X-Ray-Photoelectron Diffraction from a Free-Electron-Metal Valence Band: Evidence for Hole-State Localization

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X-ray-photoelectron diffraction has been measured from an Al(001) single crystal for the free-electron-like valence band and the well-localized 2*s* core level, using Mg *Kα* radiation. Both show the same high anisotropy of 65% in the azimuthal distribution of the photoemitted electrons at 45° away from the surface normal. Moreover, the measured intensity patterns are essentially identical, indicating a strong similarity in the photoemission final states. This similarity provides evidence for a strong degree of hole localization in high-energy valence-band photoemission.

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X-ray-photoelectron diffraction (XPD) is a phenomenon related to photoemission from solid surfaces.[1] After photoexcitation, the electrons are diffracted by the crystal lattice and therefore carry structural information about the sample. A convenient way to obtain this information is to monitor the intensity of a photoelectron signal from a single crystal as a function of the emission direction relative to the crystal axis. Strong modulations are found for these intensities, as a function of both polar and azimuthal emission angles. The presently accepted interpretations of XPD patterns associated with core-level emission start with a spherical electron wave emanating at the position of an atom in the crystal lattice.[1-4] Subsequent scattering and diffraction of this wave by other atoms within a restricted cluster lead to the observed diffraction pattern. This theory yields quite gratifying agreement with measured XPD data, which are always taken for well-localized core levels in order to assure the spherical-wave nature of the unscattered final-state wave function used in the theory.

In this Letter we will present XPD data for emission from the much more extended, free-electron-like states that form the valence band of Al. Here the initial-state electrons are essentially distributed uniformly in space with only small anisotropies which are reflected, e.g., by the small energy gaps.[5,6] In the usual interpretation of XPD the emission of a spherical electron wave from a lattice site is crucial,[1] and thus XPD effects for valence electrons might be expected to be reduced compared to those of localized core levels. However, in contrast to this reasoning, we find that the XPD effects from the integrated Al valence-band emission are very strong and that they furthermore produce patterns that are essentially identical to those measured with a core line of similar energy. These results provide evidence for hole localization in the final state of valence-band photoemission.

The XPD data were obtained from a clean Al(001) single crystal using nonmonochromatized Mg *Kα* radiation by scanning the azimuthal angle ϕ through 120° about the surface normal at a fixed polar angle of $\theta = 45°$ away from the normal, such that one quadrant of the anticipated fourfold-symmetric XPD pattern could be observed. At each setting of ϕ, intensities were directly determined during the measuring process by subtracting a linear background as indicated in the energy scans shown in Fig. 1. Care had to be taken when recording

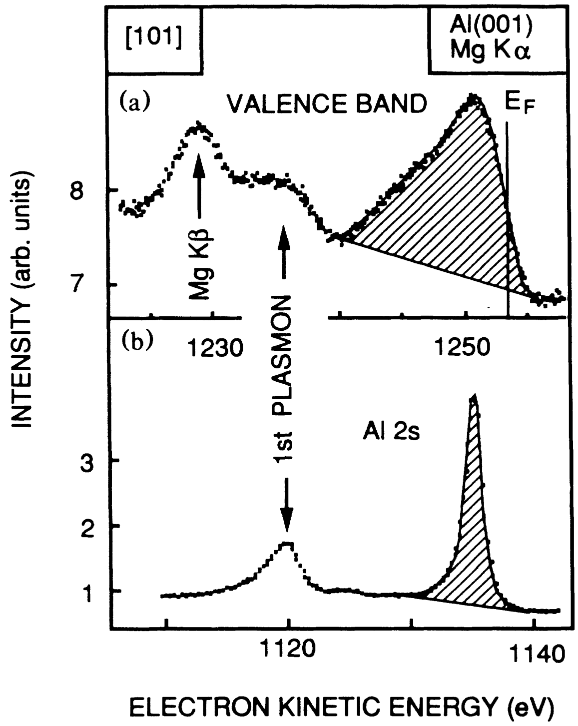

FIG. 1. Mg-*Kα*-excited XPS spectra of (a) the valence-band region and (b) the 2*s* core level of Al, recorded in the [101] direction from a clean Al(001) single crystal. Note that the two curves are not drawn to scale, with the valence-band emission being much weaker. The shaded areas represent the intensities that were calculated at each azimuthal setting to yield the XPD curves of Fig. 2. Also shown are the associated plasmon-loss peaks and, in the valence-band spectrum, the Mg-*Kβ*-excited Al 2*p* core level.

