Faraday Discuss. Chem. Soc., 1990, **89**, 65-75

GENERAL DISCUSSION

Dr A. Fontaine (*LURE, Orsay*) addressed Professor Bradshaw: Electron energy-loss spectroscopy (EELS) is a competitor of X-ray absorption spectroscopy: What should be the future of X-ray inelastic diffraction in order to probe core-level excitation? In other words, using a very high energy beam monochromatized very carefully (10^{-6}-10^{-7}) coupled to an analyser with the same resolution, it should be possible to investigate the oxygen, N, C, . . . (all the low-Z elements) using a very thick sample. Can you comment on that?

Prof. A. M. Bradshaw (*Fritz-Haber-Institut der MPG, Berlin*) replied: I agree with Dr Fontaine that there are areas in which EELS is a serious competitor of X-ray absorption spectroscopy in the study of core-level excitations. One very topical example is provided by recent work on high-T_c superconductors. This is not necessarily true, however, for studies of surfaces, in particular of adsorbed layers. Although there have been measurements of SEXAFS-type wiggles in EELS of adsorbed layers, such investigations are confined to very stable chemisorption systems not susceptible to electron beam damage. The particular experiment which Dr Fontaine describes (inelastic X-ray scattering) has already been used to examine near-edge excitations in low-Z materials by Schülke *et al.*[1] It might prove to be a useful method for bulk samples and could avoid some of the problems of sample preparation associated with XUV absorption experiments. It might conceivably provide the possibility of investigating low-Z adsorbates on bulk catalyst samples; otherwise I cannot see any surface structural applications.

1. W. Schülke, U. Bonse, H. Nagasawa, A. Kapolat and A. Berthaud, *Phys. Rev. B*, 1988, **38**, 2112.

Prof. D. P. Woodruff (*University of Warwick*) said: Although I believe extended fine structure in electron energy loss has been investigated only for atomic oxygen and carbon in the chemisorbed state, Hitchcock and co-workers have shown that near-edge structure in adsorbed benzene can be studied by this method, although the signal-to-noise ratios of their data are not very good so the experiment may be rather marginal.

Prof. Bradshaw replied: That is correct. Hitchcock and co-workers[1] have recently published some EELS near-edge spectra for adsorbed benzene and pyridine. The S/N ratio is, however, considerably worse then in a state-of-the-art soft X-ray experiment with synchrotron radiation. Furthermore, we should remember that these molecular resonances in the near-edge region are at least a factor ten stronger than the SEXAFS wiggles at higher energies.

1 T. Tyliszczak, F. Eposto and A. P. Hitchcock, *Phys. Rev. Lett.*, 1989, **62**, 2551.

Dr K. Prabhakaran (*University of Manchester*) communicated: This is just a comment on the Cu(110) (2×1)—O system. We found that oxygen is adsorbed molecularly in a peroxo form on a clean Cu(110) surface at low temperature. Adsorption of molecular oxygen on a Cu(110) (1×1) surface results in the formation of a diffuse (1×1) pattern, whereas when the adsorption is done on a Cu(110) (2×1)—O surface, it transforms back to the Cu(110) (1×1) pattern.[1] This suggests that in the presence of peroxo species the missing row reappears on the surface.

1 *Surf. Sci.*, 1986, 177, L971.

Prof. Bradshaw replied: I have no real explanation for this interesting result. One possibility is that the molecular oxygen requires a particular surface site associated with the unreconstructed surface. Molecular oxygen on Ag(110) is known[1,2] to be adsorbed in a lying-down configuration with its axis parallel to the ⟨110⟩ azimuth, presumably in the troughs of a non-restructured surface. The energy required to lift the reconstruction of the Cu(110) surface could also in this case be provided by the molecular oxygen. The amount is probably comparable with the energy difference of *ca.* 40 kJ mol^{-1} between Cu(110)(2 × 1)—O with and without the missing row, at least according to Nørskov's calculations.[3] It is, however, remarkable that the atomic oxygen, which should still give the (2 × 1) structure, then forms a disordered layer.

[1] K. C. Prince, G. Paolucci and A. M. Bradshaw, *Surf. Sci.* 1986, **175**, 101.
[2] D. A. Outka, J. Stöhr, W. Jark, P. Stevens, J. Solomon and R. J. Madix, *Phys. Rev. B*, 1987, **35**, 4119.
[3] K. W. Jacobsen and J. K. Nørskov, to be published.

