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LETTER TO THE EDITOR

High-resolution electron energy loss studies of some transition metal oxides

J P Kemp, S T P Davies and P A Cox

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

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Abstract. High resolution electron energy loss spectra have been measured for a variety of first-row transition metal oxides for loss energies of up to 5 eV. The features observed are qualitatively consistent with the electronic properties of these materials (i.e., a highly damped plasmon for metals, and local d–d excitations for insulators), with the notable exception of CuO. Quantitatively, however, the intensities of the d–d transitions are an order of magnitude greater than expected from optical dipole strengths, and we evaluate possible explanations for this.

Electron energy loss spectroscopy (EELS) is by now a well-established tool for studying vibrations at surfaces, both of adsorbates and substrates (see e.g. [1]). It has been used rather less [2–4], however, for examining electronic losses at surfaces, and thus for obtaining information about the surface electronic structure of materials. Such data is interesting from a theoretical viewpoint, and is important in determining the nature of adsorbate–substrate bonding.

As well as being far more surface-sensitive, EELS is potentially a more flexible form of electronic spectroscopy than optical absorption/reflectance, allowing the study of transitions from the infrared to the soft x-ray region, and also the observation of excitations (such as plasmons) that cannot normally be directly seen in optical spectra. The existence of several scattering mechanisms also means that selection rules in EELS may differ somewhat from optical ones. The principle drawbacks of EELS are the necessity for a UHV environment and lower resolution than conventional IR/visible/UV spectroscopy.

In this work, the EEL spectra of several first row transition metal oxides were measured, with energy losses up to 5 eV. With the exception of NiO [5], these compounds have only previously been studied using high-energy unmonochromated beams and single crystal substrates [6], and low-energy losses were consequently not resolved. The aims of our work were to investigate whether reasonable quality spectra could be recorded from polycrystalline samples, for which optical data is generally poor, to extend the work done on NiO to other oxides and thus examine more generally any differences between bulk and surface electronic structure, and finally to assess the importance of other scattering mechanisms (e.g., impact, or negative ion resonance) in the excitation of transitions which are formally dipole forbidden.

All spectra were recorded using a VG ESCALAB 5 spectrometer. This instrument is equipped with a twin-anode x-ray source (Mg K α and Al K α) for XPS, a noble gas

discharge ultra-violet lamp for UPS, and an electron monochromator unit for HREELS, with beam energy variable up to 120 eV. There is also a sample preparation chamber where samples may be heated via RF induction *in vacuo*, or in up to 1000 mbar of gases such as oxygen.

The oxides used in these studies were all in the form of high-purity (>99%) powders of commercial origin, with the exceptions of V_2O_3 and Mn_2O_3 . V_2O_3 was synthesised by reduction of V_2O_5 in hydrogen at 1100 K for 24 h [7] and Mn_2O_3 by oxidation of Mn_3O_4 in oxygen at 1100 K for 48 h [8]. In both cases, the product composition was checked by monitoring change in mass, which was within 1% of its theoretical value, and by x-ray powder diffraction, which gave patterns in good agreement with the literature. The powders were compacted at 10 tonnes force between optically flat dies, and the resultant discs were secured to platinum mounts using Pt clips and introduced into the spectrometer preparation chamber.

Prior to measurement of spectra all the samples were heat-treated for periods of up to 15 h to remove contaminants and restore correct surface stoichiometry. Temperatures quoted are all approximate since we have no way of attaching a thermocouple directly to the sample in our equipment. Conditions used were as follows. V_2O_3 was heated in 5 mbar of H_2 at 1100 K and then *in vacuo* at 1100 K; Cr_2O_3 was heated at 1000 K in 1 mbar O_2 ; Mn_2O_3 was heated at 1000 K in 50 mbar O_2 ; Fe_2O_3 was heated at 1100 K in 100 mbar O_2 ; MnO and CoO were heated to 1000 K *in vacuo*; NiO was heated to 1000 K in 100 mbar O_2 and CuO to 1000 K in 300 mbar O_2 . Surface cleanliness and composition was assessed using XPS. The above procedures yielded in all cases surfaces free from carbon and other contaminants. Calculations of surface stoichiometries using standard tables of ionisation cross sections [9] showed agreement with bulk compositions, within the accuracy of the measurements.

