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## Temperature-dependent broadening of the surface core-level spectra of W{110}

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**Abstract.** We present the first measurement of phonon broadening on a tungsten surface using surface-sensitive high-resolution photo-electron spectroscopy. We find that the core-level spectra, obtained at four different photon energies, are well fitted by two peaks: from the surface and from the bulk atoms. The surface peak is shifted to lower binding energy by  $0.29 \pm 0.1$  eV. We have determined the lineshape parameters of these peaks at 290 and 100 K by a non-linear least-squares fitting procedure in which the core levels are represented by peaks having a Doniach–Sunjic lineshape (FWHM, 50 meV;  $\alpha = 0.06$ ) convoluted with a Gaussian, representing the instrument response function and the photon broadening. We find the Gaussian width (FWHM) to be  $0.175 \pm 0.014$  eV at 100 K and  $0.185 \pm 0.011$  eV at 290 K. These values for the Gaussian broadening are in excess of the instrumental broadening of  $0.162 \pm 0.005$  eV and correspond to convolution with an additional Gaussian of width  $0.07 \pm 0.03$  eV at 100 K and  $0.09 \pm 0.02$  eV at 290 K. Because these values change with temperature, we ascribe them to phonon broadening of the photo-emission line. These latter values are in good agreement with the calculation of the expected phonon broadening of bulk tungsten by Sebilliau and co-workers. We also describe the relevance of this measurement to the decomposition of surface core-level spectra from the room temperature results for W{100} and W{111} surfaces, and to the analysis of surface core-level spectra from stepped tungsten surfaces.

### 1. Introduction

Surface core-level spectroscopy (SCLS) has been shown to be a useful technique for investigating the structure of clean adsorbate covered transition metal surfaces (Citrin *et al* 1978, Eastman *et al* 1982, Egelhoff 1987, Purcell *et al* 1988a, Spanjaard *et al* 1985). The surface core-level shifts result from changes in the electrostatic potential at the surface due to charge transfer between the surface layers and the bulk. This charge transfer is a direct consequence of the reduction in coordination number at the surface and the subsequent rearrangement of bonding charge between the surface layers and the bulk.

A characteristic feature of SCLS experimental data is the small size of the surface-induced shift in binding energy, relative to the width of the photo-emission peaks from the core levels. In tungsten, only for the closely packed {110} surface can two well separated core levels be seen (Van der Veen *et al* 1982). On the more open surfaces,

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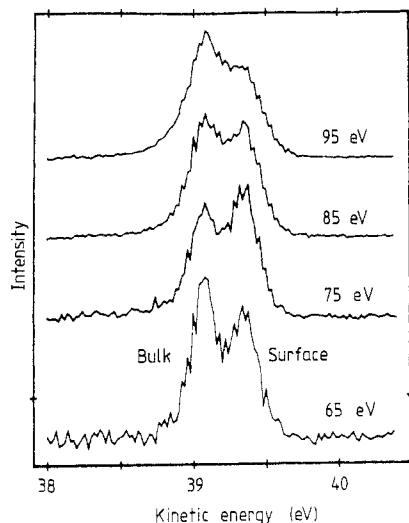
such as  $W\{100\}$ ,  $W\{111\}$  and stepped tungsten surfaces, two or more different surface atom sites have coordination numbers which differ significantly from each other and the bulk. Each of these surface atom sites gives rise to a core level at a different binding energy, resulting in a photo-emission spectrum which contains three or more strongly overlapping peaks (Purcell *et al* 1987, 1988a, b, Wertheim *et al* 1984, Guillot *et al* 1984, Jupille *et al* 1985). To extract the surface core-level binding energies from these data a non-linear least-squares fitting technique is used, in which each displaced core level is represented by a single peak. Knowledge of the lineshape of these peaks is, therefore, essential to determine accurately the core-level shifts for the more complex surfaces. It is surprising then, given the central role played by the lineshape in the analysis of SCLS data, that little experimental or theoretical effort has been applied to this area.

