Interatomic Auger transitions in transition-metal oxides

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Interatomic $L_3(M)M_{23}(M)V(0)$ and $L_3(M)V(0)V(0)$ Auger transitions of some transition-metal oxides are reported for the first time. The interatomic mode of decay becomes progressively more dominant (relative to the intra-atomic mode) as the metal d level gets depleted or as the oxidation state of the metal increases. The usefulness of interatomic Auger transitions in studying oxidation of metals has been examined.

Auger electron spectroscopy has been effectively employed to study surface oxidation and oxidation states of metals. The technique generally employs chemical shifts[1] or the relative intensities of $O(KLL)$ and metal Auger lines.[2] Relative intensities of metal Auger lines have been employed recently[3,4] to study surface oxidation and oxidation states of transition metals. We considered it most interesting to investigate the occurrence, if any, of interatomic Auger transitions in transition-metal oxides and their possible utility in investigating surface oxidation of metals. One would expect such interatomic Auger transitions involving the oxygen valence level to occur when the metal valence levels are depleted, since the transition probability of the intra-atomic process is very much higher than that of the interatomic process. Interatomic transitions of transition-metal oxides have not been reported hitherto in the literature, the reports of such transitions being limited to gases adsorbed on metals[5-7] or ionic solids.[8-10] In the study[1] of vanadium oxides, Szalkowski and Somorjai concerned themselves only with the core shifts of the *LMM* Auger transitions, but did not examine the shapes of the transitions involving the valence band.

Auger electron spectra of several oxides[11] of Ti, V, and Mn (Figs. 1 and 2) were recorded using an electron spectroscopy for chemical analysis spectrometer of VG Scientific Ltd. fitted with a sample preparation chamber. The results obtained from electron induced Auger spectra were also checked with x-ray induced spectra using Al $K\alpha$ radiation.

From Fig. 1 we see that Ti metal shows a single *LMV* Auger line, whereas the oxides show yet another peak at lower kinetic energy. The intensity of this peak relative to the higher kinetic energy signal increases progressively as the oxidation state of the metal increases, until in TiO_2 the lower ki-

netic energy transition emerges essentially as a single peak. We also find that on exposure to oxygen the intensity of the lower kinetic energy Auger peak of $TiO_{1.2}$ relative to that of the higher energy peak increases due to surface oxidation (see inset of Fig. 1). Based on these observations, we suggest that the higher kinetic energy peak arises from the normal intra-atomic $L_3(Ti)M_{23}(Ti)V(Ti)$ transition while the lower kinetic energy peak is most prob-
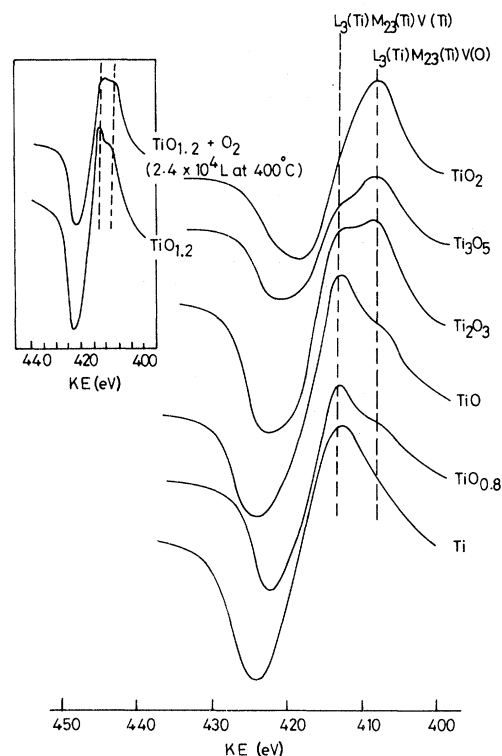

FIG. 1. *LMV* Auger spectra of Ti and its oxides showing the development of the interatomic $L(Ti)M_{23}(Ti)V(O)$ Auger peak as the metal goes into higher oxidation state. Inset shows the effect of oxygen exposure on the Auger signal of $TiO_{1.2}$ (L = langmuir $= 10^{-6}$ Torr sec).

ably due to an interatomic $L_3(Ti)M_{23}$ (Ti)$V(O)$ transition involving the oxygen valence level. This assignment is justified by the fact that Ti metal does not show the low kinetic energy Auger peak and also because the intensity of this peak increases progressively as we approach the d^0 state in TiO_2; the interatomic Auger process would be the mode of decay for the core hole localized at the metal site when the metal valence level is depleted. The energy separation between the two Auger signals in titanium oxides is about 4.5 eV which is close to the energy separation between Ti $3d$ and O $2p$ levels.

The L_3VV Auger transition of Mn and its oxides are shown in Fig. 2; in this figure we have also shown the LMV transition of vanadium oxides. The spectra of vanadium oxides show features similar to those of titanium oxides with the intensity of the low kinetic energy peak due to the interatomic $L_3(V)M_{23}(V)V(O)$ process becoming dominant as the oxidation state increases; in $V_2O_5(d^0)$ the intensity of the intra-atomic $L_3(V)M_{23}(V)V(V)$ signal is indeed negligible. The energy separation between the two signals of vanadium oxides is about 3.5 eV, as V $3d$ is energetically nearer to the O $2p$ level as compared to that in titanium oxides. The L_3VV Auger spectra of Mn oxides (Fig. 2) also clearly show the competition between the intra-atomic $L_3(Mn)V(Mn)V(Mn)$ transition and the interatomic $L_3(Mn)V(O)V(O)$ transition, the latter being entirely absent in the spec-

trum of Mn metal. The intensity of the interatomic transition increases as we go from Mn^{2+} to Mn^{4+}. The energy separation between the two Auger signals is ~ 5.0 eV. The Mn $3d$ level in MnO is separated by ~ 2.5 eV from the O $2p$ level, confirming our assignment of the low kinetic energy signal to the $L_3(Mn)V(O)V(O)$ interatomic process.

