Necessity of relativistic dipole selection rules in photoemission: A reply

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We have calculated normal photoemission spectra of Cu(110) for both spin-orbit interaction neglected and included. Our results show that the occurrence of a nonrelativistically forbidden transition of type $\Sigma_2 \rightarrow \Sigma_1$ in recent experimental photoemission data of Goldmann *et al.* is primarily a relativistic effect. It is related to a relaxation of the nonrelativistic dipole selection rules which is caused by spin-orbit interaction. Our results prove that in photoemission relativistic effects may be important even for elements of low atomic number and may dominate effects due to finite instrumental resolution.

In a recent study[1] of high-resolution angle-resolved photoemission spectra of Ag(111), we concluded that relativistic dipole selection rules (RSR) are essential for a consistent interpretation of photoemission data even for energy bands whose degeneracy is not affected by spin-orbit interaction and for elements of low atomic number, where spin-orbit splittings are difficult to be resolved energetically in photoemission experiments. Our argument was based on the fact that spin-orbit interaction causes hybridization of those spinors which belong to a distinct representation of the double group of the wave vector $\vec{k}$, but whose spatial parts are bases for different irreducible representations of the single group of $\vec{k}$. This gives rise to a relaxation of the nonrelativistic dipole selection rules[2] (NRSR), derived within the single-group formalism. As a consequence transitions which are forbidden by NRSR may become allowed by RSR and show up in photoemission experiments.

These conclusions have been criticized recently by Goldmann *et al.*[3] in a Comment on our publication. On the basis of their photoemission data from Cu(110), Cu(111), Ag(110), and Ag(111), they conclude that there is no need to invoke RSR since their data are in accordance with NRSR.

In view of the excellent series of photoemission spectra from Ag(111) shown by Goldmann *et al.* in Fig. 3 of their Comment we agree with them that our near-normal photoemission data for Ag(111) may not provide a definite answer to the question of whether RSR are important for this material or not. In fact, their spectra demonstrate that for near-normal photoemission from Ag(111), relativistic effects, if present, may interfere with effects due to the angular dependence of the photoemission intensities and thus become difficult to be separated experimentally. On the other hand, we strongly disagree with the conclusion of Goldmann *et al.* that effects due to RSR are generally not present in their data. In the following we will prove that contrary to the conclusion of these authors their spectra contain rather obvious effects due to relaxation of NRSR and thus indeed support strongly our former conclusions.

To show this we investigate the most instructive case, namely the normal photoemission spectra of Cu(110) in Fig. 2 of their Comment. Copper is generally regarded as an element with low atomic number. Along the direction Σ the electron energy bands are totally split even in the absence of spin-orbit interaction; therefore, Cu(110) is well suited for our purposes. As may be seen from their Fig. 2, three main peaks labeled *A, B,* and *C,* contribute to the spectra, which in the single-group labeling scheme correspond to transitions $\Sigma_2 \rightarrow \Sigma_1$, $\Sigma_3 \rightarrow \Sigma_1$, and $\Sigma_4 \rightarrow \Sigma_1$, respectively. According to NRSR, the transiton *A* is forbidden by symmetry arguments in normal emission. Its appearance in all spectra of Fig. 2 is explained by Goldmann *et al.* by the nonzero width of the acceptance cone of their detector, which allows off-normal emitted photoelectrons to contribute to the spectra. To check this explanation we calculate the exact-normal photoemission spectrum of Cu(110) for *s*-polarized light with energy $\hbar\omega = 21.2$ eV incident in the ΓKLU crystal plane. We choose *s* polarization since it recently has been found for Cu(111) (Ref. 4) that the agreement between theoretical and experimental photoemission intensities for reasons so far unknown is much better for *s* polarized incident light than for *p* polarized radiation. Thus by choosing the spectrum (c) in their Fig. 2 for a check we avoid the theoretical subtleties connected

with the validity of Fresnel's formulas at a vacuum-metal boundary in the case of *p*-polarized incident radiation.[4]

To calculate the required photoemission spectra we use the fcc interpolation scheme developed by Smith and Mattheiss[5] in its extended (16 plane wave) form.[6] We follow the procedure of Smith *et al.*[4] in their calculation of normal emission spectra, thereby making the following modifications: (i) To control the influence of spin-orbit interaction we use the relativistic version of the scheme.[5] (ii) Since the transitions *A*, *B*, and *C* occur within a few tenths of an electron volt, lifetime broadening is taken into account by convoluting the distribution using a Lorentzian with an energy independent full width at half maximum (FWHM) Γ. (iii) The spectra are generated on the basis of 15-meV data channels. As we are mainly concerned with intrinsic effects, no further convolution for simulation of instrumental energetic resolution is applied.