Al valence-band spectra [Fig. 1(a)]. Because of the extremely low photoelectric cross section of these valence electrons, even minor contamination with Ar remaining from the cleaning procedure produces visible features in the spectral region of interest and may give a contribution from atomiclike electrons to the XPD patterns. Annealing the sample at 400 °C for 2 min removed all of the Ar, however. Also, Mg-$K\beta$-excited Al 2*p* emission falls near the valence-band emission [Fig. 1(a)] and had to be avoided in the intensity integration, along with the plasmon-loss peak. During the measurements, the pressure was maintained at 5×10^{-11} mbar. Surface contamination amounted to a total of about 10% of a monolayer (ML) of oxygen and carbon before, and less than 20% of a ML after, a 30-h run.

The experimental results for the Al valence-band XPD ($E_{\rm kin}=1250$ eV) and those for the 2*s* core level ($E_{\rm kin}=1136$ eV) are given in Fig. 2. Apart from minor deviations, which might eventually be important to test more accurate theories in detail, the data are virtually identical, with both showing an anisotropy $A=(I_{\rm max}-I_{\rm min})/I_{\rm max}$ of 65%. The much poorer statistics in the valence-band data are simply a consequence of the low signal intensity and the background-subtraction procedure. The strong maxima along the [011] and [101] directions, corresponding to $\phi=0°$ and 90°, respectively, are associated with strong forward scattering by nearest-neighbor atoms in this fcc structure, an effect that dominates XPD patterns at photoelectron kinetic energies of more than a few hundred eV.[1,2,7] The two additional features centered at $\phi=32°$ and 58° are due to more complicated diffraction effects. As for the minor differences between the two curves, the most significant one is that the forward-scattering peaks appear to be slightly broader for the valence-band emission than for the core level.

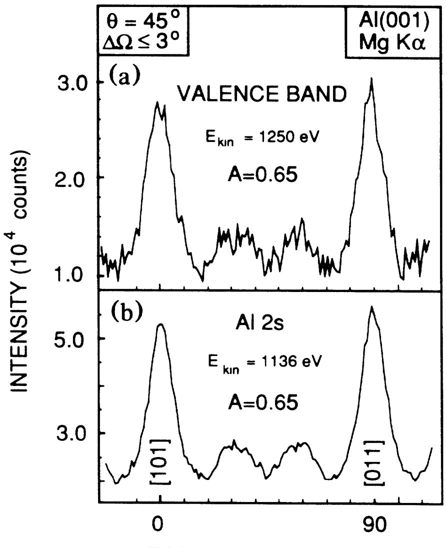

FIG. 2. (a) XPD azimuthal pattern of the integrated valence band measured from a (001) single crystal of Al at a polar angle of 45° using Mg $K\alpha$ radiation. The angular resolution $\Delta\Omega$ of the spectrometer was better than 3°. The main maxima correspond to electron detection in the [011] and [101] directions. (b) Same as (a), however, here electrons were detected from the 2*s* core line at a kinetic energy of 1136 eV.

Trying to reconcile these findings with the current understanding of photoemission and photoelectron diffraction, one must consider mechanisms that lead to this apparent localization of the hole in the final-state wave function. Both the free-electron-like initial states *and* the photoemission process have to be taken under consideration. We first note that the very first XPD experiments were also performed on valence electrons, namely, the 3*p* electrons in NaCl (Ref. 8) and the 5*d* electrons in Au.[9] In both cases, the XPD effect was as large as that of core electrons of similar kinetic energy. But here the 3*p* electrons in NaCl and also the 5*d* electrons in Au are still quite localized, which makes the assumption of a spherical-wave emitter in the interpretation a valid approximation.

It has been shown theoretically by band-structure calculations,[10] and experimentally by measuring energy-band dispersions with ultraviolet photoemission spectroscopy (UPS),[11] that the valence states in Al are essentially free-electron-like. However, there are some discrepancies between the measured and the free-electron dispersion curves, the origins of which are not completely clear at this point.[12-16] It is difficult to relate these deviations in a simple manner to the large XPD effects observed in the present paper, although hole localization could be involved.

We shall now accumulate arguments that point to the fact that high-energy photoemission from a valence-band electron leads to a localization of the photohole at a lattice site. This localization in the final state is similar to that observed in the photoionization from core states, and therefore the similarity of the diffraction patterns seen in Fig. 2 are not as surprising as it may seem at first sight.

The convenient basis for further discussion is the so-called "time-reversed LEED" formulation of photoemission.[17-20] In this theory, one starts from the "golden rule" equation with the electric dipole operator to calculate the photocurrent using LEED-type final-state wave functions in the time-reversed form. This finally produces an outgoing plane wave, running towards the detector. The initial state can be constructed, e.g., from augmented-plane-wave components at each atomic center. In this picture, the final-state scattering and interference for valence-band photoexcitation from each atomic component will not be too different from that in the core case.

