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LETTER TO THE EDITOR

Photocurrent calculations including correlations: application to Ni(110)

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Abstract. Photocurrent calculations based on a one-step model and including correlation effects have been carried out for the Ni(110) surface. An energy-dependent and complex potential was constructed using a form of the self-energy corrections developed by Tréglia and co-workers. Comparisons with experimental data for the photoemission from initial states with Σ_4/S_4 symmetry show that although the dispersion is well reproduced the lifetimes of holes in the majority-spin band are overestimated.

It has been the custom to use angle- and spin-resolved UV photoemission measurements to establish the validity, or otherwise, of band structure calculations that are based on some form of the local density approximation (LDA) in density functional theory. Such an approach relies on a number of underlying simplifications and assumptions; for example, (i) the calculations usually refer to the infinite lattice whereas photoemission probes the electronic structure in the vicinity of a surface, (ii) it is often necessary to use some form of empirical expression for the dispersion of the final states in order to 'map' the initial state bands, and (iii) it is assumed that the energetics of the photoemission process can be described in terms of the single-particle eigenvalues. The use of photocurrent calculations based on a one-step model [1] that specifically includes a surface and a suitable potential, e.g., from a slab calculation [2], has helped to overcome the problems associated with (i) and (ii). Despite there being no formal justification for (iii), it has been shown nevertheless that LDA eigenvalues provide a useful basis for describing the photoemission from a range of metals and alloys. On the other hand, there are well documented cases where, because of many-body effects, it does not give a wholly satisfactory picture and where significant discrepancies occur; for instance, the band gaps in a number of semiconductors and the valence band-widths in the simple metals Na, Mg and Al [3, 4]. Other examples include the 3d transition metals [5]; notably Ni, for which the measured d band-width and the exchange-splitting are considerably smaller than predicted [6, 7] and resonant satellite structure appears [8, 9]. The key quantity for describing the many-body correlation effects is the self-energy, which represents a generalised correction to the one-electron eigenvalues [10]. Although such effects are difficult to treat from first principles there has been considerable progress recently for some weakly scattering systems, involving the GW approximation [3, 4]. In the case of Ni,

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however, various models have been used to calculate the self-energy [5]. For example, Tréglia and co-workers [11], hereafter referred to as TDS, using perturbation methods within a single-band Hubbard model, showed that it is possible to account at least qualitatively for the discrepancies between photoemission measurements and one-electron band structure calculations by considering Coulomb correlation effects between particles in the unfilled d band.

One seeks, therefore, a calculational scheme for the photocurrent in which the surface, the electron–photon matrix elements and the many-body correlation effects, etc. are properly included. Since, in general, the self-energy operator is complex, non-local and energy-dependent, formally, this is a formidable task. However, there has been some progress, albeit inevitably involving approximations. For instance, Nilsson and Larsson [12] showed that improved agreement between photocurrent calculations and experimental spectra could be achieved for Cu(111) by including self-energy corrections for the hole and the electron calculated for a homogeneous electron gas. They constructed a modified potential which was used in a one-step model of photoemission. Clauberg [13] calculated the spin-resolved photocurrent from Ni(110) at a single photon energy but he included only the real part of the self-energy. More recently, Jordan and Hoyland [14] calculated the photocurrent from Ni(110) over a range of photon energies using the TDS self-energy. Since the latter is $\boldsymbol{k}$-independent they included both its real and imaginary parts by renormalising the one-electron photocurrent.

In this letter a series of photocurrent calculations are described for Ni(110) using a one-step model and a potential for the excited state. The calculations are based on the TDS self-energy, which is essentially only spin- and energy-dependent, i.e. $\Sigma \rightarrow \Sigma_\sigma(E)$, and whose real and imaginary parts satisfy the correct dispersion relation. In view of the single-band nature of the TDS model the calculations and comparisons with experiment are made for the bands of Σ_4/S_4 symmetry only. In principle, more sophisticated forms of the self-energy can be included in the formalism when they become available. Although the results are similar to those obtained by Jordan and Hoyland [14], the calculations here are carried out on a more rigorous footing.

The calculations were made using a modified form of the NEWPOOL code [1, 15]. In this scheme the spin-resolved, no-loss part of the angle-resolved photocurrent is calculated by layer KKR multiple-scattering techniques for a semi-infinite array of non-overlapping, muffin-tin potentials [16]. The surface barrier is modelled by a step function that is in contact with the outermost layer of muffin tins. To take account of the self-energy corrections the Green function propagators for the low- and high-energy states are renormalised separately; the vertex corrections are assumed to have no substantial effect on the elastic part of the photocurrent [17]. Accordingly, a modified excitation potential is introduced

$$V_\sigma(r, E) = \begin{cases} = V_\sigma^0(r) + \Sigma_\sigma(E) & r \leqslant r_{\mathrm{MT}} \\ = \mathrm{i}V_{0i}(E) & r > r_{\mathrm{MT}} \end{cases} \tag{1}$$

where $V_\sigma^0(r)$ is the ground-state potential with eigenvalues $\varepsilon_{\nu\sigma}(\boldsymbol{k})$ (ν is the band index), r_{MT} is the muffin-tin radius and

$$\Sigma_\sigma(E) = U^2[\Delta_\sigma^0 + \Delta_\sigma(E) + \mathrm{i}\Gamma_\sigma(E)]. \tag{2}$$

Here U is the intra-atomic Coulomb energy, Δ_σ^0 is a correction term (see below) and $\Delta_\sigma(E)$ and $\Gamma_\sigma(E)$ are given by equation (5) in TDS. Thus, equations (1) and (2) provide a method for calculating the photocurrent from Ni in the presence of correlations using

the NEWPOOL code. (The inclusion of a complex potential required some re-coding of the original program.)