EEL spectra were measured in the specular mode, at 298 K, with an incidence angle of 45° . The analyser accepts all electrons scattered through a semi-vertical angle of 6° . Owing to the polycrystalline nature of the samples, the specularly reflected beam has a considerable angular spread, reducing scattered intensity by at least an order of magnitude compared with single crystal samples. The losses studied are also rather weak. To compensate for this, the resolution of our instrument was deliberately degraded to around 75 meV to allow more rapid accumulation of data. Since the observed electronic losses tend to be rather broad (up to 500 meV), this does not significantly affect the quality of the spectra obtained.

Most of the samples were sufficiently conducting to allow spectra to be recorded at incident beam energies of 25 eV without charging problems. In some of the samples, however, it proved necessary to employ beam energies up to 50 eV to prevent these from occurring.

Figures 1 and 2 show the observed EEL spectra from the sesquioxides and the monoxides, respectively, along with spectra calculated on the basis of optical data. With the exception of V_2O_3 , all the oxides are insulators or semi-conductors. Though the exact nature of the band gap has been a matter of some dispute [10, 11], it is generally believed that strong correlations between the d electrons cause them to be localised [12]. V_2O_3 , on the other hand, shows a metal-insulator transition at 150 K, and at room temperature possesses a Fermi edge in its UVPE spectrum [13], characteristic of itinerant electrons. The EEL spectrum of V_2O_3 in figure 1 shows a broad feature at around 0.8 eV which merges with the elastic peak. Similar features have been observed in the EELS of Sr-doped $LaVO_3$ [14] and may be tentatively assigned to a conduction band plasmon.

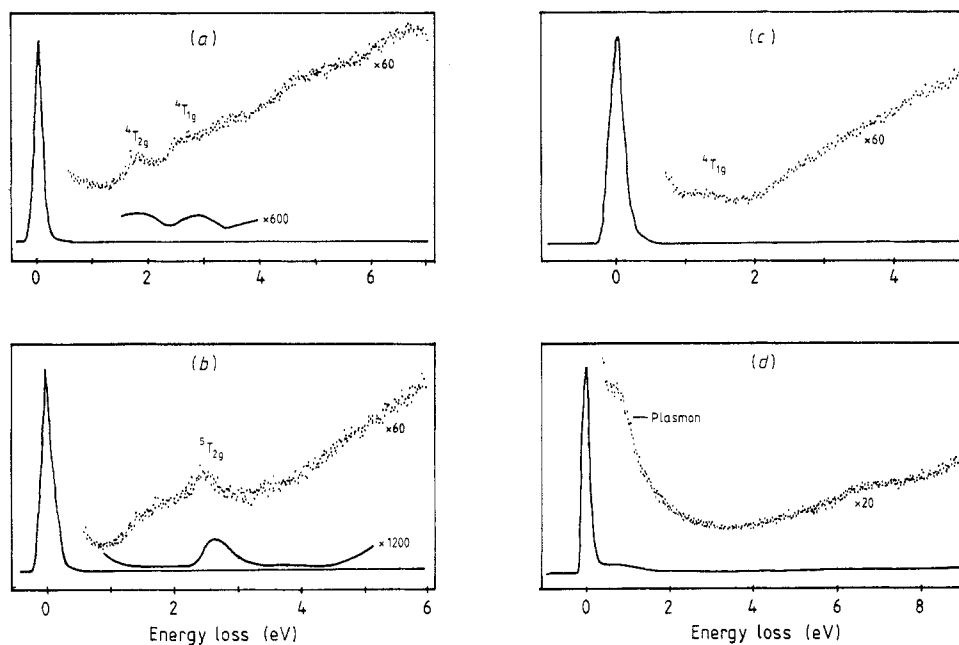


Figure 1. EEL spectra of transition-metal sesquioxides: (a) Cr_2O_3 ; (b) Mn_2O_3 ; (c) Fe_2O_3 ; (d) V_2O_3 . Expanded-scale spectra refer to measured (points) and calculated (full curves; see text) spectra. Possible assignments for d-d transitions are indicated.

