Determination of Co-ordination Number in some Compounds of Magnesium and Aluminium: a Comparison of X-Ray Photoelectron (ESCA) and X-Ray Emission Spectroscopies

By C. J. Nicholls and D. S. Urch*
(*Chemistry Department, Queen Mary College, Mile End Road, London* E1 4NS)
and A. N. L. Kay
(*Vacuum Generators Ltd., Charlwoods Road, East Grinstead, Sussex*)

Summary The effect of changes in co-ordination number (four to six, oxygen ligands) upon $2p$ and $2s$ ionisation energies of magnesium and aluminium is shown to be about ten times greater (*i.e. ca.* 2 eV) than the effect upon the Kα emission energy, X-ray photoelectron spectroscopy (ESCA) is therefore to be preferred to X-ray emission spectroscopy for the determination of co-ordination number; at constant co-ordination number orbital energies are also affected by the nature of the ligands.

Day[1] has shown that the Kα emission energy from a series of aluminium compounds can be correlated to co-ordination number. The changes are slight and are just at the limit of experimental detection. Kα, from aluminium metal is at 1486·6 eV, when surrounded by four oxygen ligands, it is at about 1486·8 eV, and if there are six oxygen ligands Kα is at about 1487·0 eV. A series of magnesium compounds was investigated to see if comparable results could be obtained for this element. A Philips PW 1410 X-ray fluorescence spectrometer with a 2·7 kW chromium X-ray tube and an ammonium dihydrogen phosphate (ADP, $2d$ = 1·065 nm) diffracting crystal was used. The magnesium Kα emission was found at the following energies (in eV): metal, 1253·6; spinel, 1253·65 (IV); magnesium oxide, 1253·80 (VI); $Mg(H_2O)_6^{2+}$ in hydrated magnesium sulphate, 1253·95 (VI); magnesium fluoride, 1254·00 (VI); the co-ordination number has been indicated by IV or VI. As in the case of aluminium these small shifts are very much less than the Kα peak width at half-height. Their accurate position was only determined with some difficulty. A step-scanning technique was employed, counting for 100 s at fixed spectrometer positions to cover the region of the peak.

It was felt that the very slight changes in Kα emission energies were associated with much larger but almost identical changes in the ionisation energies of the $2p$ and $1s$ orbitals. Such ionisation energies should therefore provide a more reliable, and easily experimentally determinable parameter for correlation with co-ordination number.

To test this idea the $2p$ (and also $2s$) ionisation energies of a representative group of aluminium and magnesium compounds were determined and the results are summarised in the Table.

Table. *Orbital ionisation energies*

Co-ordination number	IV	VI	VI
ligand	oxygen	oxygen	fluorine
Sample	Spinel	MgO	MgF_2
Mg 2p	49·8	52·2	55·1
Mg 2s	89·8	91·0	93·7
Sample	Microcline	Al_2O_3	Na_3AlF_6
Al 2p	75·0	76·4	78·8
Al 2s	119·9	121·0	124·6

The instrument used was a Vacuum Generators ESCA Mk. III with an Al Kα source. All the samples were mounted on gold plated mesh and the spectra were calibrated by reference to the gold $4f$ ionisation energies (NVI 86·4 eV; NVII 82·8 eV). Peak shifts of about 1·5—2·5 eV are associated with the change from fourfold to sixfold co-ordination (see Table); as would be expected, the bond in the latter case is more ionic. Further increases in ionisation energy are also found, retaining sixfold co-ordination, in going from oxygen to fluorine ligands. Whilst this might also be expected it is interesting to note that the Kα emission energy would seem to be dependent only on co-ordination number and to be indifferent to the nature of the ligand.

From these preliminary results it seems reasonable to suggest that more detailed investigations may succeed in establishing a correlation between orbital ionisation energies and bond lengths. Also this technique should be applicable to all elements in the periodic table enabling elements not only to be detected but also the nature and number of surrounding elements to be determined. This should be of particular value in investigations of glasses, ceramics and other non-crystalline materials.

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[1] D. E. Day, *Nature*, 1963, **200**, 649.