A central question which now has to be addressed in comparing core-level and free-electron-like valence-band XPD is that of the nature and the degree of localization of the hole left behind in the photoemission process. In the core case, localization is given "naturally." In addition, from an analysis of core-level binding energies[21] and singularity parameters,[22-24] it can be concluded that total screening of the core hole is achieved by a unit valence charge. The situation is less obvious for a valence-band hole. Theoretical considerations,[25] as reviewed by Almbladh and Hedin,[26] indicate that for the valence hole there also occur screening by a valence electron and considerable localization. An earlier analysis by Ley *et al.*[21] of the energetics of the valence electrons along the lines performed for the core energies comes to the conclusion that the data can be explained equally well by a localized and a delocalized hole and are therefore inconclusive on the question of localization.

Almbladh and Hedin[26] point out that a measure of the localization of the valence-band hole could be obtained from the strength of the intrinsic plasmon accompanying the valence bands. The reasoning behind this contention comes from the fact that the theory of intrinsic plasmon production assumes perturbation of the valence electrons by a localized hole.

The plasmons accompanying XPS valence-band spectra from aluminum have indeed been analyzed, but with conflicting results. Höchst and co-workers[27-29] find an intrinsic plasmon creation rate b of 0.11 for both the core levels and the valence band in Al, while van Attekum and Trooster[30] get $b=0.21$ for the core levels and $b=0.10$ for the valence band. However, we note that the data analyses of the two groups differ in some important aspects, which may be the reason of the discrepancy. Still, both analyses give a sizable intrinsic plasmon creation rate for the valence-band plasmons, indicating considerable localization of the valence-band hole.

A further indication of valence-hole localization comes from the observation that, while the intrinsic plasmon creation rate is between 10% and 20% of the total plasmon creation rate in the XPS data, it is only $\approx 2\%$ in the VL_{23} x-ray emission spectrum.[31] The intrinsic plasmon creation rate in the x-ray emission case samples the difference in localization of the two levels involved, and the data of Rooke[31] thus indicate a similar localization in the $2p$ core level and the valence band, in agreement with the finding of Höchst and co-workers.[27-29] Therefore we are led to the conclusion that the limited available data on the intrinsic plasmon creation strongly point to a localization of the valence-band hole.

The observed localization of the final state of x-ray-excited valence electrons can also be considered from a different point of view. If $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wave vectors of the initial and final states, respectively, momentum conservation for a direct transition means that $\mathbf{k}_f=\mathbf{k}_i+\mathbf{k}_{h\nu}+\mathbf{g}$, where $\mathbf{k}_{h\nu}$ is the photon wave vector and $\mathbf{g}$ is a reciprocal-lattice vector.[32] This equation is also the basis for determining the band structure from UPS experiments, where $\mathbf{k}_{h\nu}$ is negligible. In our high-energy case, however, $\mathbf{k}_f$ is about 10 reciprocal basis vectors long, and therefore the experimental angular acceptance angle leads to a wider sampling within the Brillouin zone. Also, the Debye-Waller factor at room temperature and at these energies gets quite small for most materials, leading predominantly to photon-induced indirect transitions.[32] For these two reasons, XPS experiments for most materials sample principally the density of states. In the case of indirect transitions, we have $\mathbf{k}_f=\mathbf{k}_i+\mathbf{k}_{h\nu}+\mathbf{g}\pm\mathbf{Q}$, where $\mathbf{Q}$ can be any sum of phonon wave vectors.

At this point we should also comment on the effect of the limited angular and energy resolution in this experiment. We are recording the *integrated* valence-band emission at an angular resolution of less than 3° full cone, which is enough to lead to an almost complete averaging over the first Brillouin zone.[32] This means that we are measuring essentially *every* occupied valence state. If, on the other hand, we could perform the same experiment with an infinitely high energy and angular resolution, and at a low enough temperature to suppress indirect transitions, we should be seeing predominantly direct transitions; i.e., at each energy within the valence-band emission we would expect a set of δ functions in the corresponding azimuthal scans, with the positions depending on the $\mathbf{k}$-conservation selection rule. As an intermediate case approaching this, we can consider the detailed angle-resolved XPS study of the W valence band,[32] a material with a high Debye temperature permitting the observation of direct transitions even in XPS. These data show marked changes in spectral form from one direction to the other, implying that different parts of the spectrum show different diffraction patterns, and in turn that all of them cannot reflect the core-level patterns at similar energy. It would certainly be of interest to see if the energy-integrated valence-band emission in W again matches the core emission. In the case of Al we did not see significant spectral changes with direction beyond the noise limit; i.e., the same diffraction occurs at any part of the valence band, at least in this low-resolution experiment.

