bandstructure and applying simple symmetry selection rules as follows:

First, the detailed geometry of the experiment prohibits the observation of odd-parity initial states. This is due to the mechanical constraints of the spectrometer, the highly polarized nature of the synchrotron radiation on beamline I-2, and our selection of a mirror-plane emission geometry.

Secondly, the bulk bandstructure suggests the possibility that for off-normal emission, only odd-parity states may remain populated for the structure of interest. The -0.4 eV peak has been associated with a doubly degenerate A1 band which just becomes populated at A. Away from A toward L, the degeneracy is lifted and one band rapidly depopulates while the other continues to disperse downward in energy. If the downward-dispersing band is the odd-parity partner, this would explain the observed behavior since as the emission direction is moved off the normal, the -0.4 eV peak could only be followed until the upward-dispersing partner depopulates.

In summary, then, we have presented results of an angle-resolved photoemission study of WC (0001). Interpretation of the results was greatly facilitated by preliminary data from a first-principles bulk bandstructure calculation for WC, using the LMTO method. The spectra from 10 eV < hv < 30 eV seem to most closely resemble a 1-D DOS of the A line. Intensity modulation of the initial-state structures is well correlated with the requirements of energy conservation within the framework of the calculated bandstructure. The strong emission-angle dependence of one initial-state feature is ascribed to the consequences of symmetry selection rules arising from a mirror-plane emission geometry and the highly polarized synchrotron light source.

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Summary Abstract: Angle-resolved photoemission study of CO/Co (0001)

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In the study reported here the techniques of LEED and angle- and energy-resolved photoemission have been used to investigate some of the properties of CO/Co (0001). The orientation of the CO molecules was determined using well-established symmetry selection rules. The CO-Co interaction was measured by mapping out the E vs k<sub>z</sub> dispersion of the 4σ and combined 5σ/1π levels of CO in several directions in the Surface Brillouin Zone (SBZ) at two coverages of CO, corresponding to the saturated room and low (170 K) temperature phases. The dispersion can be related to the size and shape of the SBZ and correspondingly to the geometry of the CO overlayer in real space.

After preliminary LEED work, a photoemission study was performed at the Synchrotron Radiation Lab of the University of Wisconsin. Two distinct peaks were seen in the UPS spectra of CO/Co (0001) with p-polarization of the incident light, as is generally observed on other transition metals. The consensus is that the level with the higher binding energy (at ~ 11 eV) corresponds to the 4σ level of the isolated CO molecule, while the level at ~ 8 eV is a superposition of the molecular 5σ and 1π levels, with the 5σ level having undergone a bonding shift of ~ 3 eV with respect to the free molecule.

We determined the orientation of the CO molecules in the room temperature phase of CO/Co (0001) by making use of the polarized nature of the radiation from the synchrotron. The almost complete disappearance of the 4σ level (and presumably the 5σ as well) in the so-called "forbidden" geometry indicates that the molecular axis is preferentially aligned parallel to the surface normal. This is in agreement with the general picture of CO bonding to metals. Further support for this picture comes from observation of resonances in the cross sections of the 4σ and 5σ/1π levels vs photon energy for p-polarized light. The cross sections peak along the surface normal and decrease significantly on going off normal. The dispersion of the 4σ and the 5σ/1π levels was measured in two directions in the SBZ for both phases of CO/Co (0001). The 5σ and 1π levels are not expected to disperse together; however, in the results presented here, we were unable to resolve two distinct peaks in the room temperature phase, although the peak width was observed to change.

The extended SBZ for the ψ 3 × ψ 3 R 30°, corresponding to the room temperature phase as seen in LEED, is given in Fig. 1. The coverage for this structure is θ = 1/3 and the CO nearest neighbor spacing is 4.35 Å. The dispersion was measured along the Γ-M-Γ and the Γ-K-M directions. The results are presented in Fig. 2. There are several observations to be made about these results: (1) The shapes of the 4σ and 5σ/1π dispersions are quite similar, indicating that the 5σ
peak dominates the $5\sigma/1\pi$ dispersion at the photon energies used. The qualitative behavior of these levels is as expected since $\pi$ levels are bonding with respect to the CO–CO interaction and should have a minimum at the $\Gamma$ point, dispersing upwards from there, as seen. On the other hand, $\pi$ levels are antibonding and will disperse downward from $\Gamma$. (2) The magnitude of the $5\sigma$ dispersion is greater than that of the $4\pi$ level. This can be explained by the greater spatial extent of the $5\sigma$ (and also the $1\pi$) level vs the $4\pi$ in real space. More overlap of the $5\sigma$ orbitals should result in a larger bandwidth. (3) In the $\Gamma-M-M'$ direction in the SBZ, the $4\pi$ dispersion is approximately symmetric about the $M$ point and drops back to its original value as $\Gamma$ is approached in the 2nd SBZ. This periodicity is in agreement with the $(\sqrt{3} \times \sqrt{3}) R 30^\circ$ observed with LEED. (4) The $5\sigma/1\pi$ level does not appear to have the same symmetry about the $M$ point. An explanation for this is that the emission of the $1\pi$ level for large collection angles, $^1$ corresponding to large values of $k_\parallel$.

At low temperatures the room temperature phase can be compressed; the dispersion results for this low temperature phase are given in Fig. 3. Shown are zone boundary crossings for the $(2\sqrt{3} \times 2\sqrt{3}) R 30^\circ$ structure proposed by Papp$^6$ (corresponding to $\theta = 0.58$ and a CO spacing of 3.52 Å at 100 K). Important features are the following: (1) The magnitude of the dispersion for both levels is larger than the corre-

![Fig. 1. Extended Surface Brillouin Zone for 2D hexagonal geometries.](image1)

![Fig. 3. Dispersion results for low temperature phase.](image3)

![Fig. 2. Dispersion along $\Gamma-M-M'$ and $\Gamma-K-M$ directions.](image2)

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