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UNOCCUPIED BAND CRITICAL POINT ENERGIES OF NOBLE METALS DETERMINED WITH BREMSSTRAHLUNG ISOCHROMAT SPECTROSCOPY

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We show that Bremsstrahlung Isochromat Spectroscopy (BIS) is a powerful and simple tool to determine unoccupied band critical point energies of solids. We determine some critical point energies of the noble metals and compare these to band structure calculations. We also determine the energy dependent lifetime broadening providing information about the imaginary part of the self energy corrections.

ONE PARTICLE ENERGY band dispersion relations and the influence of many body effects are of fundamental importance for the understanding of physical properties of solids. Modern computational methods have facilitated complete band structure calculations, the accuracy of which, as well as the validity of the one electron approximations made, have been a subject of intense investigation.

Experimental tools for studying band structres are Bremsstrahlung Isochromat Spectroscopy (BIS) and K Resolved Inverse Photoelectron Spectroscopy (KRIPES) for the unoccupied states and X-ray Photoelectron Spectroscopy (XPS) and Angle Resolved Photoelectron Spectroscopy (ARPES) for the occupied states.

In the high energy spectroscopies (BIS and XPS) the information obtained is more directly related to the density of states because of averaging over the whole Brillouin zone. In KRIPES and ARPES additional information concerning the energy dispersion relations can be obtained. However because these experiments must be carried out at low energies both initial and final states are sensitive to the crystal potentials and many body effects. To separate the contributions to the spectra from initial and final states one must resort to elaborate measurements.

BIS spectra of the noble metals are known to exhibit sharp features in the energy range up to 10 eV above the Fermi level [14, 15]. In this paper we present new data for polycrystalline Cu, Ag and Au and use the intimate connection between the observed features and calculated energy band critical points to determine the real and imaginary parts of the one particle self energies.

The BIS spectrometer is part of an XPS apparatus equipped with a large solid angle monochromator for AlKα radiation ($\hbar\omega = 1486.7$ eV) [1]. The BIS electron gun is a cylindrical Pierce gun [2], producing a wedge shaped beam with a rectangular cross section of $5 \times 1.3\,\text{mm}^2$ at the sample [3]. The polycrystalline Ag, Au and Cu samples were cleaned in ultra high vacuum by either scraping or argon ion etching. XPS was used to check for surface contamination.

The BIS spectra of Cu, Ag and Au are shown in Fig. 1. The spectra of the 3 metals are qualitatively similar as expected because of similar electronic and crystal structures [4]. The most prominent features are a plateau just above the Fermi energy followed by a sharp rise which occurs at different energies for the three metals. At even higher energies more structure is visible although the spectrum seems to gradually evolve into a structureless mononically increasing curve.

The sharp rise occurring between 3 and 4 eV above E_F is most probably a result of crossing the $L_1(L_4^+)$ critical point often referred to as the $L(7)$ point. At this critical point a rather flat band in the L–W direction begins with a corresponding high density of states. An accurate determination of the critical point energy can be made by comparing to band structure density of states calculations. Since the high energy density of states for Cu and Ag with a sufficiently small energy grid could not be found in the literature, we calculated these with the *KKR* method using 5 and 3 phase shifts for Cu and Ag respectively. In the calculations we use the self-consistent potentials of Moruzzi *et al.* [21] which are obtained by the application of the local density approximation in density functional theory. The Au density of states was taken from Christensen [5]. These are shown as solid lines in Fig. 1.

The experimental resolution was incorporated by convoluting the theoretical density of states with a Gaussian of width 0.85 eV. The width was chosen to

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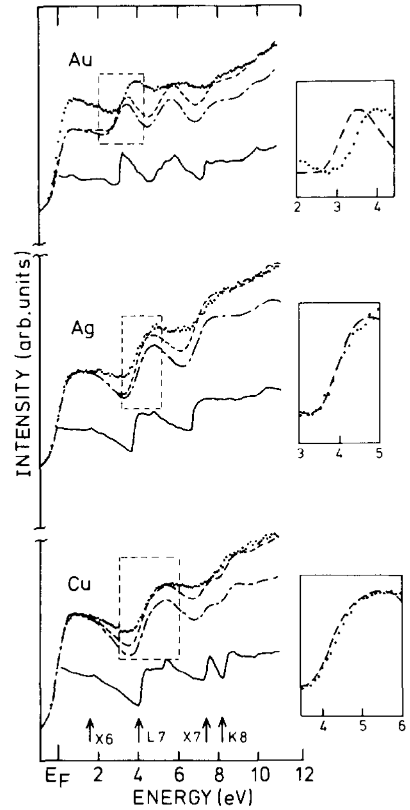

