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Abstract. The theory of temperature dependence of photoemission spectra is reviewed in a systematic manner and an attempt to identify the essential components is made. Using synchrotron light we have explored the temperature dependence of the photoemission from the valence band of Cu(111) over a broad energy range ($h\nu = 20$ to 85 eV). Remarkable differences in the thermal responses were observed as the photon energy was varied. Particularly unusual was the observation of a direct transition peak which increased in intensity as the temperature was raised. The experimental data support the idea that, under certain circumstances, phonon-assisted transitions from k-space regions where the initial-state bands are flat, e.g. at band edges, may result in spectral peaks, which compensates for the reduced intensities of direct transitions as the temperature is raised. We have also performed full numerical calculations in a time-reversed LEED formalism, and the results of these are compared with our experimental data.

1. Introduction

Angle-resolved photoelectron spectroscopy has over the last few decades become the most widely used method for the investigation of the electronic structure of solids and their surfaces. More or less advanced approximations for the photoemission process, usually assuming direct (momentum-conserving) transitions, are used to extract information from the experimental data. In most cases the effects of thermal vibrations are neglected in the analysis. However, thermal effects are, in principle, always present in the photoemission process and may in some situations even be crucial for the correct interpretation of data. As an example, in materials with low Debye temperatures, or at high temperatures, the increased relative contribution of phonon-assisted transitions may result in the appearance of additional spectral structures.

The theory of temperature effects turns out to be very complicated, because the photoemission process is affected by thermal vibrations in so many different ways. Although some promising attempts to formulate a general theory have been made, there is still no theory that provides a complete and coherent picture of these effects. If we can improve our understanding in this field, we may in photoemission find a tool for detailed studies of electron–phonon interactions away from the Fermi surface, which still today are largely unexplored.

The aim of this article is twofold. Firstly, we would like to summarise and discuss the present, incomplete, picture of thermal effects in photoemission from valence bands. Secondly, we present and discuss new data, obtained with synchrotron radiation, showing remarkable variations in the temperature dependence as the photon energy is changed.

2. Theory

In line with previous theoretical treatments of the photoemission process [1, 2], we use the following simple expression for the photocurrent as our starting point:

$$I(k_i, h\nu) \sim \sum_i |M_{fi}|^2 \, \delta(E(k_f) - E(k_i) - h\nu) \tag{1}$$

where E is the electronic energy, k_i (k_f) is the initial (final) state wavevector, $h\nu$ is the photon energy, and M_{fi} is the dipole matrix element.

For the perfectly ordered crystal we consider a tight-binding initial state:

$$\Psi_k(r) = \sum_l \exp(ik \cdot R_l)\Phi_k(r - R_l). \tag{2}$$

Here R_l is the position of atom l and Φ_k is a linear combination of atomic-like orbitals. If now the final state is taken to be a plane wave or an augmented plane wave (APW), the factor $|M_{fi}|^2$ in equation (1) will be of the form

$$|M_{fi}|^2 = |\sigma_{fi}|^2 S(k_f - k_i) \tag{3}$$

where σ_{fi} is the atomic photo-ionisation cross section, and

$$S(\Delta k) = \sum_i \delta(\Delta k - G_i) \tag{4}$$

is the structure factor, well known from diffraction theory [3]. The summation is over reciprocal-lattice vectors G_i.

The inclusion of thermal effects in the theory can be done systematically by observing Shevchik's distinction between *intra-* and *inter-*atomic contributions [4].

One may account for the *intra*-atomic effects by using tight-binding initial states, where the atomic-like orbitals Φ_k rigidly follow the atomic motions [4, 5]:

$$\Psi_k(r) = \sum_l \exp[ik \cdot (R_l + U_l)] \, \Phi_k(r - R_l - U_l). \tag{5}$$

Here U_l is the instantaneous displacement away from the equilibrium position R_l of atom l. With an initial state of this kind, a new structure factor is obtained, which has to be averaged over all possible configurations, using proper weights. Neglecting correlations in time and space, and using the Debye approximation, one finds

$$S(\Delta k) = \exp(-\Delta k^2 U_0^2) \sum_i \delta(\Delta k - G_i) + N(1 - \exp(-\Delta k^2 U_0^2)) \tag{6}$$

where N is the total number of atoms, and the mean square vibration amplitude

$$U_0^2 = (3h^2/4\pi^2 M_a k_B \theta_D^2)T. \tag{7}$$

Here M_a is the atomic mass, k_B is Boltzmann's constant, θ_D is the Debye temperature

and T is the temperature. The intensity of direct transitions is now reduced by the factor $\exp(-\Delta k^2 U_0^2)$, also known as the Debye–Waller factor [3]. The possibility of phonon-assisted indirect (non-k-conserving) transitions results in an additional contribution, weighted by the factor $(1 - \exp(-\Delta k^2 U_0^2))$ and supposedly resembling the electronic density of states (DOS) modulated by an atomic-like photo-ionisation cross section.

