Spectra and Spin Polarization of the Valence Band Auger Emission from Cr (100) Surface *

YUAN Jian-Min(袁建民)[1], L. Fritsche[2], J. Noffke[2]

[1]*Department of Applied Physics, National University of Defense Technology, Changsha 410073*
[2]*Institut für Theoretische Physik, TU Clausthal D-38678 Clausthal-Zellerfeld, F. R. Germany*

(Received 19 May 2003)

Calculations have been carried out on spin-polarized Auger electron emission from a seven-layer chromium (100)-film. The core and valence states concerning the Auger transition are obtained from a self-consistent full-potential linearized augmented plane wave calculation by using a repeated slab geometry. The calculations refer to experiments on the $L_3M_{23}V$- and L_3VV-transitions that have recently been carried out by Heinzmann et al. The Auger spectrum obtained for the L_3VV transition agrees relatively well with our calculations, whereas the observed $L_3M_{23}V$-Auger structure is considerably wider than that predicted by our theory. Nevertheless, the spin-polarization in the latter case, which is about -13%, is in fair agreement with the experiment, different from the L_3VV-transition where the experiment yields -10% as opposed to the theoretical value of -25%. We give possible reasons for the origin of these discrepancies.

PACS: 79. 20.Ḟv, 73. 20. At, 73. 20. Dx

The idea of correlating Auger-line shapes from elemental metals with their electronic structure goes back to Lander[1] who pointed out that the form of the Auger spectral line, associated with a CVV transition, results from a self-convolution of the local density of (valence) states (LDOS). In demonstrating this interrelation he had to assume that the pertinent transition matrix elements, to a good approximation, may be regarded as constant across the valence band. Although sizeable discrepancies between experimental line shapes and Lander's formula have been observed, it seems to be clear that this assumption on the constancy of the matrix elements represents the major source of error. In order to improve the theory at this point and to elucidate the influence of the actual variation of the matrix elements and their dependence on the angular momenta of the valence electrons there have been various studies based on different representations of the involved orbitals. Feibelman *et al.*[2] and Jennison *et al.*[3] use a linear combination of atomic orbitals (LCAO). Jennison *et al.* were led to atomic-like matrix elements which then occur as weighting factors in the convolution of the partial density of states. More recent work by Hörmandinger *et al.*[4] is based on a relativistic form of the orbitals and has subsequently been extended by Szunyogh *et al.*[5] The authors give a detailed and refined derivation of the dependence of the Auger transition intensity on the LDOS. Almbladh *et al.*[6] used self-consistent linear combinations of muffin-tin orbitals (LMTOs) in their calculations and allowed for finite core-hole lifetimes as well as for dynamical effects and processes at the surface. An ab-initio Green-function study of Auger emission from polyethylene has been reported by Liegener.[7] The calculation draws on quasi-particle bands and includes correlation effects by a renormalization procedure.

The present study was primarily motivated by recent experiments on spin-resolved Auger transitions that involve two itinerant states of the $3d$-valence band of Cr metal.[8] The calculations we shall present are based on the same theoretical method as described in the previous paper[9] concerned with the Auger electron emission (AES) from thin films of potassium metal. We use a scalar-relativistic Full-Potential-Linearized-Augmented-Plane-Wave (FLAPW) method[10] to calculate the valence states. As in the preceding article we include the core-hole screening by performing a self-consistent calculation on a seven-layer (100)-film where the central layer consists of Cr atoms that all contain a $2p$ core-hole. Supercell with a repeated slab geometry is used to simulate the seven-layer (100)-film. This technique was also used by other authors to calculate the defect states of acoustic waves in two-dimensional lattice.[11] To keep the film electrically neutral the valence bands are filled slightly higher up so that one ends up with one more–valence electron per atom averaged over the lateral unit cell. We assume the axis of the incoming circularly polarized light to be perpendicular to the film.

