*Faraday Discuss. Chem. Soc.*, 1990, **89**, 143–158

# *GENERAL DISCUSSION*

**Prof. A. M. Bradshaw** (*Fritz-Haber-Institut der MPG, Berlin*) said: I have three questions to Dr Thornton. (i) Is there not a discrepancy between the X-ray absorption (NEXAFS) data of fig. 5 and the photoemission spectra of fig. 10? In the former, the conversion of the adsorbed $SO_2$, including the re-adsorbed $SO_2$, to the sulphate species is not complete at 150 K. (ii) Surely the degeneracy of the S 1s $\rightarrow$ $t_2^*$ resonance in the X-ray absorption spectrum of the adsorbed sulphate species would be lifted by the lower symmetry configuration of the surface regardless of the nature of the bonding (ionic or covalent)? Whether the splitting is actually observed will depend on the intrinsic linewidth and the instrumental resolution. (iii) Is it not somewhat dangerous to base the identification of the sulphate species on the existence of a peak at 2482 eV in the X-ray absorption spectrum, particularly when the two peaks at higher energy in the model compound data are not reproduced?

**Dr G. Thornton** (*University of Manchester*) replied: The apparent discrepancies in temperature-dependent behaviour observed in the NEXAFS and photoemission data arise from the different experimental procedures used. In the NEXAFS work we annealed the sample and then re-cooled to 100 K before recording spectra. This gave rise to re-adsorption of $SO_2$. Hence, the NEXAFS data cannot be reliably used to judge the temperature of reaction. In contrast, photoemission measurements employed a temperature ramp such that data were collected at the anneal temperature.

The degeneracy of the $SO_4^{2-}$ S 1s $\rightarrow$ $t_2^*$ resonance should be lifted by interaction with the surface. The lack of an observed splitting, or of a polarisation dependence of the white line suggests that the '$t_2^*$' charge density at the two types of oxygen site is sufficiently similar to prevent us resolving the effect.

The assignment of the S K-edge NEXAFS in terms of $SO_4^{2-}$ is based on the energy position and structure of the white line, and its polarisation dependence. The higher-energy structure in the NEXAFS seen in the spectrum of $Na_2SO_4$ is not observed in spectra of other sulphates, including $CuSO_4$. Along with the consistent structure observed in the photoemission spectra, the evidence for $SO_4^{2-}$ seems rather compelling. However, surface vibrational data would provide valuable complementary information.

**Dr J. Robinson** (*University of Warwick*) communicated: We have recorded S K-edge spectra for alumina films that have been grown electrolytically from aqueous electrolytes containing sulphate ions. Films grown in this way are known to incorporate sulphur and from an analysis of the EXAFS data we have shown that it is an $SO_4^{2-}$ species that is incorporated (sulphur-oxygen bond length 1.44 Å). The near edge spectra for these films are essentially the same as those observed for $TiO_2(110)$–$SO_2$ after heat treatment (fig. 5), *i.e.* a very much stronger 'white line', relative to the post-edge amplitude, than is observed for $Na_2SO_4$ and a broad, weak feature at 2498 eV. These observations therefore support the hypothesis that it is indeed $SO_4^{2-}$ that is present on the $TiO_2$ surface. The enhanced 'white line' is presumably due to the low conductivity environment whereas our studies of the near-edge structure for a range of inorganic crystalline sulphates show that the fine features in this region vary from material to material, presumably reflecting variations in the local structure and symmetry.

**Prof. D. P. Woodruff** (*University of Warwick*) said: Dr Thornton has presented evidence for two surface reconstructions [on NiO(100) and Ni(111)] in which a pseudo-square mesh of the metal forms on the surface. Although this seems rather surprising, particularly on a substrate of different point-group symmetry, we have recently identified

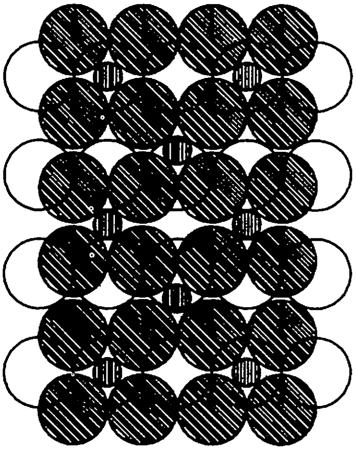

**Fig. 1.** Schematic diagram of the proposed Cu(110)(2×3)—N structure shown as a plan view of the surface with small circles representing N atoms, large hatched circles representing top (reconstructed) layer Cu atoms, and large open circles representing second-layer (unreconstructed) Cu atoms.

another example of this phenomenon; the Cu(100) (2×3)-N structure appears to be described by a slightly distorted square-mesh overlayer structure essentially identical to that seen in Cu(100)c(2×2)—N (fig. 1). The evidence for this conclusion comes from low-energy ion scattering[1] and photoelectron diffraction.[2]

---

[1] M. J. Ashwin and D. P. Woodruff, *Surf. Sci.*, in press.

[2] A. W. Robinson, D. P. Woodruff, J. S. Somers, A. L. D. Kilcoyne, D. E. Ricken and A. M. Bradshaw, *Surf. Sci.*, in press.

**Prof. D. C. Koningsberger** (*Eindhoven University of Technology*) began the discussion of Prof. Joyner's paper, and made the following points: Theoretical phase shifts obtained with MUFPOT or EXCURVE (Daresbury EXAFS data-analysis programs) for heavy scatterers (like Rh and Pt) are good, but not good enough for low $k$ ($3 < k < 5$).

The theoretically calculated EXAFS spectrum as shown in your fig. 1 does not agree with the experimental data for $7 < k < 9$. Also, by using a $k^1$ weighting instead of $k^3$ the deviations at low $k$ will be much more pronounced.

Why did you use such a short data range for your analysis of the reference compound? A larger data range would give a better judgement of the reliability of the data-analysis. The data are obtained for a bulk compound, so it must be possible to collect reliable data up to high $k$ values ($k = 15$).

Why did you not include multiple scattering in the analysis of the Rh—C—O* entity? This led to the wrong coordination number for Rh—O* and more importantly also to a completely wrong coordination distance: $R_{\text{cryst}} = 2.99$ Å *vs.* $R_{\text{EXAFS}} = 2.84$ Å.