Ground-state potentials were obtained from spin-polarised, SCF–LMTO calculations [18] and the corresponding densities of d states were used in the determination of $\Delta_\sigma(E)$ and $\Gamma_\sigma(E)$. Since the potentials were obtained from calculations involving the LDA a correction term, Δ_σ^0, is required in equation (2) to take into account the correlations already included [11, 13, 14]. However, since the real and imaginary parts of the self-energy are related by a Hilbert transformation, Δ_σ^0 is independent of energy. By using an option in the code [1] it was confirmed that in the absence of self-energy corrections the bands and critical points were very similar to those determined in previous one-electron calculations, e.g., by Moruzzi and co-workers [19].

Angle-resolved measurements of the photoemission normal to the (110) surface of Ni have been made by Heimann and co-workers [20] over the photon energy range $11\,\text{eV} \leqslant \omega \leqslant 18\,\text{eV}$. Their spectra with $\boldsymbol{A} \parallel [1\bar{1}0]$ correspond to emission from initial states with S_4 symmetry along the K–X direction near the X-point. The main points to note from the published spectra are

(i) each spectrum comprises two peaks which move towards E_F with increasing photon energy;

(ii) the spin-splitting increases as the peaks approach E_F;

(iii) the peaks are clearly resolved at a photon energy of 15 eV but much less so at lower values;

(iv) the intensities increase with photon energy to a maximum at 15 eV; thereafter, they decrease.

In figure 1 the calculated (spin-summed) photocurrents are shown for the range $12\,\text{eV} \leqslant \omega \leqslant 17\,\text{eV}$ and the same geometrical arrangement as that employed by Heimann and co-workers [20]. The self-energy corrections were only applied to initial states in the $l = 2$ channel and the values of $U = 1.8\,\text{eV}$, $\Delta_\uparrow^0 = -0.126\,\text{eV}^{-1}$ and $\Delta_\downarrow^0 = -0.149\,\text{eV}^{-1}$ were chosen to give the experimentally observed spin-splitting of the $X_2^{\uparrow\downarrow}$ states [20, 21]. (These values are slightly different from those used in [14], but they give marginally better agreement with experiment.) A constant value of $V_{0i} = -0.015\,\text{eV}$ was used in equation (1) for the low-energy state. For the final state an inverse lifetime of 2 eV was used, a value deduced from the experimental measurements [20]. Particular care was taken to ensure that a sufficiently large set of reciprocal lattice vectors was included in the plane-wave expansion in order to achieve proper convergence; in fact, 65 beams were required. To make the calculations 'realistic' a step-function cut-off was introduced at E_F and a Lorentzian function (FWHM = 0.125 eV) was folded in to simulate the experimental resolution [20].

The overall agreement with the data of Heimann and co-workers [20] is good. In particular, the dispersion of the peaks, the energy- (and hence $\boldsymbol{k}$-) dependence of the spin-splitting and the intensity variation with photon energy are reproduced. The spin-splitting remains constant for $\omega > 15\,\text{eV}$ since the emission is at the X point with the final states in the X_5'–X_3 band gap (which is some 5 eV wide), but the inclusion of a finite lifetime for the final state permits 'band-gap photoemission' [14, 22]. The loss of resolution at the lower photon energies is due to the combination of the rapid increase in $|\Gamma_\sigma(E)|$ and the reduction in spin-splitting as the initial states move away from E_F.

The major difference between the calculations and the experimental spectra concerns the relative heights of the spin-up and spin-down features. The discrepancies are due to the failure of the TDS model to give the correct relative lifetimes of holes in the majority-

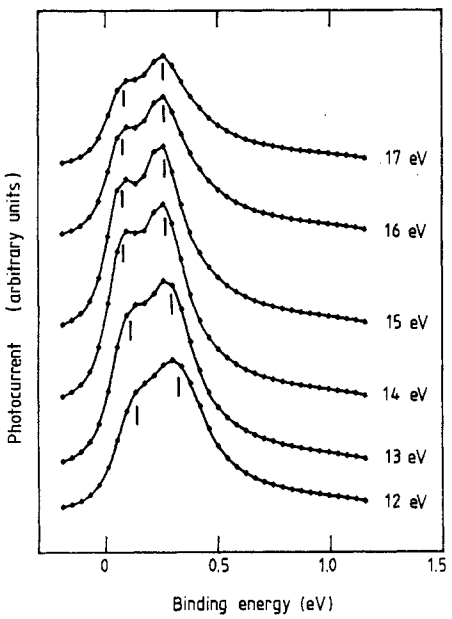

Figure 1. Calculated spin-integrated photocurrent spectra for Ni(110) with the vector potential $A \parallel [1\bar{1}0]$. The tick-marks indicate the peak positions of the spin-up and spin-down components.