An obvious weakness of the theory presented so far is the complete neglect of correlations in time and space of the atomic vibrations. The time correlations should result in energy broadenings similar in size to phonon energies. This effect is, however, negligible in comparison with other broadening mechanisms.

The space correlations are more problematic since they may affect the selection of phonons involved in the indirect transitions. White *et al* [6] have argued that, due to strong near-neighbour correlations of thermal vibrations, the indirect transitions are predominantly localised close to the expected direct transitions in k space, i.e. involving mainly phonons with wavevectors q close to zero. Accordingly the indirect contributions to the photoemission spectra should be very similar in shape to the direct contributions, rather than being a relatively featureless DOS-like background as assumed in earlier studies. The shape and temperature dependence of the direct transition contribution are not affected, but the presence of a very complex indirect contribution will make the proper decomposition of spectra almost impossible.

The form of the tight-binding initial states has been question by Mårtensson [7], who argued that the phase factors in the tight-binding initial state are generally more complicated than the $\exp[i\mathbf{k} \cdot (\mathbf{R}_l + \mathbf{U}_l)]$ factors used in equation (5), and possible highly sensitive to the instantaneous thermal displacements. The theory was applied in a simple tight-binding model, where the phase factors were determined by energy minimisation. The effect was demonstrated in principle, but the model has still not been implemented in realistic calculations.

The inter-atomic thermal effects can be calculated by perturbation theory. Shevchik showed that initial-state inter-atomic effects, i.e. vibration-induced mixing of the Bloch-type initial states, do not affect the matrix element M_{fi}, but merely introduce shifts (apart from those caused by the thermal expansion) and broadenings of the EDC peaks [4, 8].

The inter-atomic final-state effects. i.e. the scattering of the photoelectron, should, according to Shevchik [4], result in an *incoherent* spectral contribution resembling the emission from a polycrystalline sample. Photoelectron interactions with phonons as well as other electrons will affect also the *coherent*, angular-dependent part of the spectral distribution. The damping relaxes the momentum conservation perpendicular to the surface, and for strong damping the spectrum will tend towards the one-dimensional density of states (ODDOS).

Figure 1 summarises the different thermal effects discussed so far. Shevchik expressed his results in a 'Master formula' containing two matrix elements [4]. The first one is what we may call the 'primary distribution' (direct transitions), broadened and shifted due to inter-atomic effects. Moreover, a DOS-like contribution, arising from intra-atomic interactions, is also contained in this term. The second term describes a structured 'background' arising from the *incoherent* final-state scattering caused by inter-atomic interactions.

Larsson and Pendry [9] have used a different approach to introduce thermal effects into more realistic calculations of photoelectron spectra. The atoms are still assumed to vibrate independently (uncorrelated) and a Debye–Waller factor is introduced. In a multiple-scattering formalism this leads, as in LEED theory [10], to temperature-dependent phase shifts, which are introduced for both hole and electron states. The electron–
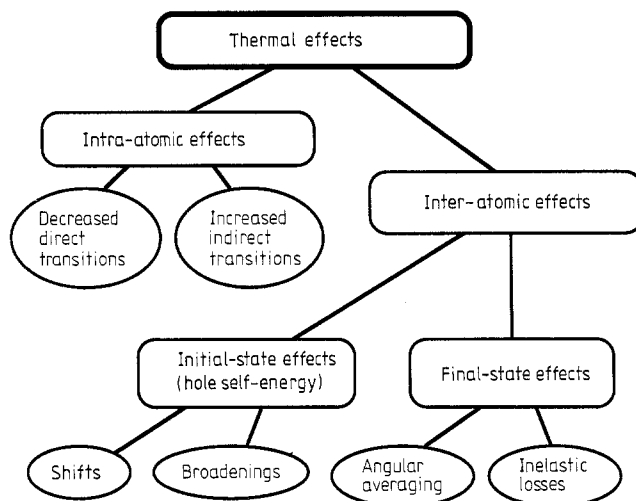
Figure 1. Schematic overview of thermal effects in photoemission.

electron interaction enters via the complex self-energy representing electron (hole) propagation. In numerical calculations we have found that the final-state contribution to the thermal response, due to the dominance of forward-scattering events, is very small.

