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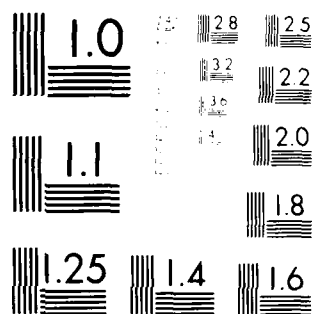
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Image Charge, Coherent Scattering, and Symmetry Effects in
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By

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Image Charge, Coherent Scattering, and Symmetry Effects in Electron Stimulated Desorption: O⁻ from O₂ Condensed on Metals

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1. Introduction

Considerable progress has been made towards our understanding of electron/photon stimulated desorption (ESD/PSD) [1]. Identification of the excited states responsible for desorption reveals that they usually are many particle excitations (i.e. n holes (h)- n electrons (e), such as $2h, 2h-1e$ etc.) and arise from widely different excitation mechanisms [2]. Furthermore, it is known that the lifetime of these localized excitations, which determine the probability for desorption, is very much altered by covalent interactions between the active site and its immediate environment [3]. In this work we shall examine "environmental" effects, which do not arise from alteration of the excited-state lifetime, but rather from: (1) the image charge induced in the metal substrate, (2) adsorbate-adsorbate interactions which reduce the symmetry and hence cause certain selection rules to breakdown, and (3) coherent scattering of electrons in the substrate.

We review previously reported [4] ESD yields of O⁻ from O₂ condensed on polycrystalline Pt in the electron energy range 0 to 40 eV. Of the various species which may desorb (O⁻, O, and O⁺), O⁻ desorption is the most convenient to study here for three reasons: 1) the O⁻ desorption yields appear to be dominated by resonant ESD processes, thus the O⁻ yields are easier to interpret quantitatively than the non-resonant ESD O⁺ yields; 2) the ESD O⁻ yields are about as straightforward to interpret as PSD O⁻ yields, but they do not require use of a synchrotron for measurement; and 3) the O⁻ yields are more difficult to observe experimentally, and they may have contributions from both resonant and nonresonant mechanisms making them more complex to interpret [2,5].

The apparatus utilized to obtain the experimental data described here has been described previously [6], and it is also fully described in the article by Sanche in this volume. The incident angle of the electron beam is 20° from the surface, and the O⁻ ions are measured by a quadrupole mass spectrometer positioned at 70° from the surface. The film thicknesses are estimated to within 20% by a method described previously [6]. A rare gas (RG) is condensed near its sublimation temperature on a clean Pt ribbon, and the O₂ gas is condensed onto the RG film at 17 K. Electron Transmission Spectra (ETS) data [7] reveal that the RG films are essentially ordered, since Bragg reflection (BR) minima are observed around 5 and 9 eV for Ar, 4, 7, and 9 eV for Kr, and 2.5, 5, and 7.5 eV for Xe. In contrast, Xe films prepared well below the sublimation temperature do not exhibit BR minimum in ETS [7]. Data also indicate that the Ar films seem to be more ordered than the Kr and Xe films [8].

The three different "environmental" effects under study in this review, can be isolated in the O⁻ yields from O₂/RG/Pt system. The effects of ion neutralization are minimized by inserting a rare gas (Ar, Kr, or Xe) layer between the Pt metal and the O₂ layer. The RG layer also serves as a spacer layer so that the distance between the ion and the metal surface can be varied, thus varying the effect of the image charge force on the desorbing ions [4]. The image charge effects are best studied for O₂(0.16 ML)/RG(1-6 ML)/Pt. Adsorbate-adsorbate interactions become important at larger O₂ coverages when symmetry breakdown effects become visible. Finally, in the range O₂(0.16 ML)/RG(6-35 ML)/Pt, coherent scattering effects dominate.

Figure 1 compares the electron-energy dependence of the ESD O⁻ yield from O₂(1 ML)/Ar(1-32 ML)/Pt as a function of incident electron energy. The electron impact O⁻ dissociation of O₂ gas is well understood [9]. In the energy range from 4.4 to 10 eV, the O⁻ ions are produced via the transient O₂($\tilde{4}\pi_g$) anion in a process referred to as dissociative attachment (DA). Above 17 eV, the O⁻ ions are produced predominantly via an excited neutral O₂⁺ molecule in a process referred to as dipolar dissociation (DD).