The observed lineshape of a peak in a photo-emission spectrum from a core level is influenced by several different processes. The underlying shape of the peak, arising from the decay of the core hole, is Lorentzian. Excitations of electron-hole pairs at the Fermi level contribute to an asymmetry in the lineshape, resulting in the well known Doniach-Sunjic (DS) (1970) lineshape. In addition to these electronic effects the photo-emitted electron may gain or lose energy to both bulk and surface phonons as it is emitted from the surface, producing a Gaussian broadening of the peak lineshape. A further contribution to the peak shape comes from the effect of inhomogeneities on the surface. These arise from a distribution in the type and geometry of different coordination sites on the surface. Although this form of broadening does not derive directly from the photo-emission process, its manifestation in the experimental data is similar. The form of this broadening has previously been assumed to be Gaussian, but for more complicated systems, such as a disordered surface resulting from an order-disorder phase transition, this broadening function will be somewhat more complex. Finally, the finite resolution of the experimental equipment used to measure the spectrum must be included. In most cases the instrument response function is taken to be Gaussian and may be calculated from the expected or measured performance of the experimental apparatus.

Recently, however, Sébilleau *et al* (1987) have calculated the lineshape expected for the surface and core levels on the  $\{100\}$  face of tungsten and tantalum. They found that phonon broadening of the core level was significant both in the bulk and at the surface compared with the lifetime broadening and that the magnitude of the broadening slightly increased at the surface. On both surfaces the broadening was found to be temperature dependent, increasing by an observable amount between 100 and 600 K.

In this paper, we present surface core-level photo-emission spectra obtained from a  $W\{110\}$  single-crystal surface at room temperature (290 K) and a low temperature (120 K). We observe different Gaussian broadenings of the core-level lineshape at these two temperatures and compare our experimental values with previous theoretical calculations of the phonon broadening at a tungsten surface.

We have examined the  $W\{110\}$  surface rather than  $W\{100\}$  used in the theoretical calculations (Sébilleau *et al* 1987) to avoid the changes induced in the surface core-level spectra associated with the thermal reconstruction of the  $W\{100\}$  surface (King 1983). The relatively small changes in lineshape due to temperature are easily confused by the changes associated with the reconstruction of the surface (Purcell *et al* 1988b). In addition, the nature of the clean high-temperature phase has not yet been fully determined, and there is the possibility of additional inhomogeneous broadening associated with a disordered surface. In contrast, the clean  $W\{110\}$  surface has been shown to be unreconstructed throughout the accessible temperature range (Chung *et al* 1986),



**Figure 1.** Tungsten  $4f_{7/2}$  core level at four different photon energies from a clean W(110) surface. All these spectra have been shifted to the same apparent kinetic energy, which is that of the 75 eV spectrum (see text).

making it an ideal surface to demonstrate the effects of the change in phonon broadening with temperature.

## 2. Experimental details

In our experiments we use a tungsten single crystal cut to within  $0.5^\circ$  of the {100} face. This crystal was bulk cleaned by repeated heating to 1800 K in oxygen at  $10^{-6}$  mbar and flashing in vacuum to 2400 K. The data were taken using a VG ADES 400 angle-resolving photo-electron spectrometer (base pressure,  $4 \times 10^{-11}$  mbar) attached to a toroidal grating monochromator on beamline 6 at the Synchrotron Radiation Source at Daresbury Laboratory. This monochromator provides high-resolution VUV radiation with photon energies 60 to 95 eV. The light was incident on the sample at  $70^\circ$  to the normal, and photo-electrons were collected at normal emission. The temperature of the crystal was measured using a (W-25% Re)-(W-3% Re) thermocouple tied to the crystal.

## 3. Results

Figure 1 shows a typical set of photo-emission data from the W{110} surface at 290 K. These spectra have been normalised in intensity after the subtraction of a linear background. The spectra have been aligned to an arbitrary binding energy based on the 75 eV spectrum by rigidly shifting the kinetic energy of each spectrum by the difference in photon energy. This procedure is required as Fermi level spectra, required to calibrate the absolute binding energy scale, could not be taken during the data collection because of technical problems.

The minimum escape depth can be seen to occur at 75 eV photon energy, corresponding to a photo-electron kinetic energy of about 39 eV, as evidenced by a maximum in the surface peak intensity. This is in good agreement with previous results.

#### 4. Fitting methodology

A non-linear least-squares fitting technique is used to analyse the experimental spectra. The photo-emission spectra are simulated by the sum of two DS peaks convolved with a Gaussian. The DS peak is expected to be a good approximation to the observed photo-emission peakshape in tungsten. Both bulk and surface peaks have the same Lorentzian widths and asymmetry parameters, as the decay process of the core-hole at the surface is identical with that in the bulk. The convolution of the DS peaks with a Gaussian represents the combined effects of instrumental resolution, phonon broadening and inhomogeneous broadening.

