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Formation of $d$-holes in the initial stages of the oxidation of Ag(001)

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Abstract. – We demonstrate that double ionisation of the Ag atoms, leading to the formation of $d$-holes, takes place in the initial oxidation stage of Ag(001). The complex formed by the Ag$^{2+}$ ion, two oxygen adatoms and one oxygen atom in the octahedral interstitial gives rise to a dipole active electron energy loss at 130 meV. Signature of the electronic origin of this loss is the inverse isotope shift and the peculiar temperature dependence of the energy loss, which can be reproduced by a theoretical model.

A striking feature of metal oxide chemistry is the unusual electronic and chemical behavior of Cu(I) and Ag(I), which is relevant for the detailed understanding of high-$T_c$ superconductivity and of the catalytic properties. The observation in many compounds of close-packed configurations with short metal-metal distances has been explained [1, 2], by invoking the participation in bonding of electronic orbitals of higher principal quantum number $(s$ or $p$ type) accompanied by the creation of $d$-orbital holes. Direct observation of such features was reported recently for Cu oxides [3], but to our best knowledge failed so far for Ag oxides [4]. Such $d$-holes could play an active role in the catalytic processes involving Ag surfaces and possibly explain the relevance of subsurface oxygen for the partial oxidation reaction of ethylene for which Ag powders show a unique selectivity [5]. Here we will show for the first time that $d$-holes form on Ag(001) during the initial stages of surface oxidation. The mode at 131 meV $(1050 \text{cm}^{-1})$, observed by high-resolution electron energy loss spectroscopy (HREELS) [6] after dissociative oxygen adsorption and generically assigned to subsurface oxygen, is due to a localised $d$-$d$ transition within a complex formed by the Ag$^{2+}$ ion, by one subsurface oxygen atom in the octahedral interstitial site and by two neighbouring oxygen adatoms.

The experimental apparatus [7] as well as the surface preparation recipe [6] were described elsewhere. As in our previous experiments, O$_2$ was dosed at a crystal temperature $T = 100 \text{K}$ with a seeded supersonic molecular beam (3% O$_2$ in He, translational energy 800 meV) in order to have a high sticking coefficient (0.6 for molecular oxygen) and thus minimising
surface contamination. The base pressure in the ultra high vacuum chamber was in the upper $10^{-11}$ mbar range. The HREEL spectra were recorded with a HREEL-spectrometer of own construction tuned to an energy resolution of about 6 meV.

In fig. 1 we show the result of an adsorption experiment at a crystal temperature of 100 K, followed by annealing at 236 K and cooling back to 100 K, performed, respectively, with $^{16}$O$_2$ and with the heavy isotope $^{18}$O$_2$. Two dipolar active losses are present: at 34 meV and 131 meV for the light isotope, and at 33 meV and 134 meV for the heavy isotope. The low-energy loss is due to the oxygen-surface stretch [8], while the high-energy loss was generically assigned to the presence of oxygen atoms in subsurface sites [6]. As discussed in ref. [6], the frequency corresponding to 131 meV is too high for an oxygen-surface vibration. Moreover, contrary to expectation for a vibrational mode [9], upon isotopic substitution of $^{16}$O with $^{18}$O, the energy of such loss increases (blue-shift). The position of the loss in case of a normal isotopic shift is marked by an arrow at 124 meV in fig. 1. The lower energy mode, on the contrary, shows a red-shift as expected for a vibrational loss. The value of the loss energy at 131 meV shows moreover little or no dependence on oxygen exposure, ruling out the possibility that our inverse isotopic shift might be connected to a difference in oxygen coverage.

Similar measurements were recorded for other $T$ values in the range between 100 K and 300 K, above which temperature the loss disappears because of the onset of bulk migration of the oxygen atoms [6]. The spectra were fitted with Gaussians in order to determine the energy loss position and the full width at half-maximum (FWHM) deconvoluted with respect to the experimental energy resolution. The result of such analysis is reported in fig. 2. The energy loss has the same inverse isotope shift of 3 meV for all temperatures (see fig. 2a). The FWHM (see fig. 2b) shows an abnormally large increment with $T$ for both isotopes, compared to the one expected for a loss of vibrational origin. For comparison no appreciable broadening

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**Fig. 1** – Sample HREEL spectra showing the O substrate vibration at 34 meV and the high-frequency mode at 131 meV for $^{16}$O and $^{18}$O. Note the inverse isotope shift. The arrow indicates the expected position of the high energy loss for normal isotopic shift.

