

## A Brief Review of the History and Use of the Daresbury 'Miyake' Monochromator for Surface Science

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This paper celebrates the 21st anniversary of the plane-grating grazing-incidence monochromator, designed at Daresbury in 1974 and in almost continuous operation ever since. The order-sorting principles [Miyake, Kato & Yamashita (1969), *Sci. Light (Tokyo)*, **18**, 39–56] are described, along with the detail of the instrument's design, followed by the history of its use on three synchrotron radiation sources (NINA, TANTALUS and SRS). A selection of scientific highlights at the SRS is given, taken from some of the experimental programmes in which the author was involved, concentrating on tunable photon-energy photoemission studies of metallic alloys. Finally, the future prospects for vacuum UV spectroscopy for surface science are briefly discussed.

**Keywords:** surface science; electron spectroscopy; vacuum UV; monochromators.

### 1. The start of photoemission studies from solids at Daresbury

The exploitation of synchrotron radiation at Daresbury started with parasitic use of NINA, the 5 GeV electron synchrotron for high-energy physics. Initial trial experiments on solid-state photoemission studied the layered semiconductor GaSe, using a simple home-built analyser with energy resolution obtained from alternating-current modulation and phase-sensitive detection. The analyser was deliberately made angle-integrating 'to avoid the possibility of complex angular effects observed with directionally sensitive electron energy analysers' (Williams, Williams, Norris, Howells & Munro, 1974). Incidentally, this publication highlights a characteristic of the early days of synchrotron radiation applications in that the words 'synchrotron radiation' were emphasized in the title of the paper: 'Photoemission from Gallium Selenide using Synchrotron Radiation'. This was an indication of the novelty of the use of synchrotron radiation, and certainly facilitated literature searching, but is a far cry from the present day when the availability of synchrotron radiation is often taken for granted.

The success of these initial photoemission experiments at the SRF (synchrotron radiation facility) on NINA led to funding for purchase of an ultra-high-vacuum surface-science system (VG ESCA-3), used with a normal-incidence monochromator (Howells, Norris & Williams, 1977). This work soon prompted a desire for higher photon energies, to study core levels in the range from *ca* 40 to 200 eV.

### 2. The 'Miyake' monochromator

The 'Miyake' scheme (Miyake, Kato & Yamashita, 1969) was described for a distant source, effectively at infinity,

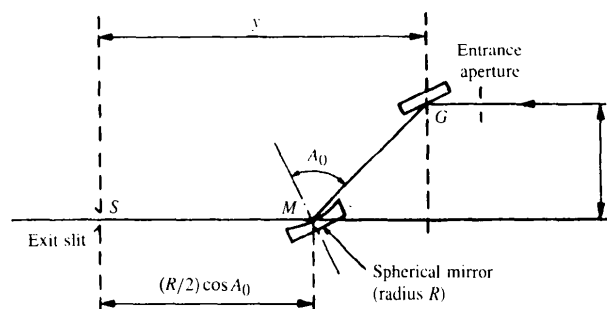
with parallel incident light, appropriate for a large synchrotron. It uses only two optical components at grazing incidence with a plane grating in negative order, and the principle of differential reflectivity for rejection of higher harmonics. The optical layout (at zero order) is shown schematically in Fig. 1. The concave mirror *M* is at a fixed position along the exit arm and wavelength is scanned by a simple rotation of the plane grating *G*. This arrangement satisfies the requirement for fixed deviation,

$$\alpha + \theta = 2\alpha_0 = \text{constant},$$

where  $\alpha$  and  $\theta$  are the grazing angles of incidence and diffraction, respectively.  $\alpha_0$  ( $= 90^\circ - A_0$ ) is the angle of grazing incidence in the zero-order position. For the spherical mirror to focus light at the exit slit,

$$y = (R/2) \cos A_0 - x \cot 2A_0.$$

For a practical design,  $x$  and  $y$  are fixed and  $A_0$  is chosen to achieve order sorting (West, Codling & Marr, 1974). For any given set of  $x$ ,  $y$  and  $R$  there are two values of  $A_0$ , and hence two positions of the mirror *M*, for which



**Figure 1** Optical arrangement of the 'Miyake' monochromator (Howells, Norman, Williams & West, 1978).

the instrument is in focus. To try to achieve a wider energy range, two mirrors can be incorporated, giving four different combinations of mirror and position and hence tuning range for the instrument. Higher orders are reflected less efficiently, and careful selection of the grating groove depth also helps to suppress the unwanted harmonics. An instrument based on this scheme was designed and used for gas-phase spectroscopy at the Daresbury SRF (West, Codling & Marr, 1974). This monochromator used two different values of  $x$  for the two mirrors, and hence two exit slits at different heights, so that the experiment had to be moved to make use of all four ranges.

