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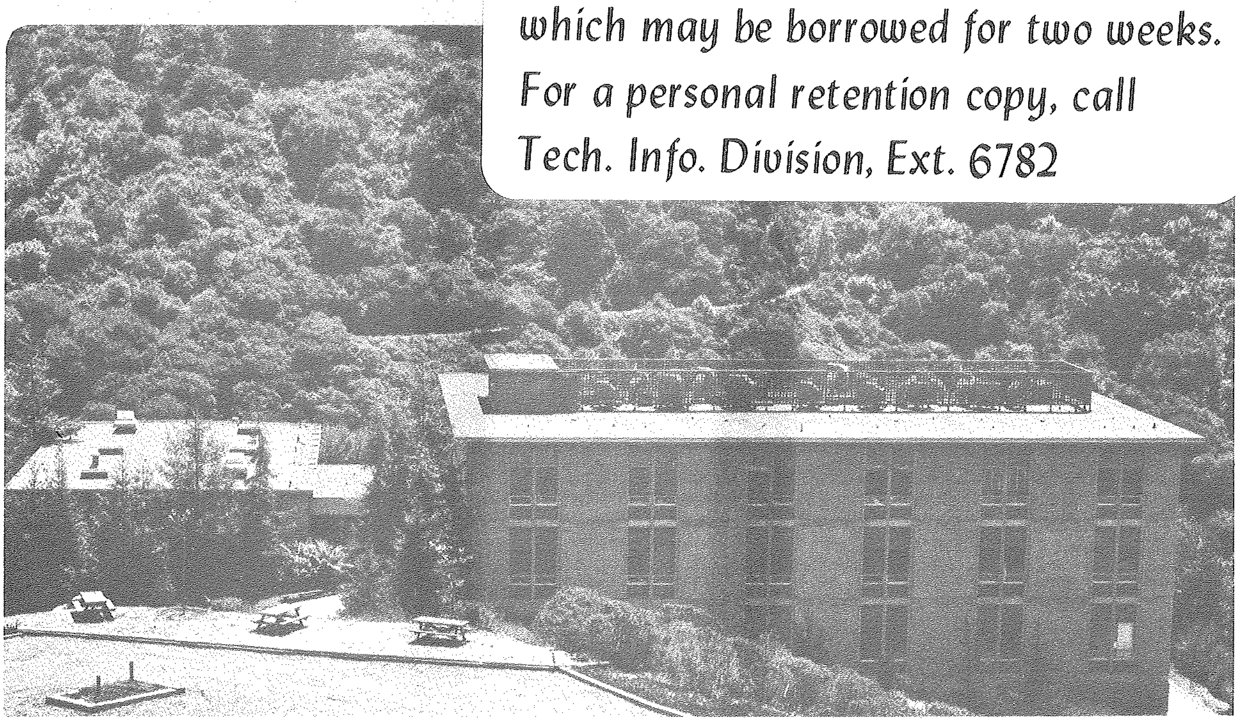

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AN ANGLE-RESOLVED PHOTOEMISSION STUDY OF THE VALENCE BANDS OF W(011) IN THE PHOTON ENERGY RANGE 1100-1250 eV: OBSERVATION OF STRONG DIRECT TRANSITIONS AND PHONON EFFECTS

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ABSTRACT

Angle-resolved photoemission spectra from valence bands of a clean W(011) single crystal, obtained using synchrotron radiation in the range 1100-1250 eV and emission normal to the surface, were observed to show strong dependences on both photon energy and temperature. The spectral variations with excitation energy at ambient temperature agree very well with the predictions of a simple bulk direct-transition model assuming free-electron final-state dispersion and constant matrix elements. The strong temperature dependence observed indicates the importance of phonon-assisted nondirect transitions in Brillouin-zone averaging.