Using the 19-parameter set given by Smith,[6] we obtain the spectra presented in Fig. 1 for both spin-orbit interaction neglected ($\xi_{3d}=0$) and included ($\xi_{3d}=0.08$ eV) (Ref. 7). According to NRSR, only the $\Sigma_4 \rightarrow \Sigma_1$ transition *C* is allowed for *s* polarized light incident in the ΓKLU crystal plane,[2] and in fact only this transition shows up in the calculated spectrum for $\xi=0$ in Fig. 1(a). If spin-orbit interaction is taken into account the initial states with symmetry Σ_2 and Σ_3 hybridizate with the Σ_4 band, i.e., they both contain now a certain fraction of spatial parts transforming according to Σ_4, which allows for a contribution to the exact-normal emission spectrum. From a group-theoretical point of view this means that restrictions due to single-group selection rules, which enter into NRSR, play no role along Σ any more. We thus expect for the case $\xi \neq 0$, three transitions *A*, *B*, and *C* to contribute to the spectrum in question. This occurs exactly, as shown in Fig. 1(b), where the transitions *B* and *C*, due to their very small energetic separation ($\Delta E \simeq 75$ meV), are not resolved despite the small linewidth $\Gamma = 50$ meV chosen for clarity in this calculation. The close resemblance of our calculated exact-normal emission spectrum in Fig. 1(b) with the spectrum (c) in Fig. 2 of Goldmann *et al.* demonstrates that the appearance of peak *A* in their data contrary to their interpretation is related to a relaxation of NRSR, and that their critique on our former conclusions is, therefore, unfounded.

The energetic separation of the peaks *A* and *C* in our Fig. 1(b) is $\Delta E \simeq 0.16$ eV, whereas from the spectra of Goldmann *et al.*, we estimate a value of 0.3 eV. This experimental value is in accordance with other photoemission data of Cu(110),[8,9] and we therefore conclude that the Cu parameters published by Smith[6] are not optimized for energy bands along Σ. The parameters were derived by Smith from a nonlinear-least-squares fit to the

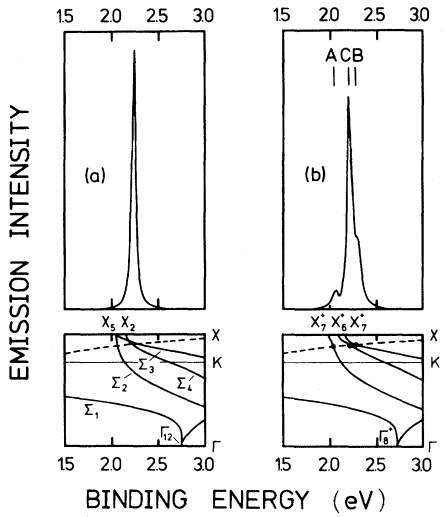

FIG. 1. Calculated Cu(110) normal photoemission spectra for *s*-polarized light ($\hbar\omega = 21.2$ eV) incident in the ΓKLU crystal plane. The lower panel shows the corresponding relevant part of the bandstructure with the final-state band (dashed line) shifted down in energy by $\hbar\omega$. (a) Spin-orbit interaction neglected, (b) spin-orbit interaction included.

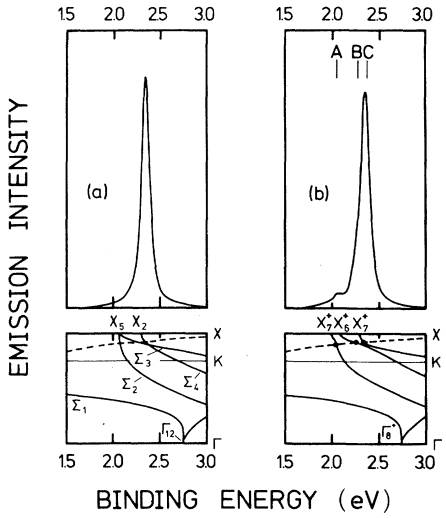

FIG. 2. Same as Fig. 1, but parameter set of interpolation scheme now modified according to experimental data of Ref. 8, as described in the text.

nonrelativistic first-principles band-structure calculation of Janak *et al.*[10] Along Σ the band structure of Janak *et al.* shows systematic deviations from experimentally determined bands, in particular with regard to the position of the Σ_4 band.[8] Therefore we present a modified calculation of the Cu(110) normal-emission spectrum which corrects for the position of this Σ_4 band.

To achieve this we observe that in the nonrelativistic limit the dispersion of the Σ_4 band $\Gamma_{12}\rightarrow X_2$ is controlled primarily by the Fletcher-Wohlfahrt parameters A_4 and A_5.[11] By slightly varying these two parameters but keeping the value of $4A_4-8A_5$ fixed, we are able to adjust the X_5-X_2 energy separation to the value of 0.25 eV without changing the energy at Γ_{12}. When spin-orbit interaction is included, this yields energetic separations at X similar to those measured by Dietz and Himpsel,[8] cf. Table I and Fig. 3 in their paper. The new parameters are $A_4=0.006\,77$, $A_5=0.001\,97$. This corresponds to a relative change of 15% and 30%, respectively.