Larsson and Pendry [9] also tried to include the temperature dependence of the optical dipole matrix elements. This is a hard task as these terms contain states at the same location, thus being 100% correlated. They found an approximation which in a limiting case gives a Debye–Waller-like factor.

It is tempting to associate the temperature-dependent phase shifts and the matrix element corrections with Shevchik's [4] inter-atomic self-energy corrections and intra-atomic effects, respectively, but because of the very different nature of the two models such analogies may be misleading.

3. Previous results

Thermal effects in photoemission spectroscopy were observed in 1970 by Lapeyre *et al* [11], as they performed angle-integrated measurements on single crystals of bismuth. They pointed out that phonon scattering of the outgoing photoelectrons as well as changes in the electronic states might contribute to the observed effects.

Bauer and co-workers [12] discussed temperature-induced changes in photoelectron spectra from partially ionic solids, which they attributed to thermal modulations of near-neighbour orbital overlaps. They also pointed out that perturbation theory is insufficient in situations where one cannot consider electron and photon states separately.

In the meantime, angle-resolved photoemission had developed into a powerful tool for band-structure probing and the drastic intensity changes with temperature observed by Williams and co-workers [13] in normal emission from Cu(100) seemed to confirm, at least qualitatively, the model put forward by Shevchik [5].

Knapp and co-workers [14] measured thermally induced shifts of features in Cu(111) spectra and interpreted these in terms of band-structure changes caused by thermal

expansion of the lattice, while Heimann and Neddermeyer [15] attributed shifts and broadenings in spectra from Au(110) to relaxation of k conservation perpendicular to the surface.

For PbS and PbSe Grandke and co-workers [16] found a striking correspondence between peak broadenings and the total DOS. This finding is consistent with inter-atomic initial-state modifications, which should result in DOS-like contributions to the imaginary part of the self-energy corrections [4].

Kevan and Shirley [17] observed that at high temperatures the intensity of the Cu(100) Tamm-type surface state decreased faster than predicted by Shevchik's model. This was viewed as an effect of anharmonic enhancement of thermal vibrations at the surface.

The Shevchik model seemed to do well in explaining the thermal effects observed by Hussain and co-workers [18] when performing angle-resolved XPS on W(100). Here a decomposition into direct and indirect transition contributions was achieved and results for different emission angles were found to be consistent.

Mårtensson and co-workers [19] studied the temperature dependence of angle-resolved photoemission from Cu(111) and found a Debye–Waller-like reduction, $I = I_0 \exp(-bT)$, of the peak intensities upon heating to 700 K. The temperature coefficient b was, however, significantly larger, in most cases, than predicted by Shevchik and it furthermore differed from peak to peak. This phenomenon was later systematically studied using Cu(110) and Ag(100) samples [20–22]. Very strong variations in temperature sensitivity were found as a function of the emission angle, in conflict with Shevchik's model. It was suggested that these irregular variations could be attributed to the mechanism put forward by Mårtensson [7], but so far this theory has not been tested in realistic calculations.

Jezequel and co-workers [23] studied temperature effects in spectra of Pb(110) and interpreted the results in terms of an effective Debye–Waller factor, accounting for the mixing of direct and 'non-direct' transitions. The latter were defined as surface-assisted transitions not conserving the perpendicular k component.

White and co-workers have presented data from Cu(100) [6] as well as W(100) and W(110) [24] which they analysed using a modified version of Shevchik's model. As mentioned in § 2, they argue that due to strong near-neighbour correlations the indirect contribution will be k-dependent and similar to the direct contribution, in contrast to the relatively featureless DOS-like background assumed in previous studies. They suggested that this more complicated indirect contribution is of importance in explaining the irregular behaviour of the temperature coefficient mentioned above. By simulating the indirect contribution by a cylindrical k-space broadening centred on the direct transition they found some qualitative agreement.

Tonner *et al* [25] investigated the temperature dependence of valence band emission from a monolayer of lead, grown epitaxially on a Ge(111) substrate. They fitted their results using a Debye–Waller factor and obtained an effective surface Debye temperature that was lower than that determined for Pb(111) by LEED. This was taken as an indication of weakened Pb–Pb bonds in the monolayer.