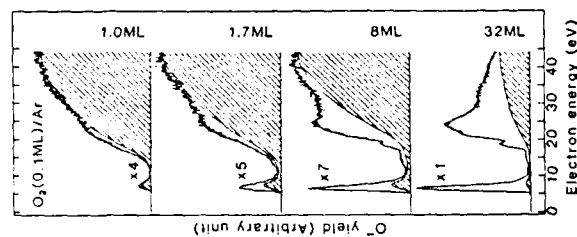


Fig. 1 Comparison of the ESD O⁻ yield curves obtained from O₂/Ar/Pt with a constant (0.1 ML) O₂ coverage and variable (1-32 ML) Ar thicknesses (4). The shaded areas indicate the estimated contributions due to the direct process.

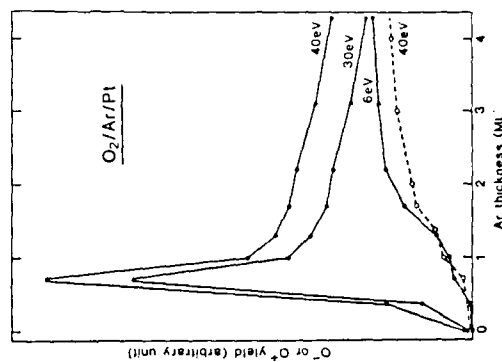


Fig. 2. Ar thickness dependence of the O⁻ yields produced by ESD from the O₂/Ar/Pt samples with a constant (0.1 ML) O₂ coverage (4). The incident electron energies are as indicated. Also shown (dotted curve) is the O⁻ yield produced by ESD with incident energy of 40 eV on O₂(0.16 ML)/Ar(variable)/Pt (4).

2. Image Charge Effects

Fig. 2 shows the Ar thickness dependence of the O⁻ yield from O₂/Ar/Pt with a constant (0.1 ML) O₂ coverage. The sharp maximum probably corresponds to the case when the Ar plus O₂ coverage forms one ML to within experimental uncertainty. Fig. 2 also shows the O⁻ yield from O₂(0.16 ML)/Ar(variable)/Pt samples produced by 40-eV electron impact. In O₂ gas, O⁻ formation by 40-eV electron impact arises predominantly via an O₂⁺ intermediate state [10]. Therefore, we expect that both the O⁻ yield and the DA contribution to the O⁻ yield are produced via charged intermediate states, O₂⁺ and O₂⁻, respectively. Fig. 2 shows that the image charge has a similar effect on these charged states and their dissociated ions.

Four effects that the image charge has on the desorption yield can be summarized using the semi-quantitative, adiabatic potential energy curves for O₂ depicted in Fig. 3 [4]. The solid curves give the ground state of O₂, the π_g , O₂⁻ state and its partner dissociating to the lowest O+O limit, and a O₂⁺ state and its partner dissociating to the lowest O+O⁻ limit [4]. The two O₂⁻ and two O₂⁺ states each form a pair of states which at large separation have

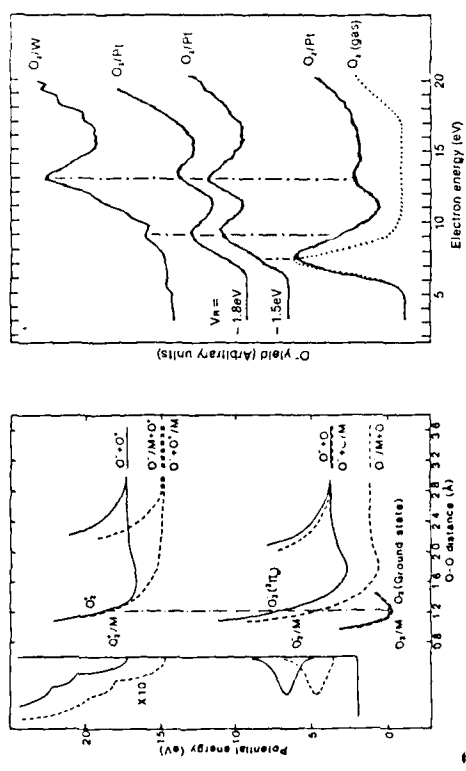


Fig. 3 Potential energy curves of O₂ gas (solid curves), and the corresponding potential energy curves under the influence of an image charge (dotted curves). Spectra on the left side show schematically the relative number of vibrational and/or electronic states which have sufficient energy to yield O⁻ ions, for O₂ gas (solid lines) and for O₂/M (dotted lines) [4].