**Fig. 2** – Energy loss (a) and loss width (FWHM) (b) of the high-frequency mode vs. $T$ for the two oxygen isotopes. In (a) the lines are the result of eqs. (5) and (7) for $^{16}$O (solid line) and $^{18}$O (dashes), respectively. In (b), on the contrary, they are a best fit to the data.
Fig. 3 – a) Model for the reconstructed Ag(001) surface drawn following the structure calculated by G. Cipriani, A. Dal Corso and S. Baroni [10] and b) proposed location of the subsurface oxygen species. The ions are depicted by circles of diameter appropriate to their charge state. The oxygen ions are at 2.56 Å from the cap atoms, while the subsurface atom is at 2.04 Å below the outermost Ag plane. The Ag cap atom is 0.45 Å higher than the same plane.

Fig. 4 – The $\text{(AgO}_3\text{)}^4^-$ complex with the independent matrix elements used in the present model (a) and the resulting $d$-hole ligand-field levels (b). The vertical arrow indicates the lowest one-hole optic-active transition polarised normal to the surface.

is observed for the 34 meV mode over the same temperature range.

The isotopic anomaly and the large value of the energy loss may be explained by associating an electronic transition to the HREELS line at 131 meV. The structure of the surface upon oxygen dissociation at low temperature was inferred by X-ray photoelectron diffraction (XPD) [11] and is reported in fig. 3. The surface exhibits a missing-row reconstruction with oxygen adatoms sitting in the channels, slightly displaced towards the missing rows (by 0.36 Å) and upwards with respect to the outermost Ag plane (by 0.15 Å) of the unreconstructed surface. The Ag atoms close to the missing rows are themselves displaced upwards by 0.30 Å and laterally towards the missing rows by less than 0.06 Å, so that the oxygen adatoms lie slightly below their nearest Ag neighbours. Moreover, X-ray photoelectron spectroscopy (XPS) shows evidence for the presence of oxygen in the immediate subsurface layer, with a slightly larger O(1s) binding energy (530.7 eV) than the adatoms (530.3 eV) [11]. Such subsurface oxygen atoms are reasonably located in the octahedral interstitial sites. We conjecture that each negatively charged subsurface oxygen and two neighboring oxygen ions in the surface plane (in either of the two electronic configurations shown in fig. 4) bring the isolated surface Ag ion sitting above the subsurface O (cap Ag) to a larger oxidation state, Ag$^{2+}$, as for an incipient AgO phase at the surface. In other words, the Coulomb potential of the three nearest oxygen ions, though partially screened, is able to lift the top $d$-level of the cap Ag ion up to the Fermi level, and to split the $4d^9$ (one $d$-hole) configuration into a five-state multiplet.
The complex \((\text{AgO}_3)^{4-}\) has altogether 14 states originating from the hybridization of the five 4\(d\) states of silver (of energy \(\varepsilon_d\)) with the nine 2\(p\) states of the three oxygen ions (of energy \(\varepsilon_p\)). For the atom arrangement and the non-zero matrix elements chosen as in fig. 4a, the energy levels induced by the ligand field of \(C_{2v}\) symmetry are

\[ E_{\pm}(b_2) = \frac{1}{2} \left( \Delta \pm \sqrt{\Delta^2 + \frac{1}{4} T_1^2} \right), \]

\[ E_{\pm}(b_1) = \frac{1}{2} \left( \Delta \pm \sqrt{\Delta^2 + \frac{1}{2} T_1^2 + \frac{1}{4} T_2^2} \right), \]

\[ E_{\pm}(a_2) = \frac{1}{2} \left( \Delta \pm \sqrt{\Delta^2 + \frac{1}{2} T_1^2} \right), \]

\[ E_{\pm}(a_1) = \frac{1}{2} \left( \Delta \pm \sqrt{\Delta^2 + A_i} \right), \quad \langle CR \rangle \]

\[ E_0(a_1) = E_{0,1}(b_1) = E_{0}(b_2) = \Delta, \]

\[ A_{\pm} = \frac{4}{3} T_1^2 + \frac{1}{6} T_2^2 \pm \sqrt{\left( \frac{4}{3} T_1^2 + \frac{1}{6} T_2^2 \right)^2 - \frac{2}{3} T_1^2 T_2^2}, \]

where \(a_{1,2}\) and \(b_{1,2}\) label the \(C_{2v}\) irreducible representations. Following Eskes \textit{et al.} [12], the energy of the unperturbed \(d\)-hole level of an isolated \(\text{Ag}^{2+}\) ion is set to zero and \(\Delta \equiv \langle p_{\alpha} | H | p_{\alpha} \rangle\) are the diagonal matrix elements of the total Hamiltonian \(H\) for oxygen atoms (taken the same for atoms \(\pm 1, 2\)). The resonance matrix elements \(T_{1,2}\) are defined in Slater and Koster notations [13] as \(T_{1,2} \equiv 2\sqrt{3}(pd\sigma)_{1,2}\), indices 1, 2 referring to the atom pairs \((0, \pm 1)\) and \((0, 2)\), respectively. The reduction to only three independent matrix elements is based on the approximations \((pd\pi) \approx (pd\sigma)/2\) [14] and of large \(pd\)-gap, where the oxygen-oxygen charge transfer integral \((pp\sigma) \sim (pp\pi)\) is neglected.