4. Experimental details

The experiments reported here were performed using a VG Scientific ADES 400 spectrometer on beamline 6 of the Synchrotron Radiation Source at the SERC Daresbury
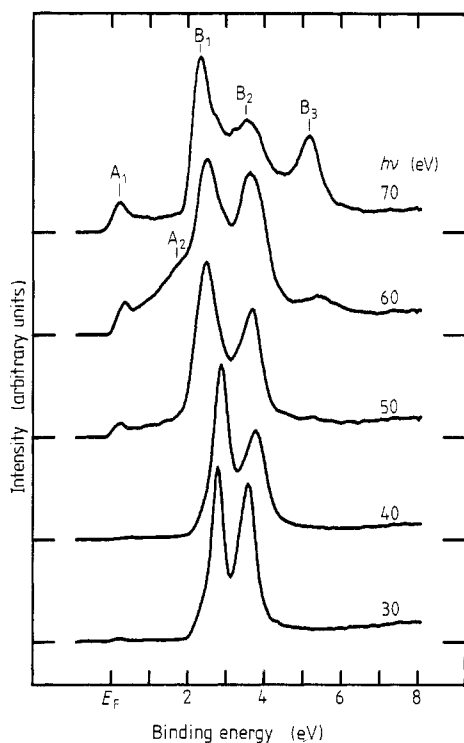
Figure 2. Room-temperature normal-emission spectra from Cu(111) for $h\nu$ in the range 30–70 eV.

Laboratory, UK. The Cu(111) surface was spark-cut to an accuracy of $\pm 1°$ and polished mechanically and electrochemically. It was further cleaned *in situ* by repeated cycles of ion sputtering and annealing. The experiments were performed at a base pressure of about 3×10^{-10} Torr. The sample was heated using a standard VG non-inductive resistive specimen heater. It was confirmed that the heating current did not influence the spectra. The temperature was monitored by a chromel/alumel thermocouple attached to the sample holder.

Synchrotron radiation was incident at 60° relative to the surface normal, and the photon energy was varied in the range 20–80 eV using a toroidal grating monochromator operated at an energy resolution of 0.1 eV. The light from this monochromator is assumed to be highly p-polarised, i.e. having the electric vector in the plane of incidence, but we cannot rule out the possibility that the optical elements depolarise the light somewhat under certain conditions [26]. As discussed in § 5, this could be of importance in explaining the different thermal sensitivities at different photon energies.

The spherical sector electron energy analyser had an angular acceptance $\pm 2°$ and typical energy resolution of 0.2 eV. All changes seen in the spectra upon varying the temperature were completely reversible in the temperature range employed (300–600 K).

5. Results and discussion

Figure 2 shows normal emission EDCs measured from Cu(111) at photon energies ranging from 30 to 70 eV. The peak labelled A_1 originates from the well known Shockley-type
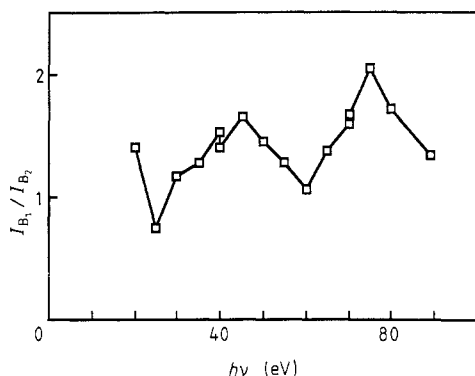
Figure 3. The intensity ratio of peaks B_1 and B_2 as a function of $h\nu$.

