Direct calculation of valence-band Auger emission: Spin polarization of Auger electrons from a potassium (110) surface

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We report calculations on spin-polarized Auger electron emission from the valence band of a potassium (110) film. In treating this process we use an N-electron scheme that is based on a generalized version of density-functional theory. The transition rate is determined by explicitly evaluating the transition matrix elements that contain the four states involved. The core and valence states are obtained from a self-consistent full-potential linearized augmented plane wave calculation on a K(110) multilayer. In the experiments that the present calculations refer to, the particular oriented core-hole state is created by photoexcitation using circularly polarized light. The observed energy spectrum and the angular dependence of the spin polarization of the emitted Auger electrons can be simply related to the character of the spinor-hole state. We compare our results for normal incidence of the light to the pertinent experiments on the Auger spin polarization referenced to the spin of the incoming photons. The results are in fair agreement with each other. [S0163-1829(97)02940-8]

Auger electron spectroscopy represents one of the standard characteristic techniques in the study of the composition of bulk materials and their interfaces.[1] There are numerous theoretical studies on the interconnection of the Auger spectrum and the electronic structure of materials.[2–17] The present study was motivated by experiments by Stoppmanns *et al.*[18] on spin-resolved Auger transitions that involve two itinerant states of the valence band of (110) alkali-metal films. By using circularly polarized light in creating a core hole below that valence band, one generates a one-particle spinor state of a well-defined total angular momentum with respect to the direction of the incoming light. The theory and the calculation we shall be presenting rest on a golden-rule–type treatment of the spin-resolved Auger transition where the valence states are itinerant. They are determined within a scalar-relativistic full-potential linearized augmented plane wave (FLAPW) calculation.[19] The results we obtain for the spin polarization show fair agreement with the experiment.

Both the initial and final Auger states are excited (mutually degenerate) N-electron states that can be described within a generalized density-functional (GDF) theory. (For a general discussion of excitations within that framework see Refs. 20 and 21.) The key idea of GDF theory resides in mapping the interacting N-electron system onto that of a noninteracting N-electron system having the same spin-resolved one-particle densities as the original one but moving in a modified external potential. The noninteracting wave function has the form of a Slater determinant. The approach used in the following is based on the assumption that the transition matrix elements describing the Auger process can, to a good approximation, be calculated by using the pertinent initial- and final-state determinants instead of the true N-electron wave function. As a consequence, the following calculations concern only one-electron states by which these Slater determinants differ. In describing the spin-resolved transition within that framework we largely rely on the work of Aschenbach.[22] As for the electronic states of the crystal, we employ the FLAPW WIEN95 code[23] to calculate the itinerant valence and semicore states. The method requires a subdivision of the crystal into sufficiently large but nonoverlapping concentric spheres (atomic spheres) around the atomic nuclei and an interstitial region between these spheres. Inside the atomic sphere the one-electron state of band index n is given by

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

where spherical harmonics are denoted by $Y_L(\hat{\vec{r}})$, $L=(l,m)$. 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 (KS-type) equation for $E=\epsilon_l$ and $R_{l1}(\epsilon_l,r)$ denotes its normalized energy derivative. To study the screening effect of the core hole on the Auger emission, we have carried out a self-consistent calculation for a fixed $3p$ hole where the screening is accounted for by including one additional valence electron.[24,25]

As has been shown by Chattarji[26] and more recently for the spin-resolved case by Aschenbach,[22] the Auger transition rate $P_{fi}^{\sigma_d}$ can be cast into the golden-rule form

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

Here $\sigma_d=\pm 1$ refers to the two spin orientations of the outgoing electron with respect to the spin direction of the in-

coming photon that creates the core-hole state and is circularly polarized. The spin quantum number of the core-hole spinor state $\psi_a(\mathbf{r})$ 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 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 we alternatively denote by $\psi_b(\mathbf{r})$ and $\psi_c(\mathbf{r})$ whenever a simplified notation is desirable. The matrix elements on the right-hand side of Eq. (2) can be split into two portions

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

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

$$D_{abcd}^{(m_{s_a})}=\int\int \frac{\psi_d^*(\mathbf{r})\psi_c(\mathbf{r})\psi_a^{(m_{s_a})*}(\mathbf{r}')\psi_b(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}d\mathbf{r}' \quad (4)$$

and

$$E_{abcd}^{(m_{s_a})}=\int\int \frac{\psi_d^*(\mathbf{r})\psi_b(\mathbf{r})\psi_a^{(m_{s_a})*}(\mathbf{r}')\psi_c(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}d\mathbf{r}'. \quad (5)$$

