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Comments

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Note on the necessity of relativistic dipole selection rules in photoemission

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In a recent study of normal photoemission from Ag(111) Borstel *et al.* [Phys. Rev. B 23, 3121 (1981)] conclude that a consistent interpretation requires the use of relativistic dipole selection rules even for elements of low atomic number where spin-orbit splittings are too small to be detected by photoemission experiments. To check these ideas we have studied polarization-dependent photoemission from Cu(110), Cu(111), Ag(110), and Ag(111). We show that our results and also the data of Borstel *et al.* which are reproduced experimentally may be interpreted in terms of nonrelativistic dipole selection rules.

The widespread use of linearly polarized ultraviolet radiation in angular resolved photoemission spectroscopy has undoubtly introduced considerable progress in that field.[1-4] The application of polarization selection rules does not only derive unique symmetry assignments in many cases, but also very often enables the experimentalist to separate and identify overlapping or energetically neighbored features in the experimental spectra. The determination of initial-state symmetry from polarization dependent photoemission spectra is based on the group-theoretical result that the optical (dipole) matrix element $\langle f \mid \vec{A}\cdot\vec{p} \mid i \rangle$ vanishes unless the integrand has an invariant component under the point group operations of the crystal. If the symmetry of the final state $\mid f \rangle$ is known[3] from the experimental arrangement (e.g., totally symmetric under point group operations about the surface normal in normal emission spectra, or $\mid f \rangle$ having even parity in case of mirror-plane emission), it is in principle easy to determine the corresponding symmetry of the initial state $\mid i \rangle$ from the direction of $\vec{A}\cdot\vec{p}$, where $\vec{A}$ is the vector potential of the incident light and $\vec{p}$ is the momentum operator. The use of these nonrelativistically derived selection rules, however, may be limited by the fact that spin-orbit coupling generally mixes single group symmetries. It is, therefore, of considerable interest to find out, in which cases relativistically derived polarization selection rules must be taken into account in order to interpret the experimental results.

Recently Borstel *et al.*[5,6] derived relativistic selection rules for space groups O_h^5 (fcc) and O_h^9 (bcc) and discussed their application to the three low-index faces of Rh (Ref. 5) and to Ag(111).[6] They conclude that nearly all prominent structures observed in normal photoemission from Rh(100) and Rh(111) can be explained on the basis of nonrelativistic dipole selection rules, but relativistic selection rules may have to be considered to interpret their results from Rh(110). In the case of near-normal emission from Ag(111), they concluded that the use of relativistic selection rules is essential for a consistent interpretation of their data even for energy bands which are not split by spin-orbit interaction.

In order to further investigate the need to use relativistic selection rules in some detail we have taken polarization-dependent photoelectron spectra from the (111) and (110) faces of Cu and Ag. These isoelectronic materials are good test candi-

dates since their bulk band structures $E(k)$ are rather well understood.[7–15] They differ, however, in that $E(k)$ for Cu is well reproduced by nonrelativistic calculations (with the small exception of the region near X along the Σ line, where a spin-orbit splitting at X_5 of about 0.1 eV is observed[7]), whereas for Ag relativistic effects must be included in the band calculations.[11] The calculated relativistic augmented plane-wave (RAPW) initial-state bands[11] for Ag have been verified experimentally[12–15] within a few tenths of an eV and the spin-orbit splitting at the upper d-band edge was estimated to be $X_{7+}-X_{6+}=0.30\pm0.05$ eV in this work. Moreover, the (110) faces are particularly well suited for tests of polarization selection rules: In the relativistic limit *all* initial states (double-group notation Σ_5) may be observed in normal photoemission,[5,6] while severe restrictions limit the number of transitions (from initial states of single-group symmetry $\Sigma_{1,2,3,4}$) under nonrelativistic selection rules.[3] Thus, from a comparison of polarization effects in photoemission from Cu and Ag we should be able to estimate the relative importance of relativistic selection rules.