surface state located around $\bar{\Gamma}$ in the surface Brillouin zone [27], while the rapidly dispersing shoulder A_2 is due to the band of mainly s–p character rising above the d band around the L point in reciprocal space. This study will focus on the d-type direct transition peaks B_1–B_3, of which the first two dominate the spectra in the entire photon energy range, while B_3 becomes prominent as $h\nu$ approaches 70 eV. This latter structure has been attributed to a surface state [28], but calculations by Nilsson and co-workers [29] indicate that it is due to direct transitions from the lowest valence band, of symmetry Λ_1. This band is largely of s–p character, but emission from it is strongly enhanced around $h\nu = 70$ eV, since it becomes d-like with a high ODDOS close to its maximum at L. The peaks B_1 and B_2 show little dispersion, but their intensities vary in a characteristic way, which may help in the identification of their origins. Figure 3 shows the height ratio of these peaks as a function of $h\nu$. The minimum at 25 eV is easily understood from the calculated behaviour of photoexcitation matrix elements for transitions from the Λ_3 valence bands to the lowest Λ_1 conduction band [30]. At this photon energy the allowed direct transitions are confined to the vicinity of Γ, where the matrix element for emission from the upper Λ_3 band (giving rise to B_1) vanishes. Simultaneously, the corresponding matrix element for emission from the lower Λ_3 band, resulting in B_2, does have a strong maximum here. As $h\nu$ is increased, the bands are probed along the Λ direction towards the L point, which is reached at about 75 eV photon energy. On doing this the B_1/B_2 ratio goes through a maximum at $h\nu \simeq 45$ eV and a minimum at $h\nu \simeq 60$ eV. We furthermore observed small discontinuities in the B_2 dispersion at $h\nu \simeq 45$ and 60 eV. From the relativistic band calculation by Eckardt and co-workers [31] one can see that the non-relativistic lower Λ_3 band is replaced by several closely spaced bands by mixing with a band of Λ_1 symmetry. As the mixing varies along the Λ direction, these 'sub-bands' may contribute to the peak B_2 in an alternating manner, thus giving rise to the observed discontinuities and intensity variations.

Our investigation of the thermal effects in normal emission from Cu(111) focused on the intensity variations of peaks B_1–B_3. Since the widths of the peaks did not change much as the temperature was changed, we evaluated their heights rather than their integrated intensities. A linear background, adjusted to fit the background levels on either side of the d band, was subtracted prior to evaluating the peak heights. The contributions to peak heights due to overlap with tails from other peaks were considered to be small and were consequently neglected in the evaluation. Although objections can be raised against the simplifications made, one would most likely introduce worse
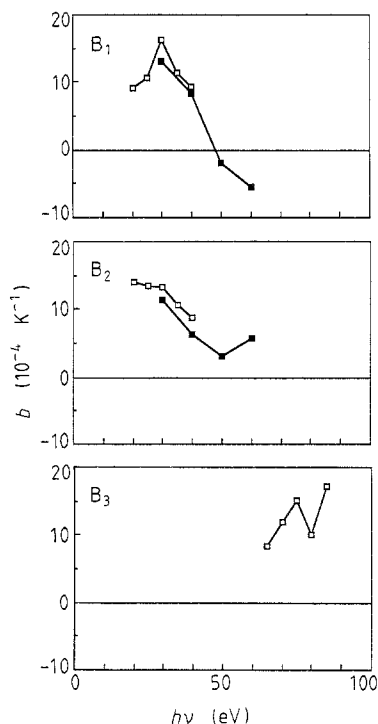
Figure 4. The 'temperature coefficient' *b* as function of *hv* for the peaks B_1, B_2, and B_3. Filled and open data points refer to different experimental runs.

uncertainties by attempting more elaborate background subtraction procedures, deconvolutions, or peak-fitting procedures. We generally found the intensity variations to be well described by the exponential law

$$I = I_0 \exp(-bT). \tag{8}$$

The coefficient *b*, the 'temperature sensitivity', is plotted in figure 4. Its dependence on photon energy deviates in a striking way from the predictions of the Debye–Waller theory (equations (6) and (7)). This is particularly so in the case for peak B_1, for which *b* has a maximum at 30 eV photon energy (i.e. transitions near Γ), but decreases rapidly as *hv* is increased and changes sign as *hv* approach 50 eV. This means that the height of B_1, at these higher photon energies, *increases* as the temperature is raised. Similar behaviour has previously been observed only in off-normal photoemission from Ag(100) using He II radiation [22]. In that experiment the polar emission angle was varied, rather than the photon energy. The negative values of the 'temperature sensitivity' *b* are hard to reconcile with Shevchik's theory or with any theory of Debye–Waller type. In the language of the LEED scattering formalism [10], there could exist a situation where two scattering processes interfere destructively at low temperature. If one of these processes is quenched by thermal vibrations more than the other, an increased total contribution from these interfering processes could result [10]. Of course, one also has to consider the possibility that contributions other than direct transitions could be peaked at the same binding energy as B_1, and thus create a false impression of direct transitions gaining strength as the temperature is increased. We will return to that below.

