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Dependence of metal Auger intensity ratios on the effective charge on metal atoms

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Abstract. Metal Auger line intensity ratios were shown by Rao and others to be directly related to the occupancy of valence states. It is now shown that these intensity ratios are more generally related to the effective charge on the metal atom. The Auger intensity ratios are also directly proportional to valence band intensities of metals. Correlations of the intensity ratios with Auger parameters have also been examined.

Keywords. Metal Auger intensity ratio ; Auger spectroscopy ; Auger parameter.

1. Introduction

Rao *et al* (1980) have recently demonstrated that the relative ratios of intensities of metal Auger lines are determined by the occupancy of the valence bands. Thus, the intensity ratio $L_{23}M_{23}M_{45}/L_{23}M_{23}M_{23}$ is proportional to N while the ratio $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ is proportional to $N(N-1)$ where N is the number of valence electrons (*e.g.*, $4s + 3d$ electrons in the case of first row transition elements and their compounds). Since oxidation affects the number of valence electrons (and hence the oxidation state of a metal), the metal Auger intensity ratios could be directly employed in the study of surface oxidation of transition metals (Hegde *et al* 1980; Rao *et al* 1980 ; Sarma *et al* 1980). Preliminary studies in this laboratory showed that in compounds of transition elements such as ZnO, ZnS, ZnSe and ZnTe, while the formal oxidation state of Zn remains the same, the metal Auger intensity ratios were quite different. This observation suggested to us that the intensity ratios should probably be related to the effective charge on the metal atom rather than N or the formal oxidation number of the metal. We have now investigated the variation of metal Auger intensity ratios with charge on the metal atom $\triangle q$ in a series of Ni, Cu and Zn compounds. Another aspect of interest was to understand the nature of the variation of the Auger parameter (Wagner 1977) in such related series of compounds.

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2. Experimental

AlK_α XPS and electron beam initiated Auger spectra were recorded with a ESCA-3 Mark II spectrometer of V.G. Scientific Ltd., U.K. Commercially available A.R. grade compounds of Ni, Cu and Zn have been used in this study. Core level binding energies reported here are with reference to $Au(4f_{7/2})$ at 83·7 eV. We have taken peak-to-peak heights in the differentiated Auger spectra to represent intensities of Auger lines.

3. Results and discussion

In figures 1 to 3, we have plotted the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ metal Auger intensity ratios in Ni, Cu and Zn compounds respectively against the charge on the metal ion $\triangle q$ taking the $\triangle q$ values estimated by the method of Pauling (1960). The plots are quite linear showing thereby that the metal Auger intensity ratios are indeed determined by the charge on the metal atom. We could also satisfactorily correlate the ratio against the difference in electronegativities of the two elements $\triangle X$ (see inset of figure 1). That the metal Auger ratio should be related to $\triangle q$ follows from the following arguments.

The intensities of the $L_{23}M_{23}M_{23}$ and $L_{23}M_{45}M_{45}$ Auger lines are given by:

$$I(L_{23}M_{23}M_{23}) = q(M_{23})(q(M_{23}) - 1)\,p(M_{23}M_{23}), \tag{1}$$

$$I(L_{23}M_{45}M_{45}) = q(M_{45})(q(M_{45}) - 1)\,p(M_{45}M_{45}), \tag{2}$$

where $q(M_{23})$ and $q(M_{45})$ are the atomic charges of M_{23} and M_{45} levels respectively while $p(M_{23}M_{23})$ and $p(M_{45}M_{45})$ denote Auger transition probabilities of

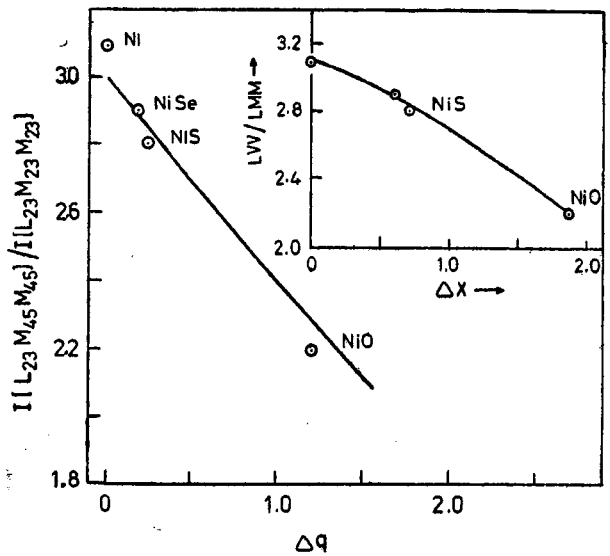

Figure 1. Plot of the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ Auger line intensity ratio against the charge, $\triangle q$ on Ni (The solid line is obtained from equation 5). Plot of the intensity ratio against the electronegativity difference ($\triangle X$) is shown in the inset.