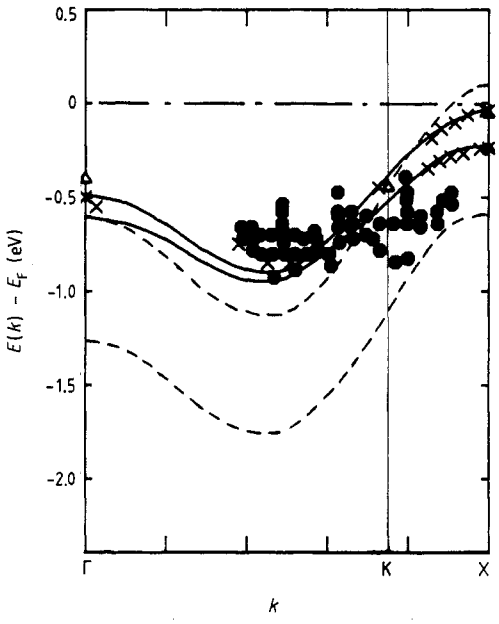

Figure 2. Comparisons of the calculated and experimentally determined dispersion for states of Σ_4/S_4 symmetry along the Γ–K–X direction. Broken curves, band calculations using ground-state potentials; full curves, loci of the maxima in the quasi-particle spectral functions. ●, from [9]; ×, from [20, 23]; ▲, from [21]; △, from [24].

and minority-spin bands [14]. The calculations suggest that the FWHM of the peaks in the different spin channels are approximately the same, which is in conflict with the experimental observations. In fact, a comparison of the calculated widths with those determined by Heimann and co-workers [20] after deconvolution of the instrumental broadening reveals that there is good agreement for the minority spins, i.e. within ±0.05 eV, over the range 11 eV $\leqslant \omega \leqslant$ 18 eV, whereas the widths of the majority-spin features here are consistently ~0.12 eV too small. However, the difference between the calculated width of the majority-spin feature at a photon energy of 16.8 eV and the corresponding spin-resolved measurement of Raue and co-workers [21] is somewhat smaller. In the latter case, Jordan and Hoyland [14] showed that if the calculated width is adjusted to the experimental value (at constant area), then the relative peak heights are correctly reproduced.

In figure 2 the dispersion of the bands of Σ_4/S_4 symmetry along the direction Γ–K–X for the ground-state potential is compared with the loci of the maxima in the corresponding quasi-particle spectral function

$$\tilde{A}_{\nu\sigma}(\boldsymbol{k}, E) = -(1/\pi)\,\mathrm{Im}[E - \varepsilon_{\nu\sigma}(\boldsymbol{k}) - \Sigma_\sigma(E)]^{-1} \tag{3}$$

for $\nu \equiv \Sigma_4/S_4$. Also included are results from several photoemission studies of the dispersion of the $\Sigma_4^{\uparrow\downarrow}/S_4^{\uparrow\downarrow}$ bands [9, 20, 21, 23, 24]. If the surface plays only a minor role in photoemission (as is the case with s-polarised light), then peak positions in experimental spectra should follow the quasi-particle bands. The overall agreement

with the data is good; in particular, the reduction in spin-splitting along X–K and the values at the Γ point are well reproduced. Furthermore, over the energy range considered here the calculated value of $\partial\Delta_\sigma(E)/\partial E$ is ~ -0.3 to -0.6, which is consistent with the analysis of other experimental data carried out by Starnberg and Nilsson [25].

It has been the practice to equate the differences between the peak positions in photoemission spectra and the ground-state eigenvalues with Re Σ_σ. Strictly speaking this is not correct since Im Σ_σ is energy-dependent and so it also plays a role in determining the maxima in equation (3). In this particular case the error introduced by neglecting the imaginary part is ~0.13 eV at the bottom of the Σ_4 bands.

In summary, photocurrent calculations including the effects of correlations have been carried out for the Ni(110) surface using a one-step model. An energy-dependent and complex potential, based on a form for the self-energy developed by Tréglia and co-workers [11], was used. Most of the experimentally observed behaviour is reproduced for the photoemission from initial states with S_4 symmetry over the photon energy range 12–17 eV [20]. Although the calculated widths of the minority-spin features are in good agreement with experiment, it appears that the lifetimes of holes in the majority-spin band are overestimated. The calculated dispersion of the quasi-particle states with Σ_4/S_4 symmetry along Γ–K–X is in good agreement with the available data. Currently, investigations are being carried out of the spin-integrated photoemission from Ni at higher photon energies and for different band symmetries. It is anticipated that spin-resolved photoemission measurements will soon be available; such data will be particularly important in quantitative studies of self-energy effects.

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