We know from the EXAFS analysis of the $Rh_2(CO)_4Cl_2$ reference compound that the difference in phase between the 'normal' Rh—O and the multiple scattering Rh—O* coordination is almost $\pi$ rad.

The analysis presented in fig. 2 is a first-order approximation and is certainly a long way from being a fit. Within this type of approximation it is possible to find all kinds of different solutions.

Our data-analysis procedure[1] is based upon the use of: reference compounds, multiple shell fits in $k$ and $r$ space using both $k^1$ and $k^3$ weighting and identification of the different scatterers by applying phase- and amplitude-corrected Fourier transforms.

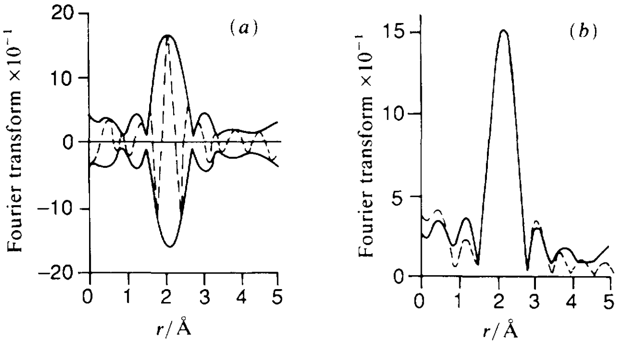

**Fig. 2.** (*a*) Magnitude (——) and imaginary part (- - -) of the Fourier transform (Rh—O phase corrected) of the difference file (raw data minus Rh—O—C* contribution). (*b*) Magnitude of Fourier transform (Rh—O phase corrected) of the difference file (——) and calculated Rh—O (support) contribution (- - -).

Our sample with a loading of 1 wt %[2] showed only a partial disruption of the metal particles after CO adsorption at room temperature just like your sample with 1 wt % loading. Our ultra-dispersed 0.5 wt % sample was completely disrupted after CO adsorption as published in ref. (1), so Rh—Rh oscillations were absent in the data, leading to a less complicated analysis. Our analysis (including the multiple scattering of the Rh—O* coordination) showed clearly that the Rh—C coordination of the Rh—C—O* entity beats with an additional scatterer present in the sample. This leads to an Rh—C peak amplitude in the Fourier transform of the experimental data that is much too low [see fig. 7(*c*) of ref. (1)]. After subtraction of the calculated Rh—C—O* contribution from the experimental EXAFS data a difference file is obtained, which gives, after Fourier-transformation with an Rh—O phase correction, an imaginary part peaking positively at 2.12 Å (fig. 2). This clearly demonstrates the presence of an oxygen scatterer instead of a chlorine scatterer as suggested in your paper. The phase of chlorine is almost $\pi$ rad different from oxygen, which should have led to a negatively peaking imaginary part of an Rh—O phase-corrected FT.

For these reasons we believe that your analysis is not reliable and the conclusions derived in your paper are questionable.

1 D. C. Koningsberger *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3139.
2 D. C. Koningsberger *et al.*, *J. Mol. Catal.*, 1984, **25**, 379.

**Prof. R. W. Joyner** (*University of Liverpool*) replied: Taking the points in the order raised: I do not accept that the theoretical phase shifts are inaccurate below $k = 5$ Å$^{-1}$. Our published fit for rhodium metal [ref (4), fig. 1 of our paper] shows an acceptable fit down to 4 Å$^{-1}$. For the catalyst samples, in any case, the region 3.5-5 Å$^{-1}$ is dominated by metal-oxygen scattering, where there is no problem with the phase shifts and excellent agreement is achieved with model compounds.

The data range analysed for the model compound was chosen to maximise the contribution of the weak scatterers, carbon, oxygen and chlorine, and hence produce optimised phase-shift corrections for these important scatterers. Above 10 Å$^{-1}$ the spectrum of the crystalline compound is dominated by Rh—Rh scattering, which is of less interest.

The question of multiple scattering is important and I will deal with it at some length. It is widely recognised that multiple scattering of the photoelectron is significant when another atom is located directly between the emitter and the backscatter. In studies of noble-metal catalysts this arises most commonly for the twice-nearest-neighbour distance in the face-centred cubic structure and for oxygen in linearly bonded carbonyls. It is also known as the focusing or searchlight effect. The consequences of the multiple scattering, as indicated in our paper, are to increase the amplitude of the EXAFS from the scattering atom, resulting in an anomalously large apparent coordination number. Also the error in the fitted interatomic distance is larger than normal. Thus multiple scattering must be included if one wishes to make statements about the environment of the carbonyl oxygen. We do not attempt to do this in our paper. It is also necessary to consider the influence of multiple scattering in one shell of neighbours on the rest of the spectrum. Here the experience of the face-centred cubic metals is instructive. Spectra, such as that shown in ref. (4), fig. 1 of our paper for rhodium metal, typically contain contributions from 4-6 shells of neighbours. Of these only the $2a$ shell, ($a$ = nearest-neighbour distance), is influenced by multiple scattering, with the consequences already indicated. This does not prevent accurate fitting of the other shells in the spectrum. Those at $a$, $2^{1/2}a$ and $3^{1/2}a$ are accurately fitted using the correct interatomic distances and coordination numbers, demonstrating that the influence of the multiple scattering is confined to the shell where it occurs. We therefore believe that our conclusions on other contributions to the spectra are unaffected by ignoring multiple scattering, which is accepted to occur in the rhodium-oxygen coordination. It is also important to note that there is no involvement of multiple scattering in the spectra from the reduced catalysts or the catalysts examined after treatment in synthesis gas. Here the particles are small, so that the contribution from the $2a$ shell is insignificant, neither is there any significant contribution from carbonyls, as discussed in the text.

It is also necessary to reiterate the account given in the paper of how we differentiate between chlorine and oxygen nearest neighbours in the spectra. We use a statistical approach which follows well established methods and which has been described in detail [ref. (12) of our paper]. These are similar to the $R$-factor analysis used in other structural methods and show clearly and quantitatively that the spectrum taken in carbon monoxide is much better described by chlorine neighbours, than by oxygen.

I am familiar with Prof. Koningsberger's methods of analysis and consider that Fourier-transform techniques are less reliable in application than he suggests. His methods claim to identify a range of very long, *ca.* 2.7 Å, metal-oxygen distances in supported catalysts [see ref. (1) of our paper] which no other group has been able to identify.[1] Another major limitation of Fourier-transform methods is that they provide no objectively quantifiable assessment of goodness of fit, of experimental error or of correlation between parameters. Resulting conclusions may thus contain a significant subjective element.