When considering a new monochromator at the Daresbury SRF for experiments on photoemission from solids in the 40–200 eV energy range, it was felt that the 'Miyake' principle would provide a suitable instrument, but that having to move any sizeable experimental apparatus for the different energy ranges would be too inconvenient and impracticable. Thus, a new instrument was designed with  $x$  and  $y$  kept fixed and mirrors chosen with two different radii  $R$ . This requires two mirrors which can be driven to any position  $M$ , automatically interchanged when appropriate and rotated to the correct angle. This problem was neatly solved in the engineering design carried out by Mr D. K. Tole, whose company (Bird & Tole Ltd) built the monochromator. The order was placed in August 1974, and the instrument was delivered in July 1975, entering service for experimental use early in 1976. This design gave quite a wide energy range ( $\sim 20$ –280 eV), high flux [ $\sim 10^{10}$  photons  $s^{-1}$  (0.1% bandwidth) $^{-1}$  (100 mA) $^{-1}$ ], medium resolution ( $h\nu/\Delta h\nu \simeq 500$  with a  $6321\text{mm}^{-1}$  grating), good order sorting, at least at the higher energy end of its range, but with a relatively large spot size of  $ca 10 \times 2\text{mm}^2$  (Howells, Norman, Williams & West, 1978). As was common at the time, polarization was a parameter that was hardly considered.

### 3. The 'Miyake' monochromator at the Daresbury SRF

The Miyake monochromator was used at the SRF on NINA for photoemission from surfaces, with experimental programmes from three institutions (University of Leicester, New University of Ulster at Coleraine, and the University of Warwick). In those early days, it was noticeable that the user groups were all from Departments of Physics.

Amongst other work at Daresbury, Woodruff and I took advantage of the variable photon energy to investigate the energy dependence of the electron inelastic scattering mean-free-path (the so-called 'universal curve') by the overlayer method. This involves monitoring the intensity of photoemission from a substrate core level as different thicknesses of an overlayer material are deposited on it. The intensity is attenuated by inelastic scattering in the overlayer: the variation of this attenuation as a function of photon energy (and thus electron kinetic energy) is the desired mean-free-path curve. The results for Ag are shown

in Fig. 2. In related work, films of Al and Mg were exposed to oxygen, leading to the new finding that the mean free path in their oxides is much longer than in the pure metals (Norman & Woodruff, 1978).

### 4. The 'Miyake' monochromator on TANTALUS at Wisconsin

The electron synchrotron NINA at Daresbury closed in April 1977, as high-energy physics research became concentrated at CERN and the decision to build a dedicated source of synchrotron radiation had already been taken. Thus, the host died but the parasite would live on. 'The Miyake' was then sent on loan to the Synchrotron Radiation Center at the University of Wisconsin to become one of the first grazing-incidence monochromators on TANTALUS. There, the monochromator was used by a variety of groups, including Montana State University, University of Pennsylvania and Cornell University, mainly for angle-resolved photoemission from surfaces.

Amongst other applications, the instrument provided the light source for early demonstrations of the technique of photoelectron diffraction from adsorbates on solid surfaces. Although there was a general expectation that diffraction effects would be seen with photoemitted electrons [following model calculations (Liebsch, 1974)], there was little agreement on the likely magnitude of the effect. Our work, in a collaboration between the University of Warwick (UK) and Bell Laboratories (USA), concentrated on the azimuthal angle dependence (Woodruff *et al.*, 1978; Smith *et al.*, 1980). At around the same time, photoelectron diffraction