As for the electronic states of the metals we are considering, we employ the FLAPW-WIEN95 code[12] to calculate the itinerant valence and semi-core solutions to the Kohn–Sham equations that result from a generalized density functional theory.[13,14] The FLAPW-method requires a subdivision of the crystal into sufficiently large, but non-overlapping concentric spheres (atomic spheres) around the atomic nuclei and

* Supported by the National Natural Science Foundation of China for Distinguished Young Scholars under Grant No 10025416, and the Research and Technology (BMBF) of the Federal Republic of Germany.
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an interstitial region between these spheres. Inside the atomic sphere the one-electron state of band index n is given by

$$\psi_n(\epsilon_n, \boldsymbol{k}, \boldsymbol{r}) = \sum_L \sum_{\nu=0}^{1} c_{L\nu}^{(n)}(\epsilon_n, \boldsymbol{k}) R_{l\nu}(\epsilon_l, r) Y_L(\hat{\boldsymbol{r}}) \chi_{\sigma_n}, \tag{1}$$

where spherical harmonics are denoted by $Y_L(\hat{\boldsymbol{r}})$, $L = (l, m)$. The quantity χ_{σ_n} represents a unit spinor for the spin orientation $\sigma_n = \pm 1$. The function $R_{l0}(\epsilon_l, r)$ is regular at the origin and solves the radial part of the Kohn–Sham-type equation for $E = \epsilon_l$, $R_{l1}(\epsilon_l, r)$ denotes its normalized energy derivative.

The Auger transition rate $P_{fi}^{\sigma_d}$ can be cast into the golden rule form[15]

$$P_{fi}^{\sigma_d}(a, d) \propto \sum_{\substack{\boldsymbol{k}', \boldsymbol{k}, n', n \\ \sigma_a, m_{s_a}}} |M_{fi}^{(\sigma_d, \sigma_a, m_{s_a})}(\boldsymbol{k}' n'; \boldsymbol{k}, n)|^2 \cdot \delta(\epsilon_d - \epsilon_{n'}(\boldsymbol{k}') - \epsilon_n(\boldsymbol{k}) + \epsilon_a), \tag{2}$$

where $\sigma_d = \pm 1$ refers to the two spin orientations of the outgoing electron with respect to the spin direction of the incoming photon that creates the core-hole state and is circularly polarized. The spin quantum number of the core-hole spinor state $\psi_a(\boldsymbol{r})$ is denoted by m_{s_a} $(= \pm\frac{1}{2})$ referring to the total angular momentum $j_a = l_a + m_{s_a}$ of the spin–orbit split core-hole doublet states. The spinor components ("up" and "down") with respect to the spin axis of the incoming photon are characterized by $\sigma_a = \pm 1$ and correspondingly by $\sigma_b = \pm 1$ and $\sigma_c = \pm 1$ for the two valence states that are alternatively denoted by $\psi_b(\boldsymbol{r})$ and $\psi_c(\boldsymbol{r})$ whenever a simplified notation is desirable. The matrix elements on the right-hand side of Eq. (2) can be split into two portions

$$M_{fi}^{(\sigma_d, \sigma_a, m_{s_a})}(\boldsymbol{k}', n'; \boldsymbol{k}, n) = D_{abcd}^{(m_{s_a})} \delta_{\sigma_a, \sigma_b} \delta_{\sigma_c, \sigma_d} - E_{abcd}^{(m_{s_a})} \delta_{\sigma_a, \sigma_c} \delta_{\sigma_b, \sigma_d}, \tag{3}$$

where $D_{abcd}^{(m_{s_a})}$ and $E_{abcd}^{(m_{s_a})}$ denote, respectively, the so-called direct and exchange portions of the transition matrix element, which are defined by

$$D_{abcd}^{(m_{s_a})} = \iint \frac{\psi_d^*(\boldsymbol{r}) \psi_c(\boldsymbol{r}) \psi_a^{(m_{s_a})*}(\boldsymbol{r}') \psi_b(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}' \tag{4}$$

and

$$E_{abcd}^{(m_{s_a})} = \iint \frac{\psi_d^*(\boldsymbol{r}) \psi_b(\boldsymbol{r}) \psi_a^{(m_{s_a})*}(\boldsymbol{r}') \psi_c(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}'. \tag{5}$$

The expressions (2)–(5) are evaluated completely along the lines of our previous paper.[9]

The experiments by Heinzmann *et al.*[8] involving in our calculations concern Auger emission from a Cr (100)-surface. We have simulated this situation by a seven-layer (100) slab.