[1] F. W. Lytle, Plenary Lecture at the 9th International Congress on Catalysis, Calgary, 1988.

**Prof. Koningsberger** then continued: Your remarks concerning the use of a statistical test is in my opinion not relevant in this case for the following reasons. (*a*) Statistical tests can differentiate between different structural models if two data sets each of high quality both extending to high $k$ values give seemingly good fits in $k$ space. Your data set is not of high quality, it does not extend to high $k$ values and the agreement between your fits and experimental data is marginal [see fig. 2(*a*) of your paper]. (*b*) The inclusion of multiple scattering in order to describe the Rh—O* coordination is of crucial importance for a reliable analysis. Describing the Rh—O* coordination with a normal Rh—O phase shift leads to faulty identification of the other scatterers present in the spectrum. This means that a systematic error dominates your statistical test, making its outcome worthless.

We did include in our analysis multiple scattering since we used the Rh—C—O* entity of the $Rh_2(CO)_4Cl_4$ compound as reference. This extensively described in ref. (1) of my last comment.

I also would like to make a remark concerning your results of the Rh(1)/$Al_2O_3$ catalysts after reduction at 473 K. Our Rh(0.5)/$Al_2O_3$ was reduced at 593 K. We have also seen chlorine neighbours after reduction at 473 K of an Rh(1)/$TiO_2$ catalyst.[1] Reduction at higher temperatures certainly leads to a decrease of chlorine neighbours from the support and this may explain in this case the observed differences.

[1] D. C. Koningsberger *et al.*, *Proc. 8th Int. Congr. Catal.* (Verlag Chemie, Basel, 1984), Vol. 5, p. 123.

**Prof. Joyner** replied: Prof. Koningsberger's comments on the application of statistical tests would be more convincing if he ever used them in his own work. His comments are wrong on several technical grounds. We are interested in identifying a neighbour, either chlorine or oxygen, which is of relatively low atomic number. For low-$Z$ scatterers the backscattering factor decays much more rapidly than for rhodium, which does indeed scatter to high $k$. The contribution of the low-$Z$ scatterers is most marked in the range we have deliberately chosen for data analysis, *i.e.* below 10 $Å^{-1}$. This maximises our chances of differentiating reliably between chlorine and oxygen, which we do with high statistical probability, as indicated in the text.

I do not accept his comments on quality of data or of fits, which are in any case irrelevant to the point he makes about statistical analysis. The advantage of the statistical approach is that it explicitly takes account of the magnitude of noise in the experimental data and of the number of data points.

**Prof. D. A. King** (*University of Cambridge*) said: Concerning fig. 1 of your paper, I would like to ask whether you have made checks on the possibility that the standard compound, $Rh_2(CO)_4Cl_2$, is decomposed by the intense X-ray beam on the wiggler line. This might explain the rather poor agreement between experiment and theory in this case. Checks could be made by, for example, checking the sample for weight loss after the EXAFS data have been collected. We have found that some organometallic compounds are particularly sensitive to X-ray beam damage.

**Prof. Joyner** replied: Other than visual inspection, no check was made for beam damage.

**Dr J. F. W. Mosselmans** (*University of Southampton*) said: We have in the past (1985/6) studied $Rh_2(CO)_4Cl_2$ [1] and fitted it using theoretical phase shifts and multiple scattering out to 17 $k$ (table 1 and fig. 3). If you record your spectra past 10 $k$, why do you not show your fits past that point? Multiple scattering in EXCURVE has been available for five years; does not using it in fitting carbonyl ligands make the whole fitting process inadequate?

Why is the first 1 Å of the Fourier transform not shown? This prevents an assessment of the quality of the background subtraction which can affect the results obtained by curve fitting?[2]

[1] R. J. Price, *PhD Thesis* (University of Southampton, 1987).

[2] I. R. Beattie, N. Binsted, W. Levason, J. S. Ogden, M. D. Spicer and N. A. Young, *High Temp. Sci.*, in press.

**Table 1.** $Rh_2(CO)_4Cl_2$ EXAFS parameters

| atom | coordination no. | shell radius /Å | Debye-Waller factor/$Å^2$ |
|---|---|---|---|
| C | 2 | 1.87 | 0.002 |
| Cl | 2 | 2.39 | 0.005 |
| O | 2 | 2.93 | 0.004 |
| Rh | 1 | 3.20 | 0.018 |

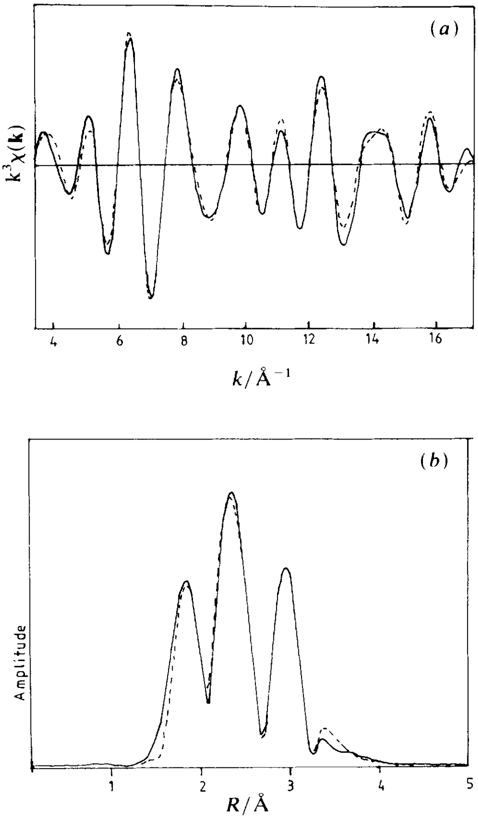

**Fig. 3.** Rh K-edge EXAFS data of $Rh_2(CO)_4Cl_2$ with multiple scattering included for the Rh—C—O unit. Refined bond angle 174(4)°. (*a*) $k^3$-weighted EXAFS and (*b*) Fourier-transform phase-corrected for carbon; (——) experimental data, (- - -) calculated fit ($R = 17.6\%$).