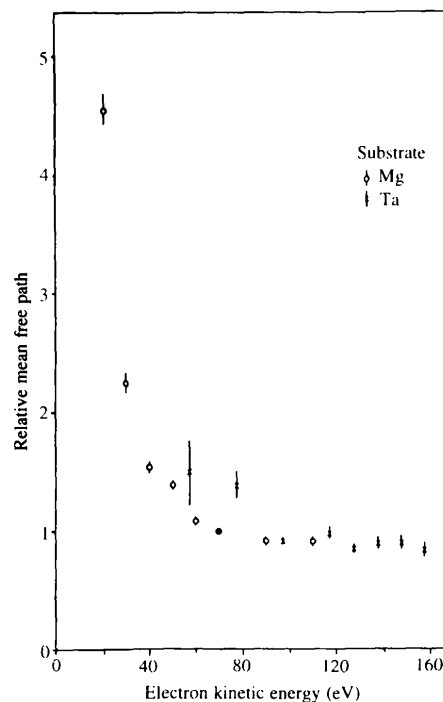


Figure 2 Relative electron scattering mean free path for Ag as a function of electron kinetic energy (Norman & Woodruff, 1978).

had been successfully demonstrated in energy-dependent spectra (Kevan, Rosenblatt, Denley, Lu & Shirley, 1978) and in scans of polar angle (Norman, Woodruff, Smith, Traum & Farrell, 1978), but in some circumstances these modes can be dominated by atomic effects (McGovern, Eberhardt & Plummer, 1979) and the azimuthal pattern is the most obvious way to isolate the photoelectron diffraction, since an isolated atom would show no such diffraction effects, and also the complications of atomic excitation and analyser geometry remain constant in this mode. The azimuthal photoelectron diffraction gives the now well known 'flower patterns' owing to the angular variation in the interference between the core-level photoemission direct from the adsorbate and the photoelectron wave backscattered from the substrate, similar to those seen in forward scattering of high-energy photoelectrons (Kono, Fadley, Hall & Hussain, 1978).

The photoelectron diffraction effects were also shown to persist in the scattered electron background. Fig. 3 shows that the blurring of the azimuthal angular pattern is only gradual as the electrons lose kinetic energy: most of the inelastic electron scattering is by plasmon creation, which takes energy but tends to be a low momentum transfer (low  $q$ ) process and thus does not change the direction of the electron by much (Woodruff, Norman, Farrell, Traum & Smith, 1980). This 'directional memory' effect was rediscovered later and dubbed 'inelastic photoelectron diffraction' (Herman & Fadley, 1991).

In the late 1970s there was much interest in multielectron effects in solid-state photoemission, especially as manifested in the apparent resonance of the satellite in nickel metal at a binding energy of 6 eV (Guillot *et al.*, 1977) when the photon energy is increased through the Ni  $M_{2,3}$  absorption edge. This observation stimulated many similar experiments, and much theoretical interest (*e.g.* Davis & Feldkamp, 1980). However, a problem with the quantitative analysis of the effect is that, at resonance ( $h\nu = 68$  eV) the Ni  $M_{2,3}$  VV Auger peak occurs at the same kinetic energy

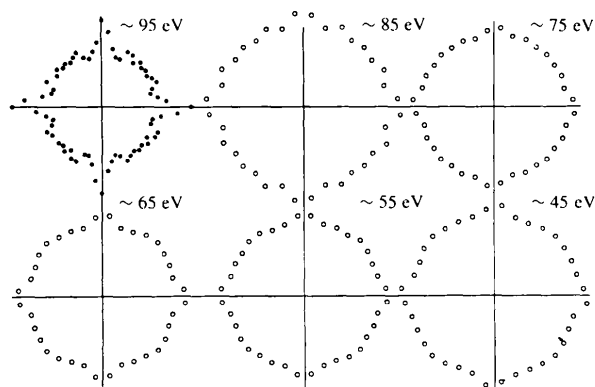
as the '6 eV' peak, thus making it difficult to disentangle the intensity of the two features. Indeed, it seemed possible that there might not be resonant enhancement at all, but merely a superposition of the Ni  $M_{2,3}$  VV Auger peak and the '6 eV' satellite. This notion was reinforced by measurements of the angular dependence of the feature (Traum, Smith, Farrell, Woodruff & Norman, 1979) which showed that the azimuthal angular variation of the '6 eV' peak at resonance closely resembled that of the electron-excited  $M_{2,3}$  VV Auger emission, suggesting that most of the intensity came from the Auger peak, not the '6 eV satellite'.

