Electronic Structures of Solids by Electron-energy-loss Spectroscopy carried out using and Electron Microscope: Oxygen-*K* and Metal-*L* Edges of Transition Metal Oxides

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Electron-energy-loss spectra, recorded from ultramicro quantities ($<10^{-12}$ g), reveal $L_{2,3}$ edges the energy and intensity of which vary systematically with oxidation state in a series of transition metal oxides; the first ever evidence for structure-sensitive features in oxygen *K*-edges is reported.

Not withstanding the pioneer work of Ruthemann[1] in the 1940s, it is only in the last few years that electron-energy-loss spectroscopy (EELS), carried out in an electron microscope, has been recognized as a potentially powerful analytical tool for the characterization of solids. The identification (by core-edge features[2] and plasmon-loss peaks[3]) of the elements present in ultramicro quantities is itself of considerable value. However, EELS becomes much more chemically useful if, in addition, it can be used to reveal information about bonding (*e.g.* from electron Compton scattering[4]), about oxidation states, and about other features of structural interest. In order to explore the potential of this technique for the elucidation of the structure of solids we have investigated the EELS spectra of a few series of transition metal oxides, using an electron microscope fitted with an electron spectrometer. In this communication we show how the metal and oxygen absorption edges in EELS of transition metal oxides provide a wealth of information of considerable chemical significance.

The experiments were carried out using a modified AEI EM6G electron microscope with a vacuum of 5×10^{-8} Torr in the specimen chamber and fitted with a Gatan model 607 magnetic prism spectrometer.

Oxides of the first-row transition metals show the characteristic L_3 and L_2 absorption edges of the metals and the *K* absorption edge of oxygen in EELS. The L_3 and L_2 edges

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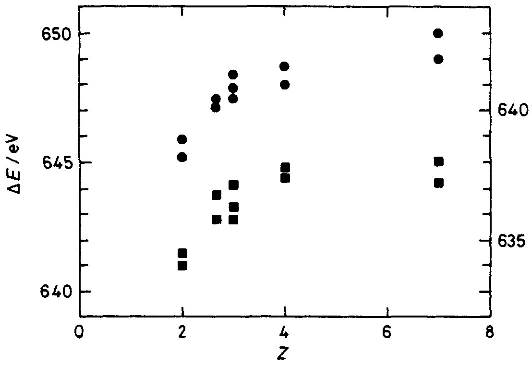

Figure 1. Variation of the L_2 and L_3 edge energies of manganese oxides with the oxidation number of manganese, *Z*. Circles and left hand energy scale are for L_2, squares and right hand energy scale are for L_3.

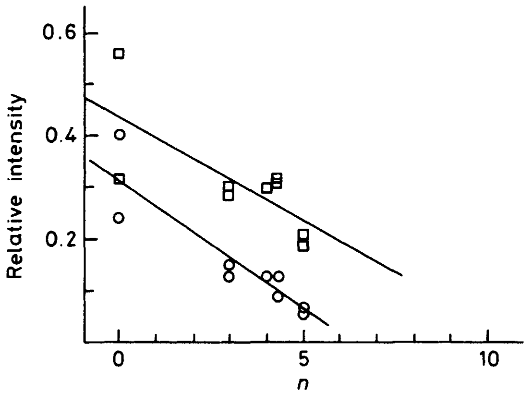

Figure 2. Variation of the L_2 (○) and L_3 (□) white-line intensities of manganese oxides with the number of d-electrons, *n*.

