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The localization of unoccupied 3d states in oxidized Sc

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Abstract. Inverse photoemission and 3p–3d giant resonance excitation in electron energy loss spectroscopy in oxidized Sc are related to 2p → 3d x-ray absorption in Sc₂O₃. The observations are shown to be consistent with 3d states being localized in both the presence and the absence of a core hole. Inverse photoemission reveals 3d crystal field splitting comparable to that found in 2p → 3d excitations, while 3p–3d excitations show in addition strong hole–electron exchange coupling.

1. Introduction

The oxides of Sc, Y and La and many of the remaining rare earths are characterized by the absence of filled d states and the availability of empty d states close to the Fermi level. It is of interest to probe whether such states are best described by a band picture or as localized quasi-atomic states modified by a crystal or ligand field. Sc, at the beginning of the first transition series, is perhaps the simplest of such systems, but the oxidation of Sc and the stoichiometric oxide Sc₂O₃ [1] have received much more limited attention than the neighbouring oxide TiO₂ [2]. In this paper we compare the results of inverse photoemission and electron energy loss spectroscopy for clean Sc and oxidized Sc, showing how they emphasize in different ways the properties of 3d levels unfilled in the ground state.

2. Experimental details

The experiments were performed in an ultra-high-vacuum system equipped with a concentric hemispherical electron energy analyser (Leybold EA10) for electron energy loss spectroscopy (EELS), an inverse photoemission spectrometer that allows spectra to be recorded in isochromat mode with $h\nu = 9.5$ eV ($\Delta E = 0.35$ eV) and that has the usual facilities for sample preparation and surface characterization [3]. EELS spectra were recorded in approximately specular reflection geometry with an overall resolution of $\Delta E \simeq 0.5$ eV [4]. Clean polycrystalline Sc surfaces have been prepared by evaporating Sc from an evaporator with a W coil surrounded by a liquid N₂ cooled CU shroud onto clean Si substrate surfaces at an ambient pressure of $< 5 \times 10^{-10}$ mbar. O₂ was introduced into the system via a leak valve and dosed from the background atmosphere.

3. Results and discussion

Figure 1 shows the inverse photoemission spectra of a thick clean Sc metal film and Sc exposed to different doses of O_2 . The metal is characterized by a sharp peak just above the Fermi edge and a broader feature at 3 eV, which is seen also prominently in the work of Hu *et al* [5]: this is in general accord with the predictions of band theory [6] and consistent with the empty d band dominating the spectrum [7]. As oxidation proceeds the d peak near E_F is suppressed and two new features evolve, a large peak at 4 eV and a smaller feature around 6 eV.

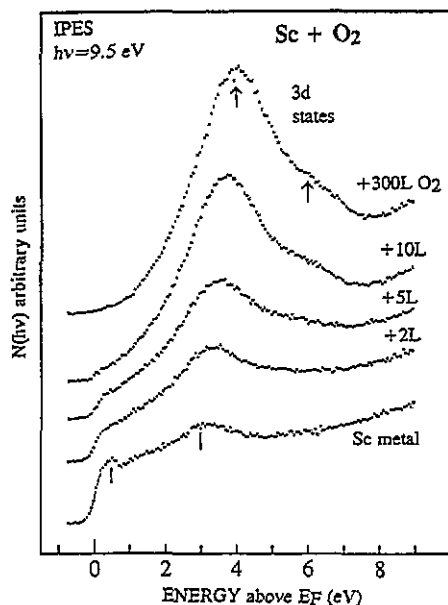


Figure 1. The inverse photoemission spectra of clean Sc and Sc exposed to various O_2 doses: a graph of photon yield versus energy of the final state electron above the Fermi level. In the oxidized sample the t_{2g} (lower) and e_g levels are marked with arrows.

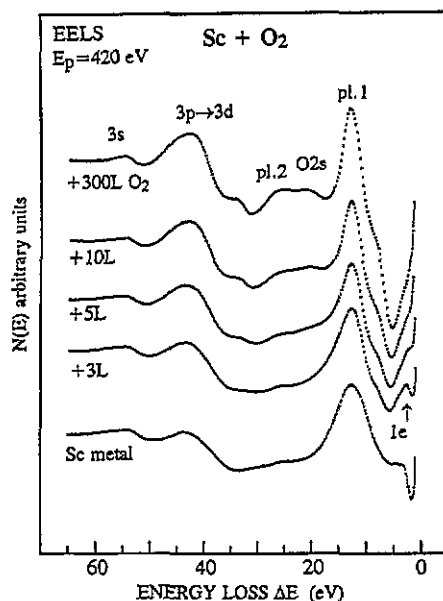


Figure 2. The electron energy loss spectra of clean Sc metal subject to varying O_2 exposure for a primary energy $E_p = 420$ eV. The spectra are presented in $N(E)$ mode.