Fig. 1. Experimental and theoretical spectra of the unoccupied bands. Solid: theoretical DOS's, dash–dotted: theoretical DOS's convoluted with a Gaussian of 0.85 eV FWHM, dashed: theoretical DOS's convoluted with experimental ELS curves and an additional Gaussian broadening of 0.4 eV, dotted: the experimental spectra. The inserts are discussed in the text.

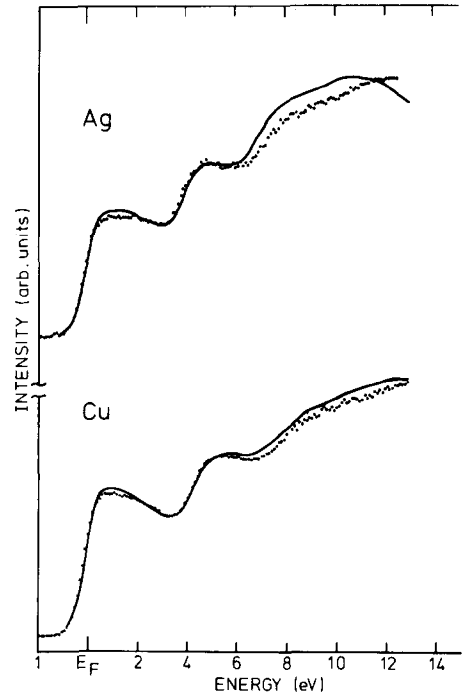

Fig. 2. Experimental and theoretical BIS spectra. Dotted: experimental, solid: theoretical spectra convoluted with an energy dependent Lorentzian discussed in the text.

best fit the shape of the Fermi level onset of the spectrum. The resulting theoretical curves are also shown in Fig. 1. In addition to the experimental broadening the measurements also contain a contribution from energy loss, suffered by the incident electron. This energy loss contribution was determined by measuring the energy loss spectrum at an incident energy of 1500 eV for each metal [6]. The dashed line is a result of a direct convolution of the theoretical density of states with the energy loss spectrum as measured. Following this procedure we see that the relative intensity at the Fermi level and at about 10 eV are in extremely good agreement with experiment for Cu and Ag, which indicates that the transition matrix elements are nearly energy independent for these materials. For Au the agreement is less satisfactory. Large differences between experiment and theory are seen in the relative intensity at E_F and high energies as well as in the overall structure in the density of states. The origin of this discrepancy is not known and should be a subject for future investigations.

In the insets of Fig. 1 an enlargement of the region around the $L(7)$ critical point is shown. Here the theoretical curve is shifted vertically and scaled to match the experimental curve allowing an accurate determination of the energy shifts. Using the tabulated $L(7)$ critical point energies and the shifts we determine experimental $L(7)$ energies. Since optical measurements can deduce the $L(6)$–$L(7)$ gap we can also determine experimental $L(6)$ critical point energies. These, together with various band structure calculated values, are given in Table 1.

The best overall agreement for Cu is the calculation of Janak *et al.* [7] but we should note that these authors include a linear energy dependent shift in the final calculation. The agreement with our calculation is surprisingly good for the $L(7)$ critical points for both Cu and Ag and reasonable for the $L(6)$ critical point. For Au the relativistic calculations of Christensen result in critical point energies which are 0.4 eV too high for $L(6)$ and 0.4 eV too low for $L(7)$ resulting in a large error in the $L(6)$–$L(7)$ gap.

It is interesting to note that the values for the $L(6)$ critical points as calculated by Jepsen *et al.* [7] are all too low which could explain why their L neck radii in the Fermi surface are consistently too large.