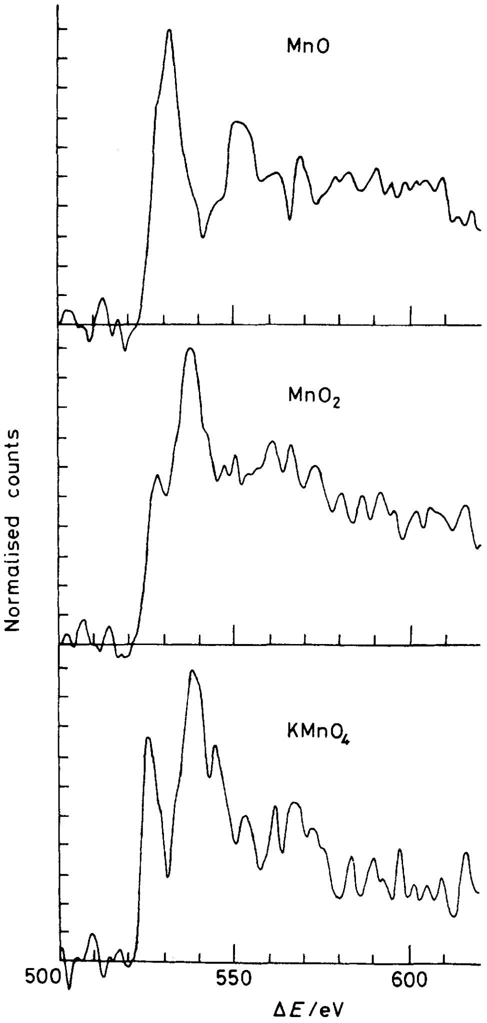

Figure 3. Oxygen *K*-edges of manganese oxides.

exhibit prominent peaks (so-called white lines) due to transitions from $2p_{3/2}$ and $2p_{1/2}$ levels respectively to the unoccupied 3d level. There are three noteworthy features in the $L_{2,3}$ edge which directly throw light on the electronic structure of the transition metal. (i) The L_3 and L_2 edge energies of the metal increase as the oxidation state of the metal increases as illustrated in the case of manganese oxides (Figure 1). This trend parallels the variation of the L_3 and L_2 binding energies from *X*-ray photoelectron spectra.[5] (ii) Since the $L_{2,3}$ transition probabilities are directly related to the occupation of the 3d level[6] the intensities of the white lines, as well as their widths, in a series of oxides of a transition metal should increase with the increase in the oxidation state of the metal, as seen in Figure 2 where the Mn shows the highest L_3 intensity in $KMnO_4$ (d^0) and the lowest in MnO (d^5). Extrapolating the best fit line through the experimental points (Figure 2) we see that the L_3 intensity goes to zero at the d^{10} configuration as in the case of Cu and Cu_2O. The L_2 intensity also decreases with increase in the oxidation state, but approaches zero at the d^5 configuration since the L_2–3d transition becomes increasingly forbidden in going from d^0 to d^5. (iii) The L_3/L_2 intensity ratio also reflects the electron state of the transition metal ion, becoming maximal at the d^5 configuration.[7]

The oxygen *K*-edges in a related series of transition metal oxides show some new, remarkable features not, to our knowledge, noticed hitherto. The transition responsible for the oxygen *K*-edge is from the 1s level to a molecular orbital involving oxygen 2p and metal 3d orbitals.[8] In the series of manganese oxides studied here, there is a feature similar to the pre-edge (1s–3d transition) peak in the *K*-edge of transition metals.[9—11] The intensity of the feature increases as the d-orbital is depleted, or the oxidation state of the Mn increases (Figure 3). The feature, present only as a shoulder in MnO, emerges as a well defined peak in $KMnO_4$. It is likely that its intensity is related to the formal valence, ionicity, and the co-ordination number, the last changing from 6 to 4 in going from MnO to $KMnO_4$: the covalency increases in the same direction. Accordingly, we see that the energy of the main feature in the *K*-edge increases while the energy of the pre-edge feature decreases in the order MnO, Mn_3O_4, Mn_2O_3, MnO_2, and $KMnO_4$. This suggests a shifting of two related molecular energy levels (possibly t_{2g} and e_g) in the opposite directions. We have noticed similar changes in the oxygen *K*-edge of the iron-oxides FeO, Fe_3O_4, and Fe_2O_3. Oxygen *K*-edges in a series of oxides of different transition metals (*e.g.* monoxides) possessing the same co-ordination show only small differences. We have also observed peaks around 550 eV attributable to a transition from 1s to a higher molecular orbital (possibly M4p–O2p).

It is clear that EELS, in view of the relative ease with which it may be carried out using a modified electron microscope, constitutes an important new technique for the characterization of solids, especially micro- or poorly-crystalline ones. While the chemical shifts of X-ray absorption edges can be employed to determine the oxidation states and effective charges of transition metals in oxides and other systems,[11,12] including catalysts,[13] EELS enables a more complete characterization of the electronic structure in addition to determining the composition.

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