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# Necessity of relativistic dipole selection rules in photoemission

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Relativistic dipole selection rules for direct interband transitions in fcc and bcc lattices are derived. High-resolution angle-resolved photoemission spectra of Ag demonstrate that these selection rules are essential for a consistent interpretation of photoemission data even for energy bands which are not split by spin-orbit interaction.

## I. INTRODUCTION

The symmetry properties of electronic states in solids can be investigated by photoemission measurements using linear or circularly polarized light. If local-field effects[1] are neglected selection rules for direct interband transitions at a wave vector $\vec{k}$ may be calculated group theoretically[2] from the symmetry properties of the electric dipole operator and the electronic states involved. For crystals with Bravais lattices this calculation can be done quite easily in terms of classical point groups, but for non-Bravais lattices like the diamond and the hexagonal close-packed structure the procedure requires coset representatives in connection with the use of subgroup formalism or the full-group concept.[3]

Nonrelativistic dipole selection rules for direct interband transitions have been published for several important space groups including the fcc,[4–6] bcc,[4–6] and hcp[7,8] structures. The effect of selection rules is clearly reflected in angle-resolved photoemission experiments for instance on Cu(110),[9] in calculations of the momentum matrix elements for Cu (Refs. 10 and 11) and for ordered adsorbate overlayers.[12] Recent photoemission data on Rh (Refs. 5 and 13) indicate that a consistent interpretation requires the inclusion of spin-orbit interaction and thus the use of relativistic selection rules derived from the corresponding double group. Such selection rules based on the double-group formalism so far have been given for the hcp lattice[7] and for the special case of normal emission for fcc and bcc crystals.[5] Their derivation requires the reduction of Kronecker products of the double-group representations. This is accomplished easily with the aid of multiplication tables available in literature.[14]

Recent high-resolution angle-resolved photoemission experiments on Ag(111) in our laboratory show that the spin-orbit split $d$-band complex in this transition metal is completely resolved resulting in five distinct peaks appearing in the spectrum for excitation with unpolarized light. It is obvious that in this case relativistic selection rules must be applied since the single-group formalism predicts three peaks only. But even if the effect of spin-orbit coupling is too small to be resolved in photoemission, its mere existence may change the selection rules for linear polarized light and thus the photoemission spectum expected. This will be made evident in the following by a clear-cut example for Ag and verified by the experimental results.

The calculational details and the relativistic selection rules are set out in Sec. II for the fcc and bcc structure (space groups $O_h^5$ and $O_h^9$) for the most general case of non-normal photoemission. Section III then deals with the application of the theory to angle-resolved photoemission data on Ag(111). Here we regard Ag mainly as a model substance for transition metals, i.e., we will concentrate on the symmetry aspects and not discuss any quantitative aspects of the spectra. A discussion of our data on the basis of band-structure calculations for Ag will be given elsewhere.[15]

## II. RELATIVISTIC SELECTION RULES

The selection rules for direct interband transitions are derived from matrix elements of the form $\langle f|\vec{A}\cdot\vec{p}|i\rangle$ where $\langle f|$ and $|i\rangle$ denote the final and initial state of the electron and $\vec{A}\cdot\vec{p}$ the electric dipole operator. If spin-orbit interaction is neglected the eigenfunctions of these states in symmorphic space groups transform as irreducible representations $\Gamma$ of the point group $G_0(\vec{k})$ of the wave vector $\vec{k}$. Introduction of spin-orbit interaction causes a correlation between symmetry operations in coordinate space and those in spin space. Therefore rotations in coordinate space and in spin space have to be referred to the same axes. The wave functions are then products of a spatial and a spin part and the direct product of the corresponding irreducible representations has to be investigated.

The product representation is a representation of the double point group $\bar{G}_0(\vec{k})$ which may be reducible with respect to the extra irreducible representa-

 

tions of $\bar{G}_0(\vec{k})$. From this the following conclusions can be drawn: Spin-orbit interaction lowers the degeneracy of an energy level if the product representation is reducible and no additional degeneracies result from time-reversal symmetry. The spin-orbit interaction operator $H_{so}$ commutes with the parity operator, therefore $H_{so}$ may connect states with equal parity. Finally, if term interaction is considered, levels belonging to equal extra representations can be mixed, and the expected spectrum may be altered. This is due to the fact, that a distinct extra representation of the double group can be derived from different representations of the single group. For a given transition energy and fixed polarization of the exciting light this may result in a transition probability which is different from that predicted by the single-group formalism. This will be discussed below in more detail by means of an example.