During the fit the width and asymmetry parameter of the DS peaks are fixed to the values obtained by Wertheim *et al* (1984) (Lorentzian FWHM, 50 meV; asymmetry parameter, 0.06) and the binding energy of the bulk peak is fixed to value determined from surface core-level spectra taken from an oxidised W{111} surface (Purcell *et al* 1988a). The width of the Gaussian, the energy position of the surface peak and the amplitudes of the bulk surface peaks are varied to obtain the best fit.

This fitting procedure assumes that both surface and bulk photo-emission peaks have the same phonon broadening and that the instrument response function is Gaussian in form. The first assumption is justified from the calculations of Sébilleau *et al* (1987) who found that the additional broadening from surface phonons is very small; for a W{100} surface an extra broadening of 20 meV is expected. The second is considered a reasonable assumption for our electron analyser, and, as its contribution does not change with temperature, any changes may be attributed to changes taking place in the sample.

The results of applying this fitting procedure are shown in figure 2 where the DS peaks are shown and summarised in table 1.

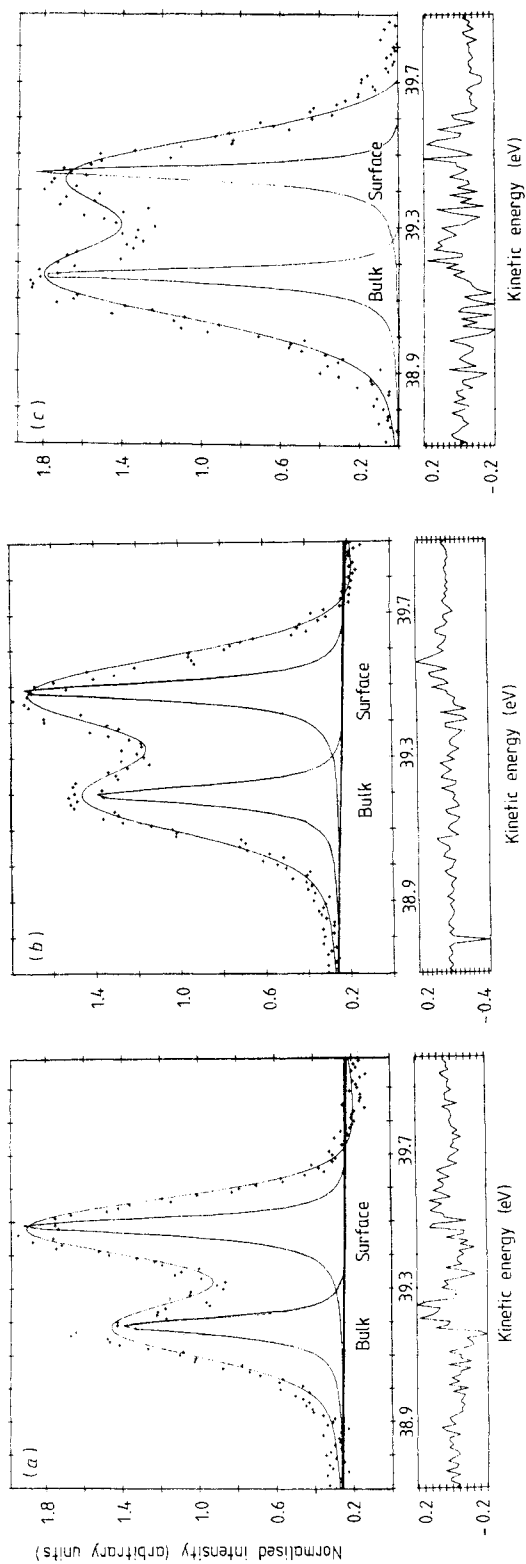
It was found that it was possible to obtain excellent fits of the spectra using only two peaks. No improvement to the fit was found if three peaks were used instead of two. Rosengren (1981) estimated that the second-layer core level on W{110} should be shifted by 20 meV from the bulk peak. In the current analysis, we are therefore effectively folding this contribution into what is described as the 'bulk peak', i.e. we are assuming that the second layer, third layer, etc, contributions are all included into a single peak. The surface core level was found to be shifted by  $0.29 \pm 0.01$  eV to lower binding energy, in close agreement with previous experimental and theoretical work. The Gaussian broadening was found to be  $0.175 \pm 0.014$  eV at 290 K and  $0.175 \pm 0.014$  eV at 100 K.