wavefunctions approaching $\psi(O_2^+)\psi(O_2) \pm \psi(O_2)\psi(O_2^+)$ and $\psi(O_2^+)\psi(O_2^-) \pm \psi(O_2)\psi(O_2^+)$ respectively, where $\psi(O_2)$ denotes the wavefunction for an isolated O atom at site "a". The dotted curves give the corresponding potential energy curves in the presence of the image charge. The symbol O₂/M in Fig. 3, for example, means that the O⁻ ion is near a metal surface. The image charge due to the Pt lowers the energies of the ionic species such as O₂⁻/M, O₂⁺/M, and O₂/M, while the energies of the neutral species such as O₂/M, O₂⁻/M, and O₂⁺/M remain the same. The magnitude of this lowering depends on the distance between the ion and the metal surface, and hence on the thickness of the rare gas spacer layer. The curves in Fig. 3 are drawn assuming the maximum energy lowering, 2.5 eV [4].

The first effect of the image charge involves the energy separation of the O + O⁻ dissociation limit into the O₂⁻/M and O₂⁺/M limits. Consequently, to desorb O⁻ ions, the lower O₂⁻/M intermediate state must undergo a non-radiative transition into its upper partner state. The mechanism for this "charge transfer" transition, O₂⁻/M to O₂⁺/M, is similar to that for symmetric charge transfer in atom-atom collisions of identical nuclei [11] and occurs because of the breakdown of the adiabatic approximation. The probability for this transition is 1/2 when the separation of the dissociation limits vanishes, and decreases quickly as the separation increases. In contrast, the separation between the O₂⁻/M and O₂⁺/M dissociation limits is negligibly small. Nevertheless, based on the relative atomic sizes of O⁻ and O⁺, we expect that the O₂⁻/M limit is slightly lower than the O₂⁺/M limit. This means that the DA contribution should increase and the DD contribution should decrease slightly as the thickness of the rare gas layer increases.

The second effect of the image charge involves the kinetic energy of the escaping O⁻ ions. As can be seen easily in Fig. 3, in comparison with the corresponding O⁻ kinetic energy from O₂ gas, the kinetic energy of the O⁻ ions via O₂⁻/M is decreased while that via O₂⁺/M is increased. The slower escaping ions have a greater chance to be recaptured or neutralized, thus decreasing the DA O⁻ yield, while the faster O⁻ ions have a greater chance for escape, thus increasing the DD O⁻ yield. However, this mechanism probably causes a relatively small effect.

The third effect of the image charge involves the number of vibrational and/or electronic intermediate states (i.e., amount of configuration space) which have sufficient energy to yield O⁻ ions. The curves on the left side of Fig. 3 schematically indicate the configuration space for production of O⁻ from O₂ gas (solid lines) and from O₂/M (dotted lines). These plots indicate that the configuration space for O₂⁻/M decreases slightly while that for the O₂⁺/M state increases significantly compared to that for O₂.

Finally, the fourth effect of the image charge involves the quenching rate of the intermediate state. Near a metal surface, some of the O₂⁻ or O₂⁺ states may be neutralized or de-excited before the desorption process can get underway. The image charge influences these destruction rates of the O₂⁻ intermediate state by attracting the ion towards the metal surface. The inward motion and subsequent neutralization are similar to the first two steps of the Antoniewicz "bounce" mechanism [12], which is known to be active for neutral desorption from physisorbed systems [13]. Again in contrast, the de-excitation rate of the O₂⁺ intermediate state is not affected by the image charge. Thus, intermediate state quenching has a greater effect on the DA process than on the DD process.