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Angle-resolved photoemission (ARP) spectroscopy is the technique of choice for studying the total valence band structures of solids. An ARP experiment yields, for each valence-band feature, its binding energy B, plus the kinetic energy E <u>and</u> momentum $\hbar\vec{q}$ of the ejected photoelectron, related by

$$h\nu = B + E = B + \frac{\hbar^2 q^2}{2m} \tag{1}$$

Here $h\nu$ is the energy of the exciting photon, and both B and E are referenced to the vacuum level (the reference level may be taken anywhere, but must be consistent throughout). Momentum conservation requires

$$\vec{k}_f = \vec{k}_i + \vec{k}_{h\nu} + \vec{g} \quad , \tag{2}$$

where $\vec{k}_f$ and $\vec{k}_i$ are the crystal momenta of the final and initial electronic states, respectively, $\vec{k}_{h\nu}$ is the photon momentum, and $\vec{g}$ is a reciprocal lattice vector. Inasmuch as $\vec{k}_{h\nu}$ is known and $\vec{g}$ can usually be assessed, the measurement of $\vec{q}$ by ARP will yield $\vec{k}_f$--hence, by Eq. (2), $\vec{k}_i$--provided that photoexcited electrons follow a known dispersion relation as they leave the solid. A bulk direct-transition model based on free-electron dispersion in the (photoexcited) final state was first proposed by Baird et al.,[1] for interpreting high-energy ARP spectra. In this model $\vec{q}$ and $\vec{k}_f$ are parallel for normal emission and are related in magnitude by

$$\frac{\hbar^2 q^2}{2m} = \frac{\hbar^2 k_f^2}{2m} - V_o \quad , \tag{3}$$

where V_o is the effective crystal potential of the final-state electron,[2] referenced to the vacuum level. If Eq. (3) is valid, this model can be used to derive valence-band dispersion relations from high-energy ARP spectra. The model has in fact proved successful for predicting most of the changes in the ARP spectra of copper throughout the range hν = 30-200 eV.[3-6] For higher photon (and thus electron) energies in the 10^3 eV range, the experimental situation is less clear. In this paper we report ARP experiments on W(011) which were carried out to address this problem. We report the first ARP experiments based on synchrotron radiation in the kilovolt x-ray range, using in this case photon energies between 1100 eV and 1250 eV.

All previous valence-band ARP studies in the kilovolt range have employed the fixed-energy photon excitation sources AlKα (1486.6 eV) and/or MgKα (1253.6 eV).[7-13] The early experiments were mostly performed on relatively "soft" metals, at room temperature. While some of the early spectra appeared to show evidence for direct transitions in Au[1] and Cu,[8] the subsequent weight of evidence has proved that, in Cu,[9] Al,[10] Au,[10,11] and Pt,[11] even Angle-resolved photoexcitation spectra at these high energies are comprised of averages over a large volume of the first Brillouin zone (BZ). In fact, a simple real-space "matrix element" model, which was predicated on such averaging, showed qualitatively better agreement with experiment for Au[7,9] and Cu[9] although it was oversimplified.[12,14]

At this point interest shifted from whether zone-averaging occurred in high-energy ARP spectra to why it did. Final-state complexity was proposed first as a mechanism for effectively averaging over much of the BZ.[7,9,11,14] This complexity could arise from bulk or surface scattering processes, or through mixing of several planewave functions by the crystal potential. This proposed explanation has a certain intuitive appeal, particularly because of the large state density and complexity of conduction-band states in the ~10^3 eV energy range.[7] However, two considerations militate against this explanation. First, it is not clear that these complexities in the wave functions of the final state will actually have the effect of zone averaging. Second, it is becoming increasingly clear that ARP spectra cannot be interpreted by simply referring to conduction band functions, because only very special (free-electron-like) functions actually propagate into the ARP detectors.

