Studies of Solids and Surfaces by Auger Electron Spectroscopy [and Discussion]

C. N. R. Rao, M. W. Roberts and P. Weightman

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Studies of solids and surfaces by Auger electron spectroscopy†

By C. N. R. Rao, F.R.S.

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, *India*

Although the applications of Auger electron spectroscopy in surface analysis have by far outweighed its use as a tool to investigate electron states of solids and surfaces, there are a variety of situations where Auger spectroscopy provides unique information. Apart from the chemical shifts, Auger intensities are useful in determining the number of d-electron states in transition metal systems. Auger spectroscopy is a good probe to investigate the surface oxidation of metals. In addition to the intra-atomic Auger transitions, inter-atomic transitions observed in oxides and other systems reveal the nature of electron states of surfaces. Charge-transfer and hybridization effects in alloys are also usefully studied by Auger spectroscopy. Auger electron spectroscopy has not been a popular technique to investigate adsorption of molecules on surfaces, but the technique is useful to obtain fingerprints of surface species.

1. Introduction

Auger electron spectroscopy has emerged as an important tool for the characterization of the surfaces of solids. Shifts of the Auger transition energies of metals on compound formation reflect the chemical state of the metal in the compound; thus, Szalkowski and Somorjai (1972) found that the metal Auger shift as well as the oxygen KLL to metal $L_{23}M_{23}M_{23}$ intensity ratio in vanadium oxides depend on the oxidation state of vanadium. The chemical shifts are generally small in transition metal compounds and significant shifts are found only in s and p band metals such as Cd and Sn. Some interesting systematics in the energies and intensities of Auger transitions were reported a few years ago by Clarke *et al.* (1971), but it is difficult to use methods based on absolute intensity measurements.

Much of the preoccupation with Auger spectroscopy until recently has been in the compositional analysis of solid surfaces. In the last few years, however, increasing attention has been directed to the study of electron states of solids by Auger spectroscopy. Davies & Weightman (1984*a*) and Davies *et al.* (1984*b*) have shown that the Auger spectra of metallic alloys reflect charge-transfer and hybridization effects. The formulation of Cini (1977) and Sawatzky (1977) has provided a simple method of finding whether an Auger transition is quasi-atomic or band-like from the effective Coulomb repulsion term, U_{eff}, and the bandwidth of the one-electron states, W. When $U_{\text{eff}}/2W > 1$, the Auger spectrum is expected to be quasi-atomic; the spectrum represents bandlike states when $U_{\text{eff}}/2W < 1$. The observed changes in the Auger profiles of alloys have been explained by Weightman *et al.* (1979) and Weightman & Andrews (1980*a*, *b*) by employing the theoretical model of Cini (1977) and Sawatzky (1977).

We have made use of metal Auger intensities for characterizing the electron states of transition metal compounds in some detail. In doing so, we have made use of the ratios of metal Auger intensities rather than their absolute values. In this article we shall discuss the systematics

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in Auger intensity ratios in transition metals and their compounds and show how the intensity ratios can be used in determining the number of d electron states in manganese oxide catalysts and in investigating surface oxidation of metals. The intensity ratios can also be used for investigating charge-transfer and hybridization effects in transition metal alloys with aluminium. Changes in the spectral features of the valence Auger transitions of copper in copper alloys have been found to reflect variations in the band-like Auger states on alloying. We have discussed inter-atomic Auger transitions observed in the spectra of transition metal oxides especially when the valence d-electrons of the metal are depleted.

Unlike other techniques of electron spectroscopy, Auger electron spectroscopy has not been employed extensively to investigate adsorption of molecules on surfaces. We would, however, expect Auger transitions involving valence levels to provide fingerprints of adsorbed molecular species, although one may not be able to exactly interpret the observed spectra in terms of specific transitions. It has been our experience in this laboratory that carefully recorded Auger spectra with X-ray and electron beam excitations are useful in characterizing adsorbed species and also in examining chemical transformations on surfaces. We shall discuss typical examples of Auger spectra of adsorbed species to illustrate these aspects.

2. Metal Auger intensity ratios

An examination of the metal Auger intensity ratios in several series of oxides of first-row transition metals, reveals the following relations between the intensity ratios and the number of valence electrons, N,

$$I(L_{23}M_{23}M_{45})/I(L_{23}M_{23}M_{23}) \propto N, \tag{1}$$

$$I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{45}) \propto (N-1), \tag{2}$$

$$I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{23}) \propto N(N-1), \tag{3}$$

In the above relations, N stands for $3d^n+4s^2$ electrons, the 4s electrons being included to account for the difference in intensity ratios of systems such as Fe and FeO, which exhibit different intensity ratios although they possess the same number of d electrons (Rao *et al.* 1980). In figure 1 we have shown the plots of various Auger intensity ratios of iron and its oxides as functions of N as well as the oxidation number, Z. Similar relations are found to be valid in oxides of Ti, V and Cr. Relations (1) to (3) are valid to some extent for the intensity ratios of the first-row transition elements, but the relations are not linear (see figure 2); the $I(L_{23}M_{23}M_{45})/I(L_{23}M_{23}M_{23})$ intensity ratios show large deviations for V and Cr.

Relations of the type (1) to (3) are found to hold for the second-row transition elements and their oxides as well. The plot of $I(M_{45}N_{45}N_{45})/I(M_{45}N_{23}N_{45})$ against $(N-1)$ for these elements is shown in figure 3. Oxides of the second-row transition elements obey such relations just as the iron oxides illustrated in figure 1. In general, it appears that the intensity ratios of the type $I(CVV)/I(CC'V)$ and $I(CVV)/I(CC'C'')$, where C, C′ and C″ denote core levels and V stands for a valence level, show progressive increase with the number of valence electrons in the metal (Yashonath *et al.* 1983). These relations hold better for a related series of oxides of the same metal where the transition probability essentially remains the same, rather than for a series of transition metals.