The coefficient *b* of peak B_2 has a less dramatic dependence on *hv*, but it should be pointed out that its almost monotonic decrease as *hv* increases is contrary to that
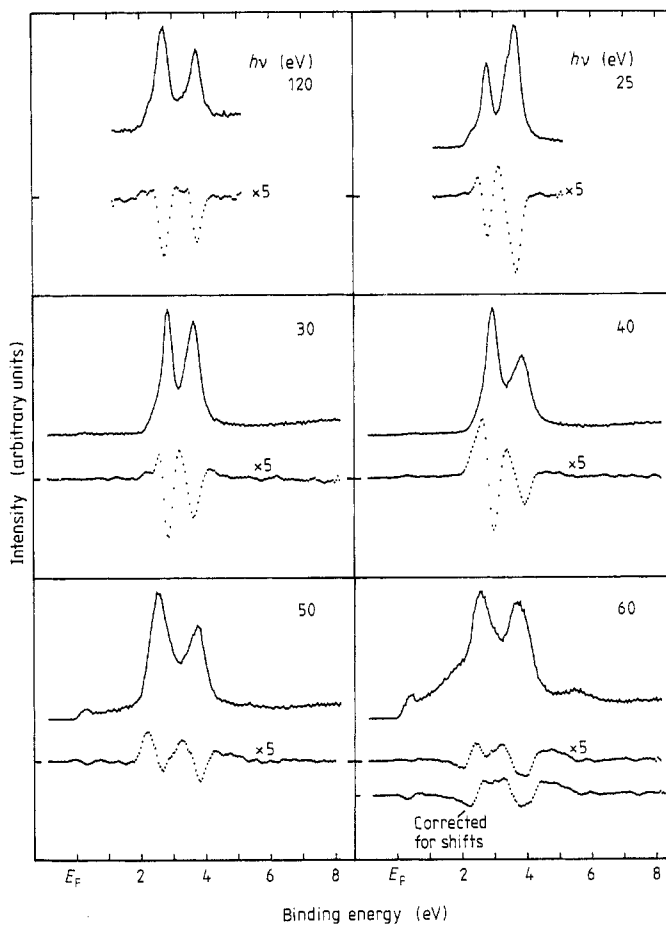
Figure 5. Room-temperature EDCs and thermal difference spectra from Cu(111) at 20 to 60 eV photon energy. The latter are obtained by subtracting at each photon energy the room-temperature EDC from the corresponding properly normalised spectrum measured at approximately 450 K. In each panel the difference spectrum is scaled by a factor five relative to the corresponding room-temperature EDC, while all room-temperature EDCs are scaled to the same maximum height. The lowest difference spectrum in the 60 eV panel is compensated for thermal shifts of the main peaks.

predicted from e.g. equation (6) (Δk^2 should be roughly proportional to $h\nu$ over a broad energy range). The increase of b found when going from 50 to 60 eV photon energy could possibly be associated with the same type of band-crossing-induced changes of initial-state character as was suggested above in the discussion of figure 3. Peak B_3 differs from the other peaks as the trend for b here is to increase with $h\nu$. There is a dip, however, around 80 eV, which is too deep to be attributed to experimental uncertainty. It seems reasonable to associate this dip with the passage through the L point in reciprocal space, although the underlying mechanism is still unclear.

We are confident that our simple analysis of peak intensities, using the coefficient b, gives a valuable representation of important thermal effects, but, to complete the picture, we need to look for other effects than changes in peak heights. Figure 5 shows room-temperature EDCs for photon energies ranging from 20 to 60 eV, together with

difference spectra obtained by subtracting the room-temperature spectra from corresponding spectra obtained at elevated temperatures ($\approx$450 K). The spectra were normalised to the light intensity prior to the differentiation. In figure 5 the room-temperature spectra are all scaled to have the same maximum height, and the difference spectra are each scaled by a factor five relative to the corresponding room-temperature spectrum. The temperature differences used to produce the difference spectra were not exactly identical at every photon energy, but still this series of difference spectra gives a reasonably correct representation of how the temperature sensitivity varies with $h\nu$.