Shevchik's[15] observation that phonon-assisted nondirect transitions should modify high-energy ARP valence-band spectra rendered the above discussion moot in the high-temperature (or high-energy) limit, which applies to the cases mentioned above. Thermal-diffuse (phonon-assisted) scattering reduces the fraction of transitions that can be direct to

$$W(T) = \exp(-1/3\langle U^2(T)\rangle g^2) \quad ,$$

the Debye-Waller factor, where $\langle U^2(T)\rangle$ is the mean-square atomic displacement. The temperature dependence of valence-band spectra expected as a result of thermal-diffuse scattering was verified experimentally in an angle-resolved photoemission study of Cu at $h\nu \cong 45$ eV by Williams et al.[16] However, later attempts to observe such effects in the x-ray photoemission spectra of Au and Pt near liquid nitrogen temperature ($\geqslant$77 K) did not show any temperature dependence, leading Dabbousi et al.[11] to conclude that final-state complexities were responsible for zone averaging at high energies. More recently, however, Hussain et al.[13] have observed both temperature-dependent and direct-transition effects in angle-resolved photoemission spectra from tungsten at a fixed photon energy of 1486.6 eV. Our present study of angle-resolved photoemission valence spectra from W(011) single crystal using synchrotron radiation in the 1100-1250 eV range agrees with their observations. It also demonstrates the existence of a very strong temperature dependence, indicating the importance of phonons for BZ averaging, as well as showing good agreement between the observed spectra and predictions based on the nearly-free-electron direct-transition model.

Experiments were carried out on the new ultra-high vacuum double crystal monochromator at the Stanford Synchrotron Radiation Laboratory using photon energies in the range of 1100-1250 eV. With beryl($10\bar{1}0$) crystals installed, this instrument provides highly monochromatic radiation in the energy range 800-1550 eV, with a photon resolution of 0.35-0.85 eV.[17] The angle-resolved spectrometer with multichannel detection capability used in these experiments have been described elsewhere.[18] Tungsten was selected for study because it has a rather high Debye-Waller factor (W) of ~0.65 at ambient temperature for excitation in the range of energy 1000-1250 eV. A tungsten single crystal was oriented to within 0.5° of (011), mechanically polished, chemically etched, and cleaned in situ by high-temperature oxygen exposure (1.0×10^{-7} Torr at ~2300 K) followed by flashing at ~2600 K. Temperatures were measured with an infrared pyrometer (Ircon Model 300 C). Operating pressures were $\leq 3 \times 10^{-10}$ Torr. Low energy electron diffraction (LEED) was used to verify high surface order, and Auger spectra confirmed surface cleanliness. Spectra were obtained for normal emission using various photon energies between 1100 eV and 1250 eV at a specimen temperature of 295 K, as well as in two cases ($h\nu$ = 1100 eV and 1250 eV) at two different temperatures of 295 K and 700 K. All the valence-band spectra were recorded at a constant analyzer pass energy of E_p = 80 eV giving a total experimental resolution of 1.2 eV for the $W4f_{7/2}$ core level. The experimental spectra were smoothed with Weiner filters using a 2.0 eV symmetric Gaussian function as the signal estimate.[19] No corrections for inelastic scattering have been made in any of the experimental data reported here. The Fermi level is specified in all spectra with respect to the $W4f_{7/2}$ binding energy, which is taken to be 31.5 eV.[20]

Experimental valence-band spectra obtained along normal-electron-emission direction (see inset in Fig. 1) at four excitation energies (1100 eV, 1150 eV, 1175 eV, and 1200 eV) are shown as solid curves in

Fig. 1. All spectra were normalized to a constant maximum height. There are marked changes in the relative intensities of the two prominent peaks at binding energies of ~2.3 eV and ~5.0 eV, but especially in the 5 eV peak.[21] This is a strong indication of the presence of direct transitions because, according to any matrix-element model, one would not expect to observe significant changes in spectra with such a relatively small change in photon energy. Figure 1 also shows the results of previously discussed direct-transition-model calculations based upon a relativistic augmented-plane-wave band structure for tungsten by Christensen and Feuerbacher.[22] Averaging over the acceptance cone of the analyzer of ~±2° has been included, together with a momentum broadening $\Delta\vec{k}^f$ parallel to $\vec{k}^f$ because of inelastic scattering with an estimated mean free path of ~10Å (Ref. 23). The latter effect has not significantly changed the curves. The contributions of phonon-assisted nondirect transitions have also been approximately included by using a procedure as described in detail by Hussain et al.[13] Briefly, the intensities as predicted by the pure direct-transition model [I_{PDT}] were added to the total density of states [I_{DOS}] after being weighted by the Debye-Waller factor W(T) according to the equation