**Prof. Joyner** replied: The spectrum which you present is very similar to that given in fig. 1(*a*), (our paper), in the range up to 10.5 $Å^{-1}$, as is the quality of fit obtained. Note that our fit uses crystallographically correct distances (Rh—C, 1.77 and 1.85 Å), whereas your single Rh—C distance is longer than either. The difference in the Fourier transform relates solely to the greater data range in your figure.

We have been concerned to optimise phase shifts in the range where light backscatterers (O, C, Cl) contribute most strongly, *i.e.* below *ca.* 10 $Å^{-1}$. As indicated in my reply to Prof. Koningsberger, we do not attempt to make detailed statements about carbonyl bonding, and therefore consider the use of single scattering to be justified.

The region of the Fourier transform below 1 Å contains nothing of structural significance and is therefore not presented.

**Prof. Koningsberger** continued: Neglecting multiple scattering leads not only to faulty coordination numbers, but also to wrong coordination distances. A deviation of 0.15 Å from the crystallographic Rh—O* distance is too large to be described as a second-order effect.

Again I would like to emphasize that it is very likely that you obtain from your analysis an Rh—Cl coordination instead of an Rh—O coordination as we found for our Rh(0.5)/$Al_2O_3$ sample after CO adsorption at room temperature. In your analysis you have to compensate the incorrectly chosen Rh—O* phase shift by including a scatterer which has a phase shift *ca.* $\pi$ rad different from oxygen; this is just the case for chlorine. Inspection of fig. 7(*c*) of our paper in ref. (1) will make this clear.

1 D. C. Koningsberger *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3139.

**Prof. Joyner** replied: I have already accepted that a multiple scattering treatment is needed to describe the oxygen moiety of the carbonyls accurately. I have also indicated why ignoring multiple scattering has no significance for the identification of the chlorine neighbour.

**Prof. G. N. Greaves** (*Daresbury Laboratory, Warrington*) said: It cannot be stressed enough that multiple scattering corrections are essential in achieving accurate parameters for metal carbonyl structures using EXAFS spectroscopy. Work by the Southampton-Daresbury group demonstrates how crystallographic coordination numbers and interatomic distances along with credible Debye-Waller factors can be obtained from model systems with precision. Moreover the effect can be exploited to obtain M—C—O bond angles where these linkages are distorted when a cluster becomes attached to a substrate. The point made earlier about the inherent instability of carbonyl clusters has been beautifully demonstrated using EXAFS in the case of the interaction of $Ru_3(CO)_{12}$ with $SiO_2$, where exposure to air results in dissociation to a single metal unit. Multiple scattering analysis is a prerequisite in unravelling from EXAFS the changing architecture of adsorbed metal carbonyl clusters reliably.

**Prof. Joyner** replied: I have nothing to add to my earlier comments on multiple scattering. I accept that carbonyl clusters can be decomposed by interaction with a support such as silica. We have not attempted to support carbonyls in our work. As with Prof. Koningsberger [ref. (1), our paper], we have observed synthesis of carbonyls *in situ*, when metal particles have been exposed to carbon monoxide. These appear to be indefinitely stable in the X-ray beam and to decompose on exposure to synthesis gas under the conditions indicated, with the reformation of metallic particles. This is the result of catalytic significance.

**Dr J. T. Gauntlett** (*ICI, Runcorn*) said: In your statistical analysis, can you be certain of your significances with such a small number of data points per *k* in the high region and a short data range?

With such high apparent signal-to-noise at the end of the data sets, why did you not extend the data range? A cynic may say that, while the data do not appear to be filtered they do appear to be 'smoothed' by removing data points.

**Prof. Joyner** replied: The statistical analysis of EXAFS data is discussed exhaustively in ref. (1). The number of data points is represented in this analysis by the number of 'degrees of freedom', and the improvement in fitting index required for significance increases as the number of degrees of freedom decreases. High levels of significance may equally be achieved by a large number of points with a relatively low signal-to-noise ratio or by a smaller number of points with better signal-to-noise. At high *k* we have collected data at *ca.* 0.01 $Å^{-1}$ intervals with suitably long collection times to achieve good signal-to-noise, as the question recognises.

Choice of data range is dictated by two main factors. (i) Accuracy required: We estimate Rh—Rh distances to be accurate to ±0.02 Å, using methods discussed in ref. (1). To improve this to 0.01 Å would approximately double data collection time and not modify our conclusions at all. (ii) Balance between low-*Z* and high-*Z* scatterers: Because we are interested in low-*Z* scatterers (O, C, Cl) as well as strong scatterers, such as rhodium, we choose a suitable data range (3.5–10 $Å^{-1}$) where both are likely to be significantly represented.

It is important to note that, in comparison to some data at this meeting, none of the data presented in our paper have been filtered or smoothed in any way.

[1] R. W. Joyner, K. J. Martin and P. Meehan, *J. Phys. C*, 1987, **20**, 4005.

**Dr R. J. Oldman** (*ICI, Runcorn*) said: I have three comments to make following the discussion which has just taken place. First, multiple scattering is not a second-order effect in these systems. In table 1 for $Rh_2(CO)_4Cl_2$, the apparent coordination number for oxygen is the largest and the apparent Debye–Waller term is the smallest, showing that this shell makes a large contribution to the spectrum. If this is not modelled correctly then the level of confidence in the rest of the model is reduced.

As a second point, why do we use model compounds for EXAFS? Model compounds are to help develop and test theory as a prelude to solving an unknown structure. In the first instance we are concerned with testing the accuracy of phase shifts. If the agreement between experiment and theory for the model compound is not perfect we cannot hope to probe the more subtle aspects of our unknown. For example in the case to hand we are trying to decide between oxygen or chlorine bonding to rhodium.

Finally, I would like to comment on the use of fitting statistics in EXAFS. These serve two purposes. First, they help to define a best fit between experiment and theory. However, this is only applicable to selecting options for structures if the fit is already quite good and there are no systematic residuals of the kind indicated in fig. 2. Secondly, having obtained a sensible solution, fitting statistics allow an estimate of the uncertainties in the derived structural parameters, especially where they are highly correlated, *e.g.* coordination number and Debye–Waller factors [ref. (12)].

**Prof. Joyner** replied: I agree that the carbonyl oxygen makes a large contribution to the spectrum measured in carbon monoxide. However, both Prof. Koningsberger and I conclude that the oxygen environment is not markedly changed between the model compound and the catalyst in carbon monoxide. In both cases it should be modelled by a similar single scattering treatment.