This suggestion did not fit in with popular understanding at the time, and this paper was ignored until identical measurements were performed almost 15 years later. Recent work has confirmed our earlier findings for Ni, and also shown that the enhanced 4*f* emission in metallic Ce at the  $N_{4,5}$  threshold has a  $\cos^2$  polar angular dependence, thus demonstrating that the resonant enhancement of the Ni 6 eV satellite is mainly due to a secondary Auger decay while for the Ce 4*f* it reflects true resonant photoemission (López, Gutiérrez, Laubschat & Kaindl, 1995).

## 5. The 'Miyake' monochromator at the Daresbury SRS

In 1979, the Miyake monochromator was returned to Daresbury to be installed on the first VUV station (6.1) at the newly built 2 GeV electron storage ring, the SRS. The experimental apparatus included an angle-resolving photoelectron energy analyser, and the first experiment studied angle-resolved photon energy-dependent photoemission from Ag(001). A comparison of the experimental results with theoretical calculations using a full multiple-scattering time-reversed LEED formalism showed that the theory reproduced the spectra quite well (Padmore, Norris, Smith, Larsson & Norman, 1982).

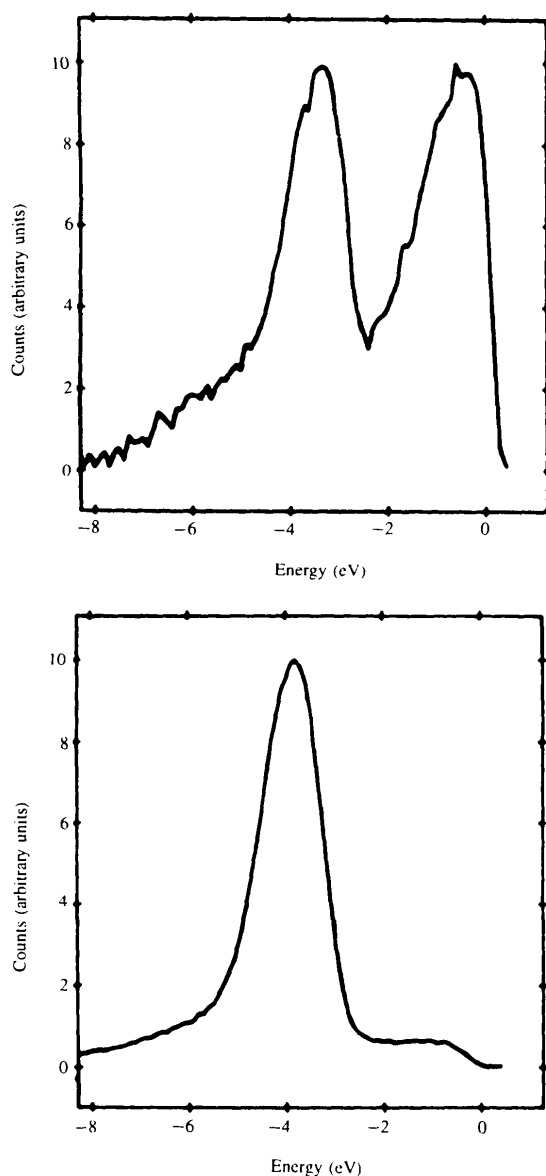
From 1981 onwards, the scientific programme at Daresbury rapidly expanded, and it was notable that the user group soon included academics from Departments of Chemistry and Materials as well as Physics, reflecting the fact that the maturing field of synchrotron radiation applications was no longer dominated by specialists in instrumentation. Various improvements to the instrument were introduced over the years, of which two have had the most benefit for users of the monochromator. A horizontal post-focusing mirror (Padmore, 1984) and a modification to the magnetic lattice of the SRS (Thompson & Suller, 1989) reduced the spot size to *ca*  $3 \times 0.3$  mm<sup>2</sup>, quite well matched to the acceptance of most electron energy analysers. Padmore (1986) also proposed slightly adjusting the mirror position  $M$  to achieve the best possible resolution at a particular wavelength, this being necessary because the source is not at infinity as the ideal Miyake design assumes. The resolution routinely achieved is  $h\nu/\Delta h\nu \approx 1000$  across the photon energy range 80–160 eV with a 1200 l mm<sup>-1</sup> grating (Bailey & Quinn, 1993).



**Figure 3** The 'directional memory effect' in the azimuthal angular variation of electron emission from a clean Ni(100) surface. The filled circles are the direct Ni 3*d* photoemission and the open circles are the inelastic background at various kinetic energies (Woodruff, Norman, Farrell, Traum & Smith, 1980).