All four image charge mechanisms predict a depletion of the DA process relative to the DD process. This is consistent with the two-orders of magnitude reduction seen in the O-(via DA)/O-(via DD) ratio for the O₂(0.37 ML)/Ar/Pt system compared with that of O₂ gas. As the thickness of the rare gas spacer layer decreases from 4 to 1 ML, the image charge force increases. Accordingly, with decreasing rare gas thickness, the O⁻ yield via the DA process should decrease and that via the DD process should increase. This is consistent with Fig. 2. As indicated above, the dissociation branching effect for the DA process, and the configuration space effect for the DD process, are primarily responsible for this behavior.

3. Symmetry Effects

Figure 4 compares the O⁻ yield from O₂ gas with that from O₂(3 ML)/Pt at 17 K [14] and O₂(1 ML)/W at 300 K [15] in the electron energy range 2-20 eV, i.e. in the range where the DA contribution dominates. The data for O₂/Pt is also shown with retarding potentials, V_r, of -1.5 and -1.8 eV. These latter data provide a measure of the kinetic energy of the desorbing O⁻, since only ions in excess of V_r can be collected. Note that application of the retarding potentials for O₂/Pt eliminates the 7 eV peak, making it comparable to that for O₂/W. The data also reveal the presence of peaks around 9 and 13 eV in the O⁻ yields from the chemisorbed systems, which are absent for O₂.

A theoretical analysis [16] indicates that the 9 and 13 eV features arise from the π_x^* and π_y^* resonances which have excitation energies in this region. These two π^* resonances do not appear in the yield from O₂ because of a selection rule which does not allow $\Sigma^- \rightarrow \Sigma^+$ transitions from the π_x ground state of O₂ in the gas phase, or even at low coverages on the RG/Pt substrate [16]. However at higher coverages, O₂-O₂ interactions on the surface, and perhaps even dimer formation, causes this selection rule to break down [16].

Image charge effects are responsible for the remaining differences seen in Fig. 4. The principal π_x DA contribution at 7 eV is absent in the yield from O₂/W primarily because of the branching ratio mechanism described above. It is present in the yield from O₂/Pt at the 3 ML O₂ thickness because the image charge effect is already decreased. The retarding potentials of 1.5 and 1.8 eV eliminate this contribution because the π_x resonance apparently produces O⁻ of kinetic energy less than these energies while the O⁻ from the two π^* resonances have larger kinetic energies [14]. Although the image charge via the branching ratio mechanism essentially eliminates the π_x contribution, it increases the two π^* contributions because these two resonances correlate to the upper O/M + O⁻ dissociation limits, while their partner states (the π_x^* and π_y^*) correlate to the lower O + O/W dissociation limits [16]. Thus the image charge effect can increase or decrease the DA yield depending on whether the excited resonance correlates to the upper or lower limit.

The data and interpretation above provides an answer to the long standing question concerning the active sites for O₂/W, i.e. are they atomic or molecular sites [17]. The presence of the two π^* resonance contributions and the similarity of the DD contributions for O₂/W and O₂ gas clearly indicate that the minority molecular sites are the active ones in this case. However, the O⁻ yields from O₂(1 ML)/Mo at 300 K [15] suggests that both the molecular and the atomic sites are active, because spectral features in the total yield align with those from O₂/W and from the OH⁻ yield from OH/TiO₂ [5]. Portions of the OH⁻ yield have been shown to arise from the DA mechanism, and

therefore must involve breaking O-Ti bonds, i.e. the OH⁻ spectral lineshape should mimic the O⁻ spectral lineshape from atomic O sites on Pt [5]. A least squares fit of the O⁻ from O₂/W and OH⁻ from OH/TiO₂ spectral lineshapes to the O⁻ yield from O₂/Mo suggest that about half of the O⁻ yield from O₂/Mo arises from the minority molecular sites and half from the predominant atomic sites [16].

4. Coherent Scattering Effects

Fig. 1 shows that for O⁻ from O₂/Ar(1-32 ML)/Pt, the three features at 6, 18, and 24 eV grow faster than the remainder of the spectrum, and at large thicknesses (>20 ML) dominate the spectrum [4]. The O⁻ yields at these three thicknesses are plotted as a function of the Ar thickness in Fig. 5. The spectral shape of the 6-eV feature depends on the RG, the thickness and structural order of the RG layer, and the O₂ coverage. It is broad and asymmetric at small RG thicknesses but sharp, asymmetric, and shifted to lower energy at larger thicknesses. It is much narrower at smaller O₂ coverages than at larger coverages (Fig. 6). The dependence on the RG and on the structural order of the RG can also be seen in Fig. 6 [4].