I am in broad agreement with your comments about statistical analysis, but reject your assumption that we could achieve fits of as good or similar quality to fig. 2 with an oxygen neighbour instead of chlorine, for the catalyst in carbon monoxide. We were unable to obtain convincing fits with an oxygen shell in the distance range 2.1–2.4 Å, and this was what led us to consider a chlorine neighbour. The improvement in fit was very marked, and the statistical result is a quantitative confirmation of this. I am not sure why you are unwilling to see statistical criteria used for choosing between structures. These are routinely used, as *R*-factor analyses, in other structural techniques. An *R*-factor analysis is currently being implemented by Daresbury staff as part of the new EXCURV90 analysis package. The *R* factor which will be generated will merely be a normalised version of the fitting index which is the input data for our statistical analysis. The criteria proposed in ref. (12) of our paper still apply.[1]

[1] S. J. Gurman, personal communication.

The discussion then moved on to Prof. Thomas's paper, and **Prof. Joyner** said: For your dehydrated sample you observe by EXAFS, an Ni—O distance of 2.02 Å. This is very similar to that reported by Morrison *et al.*[1] for trigonally coordinated $Co^{2+}$ in zeolite A, (1.9 Å) using EXAFS and by Gallezot *et al.*[2] for $Cu^{2+}$ in the $S_I{}'$ site in zeolite Y, using X-ray diffraction. You suggest that the distance deduced from XRD, 2.25 Å, is an average of this value and longer, non-bonding Ni—O distances. Is it possible to allow for this mixture of environments in the Rietveld profile analysis, and thus bring XRD and EXAFS results into clear agreement?

1 T. I. Morrison, L. E. Iton, G. K. Shenoy, G. D. Stucky, S. L. Suib and A. H. Reis, *J. Chem. Phys.*, (1980), **73**, 4705.
2 P. Gallezot, Y. Ben Taarit and B. Imelik, *J. Catal.*, 1972, **26**, 295.

**Prof. J. M. Thomas** (*The Royal Institution, London*) replied: Diffraction is intrinsically an averaging technique. We could put different types of oxygen into the refinement, but the results would have no more significance than the average Ni—O bond length that we outlined.

**Prof. J. V. Smith** (*University of Chicago*) said: For the sites I and I′ the distortion of each six-ring of oxygen atoms in response to Ni bonding produces three short and three long Ni—O distances. Do you see the long as well as the short distances in the fit of the Ni EXAFS spectra?

A second part of the discussion concerns the short Ni—O distance of 1.87 Å. This might represent an Ni atom bonded to three oxygen atoms of a six-ring and an additional oxygen species projecting away from the six-ring down the three-fold axis.

**Prof. Greaves** replied: Yes we do see the three long as well as the three short Ni—O distances in our analysis of Ni K-edge EXAFS.

As far as your second point is concerned, relating to the short 1.87 Å distance, we have in fact explored the possibility of shifting the Ni along the three-fold axis away from the centre of the regular hexagonal site. However, the Rietveld figure of merit worsens by a factor of two. All the indications from XRD are that these Ni atoms occupy near-perfect $S_I$ octahedral sites. The 1.87 Å distance we interpret as being part and parcel of the $S_{I'}$ site.

**Prof. Koningsberger** said: EXAFS seems to be more sensitive in detecting the different Ni—O distances in the dehydrated Ni—Y than high-resolution powder diffraction. I agree with your explanation of the apparent discrepancy between the results of XRD and EXAFS concerning the XRD peak at 2.25 Å. However, how do you explain that EXAFS is also seeing peaks around 2.49 and 2.68 Å with relatively high coordination numbers whereas these peaks are not detected with XRD?

**Prof. Greaves** replied: The justification for including split oxygen shells in addition to the single Ni—O distance of 2.02 Å in our EXAFS analysis comes from the XRD refinement. Here, in dehydrated Zeolite-Y, we detect not only Ni in $S_I$ sites but also in $S_{I'}$ and $S_{II}$ sites together with extra oxygens (which we call $O_W$) located just outside the framework. These split oxygen Ni environments are modelled in fig. 7 but the precise distances, as you know, can only come from Ni EXAFS.

**Dr I. K. Robinson** (*AT&T Bell Labs, Murray Hill, NJ*) said: The cause of the discrepancy between the EXAFS and XRD determinations of the $S_I$ Ni—O bond length is attributed to disorder of this site: the Ni occupied site has one bond length and the empty site another one. If the oxygen occupancy ($N$) were constrained to be the same as that of Ni, and two oxygen sites were refined, it might be possible to confirm this hypothesis.

**Prof. Greaves** replied: I agree, this would be an interesting test of the hypothesis in principle. In practice it may not be significant, adding as it will to the queue of Rietveld fitting parameters.

**Prof. Smith** said: What is the accuracy of the Al—O bond lengths given in your table 3? The bond lengths and errors can be compared with values obtained by Bragg diffraction of Al—O (tetrahedral) near 1.74 Å and Al—O (octahedral) near 1.9 Å, both of which vary somewhat depending on the stereochemistry of individual structures and on whether O occurs as $O^{2-}$, $OH^-$ or $H_2O$.

**Prof. Greaves** replied: The shorter energy range obtainable from Al K-edge EXAFS of *ca.* 280 eV, due to the proximity of the Si K-edge, clearly reduces the precision of the analysed Al—O distance. However, oxygen backscattering is limited, usually being spent by 350-400 eV. The equivalent wavevector range of around 10 $Å^{-1}$ can result in a precision of *ca.* 0.02 Å or better. With the smaller bandpass of our Al EXAFS this precision will reduce to 0.04 Å at worst, which is clearly sufficient to distinguish the 0.1-0.2 Å difference in the Al—O distance between octahedral and tetrahedral sites, but is unlikely to differentiate particular types of oxygen.

**Dr J. Robinson** (*University of Warwick*) communicated: We have been using Al K-edge X-ray absorption spectroscopy to study the structure of anodically formed oxide films on aluminium and have studied films prepared in many different ways, as well as a range of model compounds. Whilst it is true that the proximity of the Si K-edge limits the available data range for Al EXAFS (the monochromator crystal used is quartz and hence it is impossible to record data beyond the Si edge) additional structural information is available from the XANES region. If one takes the position of the half-edge height for $\alpha$-$Al_2O_3$ as a reference point (zero energy) then for all materials containing four-coordinate Al there is a strong peak in the spectrum at −2 eV effectively shifting the edge energy by 3 eV. Similarly for five-coordinate Al (in andalusite) there is a peak at *ca.* −1.5 eV. There are also other edge features that appear to provide a 'fingerprint' of the coordination. These observations have been confirmed for a wide range of materials.