In addition to the $L(7)$ critical point there are several other critical points in the energy region from the Fermi level to 10 eV, the calculated positions of which

Table 1. List of theoretical and experimental L(6) *and* L(7) *critical point energies for* Cu, Ag *and* Au. *All values are in* eV

	L_6 (th)	L_7 (th)	L_7 (exp)	L_7-L_6 (exp)	L_6 ("exp")
Cu	−1.15	4.10[a]	4.2 (0.1)[k]	5.05 (0.1)[g]	−0.85 (0.1)[a]
	−0.61	3.94[b]			−0.9 (0.2)[j]
	−0.90	4.26[c]			
	−1.22	4.44[d]			
	−1.10	3.79[e]			
Ag	−0.48	3.82[a]	3.8 (0.1)[k]	4.2[h]	−0.4 (0.1)[a]
	−0.16	3.33[f]			
	−0.62	3.55[d]			
	−0.58	3.79[c]			
Au	−0.72	3.01[f]	3.4 (0.1)[k]	4.5[i]	−1.1 (0.1)[a]
	−1.27	3.68[d]			
	−1.35	3.18[e]			

[a] Discussed in the text.
[b] Burdick, [10]
[c] Janak *et al.* [9]
[d] Lässer *et al.* [4].
[e] Jepsen *et al.* [7]
[f] Christensen [5]
[g] Beaglehole *et al.* [11].
[h] Rosei *et al.* [12].
[i] Chen *et al.* [13].
[j] Knapp *et al.* [8].
[k] Present work.

are shown in Fig. 1 for Cu. However the experimental broadening washes out these structures preventing an accurate determination of their energies.

In comparing theory with experiment as in Fig. 1 another problem is evident. Even after the experimental broadening we see that the theoretical features are still much too sharp. There must be an additional broadening which increases with energy above the Fermi level. We attribute this to lifetime broadening caused by the imaginary part of the self energy corrections to the calculated band structure. In Fig. 2 we show results of convoluting the theoretical curve for Cu and Ag (solid lines in Fig. 1) with a Lorentzian with an energy dependent width (Γ) $\Gamma = 0.09(E - E_F)$ to simulate the lifetime broadening. This results in an almost embarrassingly good agreement with experiment for both Cu and Ag. The largest discrepancies remaining are a shift of about 0.3 and 0.4 eV to higher energise of the step at about 8 and 7 eV for Cu and Ag respectively. This suggests that the theoretical $X7$ and $K8$ critical point energies are about 0.3–0.4 eV too low. The lifetime broadening as introduced above results in a width of 0.9 eV at 10 eV above E_F in good agreement with the photoemission measurement of Knapp *et al.* [8].

The good agreement up to about 5 eV might be accidental and is in any case surprising for several reasons. First of all the real part of the self-energy corrections due to many body effects is expected to be at least several tenths of an eV [16–18]. In fact the calculation of Janak *et al.* [9] for Cu includes a self-energy correction amounting to 0.32 eV at 4 eV above E_F whereas our calculation does not include any such correction. Secondly it is difficult to understand why the real part of the self-energy correction could be so small with a fairly strongly energy dependent imaginary part. Thirdly it should be noted that the agreement is only good up to about 4 or 5 eV above E_F. There is a considerable discrepancy for the L_6 energy below E_F and also the *d* band edge (the X_5 point) is found at −1.63 and −3.24 eV for Cu and Ag respectively in our calculation whereas the experimental values are −2.0 [19] and −3.8 eV [20] respectively. Also a shift due to relativistic effects (not included in our calculation) in the L_7 energies of several tenths of an eV are expected for Ag [5].

All of this shows that more theoretical work should be done on the definition of the real part of the self energy correction and its relation to the various types of band structure calculations. In conclusion we have shown that BIS provides a powerful tool for locating critical point energies of solids. The technique is simple compared to other methods used up to now and can be applied to polycrystalline samples. In addition to the determination of the critical point energies also the energy dependent lifetime broadening can be obtained providing the necessary information for determining both the real and imaginary parts of the self energy corrections to band structure calculations.

Efforts should be concentrated on improving the energy resolution of BIS so that more critical points can be located providing a detailed determination of the self energy corrections. Obviously theoretical work on both the real and imaginary part of the self-energy correction is necessary. The large discrepancies found with the band structure calculation of Au suggest that improvements in relativistic calculations are required.

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