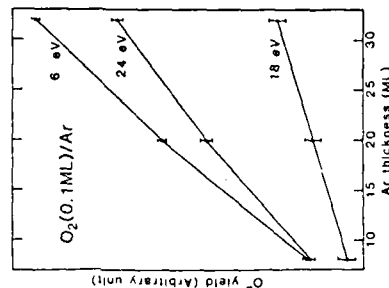


Fig. 5 Ar thickness dependence of the ESD O⁻ yields from O₂(0.1 ML)/Ar/Pt [4]. The incident electron energies are as indicated.

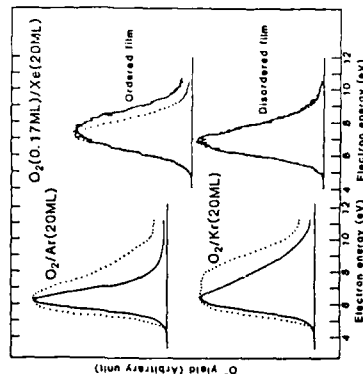


Fig. 6 LEFT Comparison of the ESD O⁻ yield curves obtained with a constant rare gas (Ar or Kr) thickness (20 ML) but with different O₂ coverages, 0.03 ML (solid curves) and 1.0 ML (dotted curves)[4]. RIGHT ESD O⁻ yield curves obtained from O₂(0.1 ML)/Xe(20 ML)/Pt but prepared at 40 K (top) and 17 K (bottom). Also shown are ESD O⁻ yield curves from O₂ gas (dotted curves) [4].

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The experimental results described above can be explained in terms of three processes which we call the direct (D), elastic-indirect (EID), and inelastic-indirect (IID) processes [4]. In the D process, an incident electron collides with an O_2 on the surface and produces an O^- directly. In the EID process, an incident electron at an energy below the O_2 layer without loss of energy (first E_{st}) of the RG, passes through the O_2 layer and returns to energy, undergoes quasi-elastic multiple scattering in the RG, and produces O^- as in the D process. The IID process is identical to the EID, except that the electron upon initial entry into the RG film suffers loss of energy by electronically exciting the RG. At electron energies above the first E_{st} , the inelastic mean free path in RG films is very short ($\sim 10 \text{ \AA}$ [4]).

The O^- yield via these processes are proportional to the following expressions [4],

$$\begin{aligned} D &= \sigma(E) \\ EID &= [1 - \sigma_{el}(E)] P_2(RG, r, E) \sigma(E), \\ IID &= [1 - \sigma_{el}(E)] P_{st}(RG, E_{st}, E) P_2(RG, r, E - E_{st}) \sigma(E - E_{st}). \end{aligned} \quad (1)$$

Here, E denotes the incident electron energy, σ the O_2 coverage, and $\sigma(E)$ the O^- yield cross section from O_2 on the RG film. $\sigma(E)$ is assumed to be independent of the RG thickness beyond 7 ML. The $[1 - \sigma_{el}(E)]$ factor gives the probability of passing through the O_2 layer without loss of energy, where $\sigma_{el}(E)$ is equal to a sum of the elastic backscattering and the total inelastic cross sections of O_2 . $P_2(RG, r, E)$ denotes the probability of the electron returning to the surface, which depends on the RG, the RG thickness (r), and the electron energy in the film. $P_{st}(RG, E_{st}, E)$ denotes the electronic excitation probability of the RG film by electron impact at energy E . Since $\sigma_{el}(E)$ and $P_2(E)$ are slowly varying functions of E [4], the E dependence of the D, EID, and IID contributions are primarily determined by $\sigma(E)$ and $P_2(E)$. Because of the short inelastic mean free path, the O^- yield, $Y(RG, E)$, below and above the first E_{st} are given by $Y = D + EID$ and $Y = D + IID$, respectively.