With *CCV* and *CVV* Auger transitions one is dealing with a core-hole state that is, to a good approximation, confined to the pertaining atom. Hence the integration over the $\mathbf{r}'$-dependent functions may be restricted to the atomic sphere of that atom. On the other hand, the integral under consideration may be viewed as a sum of multipole potentials that are of sizable magnitude only within that atomic sphere as well. We are therefore justified in performing the integrals over the $\mathbf{r}$- and $\mathbf{r}'$-dependent functions only over the atomic sphere of the atom that contains the core hole.

The core (or semicore) state may be approximated by an atomiclike two-component spinor

$$\Psi_a^{(m_{s_a})}(\mathbf{r})=\sum_{\sigma_a}\psi_a^{(m_{s_a})}(\mathbf{r})\chi_{\sigma_a}, \quad (6)$$

where

$$\psi_a^{(m_{s_a}=\pm 1/2)}=R_{l_a}(\epsilon_a,r)\times\begin{cases}\sqrt{\dfrac{l+\frac{1}{2}\pm m_j}{2l+1}}\,Y_{l_a,m_a}(\hat{\mathbf{r}}) & \text{for } \sigma_a=+1\\ \sqrt{\dfrac{l+\frac{1}{2}\mp m_J}{2l+1}}\,Y_{l_a,m_a+1}(\hat{\mathbf{r}}) & \text{for } \sigma_a=-1\end{cases} \quad (7)$$

and

$$m_a=m_j-\frac{1}{2},\quad -j\leqslant m_j\leqslant j,$$

with j denoting the total angular momentum quantum number $j=l_a+m_{s_a}$. The spinors $\Psi_a^{(m_{s_a})}$ satisfy a two-component scalar-relativistic KS-type equation with an additional spin-orbit coupling term. (For details see Ref. 27.)

The outgoing Auger electron may be described by a time-reversed low-energy electron diffraction state in the so-called single-scatterer approximation[28]

$$\psi_d(\epsilon_d,\mathbf{r})=\sum_{L_d} i^{l_d}Y_{L_d}^*(\hat{\mathbf{k}}_d)e^{i\delta_{l_d}(\epsilon_d)}R_{l_d}(\epsilon_d,r)Y_{L_d}(\hat{\mathbf{r}})\chi_{\sigma_d}, \quad (8)$$

with $R_{l_d}(\epsilon_d,r)$ denoting again a regular solution to the radial part of the scalar-relativistic KS-type equations. This function is matched smoothly at the sphere onto a linear combination of a spherical Bessel and a spherical Neumann function with a phase shift $\delta_{l_d}(\epsilon_d)$. The direction of the outgoing electron is characterized by the unit vector $\hat{\mathbf{k}}_d$.

If we employ the expansion

$$\frac{1}{|\mathbf{r}'-\mathbf{r}|}=4\pi\sum_{l,m}\frac{1}{2l+1}\gamma_l(r',r)Y_{lm}(\hat{\mathbf{r}}')Y_{lm}^*(\hat{\mathbf{r}}), \quad (9)$$

where $\gamma_l(r',r)$ is defined

$$\gamma_l(r',r)=\begin{cases}\dfrac{r'^l}{r^{l+1}} & \text{for } r'<r\\ \dfrac{r^l}{r'^{l+1}} & \text{for } r'>r\end{cases}, \quad (10)$$

the matrix elements D_{abcd} and E_{abcd} can be cast as a sum over products of one-dimensional integrals. We define

$$D^{(m_{s_a})}_{L_aL_bL_cL_d}=\sum_L G(L_c,L,L_d)G(L_a^{(m_{s_a})},L_b,L)\,\frac{4\pi}{2l+1}\sum_{\substack{\nu'=0\\ \nu=0}}^{1} c_{L_b\nu'}(\epsilon_b(\mathbf{k}'))c_{L_c\nu}(\epsilon_c(\mathbf{k}))F_{\nu\nu'}(l,l_a,l_b,l_c,l_d)\,\delta_{\sigma_a,\sigma_b}\delta_{\sigma_c,\sigma_d}, \tag{11}$$