With these two parameters modified and all other parameters retained, we obtain the normal-emission spectra shown in Fig. 2.

Here, for the linewidth a value $\Gamma=100$ meV suggested by the spectra of Goldmann *et al.* was used. Owing to the small energetic separation of the transitions B and C the effective linewidth of the corresponding peak is then approximately 120 meV. The comparison of Figs. 2(a) and 2(b) proves once more that the appearance of peak A is in fact related to relativistic effects. The very good agreement of the calculated spectrum in Fig. 2(b) with the spectrum (c) in Fig. 2 of Goldmann *et al.* furthermore suggests that effects due to off-normal emitted photoelectrons are only of minor importance in this case. To check this quantitatively we have calculated for $\xi=0$ and $\xi\neq 0$ four further spectra by rotating the direction of electron propagation by 3° out of the Σ direction in the ΓKLU and ΓKWX crystal plane, respectively. No significant differences with respect to the spectra in Fig. 2 were found, which indeed shows that the nonzero width of the acceptance cone introduces no critical effects in this case.

The atomic value of 0.08 eV chosen for ξ_{3d} in the present calculation actually represents a lower bound for the spin-orbit parameter. For solid Cu the experimental photoemission data of Dietz and Himpsel[8] suggest $\xi_{3d}=0.1$ eV to be more appropriate. If this value is used in the calculation, the height of peak A relative to that of C increases, and will produce an even better agreement with the experimental results.

To show that effects due to RSR are present in the Cu(110) spectra of Goldmann *et al.*, we have chosen an example in which relativistic effects dominate effects due to angular dependence. There are other spectra in the work of these authors where both effects interfere. As an example we cite the Cu(110) spectrum (d) in Fig. 2 of their Comment. For s polarization with respect to the ΓKWX plane, our calculations show that the height of peak A, relative to that of B, is strongly angular dependent in accordance with previous experimental results.[8,9] We obtain an intensity ratio similar to that measured[3] if we rotate the direction of electron propagation by 2° out of the Σ direction. Since the degree of light polarization in practice is never 100% this angular dependence of spectrum (d) should, in principle, show up indirectly also in spectrum (c) and affect the relative intensities there.

Calculations of the Cu(110) normal-emission spectrum in Fig. 2(b) for different values of ξ indicate that the intensity ratio of the peaks A and C is roughly proportional to ξ for small values of the spin-orbit parameter. For Ag and Cu the ratio of the spin-orbit parameters is $\xi_{4d}(\mathrm{Ag})/\xi_{3d}(\mathrm{Cu})\simeq 3$.[7] We thus expect in the case of normal photoemission from Ag(110) and s polarization with respect to the ΓKLU plane an intensity ratio of the two peaks A and C, which is roughly 3 times larger than that corresponding to Cu(110). If one compares the spectra (c) both in Figs. 1 and 2 of the work of Goldmann *et al.*, one finds indeed a comparable factor which shows that the occurrence of peak A in this Ag(110) spectrum should also be primarily a relativistic effect. For the Ag(110) spectrum (d), which in analogy to the corresponding Cu(110) spectrum should exhibit a strong angular dependence, a similar comparison cannot be made on the basis of the experimental data reported, as it is not clear to what extent different angular effects due to different acceptance cones enter these spectra. Nevertheless, the general trend in the Ag(110) spectra is obviously an increase of the peak A with respect to the other peaks when compared with Cu(110). This observed systematic shift corresponds very well to the fact that transitions which are forbidden by NRSR, but become allowed by RSR will contribute the more to a particular photoemission experiment the stronger the spin-orbit interaction. In this context it does not seem to be very convincing to realize for Ag signi-

ficant shifts in the energy eigenvalues due to spin-orbit interaction, but at the same time to disregard any hybridization for the corresponding eigenfunctions in favor of pure instrumental resolution effects, as has been done by Goldmann *et al.*

We close this reply by summarizing our essential conclusions: (i) Since spin-orbit interaction is present in every material, RSR have to be applied in any case. (ii) Selection rules provide only information on those transitions which are forbidden. As RSR are not more restrictive than NRSR, the only case of practical interest for the question of NRSR versus RSR is a transition which is forbidden by NRSR but becomes allowed by RSR. In this case the transition in question will contribute the more to a photoemission experiment the stronger the spin-orbit interaction. (iii) Present day photoemission experiments exhibit a sufficient high resolution and sensitivity to show this breakdown of NRSR even for elements with low atomic number.

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