Prof. R. W. Joyner (*University of Liverpool*) addressed Dr Heald: To the uninitiated, the growth mode shown in fig. 5(*a*) of your paper for the Ni/Al layer is unexpected. Why does the Ni/Al_3 grow to a constant thickness (of *ca.* 150 Å) in the range 250–310 °C, and why does a layer of apparently different composition grow on top with a thickness which is temperature dependent? Do you have independent corroboration, *e.g.* by electron microscopy, for the model you propose?

Dr S. M. Heald (*Brookhaven National Laboratory, New York*) replied: It is quite common for reactions in thin-film couples to form predominantly one phase (in our case $NiAl_3$). The uniformity of the growth depends on the dominant diffusion path. Our results show that the presence of O impurities in the Al suppresses the grain-boundary diffusion channel. This results in the growth of a uniform layer during the initial reaction at lower temperatures. For higher temperatures the blocking of the grain boundaries is overcome and the reaction also takes place outwards from the grain boundaries as well as from the interface. In both cases $NiAl_3$ is being formed. The changing average composition at higher temperatures is due to a changing ratio of unreacted Al to $NiAl_3$. In response to your second question: We have not applied other techniques to Ni/Al. For the case of Cu/Al RBS and TEM studies were in good agreement with the X-ray results for both the composition and roughness of the interface in unreacted samples.

Dr I. K. Robinson (*AT & T Labs, Murray Hill, NJ*) asked: With regard to your fig. 3, can you elaborate on the number of free parameters and the uniqueness of the fitting of reflectivity data? In particular, can you distinguish between a double step interface and a single broad interface (*i.e.* very 'rough')?

Dr Heald replied: For each layer there are three parameters: thickness, density and roughness. Usually three or four layers are needed to obtain a good fit. However, we found that simultaneously fitting the spectra obtained above and below the transition-metal K-edge dramatically reduces the correlations between the parameters. It is true that different models (for example an error-function roughness compared to a linear transition region) can be used to fit the reflectivity, but if the density profiles from these are compared, they are quite similar. Thus, I believe that the density profiles are uniquely determined. Regarding the approximation of the double step with a single rough interface, this fails completely to explain the data. In fact, there are distinct indications of a double step in the 250 °C data in fig. 3. Note how the lowest-angle peak is significantly higher than the second and third, which are nearly equal. This results from a critical angle intermediate between Al and Ni, and shows up only if the intermediate layer is well defined.

Dr R. J. Oldman (*ICI Chemicals and Polymers, Runcorn*) asked: Do you have an independent check on the roughness values derived from modelling reflectivity data or are they just modelling parameters necessary to get a good fit?

Dr Heald replied: We do not have an independent check for the roughness of the Ni/Al and Cr/Al samples. I believe the roughness parameters are meaningful, however, since they were checked by TEM and surface profilometry in our earlier work on Cu/Al and Au samples. In those cases good agreement was found.

Prof. J. F. van der Veen (*FOM Institute for Atomic and Molecular Physics, Amsterdam*) said: It seems to me that the Ni density profiles in your fig. 5 could just as well have been derived from a Rutherford backscattering analysis. RBS is much easier to perform. In the discussion section of your paper you mention that RBS does not have the same depth resolution as the glancing-angle reflectivity technique. What is the depth resolution in your experiments, and what specific advantages in your view does the reflectivity technique have over RBS?

Dr Heald replied: We have sent out some of the samples our for RBS analysis, and the typical depth resolution was *ca.* 100 Å, while we can easily achieve sensitivities of 10–20 Å in the interface width. I disagree with the notion that RBS is much easier to perform. We are dealing with reflectivities greater than 1%, which means the experiments could be easily performed using laboratory X-ray sources. We used a synchrotron source as we were also making EXAFS measurements. The reflectivity also has the advantage that it can be applied *in situ* to gas/solid and liquid/solid interfaces.

Prof. van der Veen then said: In RBS, one can achieve a depth resolution of *ca.* 50 Å with the use of small exit angles. Even a depth resolution of $\leqslant 10$ Å can be achieved, though I admit that the latter value is non-standard. [See *e.g.* ref. (1) for a review of high-resolution RBS.]