The experiments were performed using an ESCALAB spectrometer from VG Scientific equipped with x-rays photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) facilities and modified by a variable aperture system to obtain small acceptance angles of the lens-analyzer system between $\pm1°$ and $\pm6°$ (half-angle of acceptance cone). Angular distributions are measured by rotating the crystal through the manipulator axis, thereby keeping the angle between light source and analyzer constant (40°). In all the measurements the electrons collected, the surface normal and the direction of incident light are confined to the same mirror plane of the sample. Light from a self-built capillary discharge lamp was polarized (90%) by triple reflection from gold mirrors similar to an arrangement described in the literature.[16] The energy resolution as verified experimentally by measuring the full width at half maximum (FWHM) of the $3p$ doublet of gaseous argon may be varied continuously above 25 meV.

The samples were oriented by Laue backreflection to $\pm1°$ and cleaned by standard procedures of argon sputtering and annealing. Surface cleanliness was checked by XPS. The vacuum was better than 10^{-10} Torr and no contamination was observed after 10 h. LEED was used both to check the surface quality as indicated by very sharp diffraction patterns with low background intensity, and to achieve the desired azimuthal orientation of the samples on the precision manipulator. All spectra were collected using a multichannel analyzer system and generally more than 2×10^4 counts per 20-meV data channel were collected in the d-band maxima.

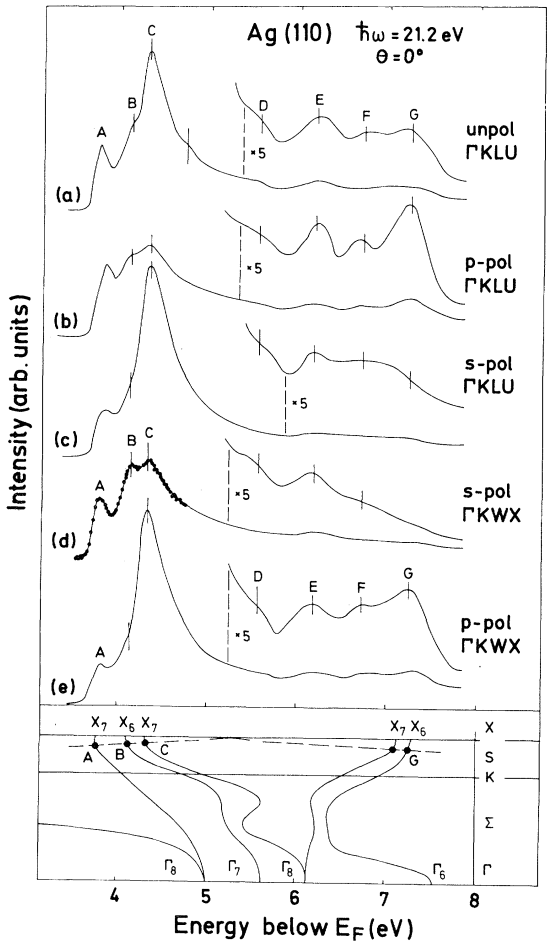

FIG. 1. Angle-resolved normal emission photoelectron spectra from Ag(110) obtained with He I (21.2 eV) radiation. Light is incident in the crystal mirror planes indicated and either unpolarized or to about 90% linearly (s,p) polarized. Some data points are given to indicate statistical accuracy. Energy resolution was set to $\Delta E=50$ meV in all spectra. Angular resolution (half angle of acceptance cone) set to 1° for unpolarized light and 3° for polarized light. Lower panel: Band structure along ΓKX as calculated (Ref. 11) and slightly modified according to recent experimental data (Ref. 15). The full circles denote direct transitions to a free-electron-like final state (dashed line) shifted down in energy by the photon energy. The spectra have neither been normalized to each other nor have any corrections for background effects been applied.