The remainder of this section describes a small selection of the science carried out using the monochromator at the Daresbury SRS, taken from some of the experimental programmes in which the author was involved, concentrating on tunable photon-energy photoemission studies of metallic alloys. Other areas are reviewed elsewhere: semiconductor surfaces (McGovern, Norman & Williams, 1987) and adsorbates on metals (Woodruff, 1995).

The first example is the determination of the density of states in amorphous Cu-Zr (Greig *et al.*, 1988). The motivation for this work derived from a long experience of studying metallic glasses at the University of Leeds, using measurements of Fermi level properties such as resistivity, thermopower, Hall effect and magnetoresistance. The photoemission experiments exploited the tunable photon energy from the SRS and the knowledge of energy-

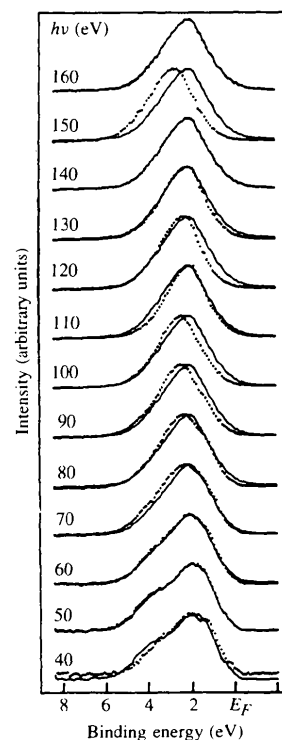


**Figure 4** Valence-band photoemission from amorphous  $\text{Cu}_{40}\text{Zr}_{60}$  at photon energies of 40 eV (top) and 120 eV (bottom) (Greig *et al.*, 1988).

dependent atomic cross sections to attribute features in the valence band to states derived from the different atoms in the alloy. The most noticeable effect is where nodes in the initial-state wavefunction lead to cancellation of matrix elements and a minimum in the photoionization cross section. This 'Cooper minimum' (Fano & Cooper, 1968) is seen for all states whose principal and angular momentum quantum numbers are related by  $n > l + 1$ , e.g.  $3p$ ,  $4d$ ,  $5d$ . Thus, in a compound or alloy where one of the constituents exhibits a Cooper minimum, it is a relatively simple task to use photon energy-dependent photoemission to separate the atom-specific density of states.

Fig. 4 shows the valence-band photoemission from amorphous  $\text{Cu}_{40}\text{Zr}_{60}$  at photon energies of 40 and 120 eV. At the higher photon energy, the peak near to the Fermi level almost disappears. It is thus very easy to see that the peak just below the Fermi level is composed of  $4d$  states, deriving from the Zr atoms, while the peak at higher binding energy is of  $3d$  character, from the Cu atoms. This is a clear example of a split-band alloy, with almost no hybridization between the two components.

The random crystalline alloy  $\text{Cu}_{95}\text{Pd}_5$  is, at first sight, more tricky, the valence states appearing as just one band (Fig. 5). However, the same technique can be used to separate out the Cu and Pd derived density of states, using the Cooper minimum in the  $4d$  states to suppress the Pd

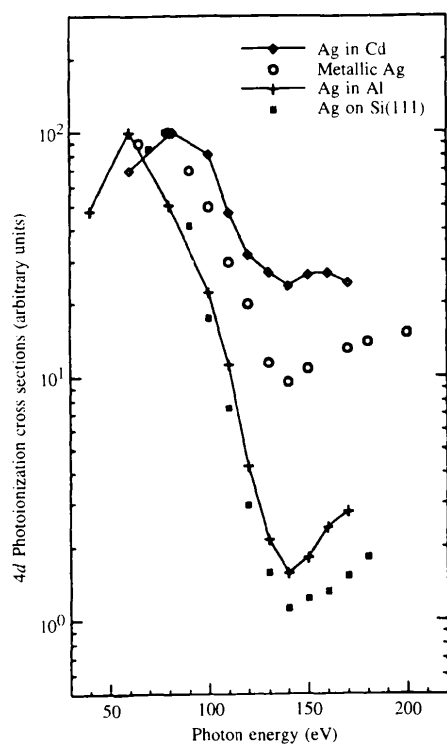


**Figure 5** Valence-band photoemission from the random crystalline alloy  $\text{Cu}_{95}\text{Pd}_5$  at a range of photon energies. The dots are the experimental spectra, after background subtraction and normalization. The full curves are theoretical profiles generated from the empirical Cu and Pd density of states (see Wright *et al.*, 1987), showing reasonable agreement except at  $h\nu = 150$  eV, where an error in setting the photon energy is suspected.