1 J. F. van der Veen, *Surf. Sci. Rep.*, 1985, **5**, 199.

Prof. P. Pershan (*Harvard University*) said: I would like to support the claim that the resolution of X-ray reflectivity is generally superior to that of Rutherford backscattering. Although Dr Heald did not measure reflectivity to large angles, we have measured specular reflectivity of the Si(100) face past the [400] position. Resolution in this case is better than 1 Å and certainly superior to anything possible by Rutherford backscattering.

Prof. D. C. Koningsberger (*Eindhoven University of Technology*) said: You did not show any coordination parameters in your paper. The quality of your data looks reasonably good. So, I would like to ask you whether it is possible really to analyse the data, which you collected with glancing-angle EXAFS and what is the accuracy you can achieve?

Dr Heald replied: The comparisons in the paper are qualitative since that was all that was needed to demonstrate the growth of $NiAl_3$. It is certainly possible to analyse the data quantitatively, as we have demonstrated for Cu/Al interfaces [see ref. (2) of our paper]. To do this the data must first be corrected for anomalous dispersion affects. For the present data anomalous dispersion reduces the EXAFS amplitude by 30–50%, and distorts the phase such that analysis would result in about a 0.03 Å error. Both the Ni and $NiAl_3$ contributions have nearly the same distortions, and, therefore, the qualitative comparisons in the paper are still valid. We have demonstrated previously that the distortions can be corrected sufficiently to have only a small additional contribution to the normal errors encountered in the EXAFS analysis.

Dr J. Jupille (*Laboratoire Maurice Letort, Villiers-les-Nancy*) said: The EXAFS analysis is performed at different angles of incidence of the X-ray beam, so as to vary the part of the sample which is probed. However, the energy scan corresponding to the EXAFS study will change the depth of the analysis (as in the combination of EXAFS with standing waves). Is that problem accounted for during the collection of EXAFS data in the present case?

Dr Heald replied: The penetration depth into the interface does vary as the energy is changed. However, for angles near the first peak, as was used for collecting the present EXAFS data, the change is quite small. It does need to be taken into account when correcting the data for anomalous dispersions distortions. For cases where the change in penetration is important, we have shown [see ref. (2) in our paper] that it is possible to vary the incidence angle as the energy is changed to maintain an approximately constant penetration.

Dr K. M. Robinson (*US Naval Research Laboratory, Washington D.C.*) said: Because α_c varies as $\sqrt{2\delta}$, the penetration depth varies as a function of E. If you do no correction for $\alpha_c(E)$, are you not continually probing a different section (depth) of your sample? Even if you do a linear correction, the penetration will vary and the same question applies.

Dr Heald replied: As mentioned in the previous response this was not a serious problem for the present measurements. It is true that for the near-edge region where the anomalous dispersion is large, additional changes in δ occur which are not so easy to remove. However, we have not used the near-edge region in the present work.

Dr K. Prabhakaran said: Could you predict anything about the reactivity of the interface, say, for example, with regard to the adsorption behaviour? The reason why I am asking is, we observed that the adsorption behaviour of a polycrystalline Ni surface can be altered by depositing Al. We also observed that Al is helping to fill the d-band holes. On the Al-deposited Ni surface we observed a precursor to dissociation of CO.

Dr Heald replied: I do not believe that our results reveal much about this question aside from the observation of a spontaneous reaction between Ni and Al at room temperature. This is consistent with your observation of Al altering the chemistry of an Ni surface.

Professor J. M. Thomas (*The Royal Institution*) addressed Dr J. Robinson: Whilst one is impressed by the strength of your argument (and the cogency of your fig. 5 in particular) that the structure of the passive film is, compositionally at least, given by $Cr(OH)_3$, I would be surprised if this were still the composition at modest temperatures. The hydrogen-bonded network that you talk of is hardly likely to survive more than a few hundred degrees Celsius. And I suppose that even at room temperature some 'fluxionality' of the OH groups might be expected.

My second point refers to your remark, with which I agree, that the passive film on iron may be regarded as disordered γ-FeOOH. My colleague, Dr Tricker when he worked with me in the University College of Wales, in the mid 1970s, showed by conversion electron Mössbauer spectroscopy—which, incidentally, *via* energy analysis, is capable of depth profiling—was among (if not) the first to show that γ-FeOOH is present at a partially oxidized iron surface.[1]

[1] M. J. Tricker and J. M. Thomas, *Appl. Surf. Sci.*, 1978, **1**, 388.

