Auger parameter and chemical state plots for copper- and zinc-containing compounds: charge distribution and screening effects

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Abstract. Cu- and Zn-containing compounds are characterised making use of the Wagner Auger parameter and of the so-called chemical state plots to obtain information on the relative initial-state charge distributions and on the relative extra-atomic relaxation energy. The position in the plots of different classes of compounds is discussed. To explain the constancy of the Auger parameter for Cu(II) compounds and metallic Cu, it is suggested that the energy involved in the electron transfer $2p^5 3d^{10} L$ is similar to the screening energy in the metallic state.

1. Introduction

It is now well established that the study of the chemical shift of Auger and photoelectron peaks is a powerful tool for characterising the electronic environment of an atom in various compounds. These shifts arise from the difference ΔV in the initial charge distributions and the difference ΔR in the relative extra-atomic relaxation energies.

Wagner (1975), Wagner and Joshi (1988) and Thomas (1980) have shown that ΔV and ΔR can be determined from measurements of the Auger parameter $\alpha = E_B + E_K$, which is the sum of the core ionisation energy E_B and of the Auger kinetic energy E_K. Wagner *et al* (1979, 1982) have also shown that the arrangement of the photoelectron and Auger energies on a two-dimensional 'chemical state plot' allows more accurate delineation of the characteristics of a chemical state. In such plots the kinetic energy of the Auger line is on the ordinate, the binding energy of the photoelectron line (in the negative direction) is on the abscissa, and the Auger parameter is shown on a diagonal grid with a slope equal to $+1$.

In this paper we apply these concepts to the characterisation of Cu- and Zn-containing compounds. A few data have been previously presented by Gaarenstroom and Winograd (1977) and by Wagner *et al* (1979).

2. Results and discussion

The line used to draw the chemical state plots are the $E_B(2p_{3/2})$ and $E_K(L_3M_{45}M_{45}, {}^1G)$ lines, the most prominent in the XPS spectra obtained with Mg or Al x-ray source.

In the simplest approximation (Wagner 1975, Thomas 1980) the shift ΔE_B in core ionisation and ΔE_K in the Auger kinetic energy are

$$\Delta E_B = \Delta V - \Delta R \tag{1}$$

$$\Delta E_K = -\Delta V + 3\,\Delta R. \tag{2}$$

The shift in the Auger parameter, given by $\Delta\alpha = \Delta E_B + \Delta E_K = 2\,\Delta R$, provides direct measurement of the extra-atomic relaxation energy. By means of equation (1) or (2) it is then possible to obtain ΔV, which reflects the initial-state charge distribution. Considering the difference between equations (2) and (1), we obtain

$$\Delta E_K = \Delta E_B - 2\,\Delta V + 2\,\Delta\alpha. \tag{3}$$

Equation (3) shows that compounds with similar Auger parameters but with different initial-state charge distribution will be found on the chemical state plots in grid lines at right angles to the Auger parameter grid. Larger ΔV-values are found as one goes down this grid from the upper right-hand corner (high E_K and low E_B) to the low left (low E_K and high E_B) (Wagner *et al* 1980, 1982). It is important to stress that ΔV-values are directly related to differences between the ionicities of the chemical bonds only when the potentials on the atom due to the different environments are similar (Broughton and Bagus 1980).

A Zn chemical state plot shows that, as expected, the metallic state has a larger value of the Auger parameter owing to the screening effect by electrons in the conduction band. The positions of the halides and chalcogenides on the plot vary qualitatively as expected from theory (Wagner 1975, Thomas 1980). The Auger parameter data follow the same trend as do the polarisabilities of both groups: $I > Br > Cl > F$ and $Te > Se > S > O$. According to chemical experience, compounds with a greater ionic character of the chemical bond are located on the lower left-hand side in the plot.

As for the Cu chemical state plot, we note that, although in Cu-containing compounds the d orbitals represent valence levels, in all the different chemical states the Auger transitions are atomic like in nature due to the localisation of the two-hole final state (Cini 1976, Sawatzky 1977, van der Laan *et al* 1981).

For the metallic state and the Cu(I) ($3d^{10}$) compounds the observed trends are similar to that reported in the Zn chemical state plot. Cu(II) compounds have, on the contrary, a constant Auger parameter, similar to the value reported for metallic Cu. To explain this fact, one has to consider that the 'main' peak of the $2p_{3/2}$ transition is represented by the electronic structure $2p^5 3d^{10}L$, where L means a ligand hole (van der Laan *et al* 1981, Ghijsen *et al* 1988, van der Marel *et al* 1988). It appears that the relaxation energy involved in this electron transfer is similar to the screening energy in the metallic state. However, the Cu(II) compounds show a different charge distribution in the initial state. The more ionic compounds present a higher $2p_{3/2}$ binding energy and lower ($L_3M_{45}M_{45}$, ^1G) Auger kinetic energy.

3. Conclusions

In this paper we have shown that the Auger parameter and the so-called chemical state plot are useful tools for characterising the electronic structure of elements in different compounds. Here we have discussed in detail the cases of Cu- and Zn-containing compounds.

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