$$I_{theory}(E) = W(T)\ I_{PDT} + [1 - W(T)]\ I_{DOS} \qquad (1)$$

All spectra shown in the Fig. 1 involve $\vec{g} = (0,6,6)2\pi/a$, where $a = 3.16$Å is the lattice constant for tungsten, and thus a Debye-Waller factor of 0.64 at the ambient temperature of 295 K. Therefore, approximately 64 percent of the transitions are expected to be direct according to the model as first proposed by Shevchik.[15] There is, in general, very good agreement as to the changes predicted and observed in the relative intensities of the main components, as well as in the energy position of the peak/shoulder at higher binding energies. This peak is observed at a binding energy of 5.5 eV for the spectrum obtained at hν = 1100 eV and is shifted to 5.0 eV at hν = 1200 eV. This energy shift noted is in full agreement with DT theory. Figure 2 further indicates the strikingly high degree of agreement between experiment and theory for the relative intensity changes of the two main peaks. In this figure, the relative intensity of the ~5 eV peak with respect to the ~2.3 eV peak is plotted against five different excitation energies ranging from 1100 eV to 1250 eV. All of the relative changes are correctly predicted by the theory. Minor discrepancies in the prediction of higher intensity for the 5 eV peak than is experimentally observed can be attributed to the matrix-element effects that are neglected in this direct-transition model. Checking the location of the initial states contributing to intensities near 5 eV in the reduced zone and inspecting the tungsten band structure[22] shows that these states contain significant components of plane-wave character, thus explaining their lower effective cross section compared to the 5d-dominated bands[24] associated with the peak at ~2.3 eV. However, the added expedient of allowing for matrix-element effects in the direct-transition model via the plane-wave final-state approximation discussed above has been shown in prior studies to be inadequate.[3,12,14] Therefore, any future improvement of the theory may require the inclusion of both direct transitions and more accurate matrix elements.[12,24,25]

Finally, in Fig. 3, we show two spectra obtained at photon energies of 1100 eV and 1250 eV which exhibit both very strong temperature dependences and a very strong sensitivity to change in excitation energy. The Debye-Waller factors are indicated at both temperatures. The $\vec{g}$ vector involved in excitation at $h\nu = 1100$ eV is $(0,6,6)2\pi/a$, whereas combinations of two, g's of $(0,6,6)2\pi/a$ and $(0,7,7)2\pi/a$, are involved for spectra at 1250 eV. The two spectra are strikingly different at the ambient temperature, especially in regards to the relative intensity of the ~5 eV peak. However, upon heating the specimen to 700 K they converge to nearly the same shape. This behavior is thus consistent with a large direct-transition component at lower temperatures and complete zone averaging due to phonon effects at higher temperatures.

In conclusion, we have very clearly demonstrated, in support of prior work,[16] that direct transitions can be observed in angle-resolved XPS valence-band spectra from materials with large Debye-Waller factors. Phonon-assisted non-direct transitions, not final-state complexity, are the dominant source of the Brillouin-zone averaging. A simple bulk direct-transition model with a plane-wave final state and constant matrix elements gives a very good first-order description of spectral changes with photon energy, although a more exact model including both direct-transition and matrix-element effects would be desirable. Furthermore, future variable-hν photoemission experiments in the presently available synchrotron radiation region of ~800-1500 eV, combined with more favorable conditions of low temperatures ($\leqslant$100 K) and higher analyzer angular resolution ($\leqslant 2^\circ$) could provide a rather straightforward technique for studying the valence-band structures of solids.