It is known from previous studies [1] that oxidation is not quite complete at such O_2 exposures: comparison of the Sc Auger spectrum obtained under these conditions with spectra obtained when Sc is deposited in an atmosphere of 10^{-6} mbar O_2 and with spectra of Sc_2O_3 [8] reveals some differences in the intensities of $L_{23}M_{23}V$ features, but there is complete correspondence in the peak structure. We therefore believe that the two peaks in inverse photoemission in figure 1 do indicate correctly the positions of empty d states in the oxide.

Adopting a naive atom in a crystal field model the peaks are interpreted, in order of energy, as the t_{2g} and e_g 3d states split by an approximately octahedral field: this splitting implies a crystal field parameter $10 Dq$ of around 2 eV, in good agreement with the value of 1.8 eV required to fit the $2p^6 \rightarrow 2p^5 3d$ x-ray absorption spectrum of Sc_2O_3 [9]. It should be noted that the behaviour of the empty 3d states of oxidized Sc differs from that of the analogous TiO_2 [10, 11], where the lowest unfilled level remains closer to the Fermi level.

The evolution of the electron energy loss curves of Sc in $N(E)$ form as a function of O_2 exposure is shown in figure 2 for a primary energy of 420 eV. For loss energies below 20 eV plasmon excitation (pl.1) at $\hbar\omega_p \simeq 12$ –13 eV dominates, with a modest shift to higher energy on oxidation, consistent with the behaviour of many rare earths [12]. At lower loss energy a sharper one-electron-loss feature declines in intensity as the oxide band gap emerges. This is in agreement with previous loss studies by Onsgaard *et al* [13]. Below the Sc 3p ionization threshold double plasmon loss (pl.2) is accompanied by some O 2s ionization contribution as oxidation proceeds.

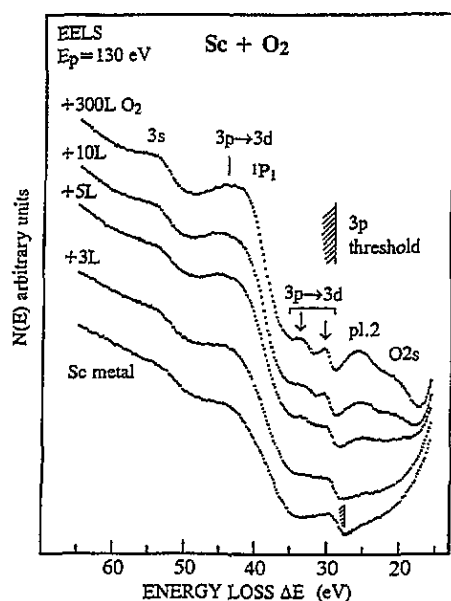


Figure 3. The 3p \rightarrow 3d excitation region of the electron energy loss spectrum in $N(E)$ form of clean Sc metal exposed to varying O_2 doses at primary energy $E_p = 130$ eV.

Of particular interest in this study is the giant dipole resonance excitation lying between the 3p threshold and the 3s ionization energy at around 55 eV, shown in greater detail in figure 3 for a primary energy of 130 eV. Note how on oxidation the main loss at $\Delta E = 43$ eV becomes more prominent while new spectral structure emerges just above the threshold. This enhancement has also been noted in Fe, Co and Ni [14] and is similar to the behaviour of oxidized Yb [15]. These intense losses arise from quasi-atomic $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ excitations, which have very large cross sections due to the localization of the 3d electrons in the presence of the core hole [16–18]. For Sc metal $n \simeq 1$ and the resulting $3p^5 3d^2$ multiplet structure is quite complex, although it is well known that optical oscillator strength is concentrated in the highest-energy multiplet well above the threshold. In stoichiometric Sc_2O_3 $n = 0$ and in L - S coupling the ionic final states are 3P , 3D and 3F . The main resonance is associated with 1P_1 , the only allowed dipole transition from 1S_0 initial state ($\Delta L = 1$, $\Delta S = 0$), while 3D_1 and 3P_1 also carry some oscillator strength through spin-orbit interaction ($\Delta J = +1$). Relativistic Hartree-Fock calculations [19] of $3p^6 \rightarrow 3p^5 3d$ transition energies are given in table 1. 1P_1 is driven to high energy by the strong exchange interaction and that transition lies well apart from the rest. Experience [20] suggests that the multiplet range may be compressed relative to single configurational predictions due to the configurational interaction, and this is in accord with the observed features in the oxide spectrum for $E_p = 130$ eV at 31, 34 and 44 eV.