Energy distribution curves for electrons emitted

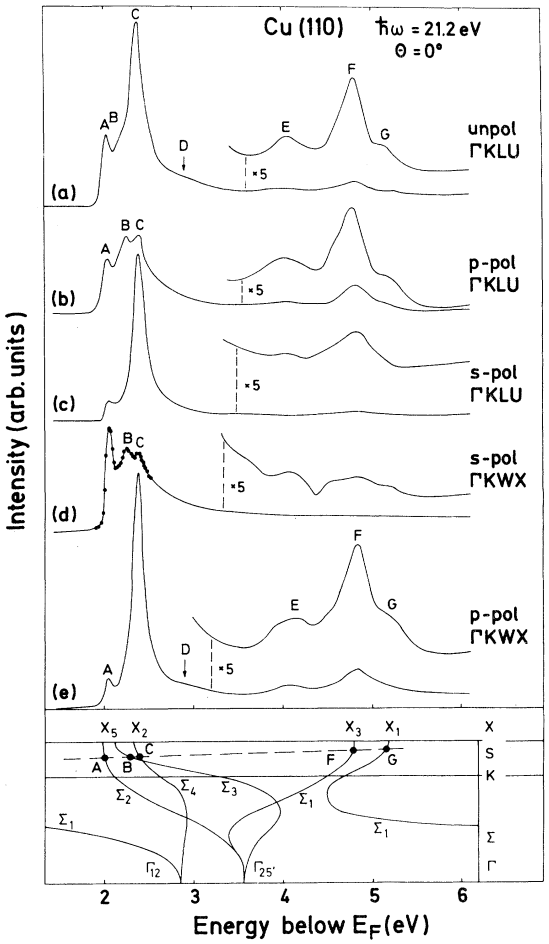

FIG. 2. Angle-resolved normal emission photoelectron spectra from Cu(110) obtained with He I radiation. For details see legend of Fig. 1 except the following details: band structure taken from Ref. 7, energy resolution was set to $\Delta E = 30$ meV.

normally at $\hbar\omega = 21.2$ eV from the Ag(110) face are presented in Fig. 1 for different polarizations in the mirror planes ΓKWX and ΓKLU. It is quite evident that strong polarization effects are observed. Before we interpret these data, we compare to the results from Cu(110) which are displayed in Fig. 2. Obviously there are striking similarities between both data sets. The spectra taken with unpolarized radiation are in excellent agreement with results obtained by other groups for Ag(110) (Refs. 12 and 17) and Cu(110) (Refs. 18 and 10). All available normal emission results from Cu(110) may be explained[7,8,10,19] completely on the basis of available bulk-band calculations[20] within the framework of the direct transition model.[8,10,19] To summarize, peaks labeled *A*, *B*, and *C* in Fig. 2 correspond to transitions from initial states with Σ_2, Σ_3, and Σ_4 symmetry[21] on the Σ/S line of the Brillouin zone (see lowest panel of Fig. 2). That assignment is immediately evident for peak *C*: This transition is allowed[3] for light *p* -polarized along ΓKWX and *s* polarized along ΓKLU, but forbidden with both *s*-polarized photons in the ΓKWX plane and *p* polarization along ΓKLU. A similar argument[3] identifies the symmetry of peak *B*. Peak *A* originates from an initial state Σ_2, which is symmetry forbidden at exactly normal emission but still contributes due to the finite solid angle of our experiment. We observe that its intensity strongly increases (while the other features remain essentially unchanged) when going off normal by a few degrees in agreement with earlier observations.[7,8,22] The symmetry of peak *A* was clearly identified recently[23] in polarization-dependent photoemission spectra from Cu(001): The same transition which generates peak *A* was observed in spectra taken at a polar angle of $\theta = 60°$ in the ΓXWK mirror plane of Cu(001) with *s*-polarized light. Its polarization behavior is thus fully consistent with the Σ_2 assignment (orbital character *xy*). Peaks *F* and *G* in Fig. 2 are obviously excited strongly only if the exciting light has a strong *z* component; they must therefore, have symmetry Σ_1 in agreement with the interpretation given earlier.[10] Peak *E* has been discussed[10] in terms of a density of states transition from the Σ_3 minimum at 4 eV. The polarization dependence of *E* in our results is consistent with this assignment, but it is seen from Fig. 2 that the polarization effects are not so pronounced for peak *E* as for the direct transitions. This might be an indication that this density of states transition is phonon assisted, thereby relaxing the polarization selection rules which require $k_{||}$ conservation during the photoemission process.