where $F_{\nu\nu'}$ is shorthand for

$$F_{\nu\nu'}(l,l_a,l_b,l_c,l_d)=\int_0^{r_0}R_{l_d}(\epsilon_d,r')R_{l_c\nu}(\epsilon_c,r')\left[\frac{1}{r'^{l+1}}\int_0^{r'}r^{l+2}R_{l_a}(\epsilon_a,r)R_{l_b\nu'}(\epsilon_b,r)dr + r'^{l}\int_{r'}^{r_0}\frac{1}{r^{l-2}}R_{l_a}(\epsilon_a,r)R_{l_b\nu'}(\epsilon_b,r)dr\right]dr', \tag{12}$$

with r_0 denoting the atomic (muffin-tin) radius of the emitter. The quantities $G(L'',L,L')$ represent Gaunt integrals. The corresponding expression $E^{(m_{s_a})}_{L_aL_bL_cL_d}$ is defined in complete analogy to Eq. (11). With these definitions at hand we are now in the position to cast the matrix elements $D^{(m_{s_a})}_{abcd}$ as

$$D^{(m_{s_a})}_{abcd}=\sum_{L_d} i^{l_d}Y^*_{L_d}(\hat{\mathbf{k}}_d)e^{i\delta_{l_d}(\epsilon_d)}\sum_{L_c}\sum_{L_b} D^{(m_{s_a})}_{L_aL_bL_cL_d}$$

$$=\sum_{L_d} i^{l_d}Y^*_{L_d}(\hat{\mathbf{k}}_d)e^{i\delta_{l_d}(\epsilon_d)}D^{(m_{s_a})}_{L_d} \tag{13}$$

where

$$D^{(m_{s_a})}_{L_d}=\sum_{L_c}\sum_{L_b} D^{(m_{s_a})}_{L_aL_bL_cL_d}.$$

Since L_a is entirely fixed by the predecessor process, we have not displayed this dependence explicitly. Again, the corresponding expression for $E^{(m_{s_a})}_{abcd}$ is defined completely analogously to Eq. (13).

The contribution of the final state to the outgoing current $I_{\sigma_d}(\hat{\mathbf{k}}_d)$ within a cone of angle $d\Omega(\hat{\mathbf{k}}_d)$ is proportional to $k_d d\Omega(\hat{\mathbf{k}}_d)$. The polarization of the outgoing Auger current is defined by

$$P=\frac{I_+-I_-}{I_++I_-}, \tag{14}$$

where the plus and minus subscripts correspond to $\sigma_d=\pm 1$. To get a rough picture of the origin of the polarization we reduce temporarily the sum over the valence band in Eq. (14) to just one term and describe the outgoing electron by one partial wave only. If we observe the spin selection rules expressed by the Kronecker symbols in expression (3), we then have for $\sigma_d=+1$ and a hole state associated with $j=\frac{3}{2}$ and $m_j=\frac{3}{2}$

$$I_+\propto|D^{(+1/2)}_{L_d}-E^{(+1/2)}_{L_d}|^2, \tag{15}$$

and for $\sigma_d=-1$

$$I_-\propto[|D^{(+1/2)}_{L_d}|^2+|E^{(+1/2)}_{L_d}|^2, \tag{16}$$

from which we obtain

$$P=\frac{|D^{(+1/2)}_{L_d}-E^{(+1/2)}_{L_d}|^2-|D^{(+1/2)}_{L_d}|^2-|E^{(+1/2)}_{L_d}|^2}{|D^{(+1/2)}_{L_d}-E^{(+1/2)}_{L_d}|^2+|D^{(+1/2)}_{L_d}|^2+|E^{(+1/2)}_{L_d}|^2}. \tag{17}$$

One recognizes that the polarization would be zero if only the direct or the indirect Auger process were to occur. For hole states where $m_j=\frac{1}{2}$ both currents I_+ and I_- contain additional expressions that arise from the fact that ψ_a now has two nonvanishing spinor components. This results in a different polarization, which, however, would also become zero if one could block one of the decay channels.