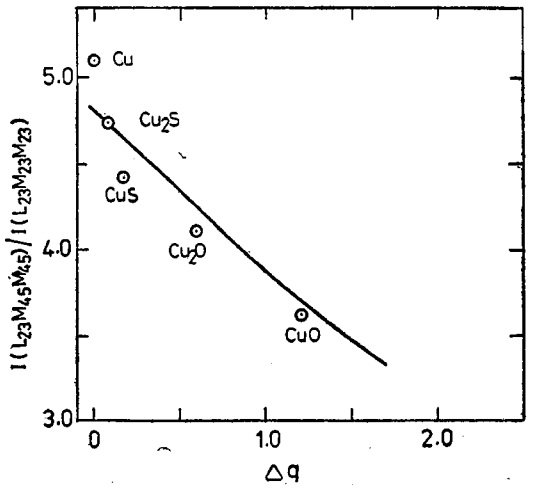

Figure 2. Plot of the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ Auger line intensity ratio against Δq of copper (solid line is obtained from equation 5).

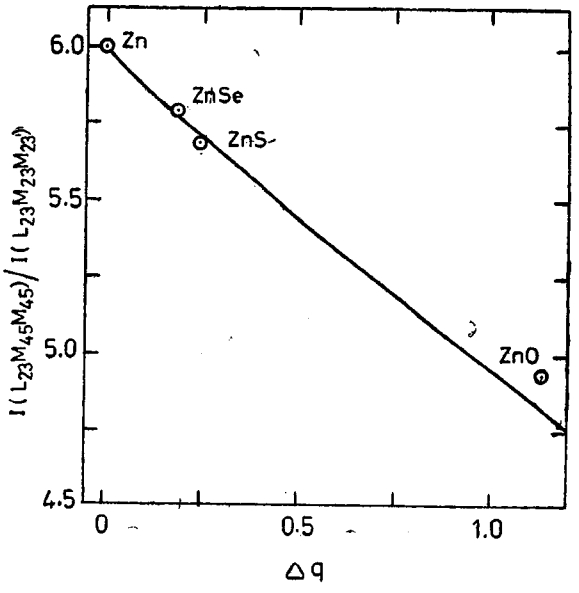

Figure 3. Plot of the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ Auger line intensity ratio against Δq of zinc (solid line is obtained from equation 5).

the respective Auger transitions. In the case of transition elements, M_{45} is taken to denote valence levels. The local charge on M_{23} (in Ni and its compounds for example) remains essentially the same since it is a core level but $q\,(M_{45})$ depends on the bonding of the metal with ligands. Thus,

$$q\,(M_{23}) = 6e = n, \tag{3}$$

and $$q(M_{45}) = (4s + 3d)\,e - \triangle q = N - \triangle q. \quad (4)$$

Here, $\triangle q$ denotes the excess positive charge on the metal atom. It, therefore follows :

$$\frac{I(L_{23}M_{45}M_{45})}{I(L_{23}M_{23}M_{23})} = \left[\frac{p(M_{45}N_{45})}{p(M_{23}M_{23})\,n(n-1)}\right][(N - \triangle q)(N - \triangle q - 1)]. \quad (5)$$

In equation (5), the first term is essentially constant if we make the reasonable assumption that the Auger transition probabilities remain constant for different compounds of the same metal (see Rao *et al* 1980). The second factor decreases with increasing $\triangle q$. The metal Auger intensity ratio calculated from (5) taking N as the total number of valence electrons, $(4s + 3d)$, of the transition metal and assuming the ratio of transition probabilities as 1·0, 1·33 and 1·36 for Ni, Cu and Zn respectively indeed show the expected variation with $\triangle q$ (see figures 1, 2 and 3). It can be readily shown that the $L_{23}M_{23}M_{45}/L_{23}M_{23}M_{23}$ and $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{45}$ Auger ratios are also similarly dependent on the charge on the metal atom.

That the metal Auger intensity ratios are dependent on the occupancy of the valence band is further supported by figure 4 where we have plotted the ratio of intensities of the valence band and the $2p_{3/2}$ core level against the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ Auger intensity ratios of transition metals. This is because the valence band in x-ray photoelectron spectra is a true representation of the density of valence states.

It has recently been established (Sarode *et al* 1979) that chemical shifts of the K absorption edges of transition metal compounds $\triangle E$ are related to $\triangle q$ by the relation $\triangle E = a(\triangle q) + b(\triangle q)^2$. Accordingly, metal Auger intensity ratios