Returning now to Fig. 1, we see that Ag(110) normal emission at $\hbar\omega = 21$ eV shows general polarization behavior in close analogy to Cu(110). We may thus conclude that peaks *A*, *B*, and *C* in Fig. 1 are due to initial states whose spatial parts of the wave function contain $xy(\Sigma_2)$, $xz(\Sigma_3)$, and $yz(\Sigma_4)$, respectively. It is also quite evident that peak *G* must possess Σ_1 symmetry. The interpretation in terms of direct transitions is given in the lowest panel of Fig. 1. The dependence of peak *F* on polarization is rather weak and it seems difficult to assign a distinct symmetry to it. What concerns *D* and *E*, which were interpreted[17] as density of states transitions along Σ, is that they show no polarization behavior at all within our accuracy, and we come back to this point later. Our experimental energies and symmetry assignments for the

TABLE I. Experimental energies (errors in parentheses given in units of last digit) and symmetry assignments of peaks observed at $\hbar\omega = 21.2$ eV in normal emission spectra from Cu(110) and Ag(110).

Peak	Symmetry	Peak energies (eV) Cu(110), Fig. 2	Ag(110), Fig. 1
A	Σ_2	2.01(5)	3.80(5)
B	Σ_3	2.15(5)	4.14(5)
C	Σ_4	2.33(5)	4.33(5)
D	?	2.9(1)	5.6(1)
E	?	4.0(1); (Σ_3 ?)	6.3(1)
F	Σ_1	4.8(1)	6.8(1); (Σ_1 ?)
G	Σ_1	5.2(1)	7.3(1)

(110) faces are summarized in Table I. We conclude at this point that all direct transitions observed here may well be understood by application of the nonrelativistic selection rules indicating that the symmetry behavior is essentially determined by the spatial part of the wave functions, not by its spin part.

Borstel *et al.*[6] concluded from their interpretation of near-normal emission from Ag(111) at $\hbar\omega = 21.2$ eV that these results can only be interpreted consistently by using relativistic polarization selection rules. We have repeated their measurements and reproduced their data quite accurately. We will now present, however, a different interpretation in terms of nonrelativistic selection rules. Our data taken with unpolarized light at several polar angles along ΓLUX from Ag(111) are displayed in Fig. 3 and the results of Borstel *et al.* (Fig. 1 of Ref. 6) are obviously reproduced by our data around $\theta = 10°$. We have therefore studied the polarization dependence at that polar angle, see our results in Fig. 4 right panel, and we nicely reproduce *all* polarization effects reported in Ref. 6. We have also repeated the same measurements with Cu(111), see Fig. 4 left panel, and find both very similar photoelectron spectra for Cu(111) and Ag(111) along comparable lines parallel to the ΓL direction in k space, and practically identical polarization behavior for both metals. We conclude that an interpretation as given in Ref. 6 in terms of emission along the Λ line is not justified since at $\theta \approx 10°$ we observe transitions along a line nearly parallel to Λ at a distance of about 0.25 Å^{-1}, not negligible as compared to $2\pi/a \approx 1.5$ Å^{-1}. We must therefore interpret the experimental results as emission in mirror planes where we can only distinguish states to be odd or even with respect to the mirror operation. Since all authors agree in that emission from Cu may be described by point group selection rules the close similarity of Cu and Ag indicates that the results presented in Fig. 4 may be interpreted without the need to apply relativistic selection rules.