Table 1. $3p^6 \rightarrow 3p^5 3d$ excitation energies from the 1S_0 ground state of Sc^{3+} calculated in the relativistic Hartree–Fock approximation.

Energy (eV)	Final state
29.2	3P_0
29.3	3P_1
29.5	3P_2
30.7	3F_4
30.8	3F_3
31.0	3F_2
33.2	$0.9^3D_3 + 0.4^1F_3$
33.2	$0.6^3D_2 + 0.8^1D_2$
33.4	3D_1
33.4	$0.8^3D_2 + 0.6^1D_2$
33.6	$0.4^3D_3 + 0.9^1F_3$
45.5	1P_1

These ionic states will be modified by the crystal field, which will both shift and split the levels and admix $J = 1$ character into other states, giving them dipole oscillator strength as in the $2p \rightarrow 3d$ x-ray absorption of Sc_2O_3 [9]. In addition at the primary energy used here non-dipole transitions will be important as in the rare earths [21, 22] and transition metals [23]. The 1P_1 feature can be unambiguously associated with the main broad loss. The additional features at 31 and 34 eV are more difficult to identify with certainty, due to the mix of crystal field and exchange effects. The 3P_1 transition tends to be weak in photon absorption [9]: the fact that the 31 eV loses intensity as the primary energy is increased suggests that it is mainly associated with non-dipole transitions to the high-multiplicity manifold of 3F states.

In contrast the 34 eV loss remains prominent not only at $E_p = 420$ eV but also in high-energy transmission electron energy loss experiments [24, 25] and must have a high dipolar component. This is consistent with a significant contribution from the crystal field modified 3D_1 final state. It should also be noted that on oxidation there is an intensification of $3p^5 3d \rightarrow 3p^6 V^{-1} + e$ autoionization emission at around 37 eV [26] where V^{-1} implies emission from the valence band (not shown). It would appear that the repulsive cage of negative O ions around Sc^{3+} leads to greater 3d localization, and filling of the core hole by the excited electron.

Combining the core binding energy shift in the oxide with the inverse photoemission results the energy differences between the t_{2g} and e_g empty 3d states and the 3p level are of order 35 and 37 eV, respectively. This may be compared with the main excitation energies of 31, 34 and 43 eV in the losses of the oxidized sample. The first two imply a positive effective hole–electron Coulomb interaction (U_{3p3d}), but the 1P state clearly has negative U_{3p3d} due to the large exchange interaction. This phenomenon is consistent with exchange control effects in other branches of electron spectroscopy of early transition metals [27].

The results presented here may be related to a similar electron energy loss/inverse photoemission study of oxides of Na and K by Bertel *et al* [28]. The superoxides NaO_2 and KO_2 also showed evidence of localized 3d excitonic states with electron–hole correlation; however, although K has atomic number only two less than Sc, the d electrons do not undergo the same degree of collapse, so that the Coulomb/exchange interaction is much smaller, while the crystal field effects are comparable to the case of oxidized Sc.

The $2p \rightarrow 3d$ x-ray absorption [9], the $3p \rightarrow 3d$ EELS and inverse photoemission of oxides of Sc all exhibit 3d localization, but the different spectroscopies show different interaction hierarchies in their spectral structure. In inverse photoemission the 3d electrons

sample a mainly spherical potential accompanied by a cubic crystal field component, which splits the levels by ~ 2 eV (figure 1): coupling to the environment broadens the quasi-atomic levels. In $3p \rightarrow 3d$ excitation the strong exchange interaction (~ 13 eV spectral range) dominates over crystal field effects, with spin-orbit interaction a small perturbation (see table 1). In $2p \rightarrow 3d$ excitation the $2p_{1/2}-2p_{3/2}$ spin-orbit splitting is the largest spectral interaction, but the crystal field and the Coulomb/exchange interaction combine to elaborate the basic spin-orbit doublet structure. Crystal fields are sometimes thought of as 'dustbins', which try to parametrize simply many complex environmental interactions including covalency effects. In this context it is heartening that x-ray absorption and inverse photoemission require comparable crystal field parameters, although, of course, they should not be identical because of the possibility of enhanced 3d localization in the presence of the 2p core hole.

4. Summary

Localization of 3d states unfilled in the ground state of oxidized Sc have been investigated by inverse photoemission and $3p \rightarrow 3d$ electron energy loss spectroscopy. To first order it is reasonable to describe the 3d electron in a quasi-atomic environment modified by a crystal field, a picture consistent with that derived from higher-energy spectroscopies such as $2p \rightarrow 3d$ x-ray absorption.

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