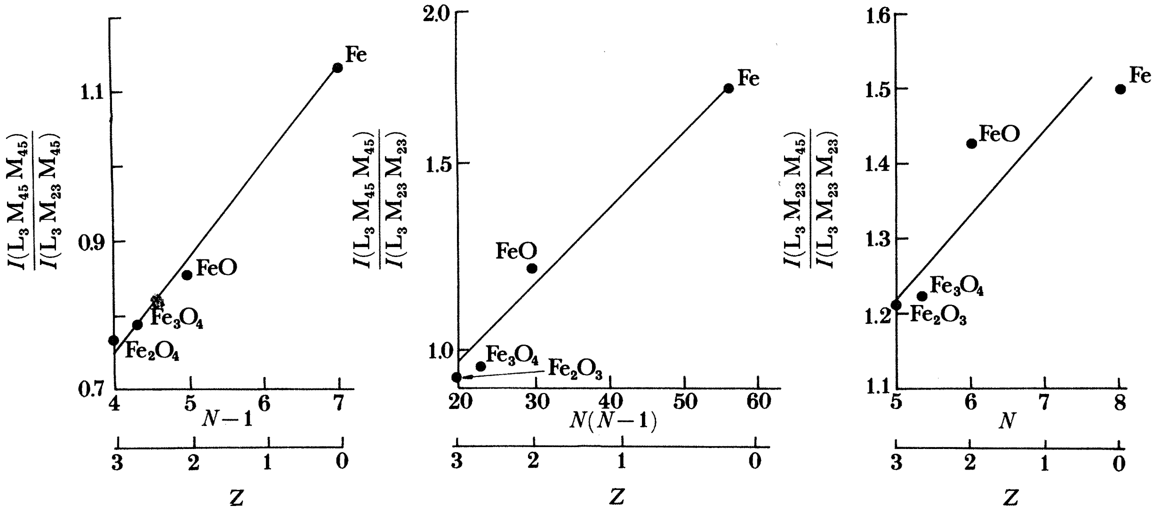

FIGURE 1. Plot of different Auger intensity ratios against the oxidation number, Z, for iron and its oxides. Relations between the intensity ratios and the number of valence electrons are also indicated.

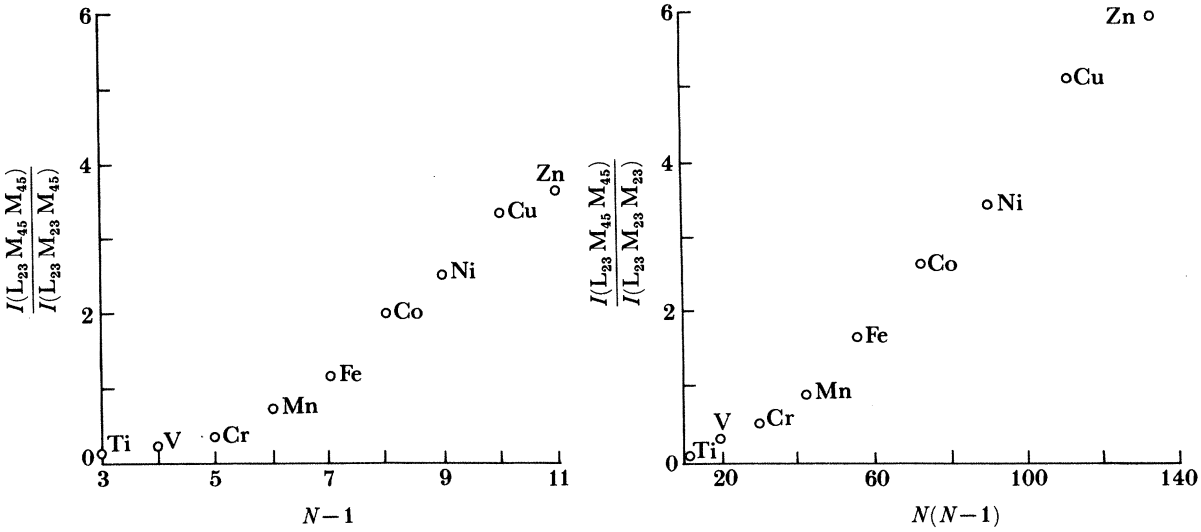

FIGURE 2. Dependence of the Auger intensity ratios of first-row transition metals on the number of valence electrons, N.

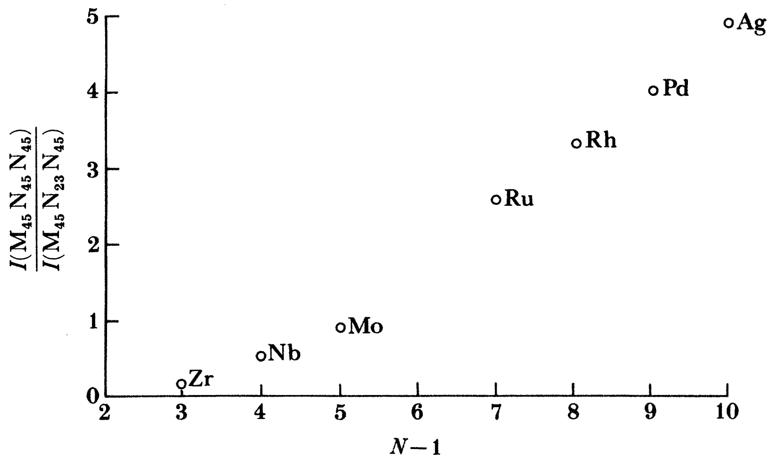

FIGURE 3. Dependence of the $I(M_{45}N_{45}N_{45})/I(M_{45}N_{23}N_{45})$ Auger intensity ratio of second-row transition metals on $(N-1)$.