When investigating the anodic aluminas (where four-, five- and six-fold coordination can be observed depending on the method of formation) it was found that conclusions drawn from the mean Al—O bond length obtained from the EXAFS were always consistent with those drawn from the near-edge features. Unfortunately Dooryhee *et al.* do not provide a spectrum of a reference material and their data appear to have rather variable backgrounds, and therefore it is difficult to draw any conclusions from their XANES data.

**Prof. Thomas** replied: We, of course, accept that XANES data provide a fingerprint for the coordination of Al in aluminosilicates. Our own data, obtained in several systems with Al in different coordinations, fully support this contention. Our data on the zeolites were refined using data from model compounds (including $\alpha$-$Al_2O_3$). The change in bond length on dealumination, which is the most important feature of our results is, we are confident, a reliable result, fully justified by the data.

**Dr Oldman** began the discussion of Prof. Koningsberger's paper: Are there any changes observable at the Ir $L_3$ white line which would help confirm changes in electronic state as a function of particle size or support interaction?

**Prof. Koningsberger** replied: We have not yet systematically investigated the white-line intensities before and after desorption of hydrogen. However, we do see a change in intensity of the $L_{III}$ white line after desorption of hydrogen.

**Dr Gauntlett** said: Given earlier experimental[1] and theoretical data which indicate that the packing in small metal particles is energetically favouring decahedral[1,2] or icosohedral[2] geometries, is it possible that your bond-length contractions on $H_2$ desorption are due to a morphology change from close-packed, stabilised by hydrogen, to a lower coordinate particle, such as icosohedral, when hydrogen is desorbed?

1 D. G. Duff, A. C. Curtis, P. P. Edwards, D. A. Jefferson, B. F. G. Johnson, A. I. Kirkland and D. E. Logan, *Angew Chem., Int. Ed. Engl.*, 1987, **26**, 676.
2 M. R. Hoare and P. Pal, *Adv. Phys.*, 1972, **9**, 209.

**Prof. Koningsberger** replied: We have not detected any icosahedral structures after desorption of chemisorbed hydrogen. However, we do see a lower coordination number after evacuation. Careful inspection of the Fourier transform of higher quality data obtained on the same catalyst after evacuation shows the decrease in the second Ir—Ir shell. This points to morphological change after evacuation from a three- dimensional to flat monolayer-type metal particles. Contraction of the metal-metal distance after desorption of chemisorbed hydrogen has been observed for more catalytic systems (see our paper).

**Dr K. Prabhakaran** (*University of Manchester*) communicated: You concluded that using EXAFS you can establish the physisorption of $O_2$. Do you not expect the beam to knock off the weakly physisorbed species instantly?

**Prof. Koningsberger** replied: The adsorption of oxygen at 77 K creates a metal-oxygen coordination with a distance of 2.19 Å. It is not clear whether the adsorption of oxygen is purely physisorption or chemisorption. The bond length of 2.19 Å points to a donation of electrons from the metal atoms to oxygen, implying some kind of oxidation, leading to the formation of a chemical bond. This may explain why the X-ray beam will not knock off the adsorbed oxygen. On the other hand I am not so sure that the X-ray beam will knock off physisorbed species from a metal surface. This brings us to the difficult problem of radiation damage by X-rays in biological materials, which is still not satisfactorily solved.

The Chairman of the session, **Prof. A. J. Leadbetter** (*Daresbury Laboratory, Warrington*) said: In trying to focus a general discussion of the morning's papers I suggest we consider separately (*a*) any scientific problems concerning the results in the papers and (*b*) the various questions which have arisen about EXAFS itself.

With respect to the latter I remember much the same arguments about interpretation of EXAFS data back in the early 70s when I first met the subject. I am a little disappointed to find apparently the same arguments continuing still. On the other hand it is clear that EXAFS is a most valuable tool when used in the right way without extravagant claims about the possibilities; and indeed in many cases of physically ill-defined systems it is the only means of addressing crucial problems of local structure. May we therefore consider and clarify where differences and problems lie, where there is consensus and what key developments or experiments are needed for future progress.

**Prof. Thomas** commented: Mr Chairman, you mentioned that some of the scientific questions to which we seek answers are accessible only *via* EXAFS. For the study of very small metal particles (supported on zeolites for example) nowadays, thanks to the work of Treacy and Rice (*J. Microsc.*, 1989) it has proved possible by using scanning transmission electron microscopy (STEM) with Rutherford scattering to count the number of atoms in a small cluster. Small aggregates of no more than three to five atoms can now be identified. This constitutes a separate, independent technique against which EXAFS can be tested.

I wonder whether Prof. Koningsberger has looked at a system like Pt in zeolite-L with both EXAFS, STEM or any other technique?

**Prof. Koningsberger** replied: Indeed, we have looked with EXAFS at the Pt/L zeolite system. We have found a Pt—Pt coordination number ($N$) of 3.9, implying particles consisting of 5-6 atoms. Moreover, we do detect Pt-Ba and Pt-Si interactions. The hydrogen chemisorption measurements confirm the EXAFS results; we found H/M = 1.55. These values agree with an earlier published H/M *vs.* $N$ curve (*J. Catal.*, 1987). EXAFS spectroscopy can be extremely powerful for structural investigations of uniformly highly dispersed catalytic systems.

