bar{f}_{\tilde{\gamma}Q}(r) \end{array} \right).
\]

In the case of core states, \(g_{\tilde{\gamma}Q}(r)\) and \(f_{\tilde{\gamma}Q}(r)\) are the solutions of the coupled Dirac equation for a given core eigenvalue \(e\) (see Ref. [2]), the \(\chi_{\tilde{\gamma}}(\hat{r})\) being spin-spherical harmonics. The valence states are described by regular scattering solutions and the DOS is given as discussed in Ref. [2]. Continuum states at energies considerably high above the Fermi level can be described in the single-site (final state) approximation.

The matrix of cross sections as introduced in Eq. (2) \(\sigma_Q^{ccv}(e; s, \hat{p})\) can be separated into three terms according...
to the three different transition processes
\[ \sigma_{Q_2}^{(s)} = \sigma_{Q_2}^{(s),D^2} + \sigma_{Q_2}^{(s),E^2} + \sigma_{Q_2}^{(s),DE}. \]  
All of them show the same formal structure, namely,
\[
\sigma_{Q_2}^{(s),D^2}(\epsilon; s, \beta) = \sum_{Q_A, Q'_A} \hat{f}_A^{-\epsilon} C(i_A 1/2 j_A; \mu_A - s, s) 
\times C(i_A 1/2 j'_A; \mu'_A - s, s) 
\times Y_{i_A j_A i'_A}^* Y_{j'_A}^{-\epsilon}(-\beta) 
\times I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]
\[
\sigma_{Q_2}^{(s),E^2}(\epsilon; s, \beta) = \sum_{Q_A, Q'_A} \hat{f}_A^{-\epsilon} C(i_A 1/2 j_A; \mu_A - s, s) 
\times Y_{i_A}^{-\epsilon} Y_{i_A j_A}^* Y_{i_A j_A}^*(-\beta) 
\times I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]
\[
\sigma_{Q_2}^{(s),DE}(\epsilon; s, \beta) = \sum_{Q_A, Q'_A} \hat{f}_A^{-\epsilon} C(i_A 1/2 j_A; \mu_A - s, s) 
\times Y_{i_A j_A}^* Y_{j_A}^{-\epsilon}(-\beta) 
\times I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]
i.e., it contains sums over the continuum states \(Q_A\) and \(Q'_A\), as well as integrals \(I\) corresponding to different combinations of initial and final states
\[
\sigma_{Q_2}^{(s)} = I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]
\[
\sigma_{Q_2}^{(s)} = I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]
\[
\sigma_{Q_2}^{(s)} = I(Q_c, Q_{c_2}) I(Q_A Q'), 
\]

The \(D^2\) term results in an Auger electron spin polarization due to the valence band while the \(E^2\) term produces a spin polarization due to the \(c_2\) core states. Thus, besides the value of the valence-band spin polarization the resulting Auger electron spin polarization also depends on the spin character of the core states weighted by the amplitudes of the radial parts in the different terms. Only for vanishing \(E^2\) and \(DE\) terms the valence-band spin is transferred to that of the Auger electron.

In the present contribution, we shall investigate AES integrated over the angle of the emitted electron \(\beta\), for which the corresponding cross sections can easily be derived from Eqs. (5) and (6). An experimentally observed cvv Auger electron spectrum results from all different atoms emitting electrons and from all possible core state combinations for one particular atom corresponding in energy
\[
I^{\exp}(\epsilon; s) = \sum_{\text{atoms}} \sum_{\epsilon_1, \epsilon_2} I^{\epsilon_1 \epsilon_2}(\epsilon; s). 
\]

Note that, the energy scale of each \(I^{\epsilon_1 \epsilon_2}(\epsilon; s)\) has to be aligned considering the different energy eigenvalues of each core state. We found the largest core state split in the Fe surface atom of 1.1 eV for the \(L_3\) (2p_{3/2}) states and of 2.5 eV for the \(M_3\) (3p_{3/2}) states. The \(L_3M_{23}V\) AES consists of 24 separate processes involving the four \(L_3\) and the six \(M_{2,3}\) states.

The electronic structure was calculated for the system BCC Fe(100)/Fe(001)/Vac using the Screened KKR method. Here, only the results for the surface Fe layer are shown. In Fig. 1, we show the total \(L_3M_{23}V\) AES for the Fe surface layer. Almost 70% of the intensity is due to transitions from only four of the 24 core-state combinations, namely, the ones with \(\Delta \epsilon_c = 0\) (\(\Delta \epsilon_c = 0\)) and \(\Delta \epsilon_c = 0\) (dashed curve). For \(Q_3 = L_3\) and \(Q_2 = M_{23}\) these are the core states with \(j_c = 3/2\) and (i) \(\mu_c = -3/2\), (ii) \(\mu_c = -1/2\), (iii) \(\mu_c = +1/2\), and (iv) \(\mu_c = +3/2\). The 8 partial spin-resolved spectra for these four cases are also shown in Fig. 1. We find most of the intensity for cases (i) and (iv) corresponding to respective opposite spins. It is interesting to mention that (i) and (iv) are the only uncoupled states and they show a spin polarization of 100% with a different sign.

In the following we compare the results for cases (i) and (iv). In Figs. 2 and 3 the spin-up and spin-down spectra and the cross sections are shown together with the corresponding DOS for the valence band. First of all it is important to note that the DOS in both figures is displayed for selected \((\kappa, \mu)\) valence states and, consequently, is not spin-polarized. Figs. 2(b) and 3(b) exhibit the largest cross sections for both spin directions for cases (i) and (iv) of the outgoing electron, respectively. The resulting unbroadered spectra are shown in (c) for case (i) and in (d) for case (iv). We find large amplitudes for opposite spins, see Figs. 2(d) and 3(c), as already pointed out.

For all spectra the respective largest partial valence-band state resolved spectra are shown. The difference in the form of the spin-up and the spin-down spectra is given by the contribution of different valence-band states, see in particular the peak around 2 eV in Fig. 3(c), which occurs only in the spin-down spectrum. Furthermore, in the spin-up case there is no dominating partial spectrum: almost all d-band partial spectra yield a comparable contribution. In the spin-down case we find in both cases (i) and (iv) a dominating contribution from the uncoupled \((j = 5/2, \mu = +5/2)\) valence state and a comparably big one from only two other states.
Summarizing, in the case of core transitions $D_{j_c} = 0$ and $D_{m_c} = 0$, we find remarkable contributions to the AES from (selected or all) d-band valence states and that the spin–resolution of the spectrum is mainly determined by the spin character of the core-states. Calculations of other AES (for $\Delta g_c \neq 0$ and/or $\Delta \mu_c \neq 0$) show couplings to s-like or p-like valence states for which the cross sections can have a very different energy dependency and amplitudes.

Financial support was provided by the TMR network on “Ab-initio calculations of magnetic properties of surfaces, interfaces, and multilayers” (contract No.: EMRX-CT96-0089), the Center of Computational Materials Science (contract No.: GZ 308.941/2-IV/95) and the Hungarian National Science Foundation (OTKA T030240 and T029813).

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