The experiments were performed by shining circularly polarized light on the (100)-chromium film with the direction of the incoming light being perpendicular to the surface. The core-hole p-states were thus created with a quantization axis parallel to the surface normal. At the threshold energy a $p_{3/2}$-electron is transferred to the Fermi level ϵ_F in the valence band. As a result of the dipole selection rule $\Delta l = \pm 1$ the number of $p_{3/2}$-holes created per second depends on the d-partial density of states at ϵ_F. For circularly polarized light we have, in addition, the selection rule $\Delta m = \pm 1$. In calculating the relative weight with which core-hole states of certain magnetic quantum numbers $-\frac{3}{2} \leq m_j \leq \frac{3}{2}$ are created under these circumstances we assume that the m-resolved d-density of states at ϵ_F is the same for any of the m-values, which constitutes a relatively good approximation. In the following, we confine ourselves to the absorption of right-hand circularly polarized light so that $\Delta m = +1$.

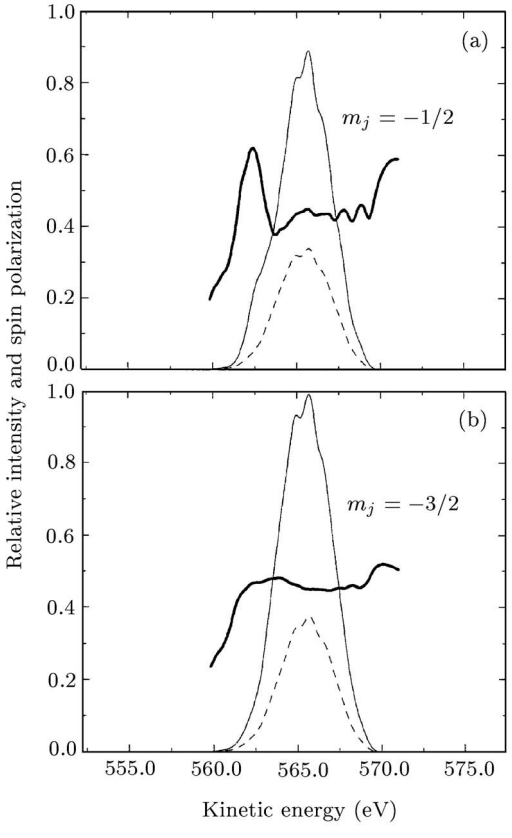

Fig. 1. Spin-dependent L_3VV-Auger transition in Cr metal: calculated relative intensities. (a) Refers to hole-states where $m_j = -1/2$ and (b) to hole-states associated with $m_j = -3/2$. The bell-shape curves represent the relative intensities as a function of the Auger electron energy (Solid curves for "spin up", dashed curves for "spin down" referenced to the spin direction of the incoming photons). All shown is the polarization of the outgoing Auger current parallel to the surface normal.

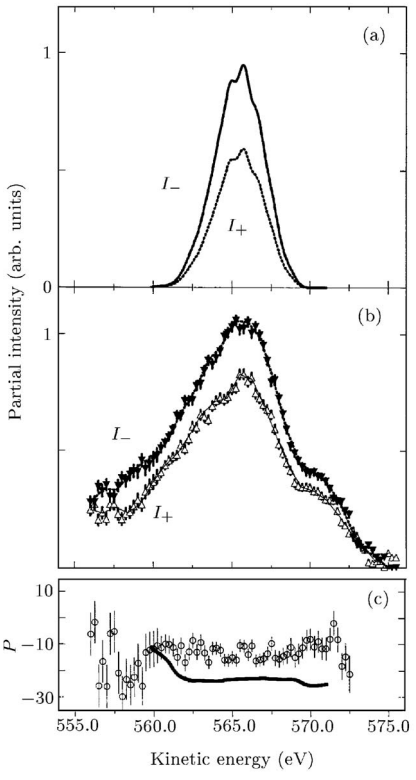

Fig. 2. Spin-dependent L_3VV-Auger transition in Cr metal: (a) calculated relative intensities and (b) measured intensities after correction for losses. (c) The resulting spin-polarization P together with the measured data.