contribution (Wright *et al.*, 1987). For the Cu partial density of states, excellent agreement is found with theory using the coherent potential approximation (CPA), but for the Pd partial density of states, this theory overstates the weight at the bottom of the band. The reason for this is still controversial (*e.g.* Nahm *et al.*, 1993; Weightman, Cole, Verdozzi & Durham, 1994), but we believe it is caused by the local lattice expansion around the Pd atoms (Weightman *et al.*, 1987; Thornton *et al.*, 1994), which is not dealt with in the standard CPA theory.

The same Cooper minimum technique has been used to suppress the Au 5d valence band, and thus relatively enhance the Fe 3d contribution in Au<sub>90</sub>Fe<sub>10</sub>. Here the intention was to study the virtual bound states of Fe (Duó *et al.*, 1991), where the real interest is in the dilute impurity limit: at the 10% concentration measured here, the Fe atoms are probably interacting, but more flux is needed to probe more dilute samples.

So far, the Cooper minimum has been referred to as if it is purely an atomic effect. In fact, there are interesting influences of the solid state that mean that the position and the depth of the Cooper minimum vary for the same atomic state in different solid environments. This effect can make the Cooper minimum a sensitive probe of the spatial extent of wavefunctions. In one study using station 6.1 at Daresbury, major differences were found in the nature of the Ag 4d Cooper minimum between bulk Ag, Ag in Cd<sub>97</sub>Ag<sub>3</sub>, Ag in Al<sub>95</sub>Ag<sub>5</sub> and a submonolayer thickness of Ag deposited on an Si(111) substrate (Cole *et al.*, 1992)

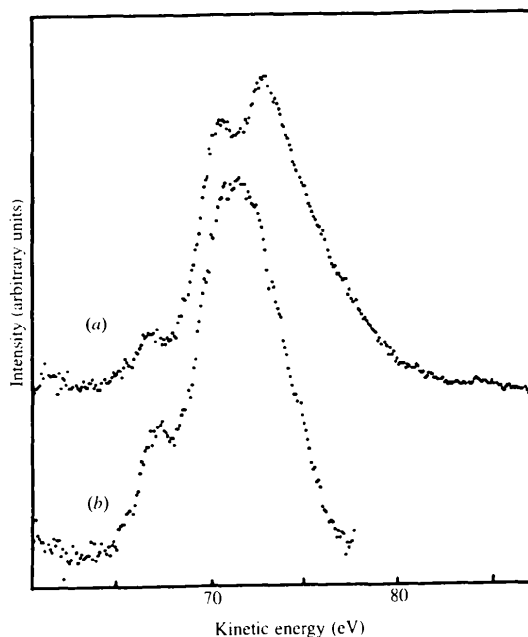


**Figure 6**

The Ag 4d Cooper minimum for bulk Ag, Ag in Cd<sub>97</sub>Ag<sub>3</sub>, Ag in Al<sub>95</sub>Ag<sub>5</sub> and a submonolayer thickness of Ag deposited on an Si(111) substrate (Cole *et al.*, 1992).

(Fig. 6). The position and depth of the minimum reflects the way in which Ag is bonded in these different systems. The Ag 4d atomic orbitals are largely unperturbed in the *sp* bonding in the Al alloy, and indeed, the Cooper minimum for Ag in the Al alloy looks very similar to that for atomic Ag. The shape of the minimum for the Ag on Si suggests that the Ag is also in an atomic-like environment. On the other hand, in the 4d systems, either pure Ag or the Cd alloy, there is significant *d-d* overlap which distorts the wavefunctions and perturbs the Cooper minimum. These experiments were a powerful demonstration that the Cooper minimum effect, depending crucially on cancellation in matrix-element integrals, is unique in its ability to detect the onset of distortion of the 4d wavefunction in the region of the radial minimum. Recent calculations for Cd–Ag have indeed shown that, even when the *d-d* hybridization is small, there is a large effect on the Ag 4d Cooper minimum (Cole, Weightman, Jennison & Stechel, 1994).