To relate the metal Auger intensity ratios in a variety of metal derivatives such as chalcogenides, it becomes necessary to take the effective atomic charge, q, of the metal into account; the effective charge itself can be estimated by employing one of several methods available. The following relations would account for the variations in the Auger intensity ratios in such situations:

$$I(L_{23}M_{23}M_{45})/I(L_{23}M_{23}M_{23}) \propto (N-q), \tag{4}$$

$$I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{45}) \propto (N-q-1), \tag{5}$$

$$I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{23}) \propto (N-q)\,(N-q-1). \tag{6}$$

In figure 4 we show plots of the intensity ratios of nickel, zinc and copper compounds to illustrate the use of the above relations. Relations similar to (4) to (6) can be written for the derivatives of second-row transition metals as well.

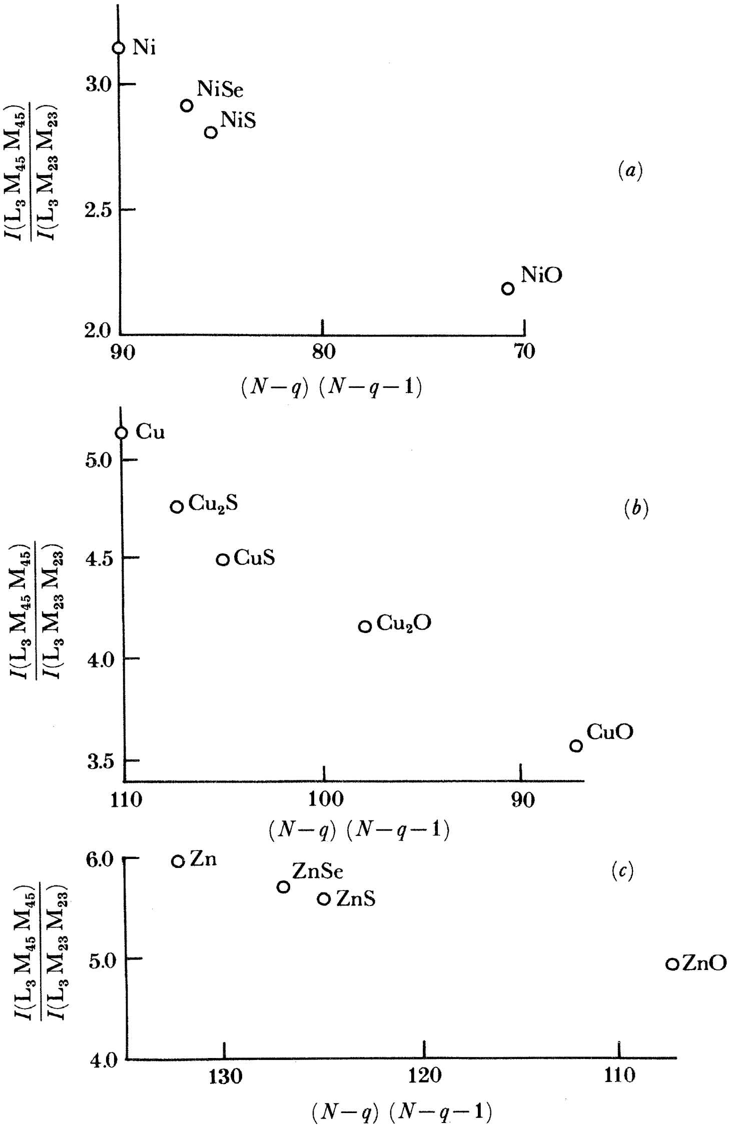

FIGURE 4. Dependence of the Auger intensity ratio $I(L_3M_{45}M_{45})/I(L_3M_{23}M_{23})$ of compounds of Ni, Cu and Zn with $(N-q)\,(N-q-1)$: (a) $N = 10$, (b) $N = 11$, (c) $N = 12$.

Metal Auger intensity ratios can be employed to determine the number of electron states in transition metal systems. We illustrate this for manganese oxide catalysts. In figure 5 we show the plot of $I(\mathrm{LVV})/I(\mathrm{LMV})$ intensity ratios of manganese in Mn metal, MnO, Mn_2O_3 and MnO_2 against the number of d-electron states, n_d. These intensity ratios were also determined for variously treated MnO_2 and MnO_2–SiO_2 catalysts. Based on the intensity ratios we could estimate the number of d electrons in the catalyst samples and the results are shown in table 1. In the reduced and deactivated catalysts, the oxidation state of manganese is lower than 4+ and the number of d electrons is greater than three. The activated catalysts, however, show significantly low n_d (1–1.6), corresponding to a high oxidation state of manganese.

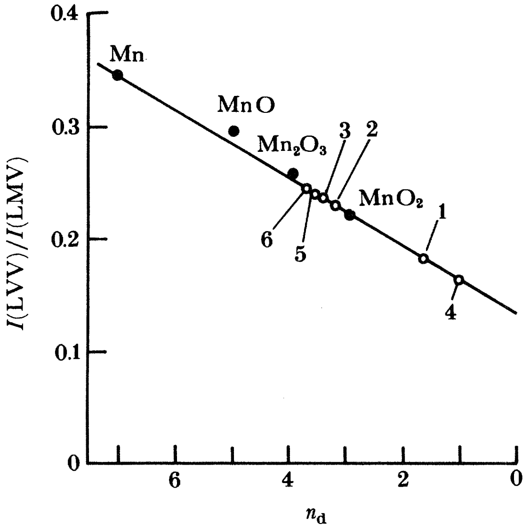

FIGURE 5. Plot of the $I(\mathrm{LVV})/I(\mathrm{LMV})$ Auger intensity ratio against the number of valence electrons, n_d: (1) MnO_2 activated; (2) MnO_2 deactivated; (3) MnO_2 reduced; (4) MnO_2–SiO_2 activated; (5) MnO_2–SiO_2 deactivated; (6) MnO_2–SiO_2 reduced.