Our calculations on a seven-layer (110) potassium film were carried out by employing the FLAPW WIEN95 code[23] and using a repeated slab geometry. The experiments by Stoppmanns *et al.* were performed by shining circularly polarized light on the (110) potassium film with the direction of the incoming light being perpendicular to the surface. Hence the core-hole p states were 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. Because of the dipole selection rule $\Delta l=\pm 1$, the transition probability and hence the number of $p_{3/2}$ holes created per second are determined by the s partial density of states at ϵ_F. For circularly polarized light we have, in addition, the selection rule $\Delta m=\pm 1$. Because of the form (6) and (7) of the spinor states, the rate at which p core-hole states $|\frac{3}{2},\pm\frac{1}{2}\rangle$ are created is, by a factor $\frac{1}{3}$, less than for states of $m_j=\pm\frac{3}{2}$. Hence, at the threshold energy of the core-hole creation process the polarization of the outgoing current is strongly dominated by Auger transitions that involve $|\frac{3}{2},\pm\frac{3}{2}\rangle$ core-hole states. At higher photon excitation energies the d partial density of states comes into play, so that one is now dealing with $\Delta l=+1$ as well, which gives rise to a change of the polarization P.

The core-hole states $|\frac{1}{2},\pm\frac{1}{2}\rangle$ practically do not contribute to the observed Auger emission if one reaches or goes beyond their excitation energy because they are immediately blocked by a very fast Coster-Kronig decay[29,30] by which electrons from the $|\frac{3}{2},\pm\frac{3}{2}\rangle$ and $|\frac{3}{2},\pm\frac{1}{2}\rangle$ states are transferred to those hole states. Despite the negligible contribution of the $|\frac{1}{2},\pm\frac{1}{2}\rangle$ states to the observed Auger current, we have calculated the spin polarization that one would obtain if the possible Auger processes associated with the states $|\frac{3}{2},-\frac{3}{2}\rangle$,

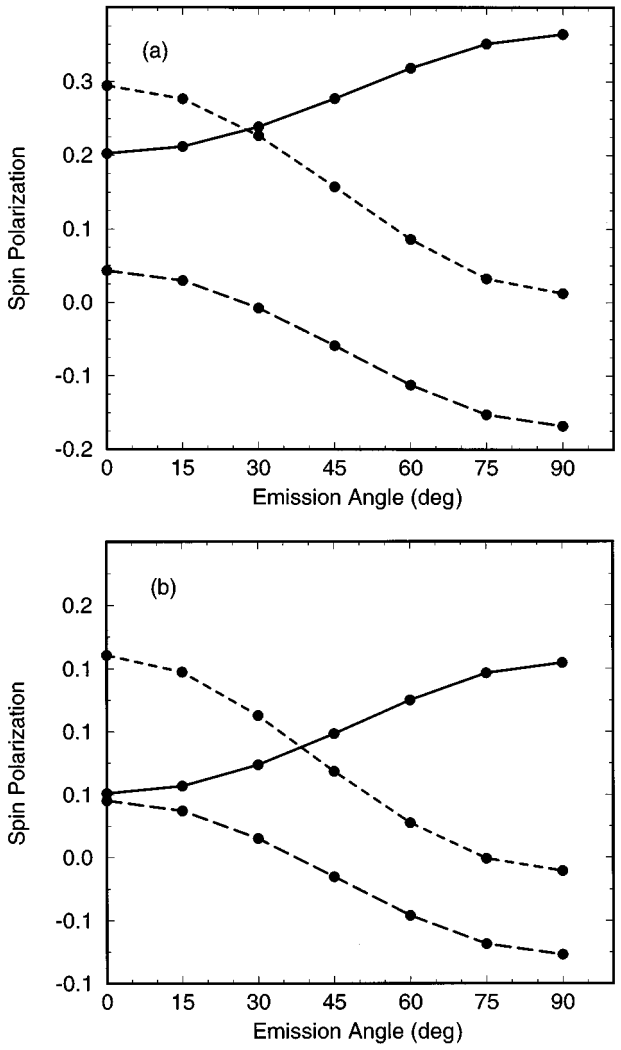

FIG. 1. Angular dependence of the spin polarization of the Auger current for the maximum peak in the Auger spectrum. The results for the different core holes $|\frac{3}{2},-\frac{3}{2}\rangle$, $|\frac{3}{2},-\frac{1}{2}\rangle$, and $|\frac{1}{2},-\frac{1}{2}\rangle$ are presented by the solid, short-dashed, and long-dashed curves, respectively. (a) shows the case of a screened core hole as explained in the text. (b) shows the result for a calculation where the valence states have been determined in the ground-state potential without core holes.