We have also studied normal emission from Cu(111) and Ag(111), see Fig. 5. The unpolarized data are in excellent agreement[24] with results of other authors.[12,18,10,17,25] Again, it is obvious in

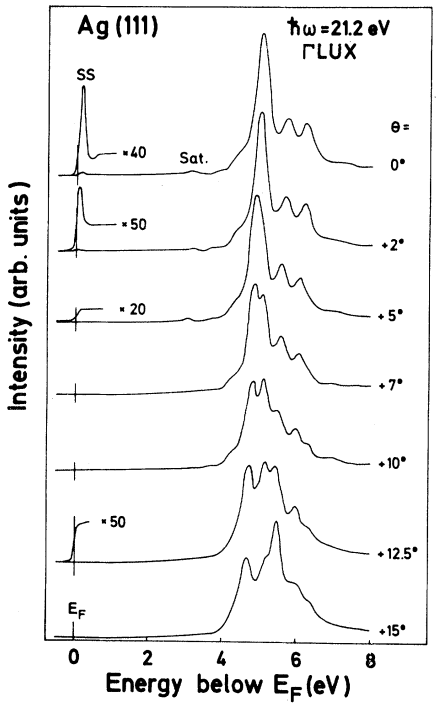

FIG. 3. Photoemission spectra taken with unpolarized He I radiation (21.1 eV) at various polar angles θ in the ΓLUX azimuth. ($\theta = 0°$ corresponds to normal emission.) Angular and energy resolution set to 1° and 100 meV, respectively. SS is the surface state observed around $k_{\|} = 0$, Sat. is the peak originating from weak satellite line of He I radiation at 23.09 eV.

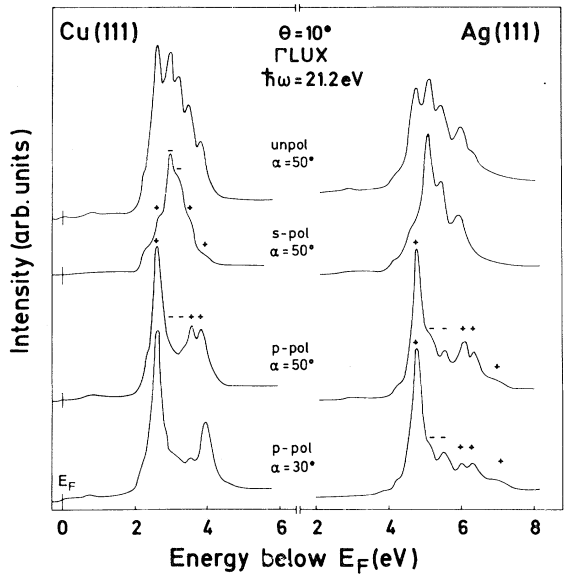

FIG. 4. Photoemission spectra taken with polarized He I radiation from Cu(111), left hand, and Ag(111), right hand, taken at a polar angle $\theta=10°$ along ΓLUX. Energy and angular resolution set to 100 meV and 1°, respectively. The angle between incident photon direction and surface normal is denoted by α. In case of $\alpha=50°$ the light is incident in the ΓLUX plane, in case of $\alpha=30°$ the light is incident in ΓLKL plane. Labels $\pm$ denote odd-even symmetry with respect to ΓLUX plane.