TABLE 1. AUGER INTENSITY RATIOS AND NUMBER OF d-ELECTRON STATES IN MANGANESE DIOXIDE CATALYSTS

	$I(\mathrm{LVV})/I(\mathrm{LMV})$	n_d
MnO_2 activated	0.18[a]	1.6
MnO_2 deactivated	0.23	3.2
MnO_2 reduced	0.24	3.5
MnO_2–SiO_2 activated	0.16	1.0
MnO_2–SiO_2 deactivated	0.24	3.5
MnO_2–SiO_2 reduced	0.25	3.7

[a] Obtained from the plot in figure 5.

Depth profile studies of chemi-plated CdS–Cu_2S solar cells have been made by measuring Auger intensity ratios (Bhide *et al.* 1981). The Cu(LVV/LMM) intensity ratios along with the $Cu(2p_{\frac{3}{2}})/S(2p)$ ratio in X.p.s. have shown that the nominal valency of Cu above the junction is +1 and that copper is essentially in the Cu_2S form. In the deeper layers, the ratios show the presence of Cu in the form of CuS. The intensity ratio corresponding to Cu^+ is considerably higher (*ca.* 4.7) compared to Cu^{2+} (*ca.* 4.2).

Auger intensity ratios have been employed to investigate the surface oxidation of metals such as Fe, Ni, Cu, Zn and Zr. Typical variations in the $I(L_3M_{45}M_{45})/I(L_3M_{23}M_{23})$ ratio of nickel is plotted against oxygen exposure (in terms of $\log L$) at two temperatures in figure 6. The plots show three distinct regions of oxidation, namely chemisorption, rapid oxidation and oxide-layer formation (Rao *et al.* 1980; Sarma *et al.* 1980). Variation in the oxidation rates with temperature can also be seen from the plots at 300 K and 500 K. In the oxidation of copper, Auger intensity ratios show minima around $\log L \approx 5$, accompanied by a significant decrease in the binding energy of the O(1s) level. This observation is explained by the suggestion that after the initial chemisorption at low exposures, oxygen diffuses into the octahedral holes of copper metal; in such a state, there could be greater transfer of electrons from copper atoms to oxygen, giving rise to the minimal values of the metal Auger intensity as well as the O(1s) binding energy. The magnitude of the surface oxidation of metals (or the number of oxide layers) estimated from Auger intensity ratios is generally in good agreement with the estimates from X.p.s. and other techniques.

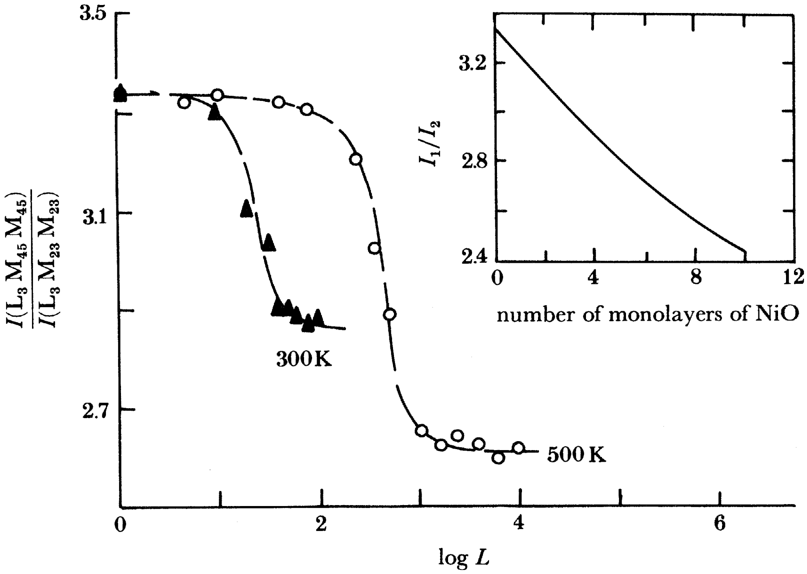

FIGURE 6. Plot of the $I(L_3M_{45}M_{45})/I(L_3M_{23}M_{23})$ intensity ratio against $\log L$ for the $Ni+O_2$ system. Inset shows the relation between the intensity ratio and the number of monolayers of NiO.

The discussion hitherto should clearly indicate how the metal Auger intensity ratios can be employed to investigate the surface oxidation states or the number of d-electron states in transition metal systems. It would be pertinent at this juncture to mention other physical methods available for this purpose. The two main techniques that can be effectively used are X-ray absorption spectroscopy and electron energy loss spectroscopy. In X-ray absorption spectroscopy, the K or L absorption edges of the transition metals are sensitive to the chemical environment and the chemical shifts depend on the oxidation state or the effective charge on the metal (Sarode *et al.* 1979). The dependence of the chemical shift on the effective charge is described by the relation $\Delta E = aq + bq^2$. The X-ray absorption near-edge structure gives information on the metal coordination and the energies of the spectral transitions vary with the effective charge on the metal (Sankar *et al.* 1983). Measurement of the intensity of the main peak near the absorption edge or of the $s \rightarrow d$ transition peak would also provide information on the number of electron states in the transition metal. Recently, it has been found that electron energy loss spectroscopy (made in an electron microscope) is very useful in determining the electron states of transition metals, a special advantage being the minute quantities (10^{-12}–10^{-20} g) of the material required (Rao *et al.* 1984*a*, *b*). Although these two techniques are very useful, the Auger intensity ratio method still provides an easy quantitative method for determining the number of valence electron states in transition metal systems.