**Prof. D. A. King** (*University of Cambridge*) said: In the EXAFS analyses referred to here the assumption is made, in writing the familiar expression:

$$\chi(k)=\sum_i A_i \sin\{2\boldsymbol{k}R_i+\phi_i(k)\} \qquad (1)$$

[where $\chi(k)$ is the normalised oscillatory part of the X-ray absorption coefficient, $A$ is a constant for a given number of scatterers at a given temperature, $\boldsymbol{k}$ is the photoelectron wavevector, $R_i$ is the distance of atoms in shell $i$ from the absorber atom, and $\phi_i(\boldsymbol{k})$ is a phase-shift term], that the pair distribution function between absorber and scatterer atoms has a Gaussian form. This is a harmonic potential approximation. If the potential is appreciably anharmonic, the pair distribution function is asymmetric, and an additional phase term $\Sigma_i(\boldsymbol{k})$ appears[1] in the sine function of eqn (1):

$$\sin\left\{2kR_i+\phi_i(\boldsymbol{k})+\sum_i(\boldsymbol{k})\right\}. \qquad (2)$$

As we have shown for Cl on Ag surfaces, and for bulk AgCl,[2] omitting this term can lead to a very significant error in bond-length determinations by EXAFS. At room temperature for Cl on Ag the error is in the region of *ca.* 0.06 Å. Typically, if the correct phase shift $\phi_i(\boldsymbol{k})$ is used, the use of eqn (1) leads to an interatomic spacing that is *too small.*

In practice, phase shifts are obtained *a priori*, by a routine based on a muffin-tin potential approximation, and these are then tweaked by fitting experimental data from a standard compound with known spacings $R_i$, to obtain an apparent function $\phi(\boldsymbol{k})$. If eqn (1) is used in the fitting procedure, this tweaking will then incorporate both the true phase-shift term and the anharmonicity term contained in eqn (2). The problem is that the latter term is strongly temperature dependent, and the use of phase shifts obtained in this way will inevitably lead to erroneous bond lengths at any other temperature. Furthermore, the procedure assumes that $\sum_i(\boldsymbol{k})$ is the same in the model compound and in the test material, an assumption of doubtful validity.

Of course, use of eqn (2) incorporates a new set of undetermined parameters into the analysis of a system where $R_i$ is not known. I very strongly urge that EXAFS data should be collected at low temperatures, where $\sum(\boldsymbol{k})$ can safely be ignored, since the bottom of the pair potential function is essentially harmonic, and the Gaussian-based expression (1) can then safely be used. Our low-temperature studies of Cl on Ag{111} and Ag{110} have been guided by this principle.[3]

[1] P. Eisenberger and G. S. Brown, *Solid State Commun.*, 1979, **29**, 481.

[2] G. M. Lamble and D. A. King, *Philos. Trans. R. Soc. London, Sect. A*, 1986, **318**, 203.

[3] G. M. Lamble, R. S. Brooks, S. Ferrer, D. A. King and D. Norman, *Phys. Rev. B*, 1986, **34**, 2975; D. J. Holmes, N. Panagiotides, C. J. Barnes, R. Dus, D. Norman, G. M. Lamble, F. Della Valle and D. A. King, *J. Vac. Sci. Technol.*, 1987, **A5**, 703.

**Dr J. C. Earnshaw** (*Queen's University of Belfast*) said to Prof. Koningsberger: In several of these papers the theoretical EXAFS spectra show deviations from the observed data which do not appear to be randomly distributed about zero. Several of the fits would probably not be acceptable to a statistical test such as the runs test. If the sequence of residuals were similar for different observations with a given instrument this would presumably indicate systematic errors. However, if this is not the case do such non-random residuals indicate shortcomings of the model used?

**Prof. Koningsberger** replied: I fully agree with you that systematic deviations point to shortcomings of the structural models used in the data analysis. Another more important problem is the use of inadequate phase shifts in the data analysis. Assuming that the phase shifts used are adequate, systematic deviations have to be minimized by a better choice of the structural model; *i.e.* the inclusion of additional neighbouring atoms in the analysis.

**Dr A. Fontaine** (*LURE, Orsay*) said: The residual which is always found between the fit based on a model and experimental data does not always mean that experiments are not accurate enough, or conversely that the model is useless because it is unable to reproduce data exactly—physics is not mathematics, there are always approximations in models. Some approximations need to be relaxed to get a better description of the real one—some other ones may be important in issues other than the actual one we are concerned with. As soon as one wants an analytical formulation of a phenomenon there is a need to classify effects according to their importance.

**Dr Fontaine** continued: The discussion on the capability of EXAFS to yield reliable information starts on the controversy for a very ill conditioned system. Poorly organised matter with many components is certainly not the perfect case.

There are many other topics where difficulties are not concentrated. A clear example was given yesterday by Prof. Bradshaw's talk, explaining how EXAFS can determine adsorbate position on a reconstructed surface. It is true also for bulky systems. Therefore, the general comment should emphasize the capability of EXAFS to extract the local order and the large benefit given by the polarised X-ray beams. In addition one has to recall that EXAFS is one part of core-level spectroscopy which has been proved to be efficient in addressing the electronic structure issue.

**Prof. D. A. King** said: I wish to raise a general point about the validity of EXAFS analyses of essentially heterodisperse systems. In EXAFS analyses of perfectly crystalline systems, the most accessible case arises where all absorber atoms occupy identical lattice sites. Then we can legitimately write down a single summation, applicable at low temperatures, of the form:

$$\chi(\boldsymbol{k}) = \sum_i A_i \sin\{2\boldsymbol{k}R_i + \phi_i(\boldsymbol{k})\}.$$

(The notation is the same as in my previous comment.)

Each interatomic spacing $R$ derived from the analysis can then be assigned to a shell around the absorber atom, and, by triangulation, a structure may be derived. If, however, just two different lattice sites are occupied by the absorber atoms, there will be *two* sets of shells, $i$ and $j$, deriving from each absorber atom and contributing to the data. Apart from the added complexity in the data due to the doubling of contributing shells, there is no means available for unscrambling the data into the two shell sets $i$ and $j$. A structural assignment becomes virtually impossible. Of course, if we extrapolate this further, it is readily seen that a multishell EXAFS analysis becomes meaningless for a system where a significant number of different lattice sites are occupied. A typical heterogeneous catalyst consists of a distribution of particle sizes, and each particle can be expected to contribute a range of adsorbate sites. Apart from some average nearest-neighbour distance, it is difficult to see that any further information can be reliably obtained.

Even in the ideal case where adsorption has been studied on single-crystal surfaces, analyses of EXAFS data can be problematic. We have conducted a detailed study of the reliability of bond lengths and coordination numbers obtained from an exhaustive SEXAFS analysis of Cl on Ag{110}.[1] We find that, while reproducible bond lengths could be obtained from four atomic shells, and that two shells separated by as little as 0.3 Å could be distinguished, large correlations between Debye-Waller factors, coordination numbers and inelastic terms in the EXAFS amplitude introduced a high degree of inaccuracy, up to ±3, on the values obtained for the coordination numbers of all shells beyond the first. We concluded that coordination numbers could not be used to infer system geometry.