Figure 5 shows that the O^- yields at 6, 18, and 24 eV all increase as the Ar layer thickness increases [4]. Equation (1) indicates that this relationship exists because of the two indirect processes. The 6, 18 and 24 eV features observed for $O_2(0.1 \text{ ML})/\text{Ar}(32 \text{ ML})$ arise predominantly from the EID, IID, and IID processes respectively. The spectral shape of $\sigma(E)$, or the D contribution, is expected to be similar to the O^- yield from O_2 gas except for the relative magnitude of the DA and DD contributions. Polarization of the thick RG layer reduces the O^- yield via the DA process, but enhances that via the DD process, compared with that for O_2 gas. Our estimates of the D contribution, indicated in Fig. 1 by the shaded areas, are based on the above considerations. The intensity ratio EID/D for $O_2(0.1 \text{ ML})/\text{Ar}(32 \text{ ML})$ is about 70 at the peak energy of the 6-eV feature which means that P_2 is around 90. For thicker and more ordered Ar films, we expect even larger values of P_2 . Since the maximum P_2 obtainable by incoherent multiple scattering is around 2, coherent scattering must be playing a dominant role.

The spectral shape of the 6-eV feature for the different RG films can be correlated with the BR minima observed in ETS data. The 6-eV line shape from a disordered Xe film is virtually identical with that from O_2 gas (Fig. 6). Since $\sigma(E)$ is virtually identical in the 5-10 eV range with that from O_2 gas, $P_2(E)$ for the disordered film must be nearly invariant with E over this same

energy range. However, $P_2(E)$ for the ordered film must vary over this energy range, since the line shape of the ordered Xe film differs from that for O_2 gas (Fig. 6). The 6-eV line shape for Ar also depends on the O_2 coverage so that at the lower coverage (0.03 ML), it is narrower than $\sigma(E)$ and its peak is shifted to lower energy (Fig. 1 and 6). All these suggest that $P_2(E)$ for Ar is strongly enhanced near the first BR minimum around 5 eV. The peak for Kr at the lower O_2 coverage is also shifted to lower energy (Fig. 6); however, the line shape is wider than $\sigma(E)$ apparently because two BR energies (4 and 7 eV) partially overlap with $\sigma(E)$. The O^- yield is enhanced for Ar more strongly than for Kr, because the first BR minimum for Ar is closer to the peak of $\sigma(E)$, and perhaps also because the Ar film is more ordered. This analysis indicates that $P_2(E)$ is enhanced near BR energies, especially strongly near the first BR minimum [4].

It is well known that for a perfect crystal the electronic wavefunctions just above and below the energy band gaps, which arise from the BR's, have standing-wave character [18]. We conclude that this standing-wave character is responsible for the large enhancement of P_2 near the BR energies. The increase of P_2 with RG thickness is also consistent with this since the standing-wave character should increase with RG thickness. However, this raises an interesting question. How does a relatively small increase in the amplitude of the electronic wavefunction (i.e. at most a factor of 2 due to the standing-wave character) cause such a dramatic increase in the O^- desorption yield (a factor of 10)? Clearly, either some quantum mechanical matrix element effect causes the $O_2 \rightarrow O_2^-$ cross-section to increase non-linearly with standing-wave character, or the $O_2 \rightarrow O^-$ desorption branching ratio increases with standing-wave character. These possibilities must still be investigated.

5. Summary

In this work we have observed the following environmental effects: 1) the image charge causes desorption yields arising from neutral intermediates to increase, while those arising from ionic intermediates may decrease or increase depending on the dissociation limit of the ionic intermediate state, 2) O_2 - O_2^- interaction effects at the surface reduce the local symmetry, cause a breakdown in the $\Sigma \rightarrow \Sigma^+$ selection rule, and thus introduce additional dissociative attachment contributions in the O^- yield, and 3) coherent scattering in the rare gas may enhance the O^- yield up to two orders of magnitude near the Bragg reflection energies. The observed image charge and adsorbate-adsorbate interaction effects should be generally observed in other systems. The coherent scattering effects will be large only for low energy desorption thresholds when the inelastic mean free path of the electrons is long. This explains why X^- desorption, which generally has higher energy thresholds, may be less affected by coherent scattering and hence has not exhibited these large effects to date.

Acknowledgements

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