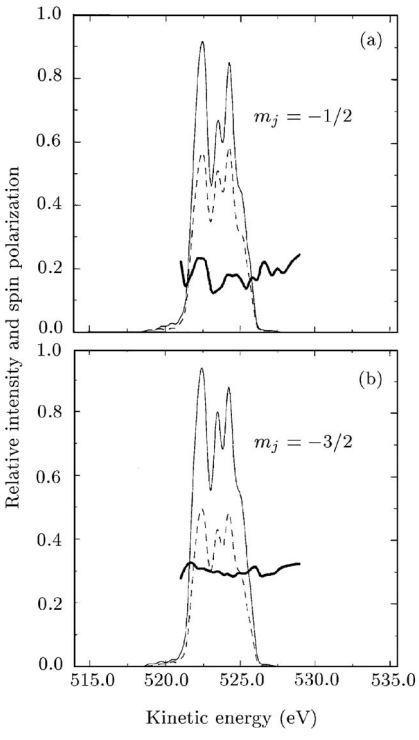

Fig. 3. Spin-dependent $L_3M_{23}V$-Auger transition: calculated relative intensities and spin-polarization. The meaning of the curves is the same as in Fig. 1.

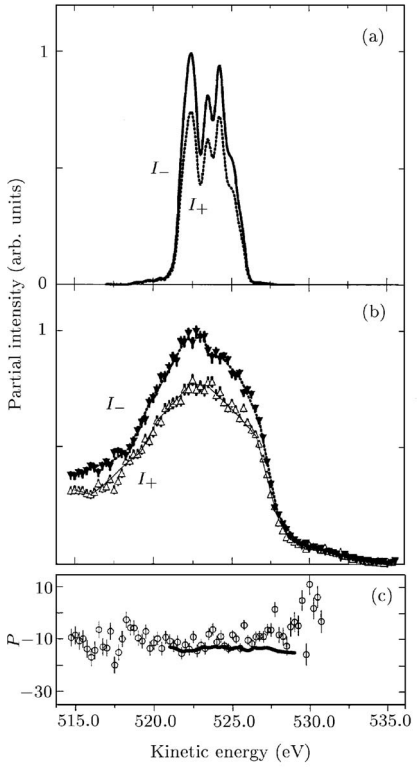

Fig. 4. Spin-dependent $L_3M_{23}V$-Auger transition: calculated and measured (multiple loss-corrected) relative intensities and the spin-polarization.

In the experiments of Heinzmann *et al.*,[8] the photon energy is slightly above the threshold of generating a $2p_{3/2}$ core-hole in the Cr atoms. We have, therefore, carried out the present calculations only for L_3VV- and $L_3M_{23}V$-Auger transitions. All the results presented in the following pertain to normal emission of the Auger electron. The occurrence of antiferromagnetic spin order has been neglected. Figure 1 shows the spin-resolved Auger spectrum for the L_3VV-transition and the associated spin-polarization. These figures refer to core-hole states with magnetic quantum numbers $m_j = -1/2$ and $m_j = -3/2$ (Transitions from states with $m_j = 1/2$ and $m_j = 3/2$ yield the same results but are associated with the opposite spin-polarization). In order to compare with the experiments, we have averaged the relative intensities and spin-polarizations for the various magnetic quantum numbers by weighting them according to the ratio of the core-state population: $n(3/2)/n(1/2)/n(-1/2)/n(-3/2) = 6/4/2.333/1$. These ratios result from the probability with which the pertinent core-hole states are created by absorbing a right-hand circularly polarized photon that propagates antiparallel to the surface normal. The result is shown in Fig. 2, in which the calculated curves were obtained by forming a weighted sum of individual contributions from core-hole states associated with m_j-values 3/2, 1/2, $-1/2$, $-3/2$; and the respective weights were chosen to be 6, 4, 2.3 and 1 according to the probability of the pertinent core-hole excitation.