Here one can easily recognise the general trend in the behaviour of peaks B_1 and B_2: a reduction of the temperature sensitivity when going from 20 to 60 eV photon energy. The simple dips in the difference curves for $h\nu = 20$ eV indicate almost pure amplitude decreases of peaks B_1 and B_2. Peak broadening would have resulted in dips with positive peaks on either side, while a pure peak shift would have created a dip/peak pair. The difficulty is to separate these contributions when they occur simultaneously, in the presence of an unknown background not directly related to the peaks. One can see in figure 5 how positive contributions to the difference spectra gain in importance as $h\nu$ is increased. These positive contributions (peaks) appear chiefly at the upper edge of the d band and in the valley between B_1 and B_2. There are some small upward (towards lower binding energies) shifts of both B_1 and B_2, but these shifts are too small to account for more than a tiny fraction of the structure seen in the difference curves. As an illustration we have redrawn the difference curve for 60 eV photon energy in figure 5 after compensating for the thermal shifts. The wiggles at the upper edge of the d band are reduced but the difference spectrum is basically still the same. Thermally induced broadenings are hard to separate out from the difference curves, but they do not appear to be major features of our data.

One possible interpretation of our data would be that the peaks in the difference spectra, as well as the reduced dips at higher photon energies, are due to a thermally induced DOS-like background. One would expect such a background to be roughly triangular in shape, with its maximum at the upper edge of the d band, and then decreasing towards the lower edge. This would explain the position of the positive difference peaks, but it would also raise serious questions about the $h\nu$ dependence of the background. Another possibility would be if the thermally induced background at the higher photon energies was dominated by two peaks at somewhat higher energy than B_1 and B_2, respectively. Such peaks could be the result of phonon-assisted transitions from regions in k space close to the L point, where the initial-state bands are flat. This kind of background would confirm the suggestion by White *et al* [6] that indirect transitions are weighted to favour transitions from states in k space close to the direct transition, rather than to average over the entire Brillouin zone. The absence, or smallness, of such thermally induced peaks at lower photon energies could be a consequence of the increasing distance in k space between L and the location of the direct transitions, although it remains to be explained why we do not encounter other thermally induced peaks, originating from the vicinity of the Γ point, as the locations of the direct transitions approach this point. Very striking is the capacity of this mechanism to explain why both the positive and negative contributions to the difference spectra in figure 5 seem to be reduced at the higher photon energies. As L is approached the direct emission peaks will eventually coincide with their indirect counterparts, and to a considerable extent the thermally induced changes will compensate out.

We now turn our attention to the other known similar case: the uppermost d-band peak in photoemission spectra from Ag(100) at 21.22 eV photon energy, which for large
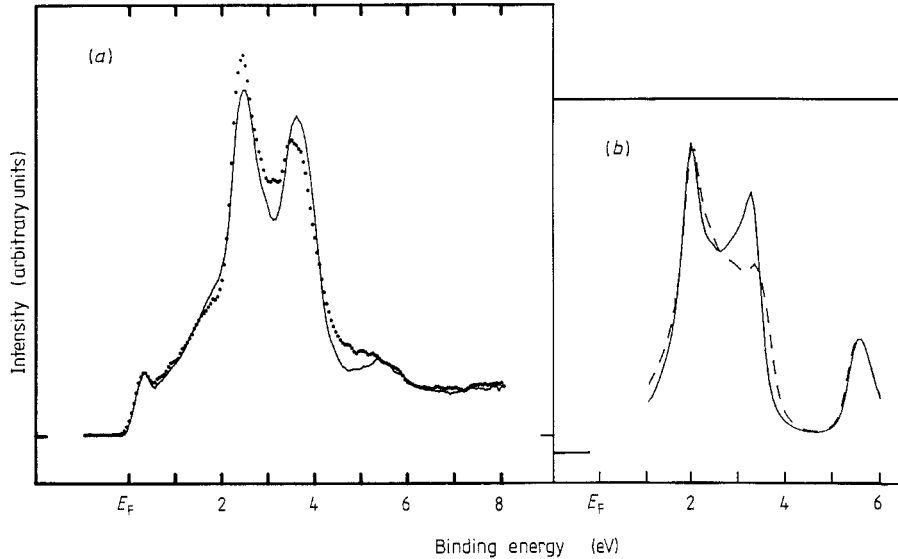
Binding energy (eV)

Figure 6. (*a*) Normal-emission EDCs from Cu(111) at 60 eV photon energy measured at room temperature (full curve) and at 456 K (full circles), respectively. (*b*) Normal-emission EDCs from Cu(111) at 60 eV photon energy calculated for absolute zero (full curve) and 700 K (broken curve), respectively. The calculation was performed using a Debye temperature of 343 K, strict p polarisation of the incident light, and assuming that only the hole-state phase shifts are affected by the temperature.