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FIGURE CAPTIONS

Fig. 1. Valence-band photoemission spectra obtained for the normal electron emission direction at four different excitation energies, compared with direct-transition theory. The theoretical curves were obtained from a weighted sum of the pure direct-transition curves and the density of states, as explained in the text and Eq. (1). The experimental geometry is also shown in the inset.

Fig. 2. Photon-energy dependence of the relative intensity of the peak near 5 eV as measured with respect to that at ~2.3 eV. Both experimental values and direct-transition theoretical values are shown.

Fig. 3. Temperature dependence of tungsten normal emission valence-band spectra for excitation energies of 1100 and 1250 eV. The temperatures and their associated Debye-Waller factors are given in the figure, together with the intensity of the ~5 eV peak as measured relative to the ~2.3 eV peak.

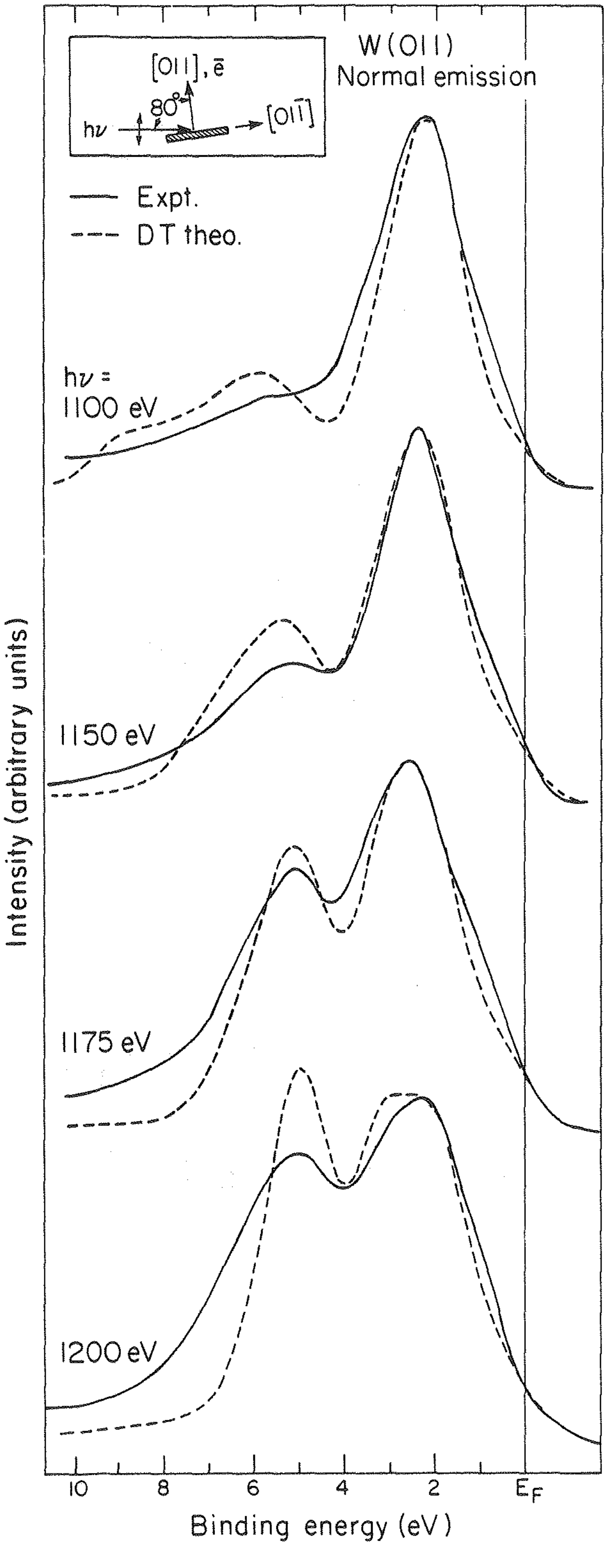

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Figure 1

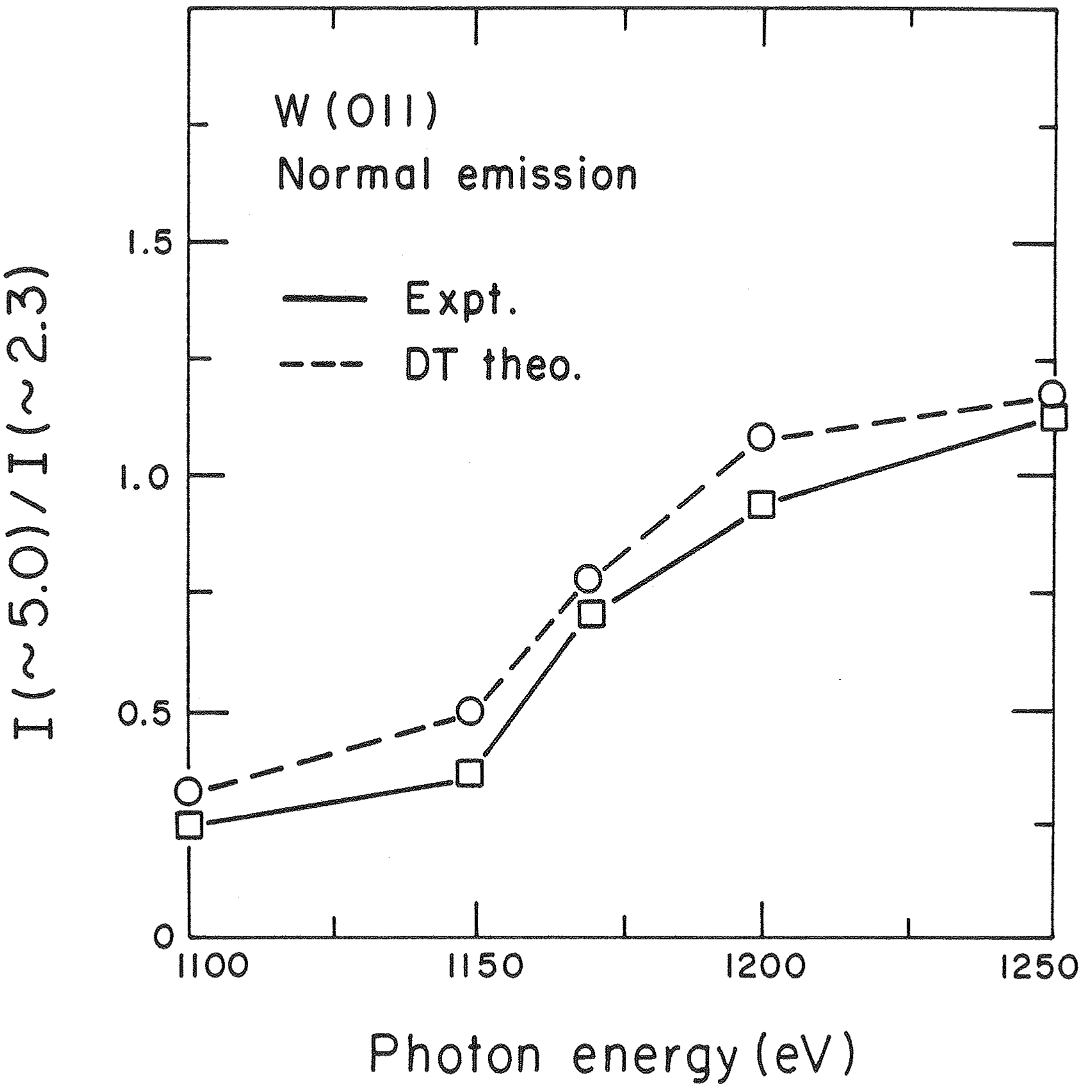

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Figure 2

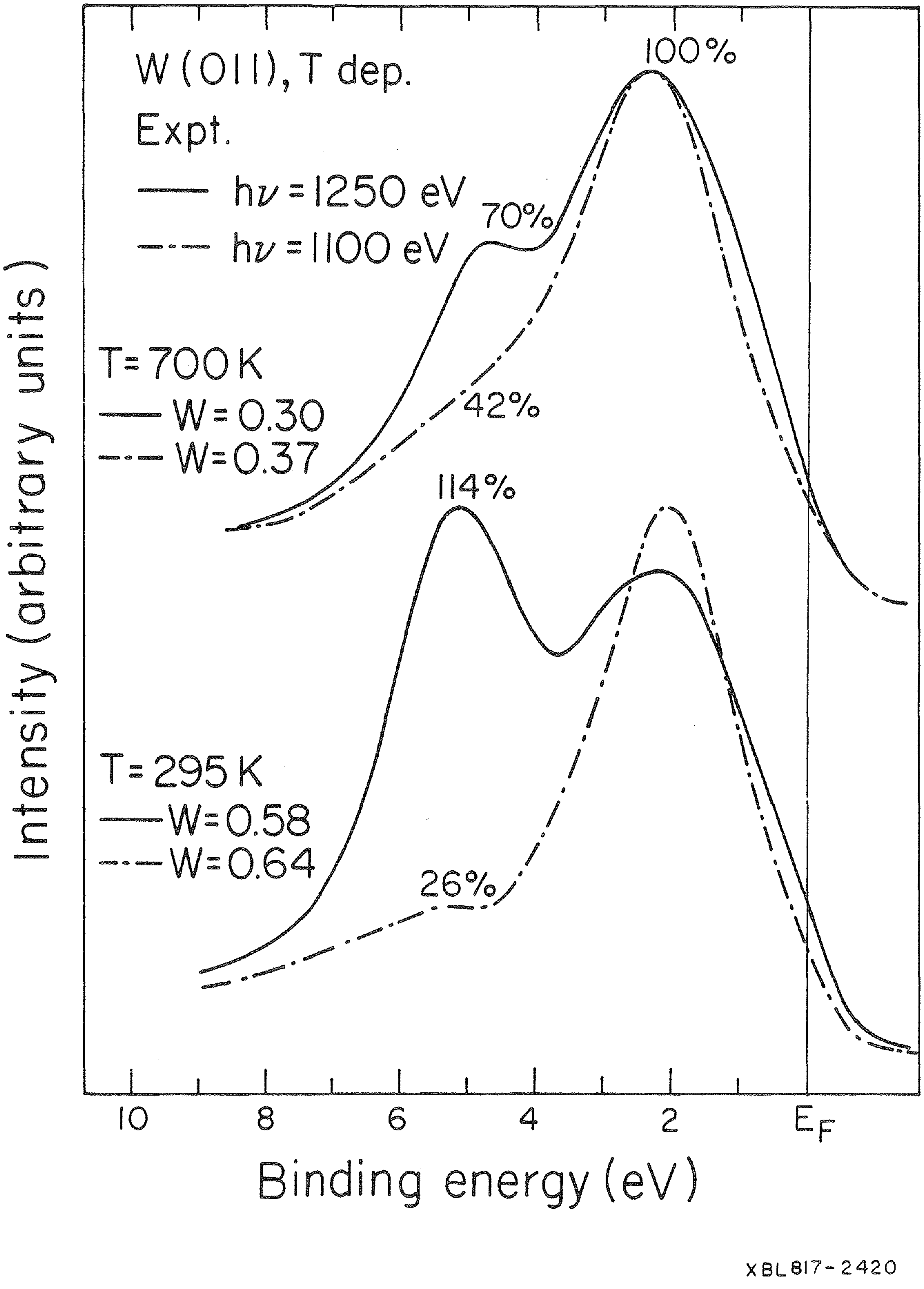

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Figure 3