#### 5. Discussion

The total broadening may be expressed as a sum of the components in quadrature, if all are Gaussian in form. So

$$\Gamma_{\text{total}}^2 = \Gamma_{\text{inst}}^2 + \Gamma_{\text{phonon}}^2 + \Gamma_{\text{inhom}}^2.$$

On the assumption that the inhomogeneous broadening, which results from disorder, is zero, then we can determine the phonon broadening if we know the width of the instrument response function. This can be evaluated from the calculated resolution of the monochromator ( $0.100 \pm 0.002$  eV) and the estimated performance of the electron analyser ( $0.123 \pm 0.002$  eV). If we assume that these are both Gaussian, a value of  $0.162 \pm 0.004$  eV is obtained for the system instrument response. This has been verified



**Figure 2.** A set of fitted W(110)  $4f_{7/2}$  core-level spectra at 75 eV photon energy and at three different crystal temperatures. The crystal has been (a) cooled to 100 K, (b) held at room temperature (290 K) and (c) heated to 700 K. The best fit curves with two peaks are shown. The energy scale is kinetic energy, with the surface peak lying to the higher kinetic energy (lower binding energy) side of the bulk. The residuals are shown beneath the spectra. In (c) the broadening in the spectrum is visible as the loss in the depth of the 'valley' between the surface and bulk peaks.

**Table 1.** Results of applying the fitting procedure.

Temperature (K)	Surface shift (eV)	$\Gamma_G$ (eV)	$\Gamma_{\text{phonon,exp}}$ (eV)	$\Gamma_{\text{phonon,theor}}$ (eV)
$100 \pm 20$	$-0.29 \pm 0.01$	$0.175 \pm 0.014$	$0.071 \pm 0.025$	0.07
$290 \pm 10$	$-0.29 \pm 0.01$	$0.185 \pm 0.011$	$0.092 \pm 0.021$	0.09

experimentally by measuring the apparent width of the Fermi level; the value was found to be  $0.16 \pm 0.01$  eV. We can now decompose the measured broadening into its components, extract the excess Gaussian broadening in the spectrum and compare it with the calculated values for the phonon broadening. The results obtained are shown in table 1. The theoretical estimates of Sébilleau *et al* (1987) for the bulk phonon broadening of the W 4f core level are also shown for comparison. The agreement is remarkably good, given the approximations made above.

The good agreement between our results and those expected on the basis of theoretical calculations have several implications. The primary cause of the broadening of the core-level line is phonon broadening and the second cause is from lifetime broadening from the decay of the 4f core-hole. We find that a value of 50 meV fits the lifetime width for both this and other data. In this particular study, we fixed this value because of the poor statistics of the data that we have collected. With better quality data, a simultaneous estimate of the DS width and the phonon broadening could be made.

We have shown that all the Gaussian broadening of the core level can be accounted for by the instrument response and a contribution from phonons, via a comparison with theory. This implies that the inhomogeneous broadening on the W{110} surface is relatively small, as expected on a smooth close-packed unreconstructed surface. This lack of additional broadening has implications for other tungsten surfaces, in particular the W{100} surface.

Wertheim *et al* (1984) have reanalysed data taken by Van der Veen *et al* (1982) on the W{111} and W{100} surfaces to obtain accurate lineshape parameters. In both cases they found that the 'surface peak' had a different Gaussian broadening from those of the underlayer and bulk peaks. This was tentatively explained as being due to crystal-field splitting at the surface. However, we have shown (Jupille *et al* 1985) that a good fit to the W{111} data is obtained using two underlayer peaks, in addition to the surface and bulk peak. For this model, all the core levels have identical lineshapes. The results obtained for the surface core-level binding energy shifts are then in considerably better agreement with theoretical expectations. We have demonstrated (Jupille *et al* 1988) that the Gaussian broadening found at the W{100} surface by Wertheim *et al* cannot be accounted for by this instrument response and the additional surface phonon broadening. In this case, we attribute the excess broadening to an inhomogeneous component, resulting from a distribution of surface core-level binding energies as a consequence of a disordered W{100} surface at room temperature. The results presented here validate the estimates used for the phonon broadening in that paper and reinforce the conclusions reached as to the nature of the high-temperature phase of the W{100} surface.

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