3. Inter-atomic Auger transitions

Inter-atomic Auger transitions have been reported in certain ionic solids and metals covered with adsorbed gases. A close examination of the metal Auger signals of transition metal oxides reveals that not only the relative intensities, but also the shapes of these signals are characteristic of the oxidation state of the metal. Auger transitions involving the valence levels of the oxides of titanium are shown in figure 7. From this figure we see that Ti metal shows a single $L_3M_{23}V$ Auger line, whereas the oxides show yet another peak at lower kinetic energy. The intensity of this peak relative to the higher kinetic energy signal increases progressively as the oxidation state of the metal increases, until in TiO_2 the lower kinetic energy transition emerges essentially as a single peak. We assign the higher kinetic energy peak to an intra-atomic $L_3(Ti)M_{23}(Ti)V(Ti)$ Auger transition, while assigning the lower kinetic energy signal to an inter-atomic $L_3(Ti)M_{23}(Ti)V(O)$ transition. Thus, we find that only the inter-atomic Auger signal appears

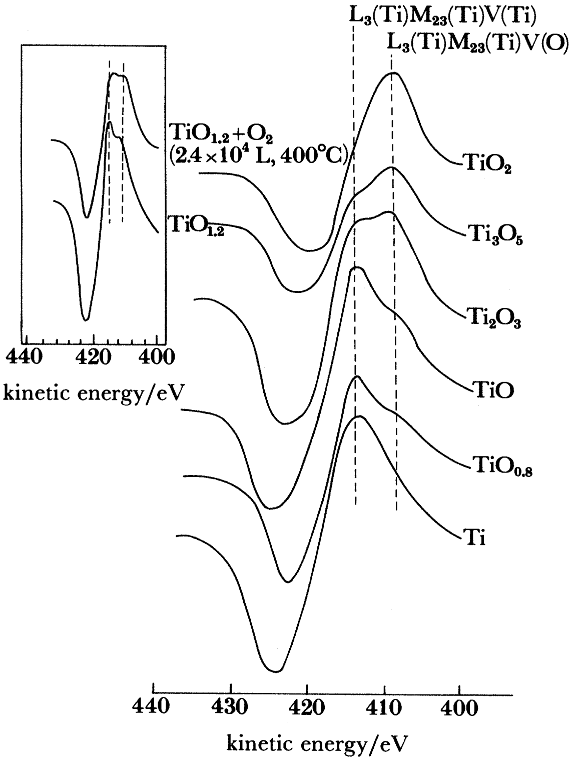

Figure 7. LMV Auger spectra of Ti and its oxides showing the development of the inter-atomic $L(Ti)M_{23}(Ti)V(O)$ Auger peak as the metal goes into the higher oxidation state. Inset shows the effect of oxygen exposure on the Auger signal of $TiO_{1.2}$.

for TiO_2, where the metal is in the d^0-state; the inter-atomic Auger process would be the mode of decay for the core hole localized at the metal site when the metal valence level is depleted. The energy separation between the two Auger signals in titanium oxides is about 4.5 eV, which is close to the energy separation between Ti(3d) and O(2p) levels in these oxides. In the inset of figure 7 we have shown the effect of oxygen exposure on the relative intensity of the inter-atomic Auger signal with respect to the intra-atomic signal in $TiO_{1.2}$, suggesting the formation of a higher oxide on oxygen exposure. We realize that it is somewhat artificial to maintain the distinction of inter-atomic and intra-atomic Auger processes since both involve molecular orbitals, but operationally this is useful.

The $L_3M_{23}V$ Auger transitions of vanadium oxides show features similar to those of titanium oxides with the intensity of the low kinetic energy peak due to the inter-atomic $L_3(V)M_{23}(V)V(O)$ process becoming dominant as the oxidation state increases. The energy separation between the two signals of $L_3M_{23}V$ transitions in vanadium oxides is about 3.5 eV, as V(3d) is energetically nearer to the O(2p) level as compared to that in titanium oxides. The L_3VV Auger spectra of manganese oxides also clearly show the competition between the intra-atomic $L_3(Mn)V(Mn)V(Mn)$ and the inter-atomic $L_3(Mn)V(O)V(O)$ transitions, the latter being entirely absent in the spectrum of Mn metal. The intensity of the inter-atomic transition increases from Mn^{2+} to Mn^{4+}. The energy separation between the two Auger signals in these oxides is about 5.0 eV. The Mn(3d) level in manganese oxides is separated by *ca.* 2.5 eV from the O(2p) level, confirming our assignment. The surface oxidation of manganese can be monitored through the intensity of the inter-atomic transition.

The present study shows that the inter-atomic mode of decay of the metal core hole state is in competition with the intra-atomic mode, the relative transition probability of the former increasing with the depletion of the d-electrons. So, we find that the relative intensity of the inter-atomic Auger signal with respect to the intra-atomic one is characteristic of the oxidation state of the metal, indicating that the intensity of the inter-atomic Auger transition can be used as a probe to the surface oxidation state of metals (Rao & Sarma 1982).

In the surface oxidation of zirconium, the formation of the sub-oxide is accompanied by an intra-atomic Auger transition of the type $M_{45}(Zr)V(Zr)V(Zr)$. When the sub-oxide transforms to ZrO_2, the intensity of the inter-atomic transition $M_{45}(Zr)V(O)V(O)$ increases at the expense of the intra-atomic transition indicating a change in the oxidation state of the metal (Sen *et al.* 1984*a*).