Dr J. Robinson (*University of Warwick*) replied: No we have not investigated what happens to the passive film on heating. We have, however, investigated the effect of transfer of the passive film to high vacuum and this does not appear to alter the structure significantly. Presumably at sufficiently high temperatures one might expect the hydroxides and oxyhydroxides to decompose to the corresponding oxides.

Prof. J. V. Smith (*University of Chicago*) said: My first question addresses the interpretation of interatomic distances. A metal-oxygen distance is *ca.* 0.05 Å shorter than an M—OH distance. The interpretation of distances in an ordered crystal structure, as studied by Bragg diffraction, depends on the relation of the centroid of measured electron density to the disorder caused by both thermal vibration and chemical substitution in the same crystallographic site. Depending on the vibration model the distances from the centroids may be increased by 0.01-0.03 Å in many inorganic materials at room temperature. The interference phenomena in EXAFS involve a different adjustment for the disorder. Hence, should your interpretation of the $Cr(OH)_3$-like phase consider these subtle effects?

A second question concerns whether the experimental data will allow a mixture of other coordinations than the value of six. For example, the possibility of some five-coordination might allow a better spatial fit on a surface.

Dr Robinson replied: In the case of the $Cr(OH)_3$-like phase I do not think there is any need to consider these subtle effects. The EXAFS and XANES of the passive film and commercial $Cr(OH)_3$ are essentially identical with the corresponding bond lengths, refining to within 0.01 Å of each other. It was found that the phase shifts were transferable between Cr_2O_3 and the hydroxide and therefore it is unlikely that anharmonicity needs to be considered in this case.

On your second point, whilst the analysis of EXAFS is rather insensitive to coordination numbers I would expect a significant reduction in the Fe—O and Cr—O bond lengths on going from six- to five-fold coordination. In addition, the XANES region is particularly sensitive to the coordination and I would again expect significant differences on going to five-fold coordination. In view of the similarities between the XANES of the passive film and that of the six-fold coordinate oxyhydroxide model compounds I think it is clear that the passive film does not contain significant quantities of five-coordinate metal centres.

In view of the strong correlation between coordination numbers and Debye-Waller factors we used a coordination number of six in all our analyses of the Fe K-edge EXAFS to make it easier to identify any possible trends in the disorder with changing alloy composition.

Prof. Koningsberger then said: An apparent deviation of the real coordination distance can be caused by not including in the EXAFS analysis an asymmetric distribution function. The result of not including an asymmetric distribution function leads to an apparent contraction of the coordination distance. Did you look in your analysis for the presence of an asymmetric distribution function?

Dr Robinson replied: Given the signal-to-noise level of the data and the rather limited data range it is quite difficult to test for anharmonicity. We have, however, checked the phase differences between the passive film and several model compounds, as a function of k, and have been unable to detect any non-linearity. This suggests that the distribution function is symmetric.

Prof. R. Parsons (*University of Southampton*) said: Does the structural investigation give any clue as to why the film is passive? Presumably it must transfer electrons either by conduction or by tunnelling. Does the chromium hydroxide have such properties?

Dr Robinson replied: The $Cr(OH)_3$-like phase is amorphous and I think it is this that gives the film its good passivating properties.

In answer to your second question. We have conducted photocurrent spectroscopy studies of the passive film on Cr-rich alloys. As with the film on pure iron, the passive layer behaves like an n-type semiconductor, but with the apparent band gap increased to *ca.* 2.5 eV. Given the thinness of the passive film, however, tunnelling seems highly probable. It should be possible to investigate this by studying electron-transfer reactions at the passive film surface, though I am not aware of any such studies having been made.

Dr G. Thornton (*University of Manchester*) said: In the experiments you describe the metal/alloy film is consumed. Do you expect your conclusions to be valid for a system in which the metal/alloy substrate is present?

Dr Robinson replied: The experiments are designed to consume all the metal film so as to facilitate the analysis of the EXAFS. If there is any unconverted metal present then this also contributes to the EXAFS. In particular the first shell of the metal overlaps with the second shell of the passive film (both of these shells contain metal atoms), making the analysis difficult. We have, however, analysed films where there is *ca.* 20 Å of metal protected by a similar thickness of passive layer and our conclusions remain the same. We therefore consider our approach to be valid.