The lowest dipole-active transition polarized normal to the surface links the one-hole ground state \(E_{\pm}^+(a_1)\) to \(E_{\pm}^-(a_1)\) with

\[ \Delta E \equiv E_{\pm}^-(a_1) - E_{\pm}^+(a_1) = \frac{1}{2} \left( \sqrt{\Delta^2 + 4A_+} - \sqrt{\Delta^2 + 4A_-} \right). \]

Since \(\Delta\) is of the order of a few eV (3.5 eV for the CuO system in the large gap case considered by Eskes \textit{et al.} [12]), a transition energy \(\Delta E\) of the order of 0.1 eV requires \(4A_\pm \ll \Delta^2\) (weak coupling). In this case

\[ \Delta E \simeq \frac{A_+ - A_-}{\Delta}. \]

For the atomic configuration depicted in fig. 3 the dependence of \(\Delta E\) on the oxygen mass \(M\) as well as on the surface temperature \(T\) occurs mostly through the thermal modulations \(u_\lambda\) of the distances \(d_\lambda\) between the oxygen atoms \((\lambda = \pm 1, 2)\) and the silver atom, whose mean-squared values are expressed as a sum over the phonon normal modes of frequency \(\omega_s\) and eigenvectors \(e_{\lambda s}\),

\[ \bar{u}_\lambda^2(T) = \sum_s |e_{\lambda s}|^2 \frac{\hbar}{2M^* \omega_s} \coth \frac{x}{2}, \quad x \equiv \frac{\hbar \omega_s}{kT}, \]

where \(\bar{u}_\lambda^2(T)\) is the mean-square displacement of the \(\lambda\)-th oxygen atom.
\( M^* \) being the normal-mode effective mass. The temperature dependence of \( \Delta E \) and its isotope shift for the replacement \( ^{16}\text{O} \to ^{18}\text{O} \) are, respectively, given by

\[
\Delta E = \Delta E_0 + \sum_{\lambda i} \frac{\partial \Delta E}{\partial A_i} \frac{\partial A_i}{\partial d_\lambda} \tilde{u}_\lambda(T),
\]

\[
\Delta(\Delta E) = \frac{1}{8} \frac{\partial \Delta E}{\partial \ln M} = \frac{1}{8} \sum_{\lambda i} \frac{\partial \Delta E}{\partial A_i} \frac{\partial A_i}{\partial d_\lambda} \frac{\partial d_\lambda}{\partial \ln M}
\]

with \( \Delta E_0 \) the electronic transition energy for an ideally rigid lattice (where also zero-point vibrations are neglected and \( d_\lambda \) is minimal). For the resonance \( p\delta \) integrals depending on the interatomic distance as \( d^{-5}_f \) [15] one has \( (\partial A_i/\partial d_\lambda) = -10(A_i/d_\lambda) \), so that

\[
\sum_i \frac{\partial \Delta E}{\partial A_i} \frac{\partial A_i}{\partial d_\lambda} = -\frac{20}{d_\lambda} \left( \frac{A_+}{\sqrt{\Delta^2 + 4A_+}} - \frac{A_-}{\sqrt{\Delta^2 + 4A_-}} \right) \approx -\frac{20}{d_\lambda} \Delta E_0,
\]

where the last expression holds in the weak-coupling limit \( (4A_i \ll \Delta^2) \). For a further qualitative analysis we work with one single coordinate, the stretching of \( d_2 \) (subsurface oxygen to silver atom distance), and express its frequency as \( \omega_s = (f_s/M^*)^{1/2} \), where \( f_s \) is a force constant and \( M^* = M M'/(M + M') = 0.87M \) (\( M' \) being the silver mass), so that

\[
\frac{\partial d_2}{\partial \ln M} = -0.19\tilde{u}_2 \left( 1 - \frac{x}{\sinh x} \right).
\]

As shown in fig. 2(a), the experimental \( \Delta E \) as a function of temperature is well reproduced by eqs. (10), (11) for both isotopes in the whole measured temperature range within the weak-coupling and single-oscillator approximations, eqs. (12), (13), with \( \hbar \omega_s = 86\text{meV} \) (for \( ^{16}\text{O} \)) and \( \Delta E_0 = 219.7\text{meV} \). The corresponding values of \( \tilde{u}_2 = 0.0410\text{A} \) and \( 0.0398\text{A} \), respectively, such a small difference being enough to account for the anomalous isotope shift. The reliability of the oscillator frequency and amplitude obtained in this analysis appears to be a strong argument in favor of an electronic mechanism associated to a \( d\)-hole transition for the observed EELS line at 131 meV and its anomalous isotope shift.