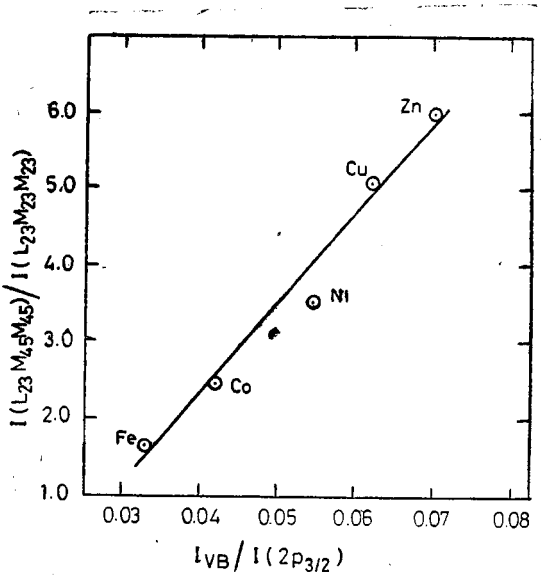

Figure 4. Plot of the $L_{23}M_{45}M_{45}/L_{23}M_{22}M_{23}$ Auger line intensity ratio in transition metals against the relative intensities of valence bands.

give a smooth relation (though not directly linear) with $\triangle E$ values in the case of Ni, Cu and Zn compounds.

Wagner (1977) has described the Auger parameter as the difference between the kinetic energy of the strongest Auger line and the kinetic energy of the strongest photoline. This parameter was suggested to be characteristic of a molecular or solid state and chemical shifts in this quantity represent differences in polarisation energy in the final state. The parameter was expected to be of analytical value since it is independent of static charge referencing. The parameter is of particular value for elements Mg, Cu, Zn, Ag and Cd where photoelectron chemical shifts are quite small. Auger parameters were available in the literature (Wagner 1977) for Zn compounds. We determined these Auger parameters for the Cu and Ni compounds listed in table 1. Although the binding energies of core levels of Ni, Cu and Zn generally vary with the effective charge on the metal atom, the variation of the metal $2p_{3/2}$ binding energies is small in the series of compounds studied by us and does not show any marked trend. The Auger kinetic energy however, shows systematic variation with $\triangle q$ in the case of Zn compounds (see figure 5). It is, therefore, apparent that any relation of the Auger parameter with $\triangle q$ (or $\triangle X$) is essentially due to the variation of the Auger kinetic energy term. Neither the Auger kinetic energy nor the Auger parameter showed any sensible variation in the case of Ni and Cu compounds where the change in the Auger parameter is rather small. Even in the case of Zn where Auger parameters are reliable (Wagner 1977), we see no particular adva tage in using these parameters. It appears that the metal Auger intensity ratios more truly reflect the bonding or variation in charge on the metal atom than the chemical shifts of core level binding energies or Auger kinetic energies which are almost always small.

Table 1. $2p_{3/2}$ binding energies, Auger kinetic energies and Auger parameters in Ni and Cu compound (values in eV).

	E $(2p_{3/2})$	E_{KE} $(L_{23}M_{45}M_{45})$	Auger parameter
Ni	852·2	846·3	211·9
NiSe	852·2	846·5	212·1
NiS	852·3	846·3	212·0
NiO	854·0	845·7	213·1
Cu	931·8	918·2	363·4
Cu_2S	931·7	918·4	363·5
CuS	931·8	918·5	363·7
Cu_2O	931·8	917·5	362·7
CuO	932·8	917·0	363·2

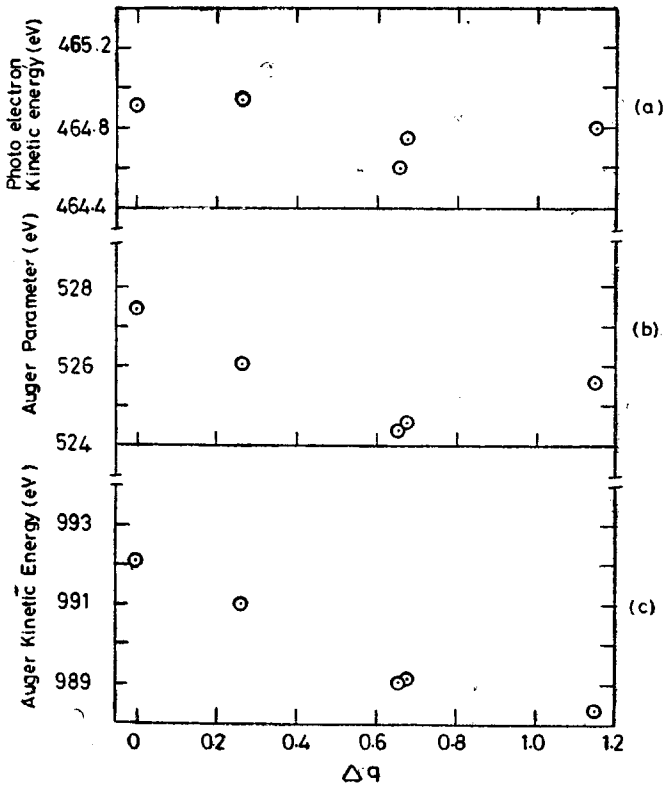

Figure 5. Plots of (a) photoelectron kinetic energy of Zn ($2p_{3/2}$), (b) Auger parameter and (c) Auger kinetic energy of Zn $L_{23}M_{45}M_{45}$ Auger line against charge on Zn.

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