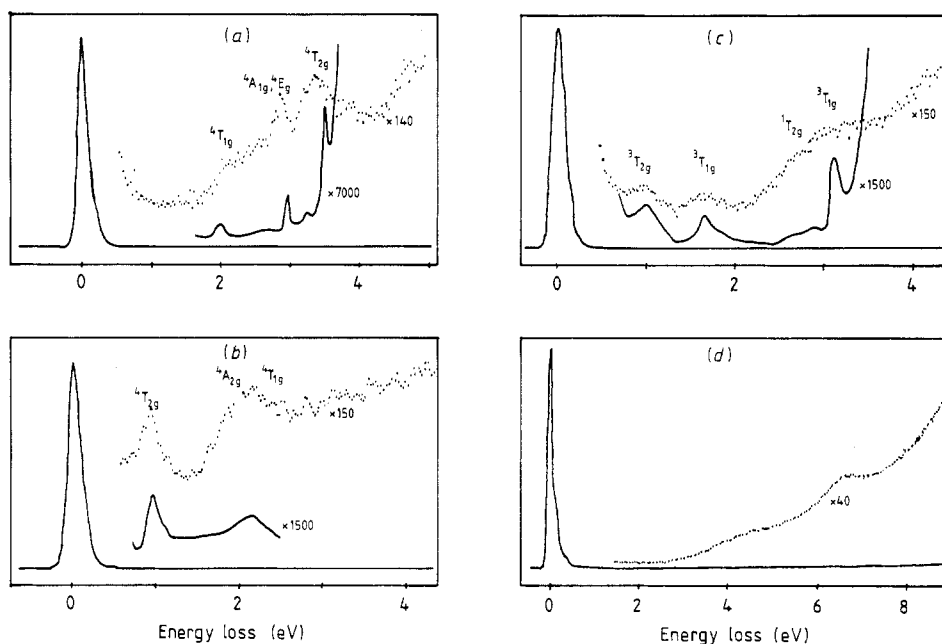


Figure 2. EEL spectra of transition-metal monoxides: (a) MnO ; (b) CoO ; (c) NiO ; (d) CuO . Expanded-scale spectra refer to measured (points) and calculated (full curves; see text) spectra. Possible assignments for d-d transitions are indicated.

If the dielectric function for the conduction electrons is represented by a Drude-type formula

$$\epsilon_{cl} = -\epsilon_{\infty}\Omega_p^2/(\omega^2 + i\omega/\tau) \quad (1)$$

then the lineshape suggests a regime where $\tau\Omega_p < 1$. The magnetic properties of this material are indicative of considerable correlation, which may provide an additional means whereby plasmons can decay into electron-hole pairs [15], so reducing the lifetime.

A localised d-electron configuration would be expected to give rise to ligand field type excitations below the charge transfer threshold. This expectation is borne out by optical spectra [16] and also by many of the EEL spectra in figures 1 and 2. Where possible, states have been assigned, based on assignments of the optical spectra of the oxides or of the hexaquo-ions. CuO does not, however, fit this pattern: a localised d^9 configuration should give rise to a single ligand field band, corresponding to the transition ${}^2E_g \rightarrow {}^2T_{2g}$. No features are observed below what is presumably the charge transfer threshold at 3–4 eV. This is supported by some reflectance studies [17]. Others, however, have observed a band at around 2 eV, which they assigned to this transition [18]. In a future publication, it will be demonstrated how the lack of ligand-field-type excitations in CuO arises naturally from the application of recent theories (the impurity model [19, 20, 21]) of electronic structure of transition metal compounds to EELS and optical spectroscopies.

In order to study the ligand field losses in more detail, calculations were carried out based on optical spectra. For CoO [16], NiO [22], MnO [23, 24] and Cr_2O_3 [25] absorption data for the thin-film oxides was used. For Mn_2O_3 this data was not available, so that for $CsMn(SO_4)_2 \cdot 12H_2O$ [26] was used. It must be noted here that water is a stronger field ligand than oxide, and thus the transitions occur at slightly higher energies.

The optical spectra were digitised, and treated as follows. The absorption coefficient κ is related to the extinction coefficient χ via

$$\chi(\omega) = \kappa(\omega)\lambda_m/4\pi. \quad (2)$$

This is related to the imaginary part of the refractive index N

$$N(\omega) = n(\omega)(1 - i\chi(\omega)) \quad (3)$$

which is simply the square root of the dielectric function. Over the region of interest the real part of the refractive index, $n(\omega)$, is virtually constant [27], and may thus be estimated from the high-frequency dielectric constant for the material concerned. The probability density for scattering in EELS (assuming integration over all scattered wavevectors) is

$$P(\omega) = (e^2/4\pi\epsilon_0 h v) \text{Im}[(\epsilon(\omega) - 1)/(\epsilon(\omega) + 1)] \quad (4)$$

where v is the velocity of the incident electron, and ϵ the dielectric function from (3).

As can be seen from figures 1 and 2, agreement between the calculated and observed spectra is very good in qualitative terms, but the calculated intensities are generally an order of magnitude too small, with the exception of MnO, where the discrepancy is rather greater. However, if the calculation is performed for the charge-transfer threshold (e.g. for NiO [28]), then there is no such discrepancy in the region. This implies that whereas the dipole scattering theory detailed above is adequate for dipole-allowed transitions such as charge transfer, it is inadequate for the d–d transitions, which are dipole forbidden, but appear to be relatively more allowed in EELS than in optical spectra.