4. ALLOYS

Metal Auger intensity ratios also reveal the magnitude of charge-transfer and hybridization in metal alloys. Accordingly, the intensity ratios $I(LVV)/I(LMV)$ and $I(LVV)/I(LMM)$ in elements like Ni and Co increase as aluminium is deposited on the surface. Plots of the $I(LVV)/I(LMV)$ and $I(LVV)/I(LMM)$ intensity ratios of Ni and Co against Al coverage, shown in figure 8, clearly indicate how the intensity ratios increase with Al coverage. For Co, the ratios seem to reach a limiting value; this is expected since the Auger technique is sensitive to the immediate environment of the Co atoms where two monolayers of Al are sufficient to induce the observed increase in the d-band electron density. Furthermore, the ratios at saturation coverage on Co nearly equal those of the next element in the periodic table, Ni, indicating thereby that the valence electron density of states on the Co site tends to be rather Ni-like.

We have examined hybridization and charge transfer between Al and the various transition metal substrates by means of plasmon losses suffered by the Auger electrons while passing through the Al overlayer. These losses are aluminium plasmon losses, the loss value depending on the substrate and coverage of aluminium. While the loss feature appeared at the Al bulk plasmon value of 15.3 for Zn, it varied between 16 and 20 eV for different coverages on Co, Ni and Cu. There is no charge transfer and hybridization for Zn, because both the d- and s-bands are full. Absence of Al–Zn hybridization has been noted on the basis of soft X-ray emission studies as well; a similar situation holds for Mg–Zn alloys.

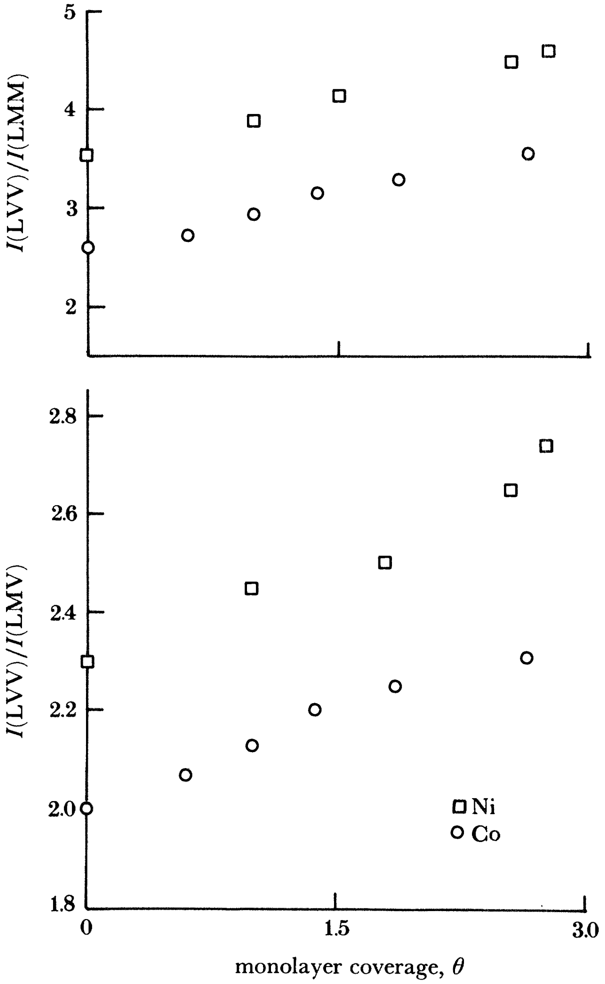

FIGURE 8. Plots of I(LVV)/I(LMV) and I(LVV)/I(LMM) Auger intensity ratios against the coverage of aluminium.

Band-like, as well as quasi-atomic types of Auger transitions have been found in metal alloys, depending on the magnitudes of the bandwidth of one-electron states, W, and the Coulomb repulsion term U_{eff}. We have examined the band-derived feature of the Cu($L_3M_{45}M_{45}$) transition in several alloys of Cu with Mn and Ni as well as in metglasses of Cu with Zr (Sen *et al.* 1984) and find that the shape and intensity of the band-like feature change from alloy to alloy (figure 9*a*). For Cu–Zr alloys the feature becomes narrower with decreasing copper concentration, suggesting an increased atomic impurity-like behaviour of Cu in the matrix of

Zr. For Cu–Ni alloys, however, the intensity of the feature decreases with decreasing Cu concentration with no evidence of band localization. We have found similar changes in Cu–Al and Cu–Mn alloys. These changes are likely to arise from a local density of band-like states at the Cu site.

In figure 9 we have also plotted the energy difference $(E_G - E_C)$ between the most intense peak of the $Cu(L_3M_{45}M_{45})$ transition and the beginning of the band-derived structure and find that it increases progressively with increasing Cu concentration regardless of the alloy system. It is noteworthy that the Cu–Zr system exhibits a more pronounced decrease in $(E_G - E_C)$ as compared to other alloys. This is in accord with the fact that the Cu(3d) signal in X.p.s. shifts away from E_F when alloyed to Zr.