In summary, we have found very high anisotropies in XPS intensities from the delocalized valence band of the free-electron-metal Al. These energy-integrated intensities show essentially the same diffraction patterns as the $2s$ core level at a similar kinetic energy. This similarity is explained by assuming that the final-state wave function involves a highly localized hole on an atomic center. These experimental results therefore provide clear evidence that, at energies of the order of 1 keV, the photoemission process produces a highly localized valence-state hole even in nearly-free-electron materials.

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[1] C. S. Fadley, Prog. Surf. Sci. **16**, 275 (1984); Phys. Scr. **T17**, 39 (1987).

[2] S. Kono, S. M. Goldberg, N. F. T. Hall, and C. S. Fadley, Phys. Rev. **22**, 6085 (1980).

[3] J. J. Barton, S. W. Robey, and D. A. Shirley, Phys. Rev. B **34**, 778 (1986).

[4] M. Sagurton, E. L. Bullock, and C. S. Fadley, Surf. Sci. **182**, 287 (1987).

[5] F. S. Szmulowicz and B. Segall, Phys. Rev. B **21**, 5628 (1980).

[6] S. P. Singhal and J. Callaway, Phys. Rev. B **16**, 1744 (1977).

[7] W. F. Egelhoff, Jr., Phys. Rev. B **30**, 1052 (1984).

[8] K. Siegbahn, U. Gelins, H. Siegbahn, and E. Olson, Phys. Scr. **1**, 272 (1970).

[9] R. J. Baird, C. S. Fadley, and L. F. Wagner, Phys. Rev. B **15**, 666 (1977).

[10] H. Hoffstein and D. J. Boudreaux, Phys. Rev. B **2**, 3013 (1970).

[11] H. J. Levinson, F. Greuter, and E. W. Plummer, Phys. Rev. B **27**, 727 (1983).

[12] I. W. Lyo and E. W. Plummer, Phys. Rev. Lett. **60**, 1558 (1988).

[13] X. Zhu and A. W. Overhauser, Phys. Rev. B **33**, 925 (1986).

[14] J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **59**, 819 (1987).

[15] K. W. K. Shung, B. E. Sernelius, and G. D. Mahan, Phys. Rev. B **36**, 4499 (1987).

[16] S. Hüfner, Solid State Commun. **59**, 639 (1986).

[17] W. L. Schaich, in *Photoemission in Solids I*, edited by M. Cardona and L. Ley, Topics of Applied Physics Vol. 26 (Springer-Verlag, Berlin, 1978), p. 105.

[18] G. D. Mahan, Phys. Rev. B **2**, 4334 (1970).

[19] I. Adawi, Phys. Rev. **134**, A788 (1964).

[20] P. J. Feibelman and D. E. Eastman, Phys. Rev. B **10**, 4932 (1974).

[21] L. Ley, F. R. Mc Feely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, Phys. Rev. B **11**, 600 (1975).

[22] G. D. Mahan, Phys. Rev. **163**, 612 (1967).

[23] P. Nozière and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).

[24] P. Steiner, H. Höchst, and S. Hüfner, Z. Phys. B **30**, 129 (1978).

[25] L. Hedin, B. I. Lundquist, and S. Lundquist, Solid State Commun. **5**, 237 (1967).

[26] C. O. Almbladh and L. Hedin, in *Handbook on Synchrotron Radiation,* edited by E. E. Koch (North-Holland, Amsterdam, 1983), Vol. 1B, p. 611.

[27] H. Höchst, P. Steiner, and S. Hüfner, J. Phys. F **7**, L309 (1977).

[28] H. Höchst, P. Steiner, and S. Hüfner, Z. Phys. B **30**, 145 (1978).

[29] P. Shenin, H. Höchst, and S. Hüfner, in *Photoemission in Solids II,* edited by L. Ley and M. Cardona, Topics in Applied Physics Vol. 27 (Springer-Verlag, Berlin, 1979), p. 349.

[30] P. M. Th. M. van Attekum and J. M. Trooster, Phys. Rev. B **18**, 3872 (1978).

[31] G. A. Rooke, Phys. Lett. **3**, 234 (1963).

[32] R. C. White, C. S. Fadley, M. Sagurton, and Z. Hussain, Phys. Rev. B **34**, 5226 (1986).