There are several possible explanations for this. (i) EELS is a surface-sensitive technique, and the additional intensity could arise from the reduced symmetry at the surface

making the transitions more allowed by relaxing the $g \leftrightarrow u$ selection rule. (ii) The transitions could be quadrupolar or higher multipolar in nature. (iii) A short-range scattering mechanism such as impact scattering, or via a negative-ion resonance could be occurring.

Explanation (i) seems unlikely, on the basis of the qualitative similarity between the optical and EELS data. For the transitions of the surface ions to have the necessary dipole strengths to account for the extra intensity, a symmetry radically different from the bulk (octahedral) would be required. This would be expected to give rise to qualitative differences between the optical spectra (which reflect bulk properties) and the EELS. Furthermore, reduction of symmetry at the surface will not alter the spin-selection rule and so cannot account for the greater enhancement of intensity, relative to the optical data, in the spectrum of MnO.

Explanation (ii) could arise due to the short wavelength of the perturbation in EELS compared with an optical experiment. For visible light, the perturbing potential is of the form $\exp(ik \cdot r)$, and since the wavelength is of the order of 500 nm, the ratio of linear (dipolar) to quadratic (quadrupolar) terms in the potential over an atomic diameter is of the order of 10^{-4} . In practice, however, the d-d transitions are typically a factor of only 10^3 lower in intensity than the dipole-allowed, charge-transfer transitions due to vibronic coupling. In EELS, at 25 eV incident energy and for losses of 2 eV, the range of the potential is around 2–3 nm, giving the same ratio in the range 10^{-1} – 10^{-2} . Since some d-d transitions are quadrupole allowed, this is expected to be the order of magnitude of the intensity difference between the d-d and charge transfer transition, i.e. an approximately tenfold enhancement in intensity when compared with optical spectra. If this is the dominant mechanism, however, there are selection rules which would forbid the appearance of certain lines. For example, ${}^3A_{2g} \rightarrow {}^3T_{2g}$, which is observed in the spectrum of NiO, is not allowed as a quadrupole transition.

Explanation (iii) is quite possible given the low absolute count rates for these samples. A spectrum arising from this mechanism is difficult to predict without extensive calculation (see, e.g., [29]), but would be expected to give rise to significant scattered intensity away from the specular direction. This was impossible to test with polycrystalline samples as the specular direction is poorly defined. Attempts to study the angular variation of intensity using an NiO(100) single crystal were carried out, but the specular direction on this substrate was little sharper, possibly due to inhomogeneous charging across the surface. We hope in future to perform these experiments on substrates with a well-defined specular angle. Additionally, impact and resonance scattering should be distinguishable as the latter should show a strong dependence on incident-beam energy. Some evidence for this mechanism is afforded by the spectra of MnO. A d^5 high-spin ion such as Mn^{2+} has only spin-forbidden transitions available. These are not as weak in the oxide as they are in solution, since the antiferromagnetic coupling introduces the possibility of allowed coupled exciton-magnon transitions [30]. However, these are still weaker than the d-d transitions in the optical spectra of the other oxides. This intensity difference is not seen in the EEL spectra. Impact or resonance scattering can excite transitions with $\Delta S = 1$ while still conserving total spin for the electron-ion system, and therefore such transitions are expected to show the greatest enhancement of intensity between the EEL and optical data. To provide more concrete evidence for this conclusion, it will be necessary to do further EELS studies on manganese compounds, especially on ones that are magnetically dilute, or that possess a substantially lower Néel temperature than the oxide. In these cases, the enhancement in intensity should be even greater.

In conclusion, we have shown that EELS is capable of yielding electronic spectra of quality comparable with those from optical experiments, off polycrystalline substrates, but with the advantage of covering a much wider spectral range. Such spectra provide useful information on the electronic structure of solids, though obviously care is needed in making deductions concerning bulk electronic structure from a spectroscopy which is highly surface sensitive.

It is clear, however, that the selection rules in EELS may be rather different from those in optical spectra, especially where dipole forbidden transitions are concerned. In particular, the ability to excite spectra via impact and resonance mechanisms may play an important role in the above, and since observations of these processes are still somewhat rare, and understanding of them similarly limited, we believe that further study of EEL spectra of these compounds, employing better quality substrates, is called for.

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