($\approx 60°$) polar emission angles in the ΓXWK symmetry plane seemingly increase with temperature [22]. The coefficient b becomes negative here as the direct transition approaches the upper edge of the d band close to the Z symmetry line in k space. It is striking that also in this case the negative value of b is associated with initial states located in k space very close to a band maximum.

Figure 6(*a*) shows explicitly the two spectra (at room temperature and 456 K) obtained at $h\nu = 60$ eV, at which photon energy the intensity of peak B_1 increases with temperature. We now will compare these experimental results with calculations based on the theory by Larsson and Pendry [9], and the self-consistent potential by Moruzzi and co-workers [32]. For the temperature calculations a Debye temperature of 343 K was chosen [10]. As mentioned before, the results were not sensitive to the thermal scattering in the photoelectron state. The dominance of forward scattering appears to be the reason for this. Instead the most important effects of temperature are those related to the scattering in the hole state. The thermal correction to the matrix element will result in a uniform but small reduction of the intensities with temperature. However, due to the crude approximations involved we have excluded this contribution from our present calculations. Figure 6(*b*) shows calculated EDCs at $h\nu = 60$ eV for $T = 0$ and 700 K. The incoming light was assumed to be strictly p-polarised. Also, the calculations indicated a difference in the thermal sensitivity of the peaks A and B, although the calculated intensity of peak A remained constant rather than increased as the temperature increased. In contrast, admixture of s-polarised light would, according to the calculations, have reduced the intensity of peak A upon temperature increases. Calculations for $h\nu = 30$ eV yield thermal effects very similar to those calculated for 60 eV. Some agreement with experimental trends would still be possible assuming that

the light from the monochromator was partially depolarised in the low-photon-energy range, but more ideally p-polarised at 60 eV. Although it has been verified that the 30 eV light is not perfectly p-polarised [26], this explanation appears less likely. It is interesting, however, that the calculations predict a polarisation dependence of the thermal sensitivity.

6. Conclusions

It can be concluded that, due to the complexity of the field, little is known about the correctness and relative importance of the many different temperature-related effects which have been suggested as important in photoemission spectroscopy. The 'master formula' introduced by Shevchik [4] seems to be a very useful starting point for any discussion about general thermal effects in photoemission, but many further details are required for a complete understanding. When discussing thermal effects in photoemission from Cu and other d-band metals, it appears reasonable to concentrate on the initial-state effects and the relative importance of direct and phonon-assisted transitions. An appropriate starting point would then be the theory outlined in Shevchik's earlier papers [5]. This theory is, however, unable to predict the drastic variations of the coefficient b with band index, emission angle [19–22] and, as demonstrated in our present paper, photon energy.

Some of these variations can possibly be accounted for by modification of initial-state phase factors as proposed by Mårtensson [7]. The suggestion by White *et al* [6], that the indirect spectral contribution may be more complex and sharply peaked than previously assumed, should also be taken very seriously. In particular, one can tentatively understand the spectacular $h\nu$-dependent changes in the thermal response of peak B_1 as resulting from phonon-assisted transitions from the L point and nearby regions of the k space. Similarly, this type of mechanism might equally well explain the previously reported case of a negative b coefficient in off-normal emission from Ag(100) [22]. Our data indicate that such effects are important only in k-space regions where the initial states are confined enough in energy to produce sharp structures in the indirect spectral contribution. Such regions are principally found in k space close to symmetry points, and sometimes also close to symmetry lines if there are any energy bands which are non-dispersive along these lines. It is somewhat surprising, however, that no sharp thermally induced structures can be identified at photon energies corresponding to transitions from the neighbourhood of Γ. Possibly, indirect transitions from that region are suppressed by cross section effects. As the transitions observed in photoemission usually are close to the above-mentioned special symmetry points only at certain photon energies and emission angles, this kind of mechanism does not seem to be a universal explanation of the drastic variations in thermal response found as the emission angle is altered [19–22].

The LEED-type calculations presented here are difficult to relate to the other models and mechanisms discussed here, in that the fundamental approach (scattering formalism) is so different from the approach used by, for example, Shevchik [4]. Some of the approximations made in order to incorporate thermal effects may also be too extensive. It is still interesting that a difference in thermal response of peaks B_1 and B_2 could be reproduced, and a further analysis of the calculations may contribute to the understanding of thermal effects. In particular, it is interesting that the calculated thermal responses were strongly dependent on the polarisation of the incoming light.

Further advances in the understanding of thermal effects will require both carefully designed experiment to single out and quantify the mechanisms in action, and continued efforts to improve the underlying theory.

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