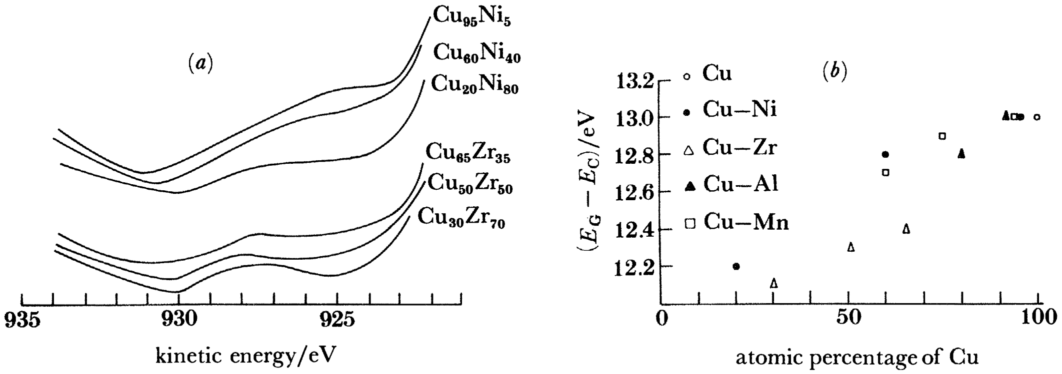

FIGURE 9. (*a*) Band part of $Cu(L_3M_{45}M_{45})$ Auger transition in crystalline Cu–Ni alloys and Cu–Zr metglasses. The spectral intensity is normalized to have the same integrated intensity of the $L_3M_{45}M_{45}$ transition in all cases. (*b*) Plot of $E_G - E_C$ against atomic percentage of Cu in Cu alloys.

5. ADSORBED MOLECULES

Auger spectra of molecules show distinct differences from those of atomic species. In figure 10 we compare the Auger spectra of atomic oxygen adsorbed on Ag with the spectra of molecular oxygen, and other oxygen-containing molecules. A similar comparison of the spectra of atomic carbon with the carbon Auger spectra of a few carbon compounds is made in figure 11. These spectra should allay the fears of some investigators that Auger spectra of all molecules look alike; similar observations have been made by Canning *et al.* (1981) and Baker *et al.* (1981).

It is advisable to record the X-ray excited Auger spectra in addition to the electron-beam excited spectra to identify the spectral changes occurring due to beam damage. We have recorded both X-ray induced and electron-beam induced Auger spectra of various molecules such as oxygen, water, carbon monoxide, methanol, formaldehyde, acetone, formic acid and methylacetate, and verified the reproducibility of the various features observed in the spectra. We also find some advantage in comparing the integrated Auger spectra obtained from the two sources.

We have compared the Auger spectra of adsorbed molecules with those of the free molecules wherever possible. In the absence of the spectra of free molecules, it becomes difficult to fully understand the spectra of the adsorbed species, especially since inter-atomic transitions involving the adsorbate levels also occur. This, however, does not prevent one from using the Auger spectra of complex molecules as fingerprints.

The first line in the O(KLL) region of atomic oxygen adsorbed on Ag (figure 10) is a broad, featureless line appearing around 516 eV, while the spectrum of molecular oxygen shows an additional high kinetic energy feature at 523 eV (figure 10). This is found to disappear on dissociation of the absorbed O_2 molecule and we assign it to the $K\pi^*\pi^*$ Auger transition of the O_2 molecule. This assignment is further substantiated with the knowledge of the photoelectron spectrum of adsorbed O_2 (Rao *et al.* 1982).

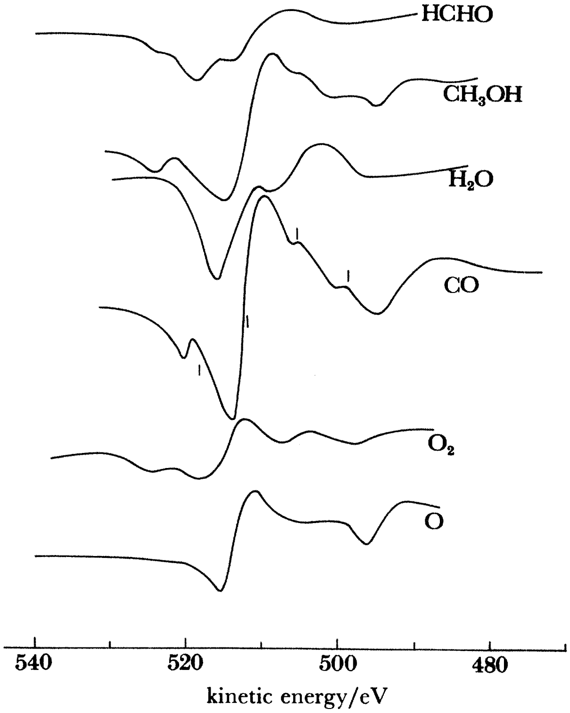

FIGURE 10. Typical oxygen Auger spectra of a few adsorbed chemical species.

Carbon monoxide shows a characteristic spectrum different from the spectra of both atomic and molecular oxygen species. This compares well with the spectrum of adsorbed CO reported by Baker *et al.* (1981). Since this spectrum matches well with that of CO in the gas phase, the assignment of Moddeman *et al.* (1971) would be valid for adsorbed CO as well.

The spectrum of adsorbed water (figure 10) shows two main features that compare well with the two most intense peaks seen in the spectrum of water in the gas phase (Moddeman *et al.* 1971). We assign the highest kinetic energy feature to the $K1b_1 1b_1$ Auger transition of adsorbed H_2O, while the other is assigned to the $K3a_1 3a_1$ transition based on the binding energy differences of the $1b_1$ and $3a_1$ levels.

The spectrum of methanol adsorbed on metals shows a high kinetic energy feature around 521 eV, which we can assign to the $K2a''2a''$ transition of molecular methanol (Rye *et al.* 1978). Methanol exhibits a variety of reactions on transition metal surfaces. Thus, on a silver surface, methanol transforms to formaldehyde, while on a nickel surface, it transforms to carbon monoxide. On a copper surface, it transforms first to HCHO and subsequently to an ester type of species. The oxygen Auger spectra given in figures 11 and 12 reflect these transformations; such changes are also seen in the carbon Auger spectra.