In order to calculate the nonvanishing matrix elements we applied conventional group-theoretical methods. A nonvanishing matrix element exists, if the direct product of the representations of the final and initial state contains the representation of the dipole operator.[14] The notation of the representations is the common one, see Ref. 2. In the calculation we profit from the fact that some groups can be considered as direct products of a subgroup and the group $C_i$ (containing unity and inversion). These are, for example, $O_h = T_d \times C_i$; $D_{3d} = C_{3v} \times C_i$ and $D_{4h} = C_{4v} \times C_i$. The existence of the inversion as an element of the group results in representations with even or odd parity. Since the electric dipole operator has odd parity, electric dipole transitions connect states with different parity. This is known as Laporte's rule. Therefore the selection rules obtained for a subgroup hold for the larger group too, if the Laporte rule is applied.

For a distinct interband transition an inspection of the coupling coefficients predicts equal transition probabilities for dipole components belonging to the same representation. This means, that in $O_h$ and $T_d$ equal transition probabilities are expected for $x$, $y$, or $z$ polarization, while in $D_{4h}$, $C_{4v}$, $D_{2d}$, $D_{3d}$, and $C_{3v}$ transitions excited with $x,y$ polarization are equal but in general different from the $z$ polarization. Transitions in $D_{2h}$, $C_{2v}$, and $C_2$ symmetry should be different for the three independent directions of the polarization vector.

The selection rules are tabulated in Table I. A tabulation of the symmetry points, their location and point group is given elsewhere.[2,6] As an example of the use of the table, consider transitions from state $\Delta_6$ caused by light with polarization vector in $x$ direction. According to Table I, line four, transitions are allowed to the states $\Delta_6$, $\Delta_7$, while a corresponding transition starting with $X_6^-$ can have final states $X_6^+, X_7^+$ (see line three of Table I). For the special case of normal photoemission the spatial part of the final-state wave function must transform as the totally symmetric representation $\Gamma_1$ of $G_0(\vec{k})$.[4] The selection rules in Table I then reduce to those given previously in Ref. 5.

TABLE I. Selection rules for direct interband transitions between electronic states transforming according to the irreducible representations of the double group.

| $O_h$ | $\Gamma_6^\mp$ | $\Gamma_7^\mp$ | $\Gamma_8^\mp$ |
|---|---|---|---|
| $x,y,z$ | $\Gamma_6^\pm, \Gamma_8^\pm$ | $\Gamma_7^\pm, \Gamma_8^\pm$ | $\Gamma_6^\pm, \Gamma_7^\pm, \Gamma_8^\pm$ |

| $T_d$ | $P_6$ | $P_7$ | $P_8$ |
|---|---|---|---|
| $x,y,z$ | $P_7, P_8$ | $P_6, P_8$ | $P_6, P_7, P_8$ |

| $D_{4h}$ | $X_6^\mp$ | $X_7^\mp$ |
|---|---|---|
| $x,y$ | $X_6^\pm, X_7^\pm$ | $X_6^\pm, X_7^\pm$ |
| $z$ | $X_6^\pm$ | $X_7^\pm$ |

| $C_{4v}$ | $\Delta_6$ | $\Delta_7$ |
|---|---|---|
| $x,y$ | $\Delta_6, \Delta_7$ | $\Delta_6, \Delta_7$ |
| $z$ | $\Delta_6$ | $\Delta_7$ |

| $D_{2d}$ | $W_6$ | $W_7$ |
|---|---|---|
| $x,y$ | $W_6, W_7$ | $W_6$ |
| $z$ | $W_7$ | $W_6, W_7$ |

| $D_{3d}$ | $L_4^\mp L_5^\mp$ | $L_6^\mp$ |
|---|---|---|
| $x,y$ | $L_6^\pm$ | $L_4^\pm L_5^\pm, L_6^\pm$ |
| $z$ | $L_4^\pm L_5^\pm$ | $L_6^\pm$ |