As for the L_3VV-transition our calculation agrees quite reasonably with the experimental results of Heinzmann *et al.*[8] That is, the position as well as the width of the main peak is well reproduced by our calculation. The observed shoulder around 570 eV might be caused by a splitting of the main peak due to some unidentified mechanisms which escapes the present theoretical framework. Our results for the $L_3M_{23}V$-transition are presented in Figs. 3 and 4 The relative intensities display the general features of the valence density of states with some corrections due to matrix element effects. The corresponding structure found in the experiments[8] is much wider than the range of the d-valence band. In Fig. 4, the meaning of the curves and the weights used in forming the sum of the core-hole contributions are identical to those in Fig. 2. Since the $L_3M_{23}V$-transition involves two core-hole states and is hence faster than the L_3VV-transition, it is conceivable that the associated Auger electron is created as a strongly localized wavepacket around the emitting atom that originally contains the core-hole. This would also apply then to the valence

state involved in the transition. Both effects would result in a considerable broadening of the Auger peak comparable to that observed in the experiments. The spin-polarization constitutes another important experimental result. Surprisingly, our theory predicts for the otherwise problematic $L_3M_{23}V$-transition -13% which agrees well with the experiment which yields -10% spin-polarization. In contrast, in the case of the L_3VV-transition we obtain about -25% polarization versus an experimental value of -10%. There are mainly two reasons that might be the cause of this discrepancy: one is the core-hole state distribution which is calculated by assuming that the d-valence states above the Fermi energy possess m-dependent d-partial waves whose amplitude square moduli averaged over the Fermi surface are the same. The other reason is the omission of antiferromagnetic order in calculating the valence states.

It is well known that the difference between the one-electron orbital energies obtained by using the density functional theory with local density approximation for the exchange cannot give correct values for the excitation energies. The kinetic energy of the Auger electron has been corrected by using the lattice atom model of Eckardt and Fritsche,[16] which is proved to be quite successful in the calculation of local electronic excitations in solids. In this model one mimics the embedding of an atom in a matrix of chemically identical atoms by performing a self-consistent atomic structure calculation where one gives the occupation numbers of the valence states fractional values that are obtained from a separate, for example FLAPW-calculation on the pertinent solid. Local excitations can then be mimicked by changing the occupation number of some core-level by one and by correspondingly increasing the occupation numbers in the valence states. The lattice atom thus modified has to be recalculated then self-consistently and the excitation energy is obtained by forming the total energy, rather than the orbital energy, difference between the two configurations of this model atom. In the L_3VV Auger transition, the total energy of the initial state is calculated with an electron configuration of one less electron in the L_3 orbital and one more electron in the valence orbital, while the total energy of the final state is obtained just with one less electron in the valence orbital. For the $L_3M_{23}V$ Auger transition, the initial state is the same as before, the final state is with one less electron in the M_{23} orbital. The changes of the electron occupation numbers are made relative the ground state of the FLAPW-calculation on the pertinent solid. The kinetic energy of the Auger electron obtained from this model has been used to correct the central kinetic energy that results from the one-particle energy conservation expressed by the delta-function in Eq. (2). The predicted position of the Auger peaks agrees reasonably well with the experiments. The electron binding energies of the relevant energy levels[17] are given in Table 1 for the reader's convenience.

Table 1. Electron binding energies of the relevant energy levels relative to the Fermi level.[17]

Label	Orbital	E (eV)
L_1	$2s$	696.0
L_2	$2p_{1/2}$	583.8
L_3	$2p_{3/2}$	574.1
M_1	$3s$	74.1
M_2	$3p_{1/2}$	42.2
M_3	$3p_{3/2}$	42.2

In summary, it may be stated that our calculations on the Auger emission from a Cr (100)-surface yield spectra and spin-polarizations in reasonably well agreement with the experiments.

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