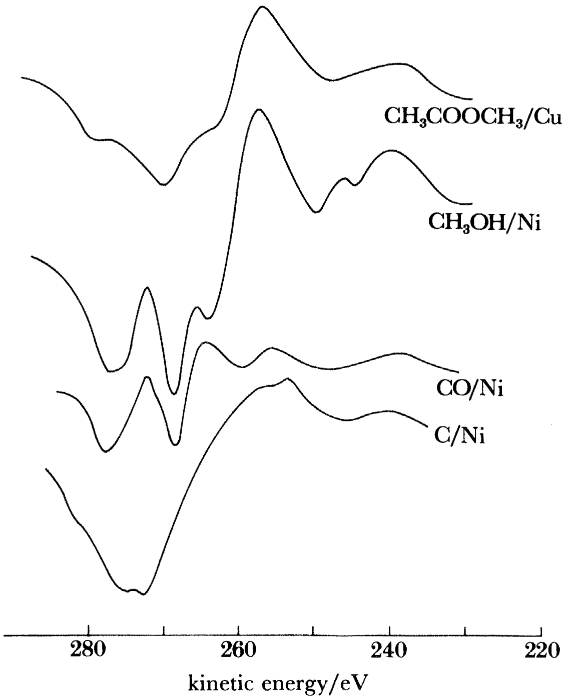

FIGURE 11. Typical carbon Auger spectra of a few adsorbed chemical species.

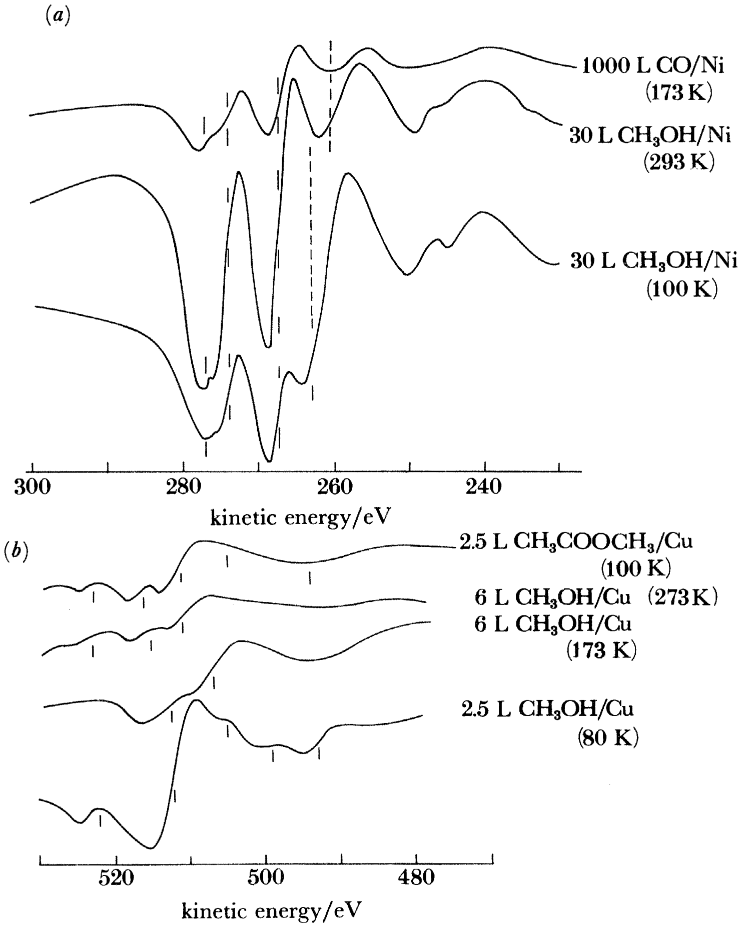

FIGURE 12. (*a*) Carbon Auger spectra of methanol adsorbed on Ni at different temperatures, showing the formation of adsorbed CO. A spectrum of CO adsorbed on Ni is shown for comparison. (*b*) Oxygen Auger spectra of methanol adsorbed on Cu showing the transformation of methanol to an ester-like species. The spectrum of methylacetate adsorbed on Cu is shown for comparison.

The Auger spectrum of molecular nitrogen adsorbed on Ni at 80 K is not unlike the carbon Auger spectrum of adsorbed carbon monoxide. NH_3 adsorbed on Ni or Cu gives a characteristic nitrogen Auger spectrum. If the copper surface contains oxygen, there is evidence for the formation of H_2O (Matloob & Roberts 1977), as revealed by the characteristic oxygen Auger spectrum.

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Discussion

M. W. Roberts (*Department of Chemistry, University College, Cardiff, U.K.*). The spectrum of the chemisorptive replacement of chemisorbed oxygen at a copper surface by exposure to ammonia should presumably reflect the presence of an imide species (NH). Was Professor Rao able to discern this in his spectrum?

C. N. R. Rao. Auger spectroscopy cannot provide information on the details of the reaction and the intermediate. However, our studies of this system with electron energy loss spectroscopy clearly shows the formation of imide species along with water.

P. Weightman (*Physics Department, Liverpool University, U.K.*). The identification of features in the Auger spectra of oxides of transition metals with inter-atomic processes involving the d electrons is incorrect. It is difficult to identify features in differentiated Auger spectra. The best way to do the experiment is to look at the Auger profile directly without differentiating. If this is done then it is observed that oxide shifts the Auger profile of any metal to lower kinetic energy. This effect can be understood in terms of an initial state chemical shift and a final state relaxation shift consequent on the change in chemical environment. That the effect is not due to inter-atomic processes involving the d electrons is confirmed by the fact that it is observed for Mg, Al and Zn.

C. N. R. Rao. I do not agree with some of the points made. There is no doubt that relaxation shift is the main factor in oxides of metals such as Mg and Zn. The chemical shifts and relaxation shifts would be rather small in a series of transition metal oxides such as the oxides of titanium. The presence of two Auger signals in some of these oxides, the intensity of one increasing with the depletion of d electrons prompts us to propose an inter-atomic mechanism.