Dr J. W. Couves (*The Royal Institution*) addressed Dr Fontaine: Is there any evidence for the degradation of the polymer integrity during the reduction of the PMeT-$FeCl_3$ system? This could account for the decrease in macroscopic conductivity at long polarisation times, as well as the proposed loss of bridging Fe^{3+} and de-doping of the polymer.

Dr Fontaine replied: In this case the distinction between incoming neighbours during the polarization is very favoured by the (π) out of phase backscattering amplitudes of S and O.

Dr Jupille then said: The increase of conductivity of the polymer is related to the appearance of Cu^I ions interacting with the sulphur atoms of the thiophene unit. This is in a second stage of the reduction process. In the first stage of that process, the Cu^I ions are surrounded by oxygen. Do these environments lead to differences within the Cu K-edge absorption spectrum?

Dr Fontaine replied: It is true that the increase in conductivity is correlated with interchain connection, which occurs through Cu^I bridging. Cu^I in a linear configuration is identified in the Cu K-edge because of the non-bonding orbitals. Therefore XANES is not sensitive to the nature of the ligand. However, this is no longer the case when using EXAFS because Cu—S and Cu—O appear as oscillations out of phase.

Prof. Koningsberger said: The S/N value of your experimental data collected with the dispersive EXAFS method seems to be excellent, certainly taking into account the short data collecting time. Is it possible really to analyse these data and to obtain reliable coordination parameters?

Dr Fontaine replied: I should have given more details about the EXAFS analysis, but because of the lack of time, I didn't show slides. But the paper contains figures showing how sensitive the dispersive geometry can be to trace tiny changes in short time. The lack of mechanical movement during data collection is of great advantage. It eliminates one of the main sources of noise given by the scanning mode.

Dr I. K. Robinson then asked Dr Roberts: First, can you summarise what is learned about the depth distributions obtained by variation of the grazing angle? In your experience, is this as useful a tool as advertised?

Secondly, could you elaborate on the surface preparation? You might expect to see As–As distances in an interface made with freshly grown GaAs.

Dr K. J. Roberts (*University of Strathclyde*) replied: As far as the Cu films are concerned, no *major* structural changes were observed by changing the glancing angle below the critical angle. However, the oxide phase appeared to be more pronounced at the outermost surface and there was an indication of a greater proportion of Cu^{II} in this top layer. The angle-dependent ReflEXAFS spectra probed the surface structure from a minimum of *ca.* 15 Å to a maximum of only *ca.* 30 Å below the air/film interface. These penetration depths are imposed by the reflection geometry, since we are forced to work below the critical angle if we want to avoid correcting the measured data for the distortions introduced by anomalous dispersion. Nevertheless this is the most interesting region, and we have shown that structural changes can be recorded even in such a small range of penetration depths. Of course, whether angle-dependent measurements will be useful or not very much depends on the system and on the depth scale for which structural changes are expected to occur.

The variation in the glancing angle was particularly useful in our ReflEXAFS study of GaAs(100). Here dramatic changes were observed in the environment of Ga atoms. In particular the coordination of Ga to O increases considerably at the outermost surface. The surface is observed to be depleted of As atoms in the surface, as evidenced by a comparison of the step edge thresholds (arbitrary units) which were:

	Z/Å	As K-edge	Ga K-edge
ϕ_1	25	0.14	0.16
ϕ_2	30	0.21	0.18

In answer to your second question, surprisingly the surface science community has, as far as we know, yet to see the advantages of total external reflection geometry for SEXAFS-type measurements. Should such measurements be carried out one might well expect to see the formation of As–As dimers on such clean GaAs surfaces.

For our work we examined GaAs(100) as-received from ICI Wafer Technology. A native oxide *ca.* 10 Å thick was therefore expected on the surface. As–As distances are unlikely at the GaAs/oxide interface but we cannot show this conclusively as, owing to the closeness in the atomic numbers of Ga and As and in the corresponding backscattering amplitudes, it is difficult to distinguish unambiguously between these two atoms. This is certainly one of the limitations of the EXAFS technique. Were we to examine other III–V compounds such as InP or GaSb then the analysis of group V dimer formation would be easier.

Dr Heald asked: Did you have a problem with Bragg reflections interfering with the single crystal EXAFS?

Dr Roberts replied: We did not have any problem with the GaAs(100) measurements since we recorded the spectrum in the reflected signal. The angle (typically 7°) subtended by the detector window is too small to enable the first diffraction peak expected from the GaAs substrate to be recorded.