| $C_{3v}$ | $\Lambda_4\Lambda_5$ | $\Lambda_6$ |
|---|---|---|
| $x,y$ | $\Lambda_6$ | $\Lambda_4\Lambda_5, \Lambda_6$ |
| $z$ | $\Lambda_4\Lambda_5$ | $\Lambda_6$ |

| $C_{2v}$ | $\Sigma_5$ |
|---|---|
| $x,y,z$ | $\Sigma_5$ |

| $D_{2h}$ | $N_5$ | $N_{5'}$ |
|---|---|---|
| $x,y,z$ | $N_{5'}$ | $N_5$ |

| $C_2$ | $Q_3Q_4$ |
|---|---|
| $x,y,z$ | $Q_3Q_4$ |

## III. DISCUSSION

To find out whether relativistic dipole selection rules play an important role in photoemission processes ultraviolet photoelectron spectra (UPS) of a clean Ag(111) surface have been measured. Silver is well suited as a testing material, as the $d$ bands have a relatively high binding energy (about 4 to 6 eV) and are quite flat. Thus in UPS spectra peaks with small half widths can be observed. Spectra of an Ag(111) surface excited with differently polarized light are shown in Fig. 1. The excitation energy was 21.2 eV. A description of the apparatus is given in Ref. 13. The light emitted from a cold cathode gas discharge lamp was polarized using a three reflection Au mirror polarizer with a degree of polarization of

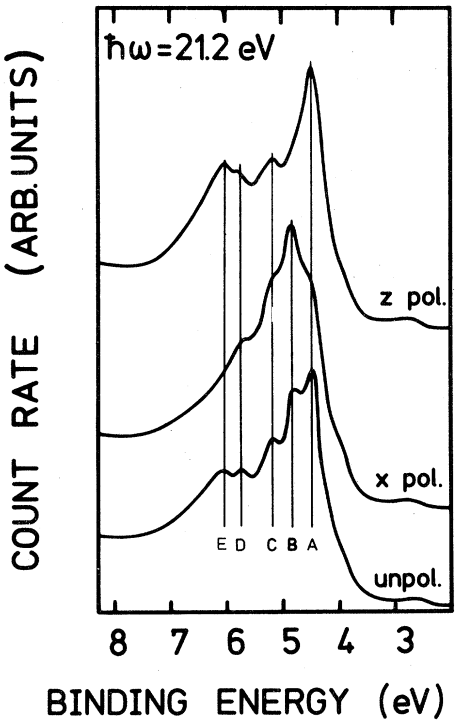


FIG. 1. Photoelectron spectra of Ag(111) for different polarization vectors. Binding energies are referred to the Fermi level.

more than 90%. The angle of incidence of the light was 80°, thus a strong component of the electric field vector normal to the sample surface could be achieved using $p$ polarized light. The emitted photoelectrons have been analyzed in a direction normal to the surface. Therefore states along $\Lambda$ in the Brillouin zone could be detected. The resolution in energy was about 60 meV and the acceptance angle about $\pm 2°$. To observe transitions from each of the five $d$ bands we tilted the crystal by 5°. This lifts accidental degeneracies in energy. Due to this tilt and the high resolution in energy *and* acceptance angle, we have been able to detect five peaks instead of three peaks which have been reported by other groups.[16]

In a fcc crystal like Ag, $d$ states along $\Lambda$ are split into two twofold $\Lambda_3$ bands and one $\Lambda_1$ band. Spin-orbit coupling leads to a splitting of the $\Lambda_3$ bands into $\Lambda_6^3$ and $\Lambda_{4,5}^3$ (time degenerated) bands, while $\Lambda_1$ is changed to $\Lambda_6^1$. According to Table I, for unpolarized light direct transitions to a totally symmetric final-state band $\Lambda_6$ are allowed from initial bands with symmetry $\Lambda_6$ and $\Lambda_{4,5}$. For energetic reasons there is only one $\Lambda_6$ final-state band available for $d$-like electrons in Ag along $\Lambda$ for an excitation energy of 21.2 eV. Thus we expect five transitions from the spin-orbit split $d$-band complex which in fact are seen in our UPS spectrum for unpolarized light. With respect to the number of observed peaks there is agreement between this experimental result and the theoretical energy distributions of the joint density of states for unpolarized light, though these were calculated only for excitation energies up to 10.8 eV.[17]