I wish to make a plea for a systematic EXAFS study of a well defined model catalyst system, preferably a homodisperse system, to evaluate critically the potential of EXAFS as a tool for the study of catalysts generally.

[1] D. J. Homes, D. R. Batchelor and D. A. King, *Surf. Sci.*, 1988, **199**, 476.

**Prof. Joyner** then said: The problem of characterising heterodisperse supported catalysts which Prof. King poses is rather more intractable and also slightly different from that he suggests. EXAFS is at its most useful for relatively small particle sizes, *e.g.* with diameters $<15$ Å. There seems to be no sure way to prepare or characterise a monodisperse sample in this size range. In practice EXAFS appears to be the most reliable method currently available for determining average particle coordination number, from which an average particle size may be inferred. The unique advantage of EXAFS is that it yields a true average of the environment. This is not true of X-ray diffraction, which accentuates the contribution of long-range order, or of electron microscopy, where the smallest particles, (typically $d<6$–8 Å), are not imaged. It is important to have use of an additional technique which can examine the range of structures present, and electron microscopy is clearly the best method to do this. Thus electron microscopy confirms that our $Rh/Al_2O_3$ sample is reasonably monodisperse, (most particles $<10$ Å diameter, no detectable particles $>15$ Å diameter), while the $Rh/V_2O_3$ catalyst contains some very large particles, ($d>100$ Å), as already inferred from EXAFS.

**Prof. Thomas** added: Prof. King raises an important issue when he makes a plea for an analysis of model (small) metal catalysts. The desire is for a definitive study involving small, well defined particles of metal of colloidal (or sub-colloidal) dimension. Specifically one should compare EXAFS data (of the kind that lead to metal–metal distances) with high-resolution electron microscopy (that leads to information concerning the morphology. When the size range of small metal particles is very narrow, one feels happier about statements (based on EXAFS) relating metal–metal distance to size.

There is much to be said for taking, as Gallezot has done in his elegant radial-distribution curves, a zeolite of well defined cage size loaded with Pt or Pd. Combined EXAFS, RDF and HREM studies of these would be very helpful.

**Prof. Greaves** said: The discussion so far has centred on the difficulties and uncertainties inherent in EXAFS analysis and has not stressed the advantages and strategy for exploiting the technique. In the first place, of course, appropriate model systems must be incorporated in EXAFS measurements; most good experiments are comparative and seek to minimize fitting parameters by the use of well characterised crystalline models. Secondly, incorporating multiple scattering and also asymmetry in the central atom potential have been considered as added complications to analysis and the benefits they offer have been understressed. The multiple-scattering phenomenon enables bond angles in the 150–180° range (*e.g.* bridging units) to be analysed very precisely. This has been used to great effect in studying adsorbed metal cluster carbonyls. Non-Gaussian atomic distributions can reflect important anharmonicity effects in atomic vibrations relative to the excited atom that are averaged out in XRD. These can be revealed by measuring EXAFS at a variety of temperatures, not just at low temperature. Thirdly, and this can't be over emphasised, X-ray absorption spectroscopy is an *underdetermined* structural technique. As such, curve fitting is inevitable and people will argue until Doomsday about how equivocal or otherwise a particular model structure is. Nevertheless the most sensible strategy is to shore up against the uncertainties of a given EXAFS spectrum by making other independent measurements. For example, obtaining spectra from other elements in the same material, for single crystals (non-centrosymmetric) comparing polarised spectra for different orientations and for crystalline powders combining EXAFS with XRD as in the last paper. Use can be made of indirect structural probes like spin resonance, ionic transport, optical spectroscopy *etc.* Combined experiments like these are mutually beneficial because most structural techniques, perhaps with the exception of single-crystal diffraction, all share a measure of indeterminacy.

**Dr K. M. Robinson** (*US Naval Research Laboratory*) said: What effect, if any, does the variable coherence length of the X-rays have on the minimum particle size observable with EXAFS?

**Prof. Koningsberger** replied: No effect at all. The mean free path of the photoelectron is of the order of 8–10 Å. In bulk compounds like metal foils up to 7–8 coordination shells are observable in the Fourier transform of good quality EXAFS data. On the other hand, EXAFS have been observed on diatomic molecules like $Br_2$ which also show that the coherence length of the photoelectron does not determine the minimum particle size observable with EXAFS. The minimum particle size observable with X-ray diffraction is of the order of 20–30 Å.

**Dr Fontaine** said: The small particle investigation has to be carried out using the two usual routes: (1) The study of real systems which are appealing issues, the response of which cannot be delayed until all new modern tools are developed; (2) we need to develop fundamental studies where the metallic clusters are formed in flight, selected by a mass spectrometer, and later eventually condensed and isolated within a rare-gas matrix. This is a new class of experiments which is just starting and can provide answers to questions such as when metallisation begins.

**Dr Gauntlett** said: Prof. Thomas mentioned an electron microscopic/EXAFS study of colloidal sols. We too were involved in such a study with the microscopists coming to us at Southampton to confirm that their electron microscopy was relevant to the structures of the sols.

I think, also that if we are to study small particles and perturb the theory to account for anharmonicity and particle size distributions, as suggested by Prof. King, the working part, on EXAFS standards must define a minimum data length and point frequency in order that we have good data from around 5 Å to fit.

**Dr Fontaine** said: At the very beginning of surface EXAFS J. Sthör was not able to produce data of good quality within a range larger than 3/4 of the oscillation. Nowadays this field is very active and unique results have been produced, as demonstrated by Prof. Bradshaw yesterday. Therefore if new domains appear and do not convince immediately because of their sin of infancy, let us wait a couple of years to see what the developments are.

**Prof. Koningsberger** said: It is of extreme importance for the credibility of the outcome of EXAFS studies that the international community of X-ray absorption spectroscopists reaches consensus about data-analysis procedures and minimum requirements for EXAFS papers. The coming workshop in Brookhaven (May 1990) organized by Prof. Stern on standards and criteria in X-ray absorption spectroscopy will discuss a comparison of existing programs for calculating *ab initio* phase shifts used for analysis of EXAFS data. Also a list with minimum requirements for EXAFS papers will be discussed and this list will be widely spread amongst researchers in the field and editorial boards of important scientific journals.