The same is not true when working in fluorescence geometry where to maximise count rate from dilute analytes a detector subtending a large solid angle is used. So far we have adopted two approaches to get round this problem: when working at glancing angles greater than ϕ_c we can spin the sample to 'average' out these effects;[1,2] for total reflection geometry the goniometric requirements are too severe to enable sample rotation at constant Z. Recently, in collaboration with Professor Regnard's group in Grenoble, we have examined the local environment around ion-implanted As in crystalline Si. On that occasion a multi-element solid-state detector was used to discriminate in terms of energy between Bragg reflections and fluorescent radiation. Even in this case there have been problems as the Bragg peaks can saturate the individual detectors and the resulting non-linearities in the detector response (due to count pile-up) can make the data unanalysable. In such cases we eliminated the non-linear channels from the final summed up data set.

1 G. N. Greaves, P. J. Halfpenny, G. M. Lamble and K. J. Roberts, *J. Phys. (Paris)*, 1986, **12**, 901, C8 suppl.
2 N. Barrett, G. M. Lamble, K. J. Roberts, J. N. Sherwood, G. N. Greaves, R. J. Davey, R. J. Oldman and D. Jones, *J. Crystal Growth*, 1989, **94**, 689.

Prof. R. W. Joyner said: The 'catalytic' effect for copper oxidation, which you ascribe to the GaAs surface may be morphological. The reactivity of oxygen with copper is very surface-specific. Thus the oxygen sticking probability varies from *ca.* unity on Cu(110) to $<10^{-6}$ on Cu(111).

Dr Roberts replied: This might be the case if the Cu films had a preferred orientation. Texture measurements have been made on the Cu/float glass samples and no preferred orientation was found. Given the disordered nature of the native oxide on GaAs(100), we doubt also that there is a preferred orientation on the Cu/GaAs samples, but we have no evidence as yet.

This question highlights the obvious need to carry out diffraction measurements *at the same time* as the ReflEXAFS measurements. Whilst such an experiment has yet, to our knowledge, to be performed, there is *no technical reason* why it could not be carried out. In our view the combination of diffraction measurements (to reveal long-range order as well as texture) is the next priority in the development of this technique.

Prof. J. M. Thomas said: Your suggestion that the surface of commercial-grade GaAs(100) has an oxide in which Ga coordinates to oxygen both tetrahedrally and octahedrally whilst As is only tetrahedrally bonded is eminently reasonable in the light of recent work by my Chinese collaborator Prof. Ruren Xu and his colleagues in Jilin University. $AlAsO_4$ (which is similar to $GaAsO_4$) forms a number of open, continuous network structures. Ruren Xu and co-workers[1] have determined the structure of this zeolite—like solid, and indeed they see four- and six-coordinated Al but only four-coordinated As, with the tetrahedral and octahedral arrangements involving bridging oxygens. My colleague Dr Richard Jones at the Davy Faraday Laboratory has recently established[2] that $AlPO_4$ sometimes crystallizes with this same structure.

1 G. Yang, L. Li, J. Chen, R. Xu, *J. Chem. Soc., Chem. Commun.*, 1989, 810.
2 R. H. Jones, Ruren Xu, J. M. Thomas, Yan Xu and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1990, in press.

Dr Roberts replied: It is most interesting to hear of this corroborating evidence from Professor Thomas's group. The structure reported by Yang *et al.* is for $Al_2As_2O_8$·ethanolamine (AAE) which seems to exhibit essentially the same local structure as we observed in the surface oxide on GaAs(100). In AAE the Group III aluminium is both tetrahedrally and octahedrally coordinated whilst the Group V arsenic is only tetrahedral. The bond lengths too are comparable with our data, *e.g.*:

	R/Å	
	our work	Yang *et al.*
Group III-O (tetrahedral)	1.69	1.718-1.751
Group III-O (octahedral)	1.95	1.844-1.947
Group V-O (tetrahedral)	1.68	1.649-1.698

However, in a more direct comparison one should be more cautious. AAE is a highly crystalline structure exhibiting a well defined long-range order whilst our material is only *ca.* 10 Å thick and variable in stoichiometry. It is quite different from AAE or $GaAsO_4$. The surface shows significant As depletion and there is a general lack of the long-range order of AAE. Also the kind of cage-like structure described by Yang *et al.* for AAE would, we believe, be easily detected by EXAFS through the backscattering enhancement provided by multiple scattering effects in ring-like structures such as this.