The final example given here is a study of the Auger lineshape in metallic gold. Using a photon energy ( $h\nu = 86$  eV) between the N<sub>6</sub> (4f<sub>5/2</sub>) and N<sub>7</sub> (4f<sub>7/2</sub>) absorption edges, the N<sub>6,7</sub>O<sub>4,5</sub>O<sub>4,5</sub> and N<sub>7</sub>O<sub>4,5</sub>O<sub>4,5</sub> Auger lines can be separated out (Evans *et al.*, 1990; Verdozzi, Cini, McGilp *et al.*, 1991), as shown in Fig. 7. The Cini–Sawatzky model for the Hubbard Hamiltonian gave a very good description of the profile for the Auger lines, but failed to give simultaneous agreement with the kinetic energy, with the energy wrong by 1.2 eV. This theory succeeds for band-like systems where the on-site interaction energy  $U$  is less than the single-electron bandwidth  $W$ . However, this work showed that in the quasi-atomic case where  $U > W$ , such as Au, off-site (interatomic) correlation effects need



**Figure 7**

The spectra of (a) the N<sub>6,7</sub>O<sub>4,5</sub>O<sub>4,5</sub> and (b) the N<sub>7</sub>O<sub>4,5</sub>O<sub>4,5</sub> Auger transitions of Au, excited with photon energies of 115 and 86 eV [between the N<sub>6</sub> (4f<sub>5/2</sub>) and N<sub>7</sub> (4f<sub>7/2</sub>) core levels], respectively (Evans *et al.*, 1990).

to be included in the Hamiltonian (Verdozzi, Cini, Evans *et al.*, 1991). A similar discrepancy has recently been found for Auger transitions in Ag, where the magnitude of the difference is 2.2 eV, even greater than for Au. This is understood in terms of the difference in the ratio of the off-site correlation energy to *d*-band width in the two metals (Cole, Verdozzi, Cini & Weightman, 1994).

## 6. The future of VUV spectroscopy for surface science

Photoemission from solids was one of the first techniques to make widespread use of synchrotron radiation. Indeed, it is interesting to note that the current Scientific Directors of many of the world's synchrotron radiation sources originally specialized in using this technique. The demand for it has not lessened over the years, and almost every synchrotron radiation source has several experimental stations dedicated to this area. The Daresbury Miyake monochromator has had an exceptional record, with 20 years of almost daily use as an excellent workhorse on three different synchrotron radiation sources. A bibliography shows over 200 publications using it (Teehan, 1995).

Now, however, we know that there are better designs. Surfaces are dilute systems and thus quite demanding in flux. Every significant improvement in spectral resolution has revealed new science, despite the anticipation that natural linewidths and solid-state broadening would negate the effects of reduced bandpass. Electron energy analysers have improved in throughput and resolving power, and spin detection is becoming more common. Polarization has become a crucial parameter for many techniques. Imaging methods are starting to reach realistic spatial resolution for many real problems.

Thus, a 'wish list' for the performance of a future monochromator for VUV spectroscopy would include a wide energy range, high flux, high resolution, well defined and variable (linear to circular) polarization, good ordering and a small spot size. All current designs have to compromise between these characteristics and it is clear that the only way to achieve most of these desired features is to have an optimized VUV synchrotron radiation source. Some second-generation storage rings have plans to fit VUV undulators but there is no source operational anywhere that has been designed for insertion device beamlines in the vacuum UV (as opposed to soft X-ray) spectral region: SINBAD, proposed for Daresbury, would fill this gap (Suller, 1994). A recent review of monochromators for third-generation sources (Padmore & Warwick, 1994) summarized the possibilities for innovative instruments for soft X-rays. There are similar prospects in the VUV region: with improvements in fabrication of optics, such as variable line spacing gratings and low slope errors on mirrors, novel instrumentation will surely open up new horizons for surface science.

The success of this monochromator, and the science achieved with it, owes much to the fine engineering skills

of Mr D. K. Tole, and to the dedication of the instrument scientists who were responsible for installing and tending it over the years: Malcolm Howells and the author at the Daresbury SRF, John West and Gwyn Williams at TANTALUS, and lately the SRS station scientists for station 6.1 over the period 1981–1995: the author, followed by Howard Padmore, Daniel Law, Frances Quinn, Paul Bailey and Dave Teehan.

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