Incidentally, we note that also in the strong limit case \( (4A_i \gg \Delta^2) \), more appropriate to a crystalline oxide such as CuO [12], the last expression in eq. (7) becomes \( -10\Delta E_0/d_\lambda \), which also gives an anomalous isotope shift, though a factor 2 smaller. The weak-coupling limit adopted in the present analysis may be justified, however, by the partial screening of the crystal field exerted by the free electrons surrounding the complex \( (\text{AgO}_3)^{4-} \).

Free electrons are also expected to make a substantial contribution \( (\Gamma_e) \) to the linewidth of the \( d\)-hole transition. \( \Gamma_e \) strongly depends on the free electron density at the center of the \( (\text{AgO}_3)^{4-} \) complex and should be smaller for \( ^{16}\text{O} \) than for \( ^{18}\text{O} \) due to the slightly larger outward relaxation of the Ag atom above \( ^{16}\text{O} \) than that above \( ^{18}\text{O} \). This is what is actually seen at low temperature (fig. 2b). On the other hand, the phonon contribution \( \Gamma_{ph} \) to the linewidth, proportional to \( \tilde{u}_2^2(T) \), is larger for \( ^{16}\text{O} \) than for \( ^{18}\text{O} \) and increases with \( T \) so that the total linewidths \( \Gamma = (\Gamma_e^2 + \Gamma_{ph}^2)^{1/2} \) for the two isotopes should have a crossover for increasing temperature. This effect is indeed seen in fig. 2b. A further remark is that experimentally the increase of the halfwidth and the decrease of the loss energy have about the same absolute values over the measured temperature range. Such effect would be incidental for a vibrational transition but is necessary for the proposed electronic mechanism because the lower turning point of the O sub-Ag stretching vibration, corresponding to the transition energy at the upper half-maximum of the loss peak, keeps almost fixed for increasing temperature...
due to the steepness of the repulsive potential. The observed linewidths are also small for
an interband transition, indicating a localisation also with respect to other complexes. This
means that the complexes under investigation should be quite diluted and therefore cannot
interact. Indeed the present experiments correspond to oxygen coverages of the order of few
percent of a monolayer. Similar very sharp interband transitions at relatively low frequency
were previously reported with HREELS for NiO [16] and especially for CoO(001) [17]. However
in that case the interpretation of the data was more straightforward as the studied material
was a transition metal oxide.

To our best knowledge, the observation of localised interband transitions on metal surfaces
was never reported so far. Similar high-frequency losses were however previously reported by
Raman spectroscopy investigations of highly oxidised Ag(111) surfaces [18] and of AgO films
deposited on glass [19,20] in the range 79–123 meV and generically assigned to bulk-dissolved
and/or subsurface oxygen. The isotope shift was not investigated. In the light of the present
study the reported Raman line at 79 meV [18] can be associated with a subsurface oxygen
vibrational mode, whereas the lines above 100 meV are likely to bear an electronic origin as
discussed above for O/Ag(001).

The presence of Ag$^{2+}$ ions at the Ag surface induced by subsurface oxygen could explain
some of the peculiar catalytic properties of Ag surfaces, providing adsorption sites for CO
or C$_2$H$_4$ molecules. Indeed stabilisation of CO adsorption up to $T = 160$ K was reported
several times in the literature [21,22] without a convincing explanation, as CO desorption is
expected at 65 K [23]. The positively charged Ag ions would however be perfectly suited as
active sites [24]. The occurrence of such phenomena for crystallographic symmetries other
than (001) suggests that the phenomenon of $d$-hole formation could be rather general and not
limited to Ag(001). However, no dipole active modes associated to $d$-$d$ interband transitions
were found by HREELS for the other known geometries of oxygen on low-index Ag surfaces.

In conclusion, we have demonstrated that $d$-holes form on Ag(001) and that localised $d$-$d$
transitions can be observed during the initial stages of surface oxidation. The phenomenon
is totally unexpected in view of the depth of the Ag 4$d$-bands below the Fermi level for the
unperturbed system. Its occurrence is relevant for the understanding of the peculiar electronic
and chemical properties of the Ag surfaces.

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find for the internal mode of the superoxide 131.6 meV for O$^{16}$ and 125.5 meV for O$^{18}$,
respectively, with the regular isotopic shift.