The Chairman then invited discussion on all the papers.

Prof. S. A. Rice (*The James Franck Institute, Chicago*) asked Prof. Bradshaw: Do you think it possible to extend the study of elastic light scattering to the soft X-ray range, say 10-20 Å, so as to be able to study the configurations of, say 20-30 long linear hydrocarbons or partially fluorinated hydrocarbons adsorbed at an interface? The issue turns on the available X-ray flux and the efficiency of the detectors, and on suppression of background scattering. Have you any feeling for what is possible now, or with new synchrotrons, or with new detectors?

Prof. Bradshaw replied: In principle, I think it is already possible to perform such measurements at existing synchrotron radiation facilities, although the spectral brilliance of undulators at sources such as the ALS or BESSY II (*ca.* 10^{18} photons s^{-1} mm^{-2} $mrad^{-2}$, 0.1 % bw^{-1}) would be of clear advantage. The main problem will be finding position-sensitive detectors. It would appear that phosphor-coated CCD detectors[1] are at present most suitable. These have recently been used for applications in soft X-ray microscopy with Gd_2O_2S: Tb as phosphor.[2] However, at the relatively large scattering angles expected for such photon energies, these detectors of typically <1 cm^2 surface area will cover only a relatively small solid angle.

[1] S. M. Grunner, *Rev. Sci. Instr.*, 1989, **60**, 1545.

[2] W. Meyer-Ilse, in *X-Ray Microscopy II*, ed. D. Sayre, M. Howells, J. Kirz and H. Harbach (Springer-Verlag, Berlin, 1988), p. 124.

Dr Fontaine asked Dr Bradshaw: What forthcoming developments can you envisage in connection with spin-polarized photoemission and with circularly polarized X-rays to investigate the magnetism of interfaces and surfaces?

Prof. Bradshaw replied: There is a whole variety of possible experiments here, some of which are already being performed, or at least planned, at several synchrotron radiation facilities. The availability of elliptically polarised undulator radiation will promote considerable activity in this area in future. The first photoemission measurements on non-magnetic materials using circularly polarised light were performed some years ago by Heinzmann, Kirschner and co-workers.[1] The emission from a particular spin-orbit split component of a bulk electronic band shows a preferential spin orientation, parallel or anti-parallel to the electron momentum. From the sign of the spin polarisation and the helicity of the light the double-group symmetry of the occupied bands can be determined. The effect has proved useful in band-mapping studies of heavier metals. Similar experiments have also been performed on adsorbed rare gases.[2] Another interesting result from non-magnetic systems is the observation of circular dichroism in the angular distribution of photoelectrons from both oriented molecules and crystalline solids[3]. The effect requires no spin detection and is not restricted to systems showing strong spin-orbit coupling.

In connection with magnetic materials there are two recent results which I think have important implications for future work. The first is the measurement by Schütz *et al.*[4] of different absorption coefficients for left- and right-hand polarised synchrotron radiation in the K and L near-edge spectra of ferromagnets. This technique probes the spin density of unoccupied valence bands and might be described as magnetic circular dichroism. The second result, again from Kirschner's group, is the observation of exchange splitting in Fe 2p core-level photoemission. Depending on the helicity of the light and the sample magnetisation the two spin-orbit split components are each resolved into lines of different intensity. Spin detection of the photoemitted electrons is not required. Similar results have apparently also been obtained in the valence region.

1 A. Eyers, F. Schäfers, G. Schönhense, U. Heinzmann, H. P. Oepen, K. Hünlich, J. Kirschner and G. Borstel, *Phys. Rev. Lett.*, 1984, **52**, 1559.
2 G. Schönhense, A. Eyers, U. Friess, F. Schäfers and U. Heinzmann, *Phys. Rev. Lett.*, 1985, **54**, 547.
3 G. Schönhense, *Phys. Scr.*, 1990, **T31**, 255.
4 G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, L. Zeller, R. Frahm and G. Materlik, *Phys. Rev. Lett.*, 1987, **58**, 737.
5 L. Baumgarten, L. M. Schneider, H. Petersen, F. Schäfers and J. Kirschner, *Phys. Rev. Lett.*, 1990, **65**, 492.