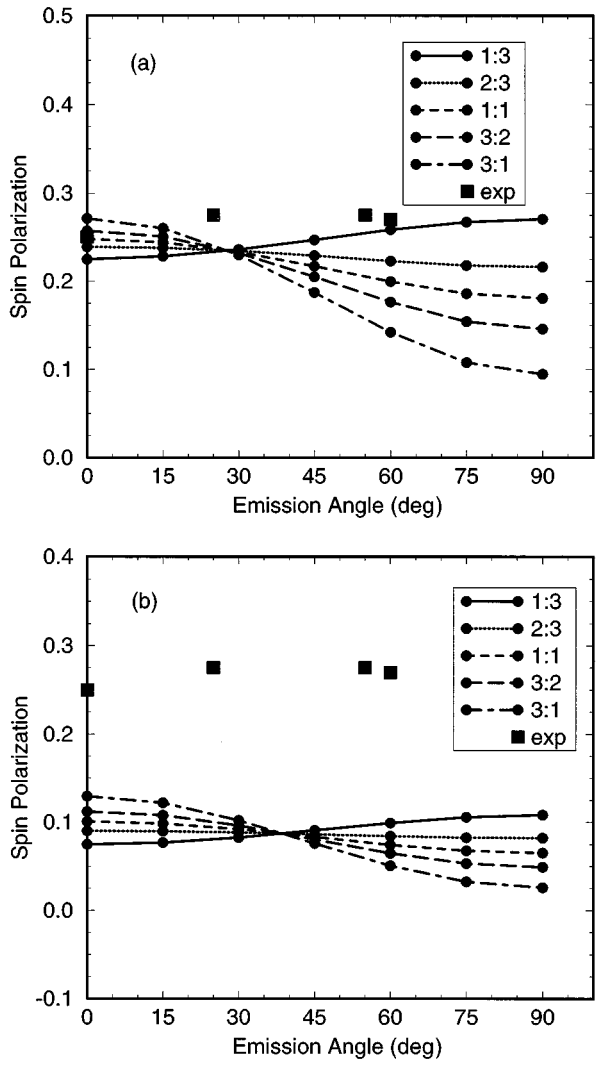

FIG. 2. Angular dependence of the resulting spin polarization from the calculations of the two core-hole states $|\frac{3}{2},-\frac{3}{2}\rangle$ and $|\frac{3}{2},-\frac{1}{2}\rangle$. The curves shown pertain to different ratios of the number of the pertinent core holes. As in Fig. 1, the curves in (a) and (b) refer to the results with and without the inclusion of core holes.

$|\frac{3}{2},-\frac{1}{2}\rangle$, and $|\frac{1}{2},-\frac{1}{2}\rangle$ could be observed individually and if the Coster-Kronig decay would not occur. The result is shown in Fig. 1, where we have plotted the dependence on the emission angle of the Auger spin polarization that refers to the three core holes. The angle dependence for the core-hole state $|\frac{3}{2},-\frac{3}{2}\rangle$ displays a distinctly different behavior.

Figure 2 shows the angle dependence of the polarization for the sum of the Auger currents that are associated with the core-hole states $|\frac{3}{2},-\frac{3}{2}\rangle$ and $|\frac{3}{2},-\frac{1}{2}\rangle$. The five curves refer to five ratios $n_{-1/2}/n_{-3/2}$, where $n_{-1/2}$ and $n_{-3/2}$ pertain to the respective number of core holes contributing to the outgoing current. The experimental results are marked by closed squares. Though the curve with a ratio $n_{-1/2}/n_{-3/2}=2/3$ shows slightly better agreement with the measured data at 0°, the best agreement with respect to the general tendency of angular dependence, i.e., going slightly higher with the emission angle, is obtained if one assumes a ratio $n_{-1/2}/n_{-3/2}=1/3$ in accord with the above theoretical consideration.

The results shown in Figs. 1(a) and 2(a) have been obtained by allowing the seven-layer film to screen the core hole in a particular way: The central layer was throughout the iterations assumed to consist solely of K atoms that all contained a $3p$ core hole and one additional valence electron distributed over the entire layer system. We have used this screening model as an initial rough approximation to demonstrate the significance of screening. Figures 1(b) and 2(b) refer to the case without screening. Obviously, the polarization is now much smaller. The origin of the enhancement of polarization by a screened core hole may be seen in the dramatic change of the local partial density of states (LPDOS).

This change consists in a massive reduction of the s-type LPDOS near ϵ_F in favor of the p- and d-type LPDOS, which indicates that a valence electron alters sizably the partial-wave components of its wave function as it goes across an atom containing a screened core hole. It is conceivable that the agreement with the experiment may be further improved by using a more realistic screening model. Work in this direction is under way.

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