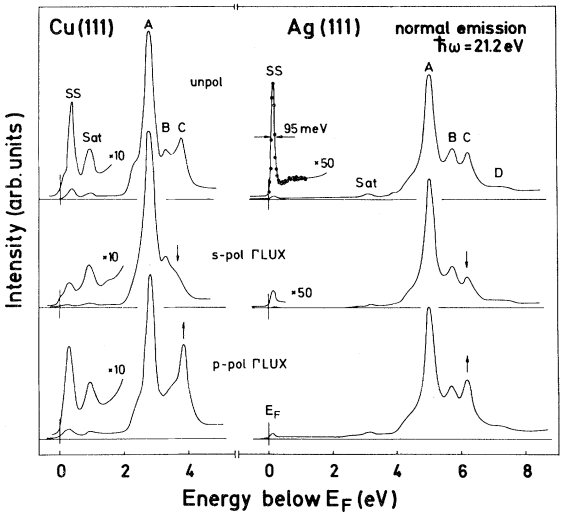

FIG. 5. Polarization dependence of normal emission spectra from Cu(111) and Ag(111). Angular resolution set to 1° in all cases. Energy resolution was 100 meV for polarized light and 50 meV for unpolarized light.

both metals that peaks A, B show a Λ_3-like polarization dependence,[3] whereas C indicates Λ_1 behavior. According to an analysis where calculated momentum matrix elements are explicitly taken into account[25] the polarization behavior of the Cu(111) results in Fig. 5 is in full agreement with the available band structures. If we use Christensen's relativistic band-structure calculation[11] to interpret the Ag(111) results in Fig. 5 we will assign double-group symmetries $\Lambda_{4,5}+\Lambda_6$, Λ_6, $\Lambda_{4,5}+\Lambda_6$, and Λ_6 to peaks labeled A, B, C, and D, respectively. (Peaks A and C are then unresolved doublets; we use here the double-group notation of Borstel *etal.*[6]) If we instead use the experimental data of Courths *et al.*,[15] we will label peaks $A-D$ as $\Lambda_{4,5}+\Lambda_6$, $\Lambda_{4,5}+\Lambda_6$ (unresolved doublets), Λ_6, and Λ_6, respectively. In both cases the relativistic selection rules would allow *all* transitions with s-polarized light. We observe, however, that C and D are attenuated in s-polarized light.

In agreement with nonrelativistic band-structure calculations[26] we may thus label peaks C and D as originating from initial states with a Λ_1-like spatial part of the wave function. In this context we note that a pronounced polarization effect in normal emission from Ag(111) has also been observed[13] at $\hbar\omega=7.8$ eV: With s-polarized light a transition at an initial energy of about 1.8 eV below E_F (symmetry Λ_6 in relativistic limit) definitely exhibits Λ_1-like behavior. The same symmetry assignment is also found[13] for the well-known surface state localized in the L gap just below the Fermi level in agreement with the results presented here, see peak SS in Fig. 5.

We must state, however, that (in Fig. 5) the polarization effects in Ag are not as pronounced as in Cu. This might well be an indication that the nonrelativistic selection rules are somewhat relaxed due to admixtures of other single group symmetries as caused by spin-orbit coupling. An alternate explanation for the attenuated polarization effect of peak C in Ag would be a rather strong contribution of density of states transitions. This would be not unreasonable since the Ag d bands are very flat near Γ along the ΓL direction. We further note that the shoulders observed clearly in Fig. 5 at $\sim$ 4.2 eV for Ag (2.5 eV for Cu) have also been interpreted as originating from density of states transitions at $L_{4,5}$. If we assume that these density of states transitions are phonon assisted they will not show strong polarization effects. In a similar way we could explain that essentially all density of states transitions identified in Ag(110) show no or only weak polarization dependence.

To summarize, we arrive at the following conclusions: All direct transitions observed in the present work may well be understood by the use of

nonrelativistic polarization selection rules. Features originating from density of states transitions show no or only weak polarization dependence. This might be due to the influence of relativistic effects but may be understood as well by the assumption that those transitions are phonon assisted. To gain further insight into the problem, two different types of investigation have to be performed. On one hand, we must try to distinguish experimentally between direct transitions and phonon assisted density of states transitions. On the other hand, one must check the polarization dependence of normal emission when going along the initial-state bands in high-symmetry directions, thus tuning the sensitivity to spin-orbit effects near the appropriate band crossings. We will do such work in the near future.

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