Prof. G. N. Greaves (*SERC, Daresbury*) then said: I would like to pick up Stuart Rice's remark about light scattering from surfaces by drawing attention to the possible utility of combining X-ray glancing-angle geometry with a two channel-cut-crystal arrangement to record surface diffuse scattering. In principle this would enable angles as small as the crystal rocking curve to be approached (*ca.* arc sec or 8×10^{-5} Å at 1.5 Å). In practice it has been used by Bonse, Hart, Bordas and others to measure conventional small-angle scattering at normal incidence. By using near-perfect crystals and multiple reflections, X-ray scattering can be extended into the Brillouin scattering regime. The use of grazing incidence would facilitate the study of molecules on surfaces and their aggregation with coverage. SR offers the advantage of choosing the wavelength to match the size of the scattering centre and the k range to determine the dimensionality of the assembly.

Dr Roberts concluded: Over the past few years glancing-angle X-ray absorption spectroscopy has developed into an extremely promising technique for the structural characterisation of condensed interfaces. Structural information on solid-liquid interfaces (e.g. electro-chemical, crystal growth interfaces) and solid-solid interfaces (*e.g.* surface-reacted layers, thin films and coatings) is at present extremely limited. Glancing-angle X-ray techniques have the potential to form a bridge between the classical surface science (UHV) techniques and the more realistic interfaces as typified by many technological and industrial systems. However, this technique is still in its infancy and significant further developments can be expected; these are likely to include: improvements in X-ray collimation and reduction in air scatter paths to enable data with improved signal-to-noise ratios to be collected; fluorescence data collection using multi-element solid-state detectors to enable dilute analytes to be examined; total electron yield detection to enable data collection of concentrated analytes to be collected at glancing

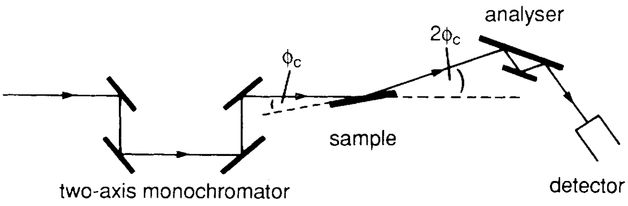

Fig. 1. Schematic representation of a four-axis scattering system. The two-axis monochromator provides a 'tail-less' tunable and non-deviating incident beam and the fourth axis (analyser) provides an exact definition of the scattered X-ray beam direction.

angles greater than the critical angle, ϕ_c; fast scanning monochromators and high-resolution position-sensitive solid-state detectors for time-resolved X-ray absorption spectroscopy measurements; environmental cells for *in situ* measurements. These developments will be significantly aided by moving from the current double-axis to the quadruple-axis scattering geometry shown in fig. 1.

This set-up has the following features: an undeviating, tail-less tunable X-ray beam is provided by a pair of oppositely handed Si channel-cut monochromators mounted on the first two axes; the scattered beam is collimated by a three-bounce Si analyser mounted on a scanable 2θ arm. Such a set up will enable the separation of the small-angle/diffuse scattering components from the reflected signals used in the ReflEXAFS technique.

Such an instrumental development will enable high-resolution X-ray diffraction and reflectivity data to be collected in the *same series of measurements* that are used to collect the glancing angle X-ray absorption spectroscopy data. It will also, by virtue of a better definition of the scattered beam path, enable rougher interfaces to be examined. Such an instrument potentially provides a research capability which directly mirrors but complements that routinely available (*e.g.* ESCALAB) to surface scientists.

Improvements in source characteristics can also be expected in the next generation of electron storage rings. The proposed Daresbury Advanced Photon Source (DAPS) will provide a projected reduction in source size and resultant improvement in spectral brightness of two orders of magnitude. This has the following implications for ReflEXAFS measurements: currently the large source size provided by first-generation storage rings has to be significantly collimated to satisfy glancing-angle requirements and typically *ca.* 95% of available beam flux cannot be used; the projected DAPS facility will provided high-intensity photons around 1000 eV and we can expect to be able to study light elements such as Mg, Al, P, S and Cl in adsorbates and surface coatings.

Thus the future for the continuing development of glancing-angle synchrotron X-ray techniques for the structural characterisation of interfaces looks good. We can expect that these will provide information to *extend and complement* that provided by conventional surface science techniques.