The initial-state symmetry of the observed transitions $A$-$E$ could be determined using polarized light. The Ag(111) surface shows $C_{3v}$ symmetry, therefore two different spectra in normal emission are expected and observed. One spectrum is excited with $x$ polarized light (the electric field vector is parallel to the surface) and the other with $z$ polarized light (the electric field vector is parallel to the surface normal). The essential point is now the fact that nonrelativistic (NRSR) and relativistic selection rules (RSR) for normal emission along $\Lambda$ differ in the following respect: (1) Emission from a $\Lambda_1$ band in $x$ polarization is forbidden by NRSR but it is allowed by RSR for the corresponding $\Lambda_6^1$ band. (2) Similarly emission from a $\Lambda_3$ band in $z$ polarization is forbidden by NRSR but it is allowed by RSR for its $\Lambda_6^3$ part.

An inspection of the measured spectra shows that the initial states correspond to the following symmetries: $A$, $\Lambda_6^1$; $B$, $\Lambda_{4,5}^3$; $C$, $\Lambda_6^3$; $D$, $\Lambda_{4,5}^3$; $E$, $\Lambda_6^3$. Thus the peaks $C$ and $B$ as well as the peaks $D$ and $E$ result from two spin-orbit split $\Lambda_3$ bands. The spin-orbit splitting is $\Delta E \sim 0.4$ eV which agrees with theoretical results.[17] The appearance of the $\Lambda_6^3$ state $C$ in both the $x$ and $z$ polarized spectrum and the quenching of the $\Lambda_{4,5}^3$ states ($B$,$D$) in the $z$ polarized spectrum is in complete accordance with RSR. Moreover, the appearance of the $\Lambda_6^1$ state ($A$) in both spectra makes evident that an application of NRSR instead of RSR to photoemission spectra may result in wrong predictions, since the transition $A$ would then be forbidden for $x$ polarization. As there is no spin-orbit splitting for a $\Lambda_1$ state, this further demonstrates that it is not the magnitude of the spin-orbit splitting in the Ag atom but merely the existence of spin-orbit interaction which enforces the use of RSR. We thus conclude that a consistent interpretation of photoemission data requires the use of RSR even for elements of low atomic number where spin-orbit splitting in the valence bands may not be resolved in UPS.

From Table I may be seen that RSR for normal emission along $\Lambda$ provide restrictions only for $z$ polarization where transitions $\Lambda_{4,5} \rightarrow \Lambda_6$ are forbidden. Unfortunately in UPS $z$ polarization can be achieved only approximately even if a large angle of incidence for $p$ polarized light is chosen.[11] Thus in an actual experiment there will always exist a component of the electric field vector along $x$ parallel to the surface which may introduce $\Lambda_{4,5} \rightarrow \Lambda_6$ transitions into the photoemission spectrum. In the spectrum for $z$ polarization in Fig. 1 this occurs in the case of the $\Lambda_{4,5}$ state $D$ which shows up as a very weak peak. On the other hand the disappearance of the $\Lambda_{4,5}$ state $B$ in this spectrum shows that the $x$ component of the

electric field must be small compared to the $z$ component, i.e., there is no indication for a large suppression of the $z$ component compared to the $x$ component due to local-field effects as has been claimed in the case of Cu(111).[11] Since in normal photoemission RSR provide less restrictions for allowed interband transitions than NRSR, one may expect modifications in the momentum matrix elements[10] as well as in theoretical photoemission spectra[11] from this source in a relativistic calculation.

## IV. CONCLUSIONS

Our photoemission spectra of Ag demonstrate that relativistic selection rules for direct interband transitions are essential for a consistent interpretation of photoemission data. This is also true for transitions involving energy bands which are not split by spin-orbit interaction, i.e., nonrelativistic selection rules based on the single-group formalism may even fail in cases where spin-orbit splitting is small.

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