The above results on Ti, V, and Mn oxides clearly show that the interatomic Auger transition involving oxygen valence levels occur in all these systems in competetion with the intra-atomic Auger transitions of the metal, the relative transition probablity of the former increasing with the depletion of the d electrons. The interatomic Auger transition found in different oxides of the same metal cannot be due to the presence of a common surface oxide layer since the intensity of the peak varies progressively with the oxidation state and also because the peak is absent in the metal; x-ray photoelectron spectra of the oxides also rule out such a possibility. Since the interatomic Auger transitions in the transition-metal oxides studied by us are sufficiently intense, we have tested their usefulness in the study of metal oxidation by investigating the $Mn+O_2$ system.

The L_3VV spectra of the $Mn+O_2$ system are shown in Fig. 3 at different oxygen exposures. We see that even at very low oxygen exposures, a shoulder develops on the low kinetic energy side of the main signal. Since we know from the L_3VV spectra of Mn and its oxides (Fig. 2) that there is
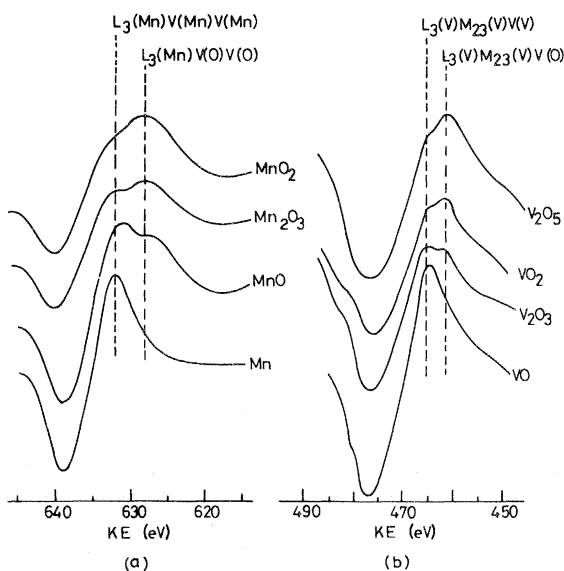

FIG. 2. (a) LVV intra-atomic and interatomic transitions in manganese oxides. (b) LMV intra-atomic and interatomic transitions of vanadium oxides.
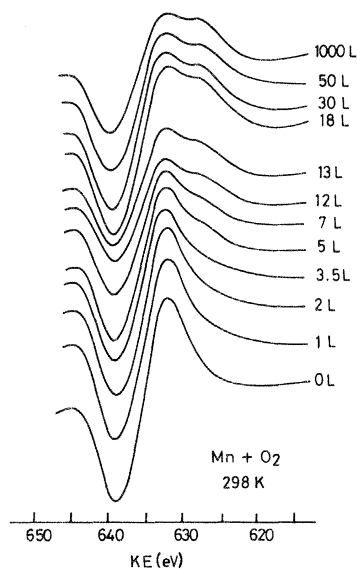

FIG. 3. LVV Auger spectra of the $Mn+O_2$ system at various exposures of oxygen.

negligible chemical shift between the various ox-
ides, the shoulder appearing about 5 eV away from
the main signal can be safely assigned to the in-
teratomic Auger transition. With increasing expo-
sure to oxygen, this shoulder rapidly develops in
intensity indicating the facile oxidation of Mn even
at low oxygen exposures. At high exposures [$\sim$
1000 L (langmuir)], the L_3VV spectrum looks very
much like that of MnO and does not change with
further oxygen exposures suggesting that the sur-
face oxide layer corresponds to MnO in this expo-
sure range. This was confirmed by examining the
x-ray photoelectron spectroscopy (XPS) of core lev-
els; thus, the surface oxide layer showed an ex-
change splitting of 6.2 eV in the 3s core-hole spec-
tra. As the chemical shift between the intra-
atomic LVV spectra of Mn and its oxides is very
small, it is difficult to establish the nature of the
surface oxide by conventional Auger electron spec-
troscopy.

In order to understand the kinetics of the oxida-
tion of Mn more quantitatively, we have plotted
the ratio of the intensity of the interatomic Auger
signal to that of the intra-atomic signal as a func-
tion of oxygen exposure in Fig. 4. The plot clearly
shows the dissociative chemisorption region
($L \leq 2$), the region of rapid oxidation ($2 < L \leq 20$),
and the region ($L > 20$) where oxidation proceeds
slowly through ion transport across the surface oxi-
dized layer, the ratio I (inter)/I (intra) asymptoti-
cally approaching the value of that in MnO.

The interatomic Auger transitions in transition-
metal oxides show unusually high intensities com-
pared to those in ionic crystals.[8-10] Thus, even in
MnO d^5, this intensity is about one-fourth the in-
tensity of the intra-atomic transition, although the
intra-atomic channel for core-hole decay is allowed.
This is probably because of the large overlap be-
tween the metal and the ligand orbitals in
transition-metal oxides. In this sense, the intera-
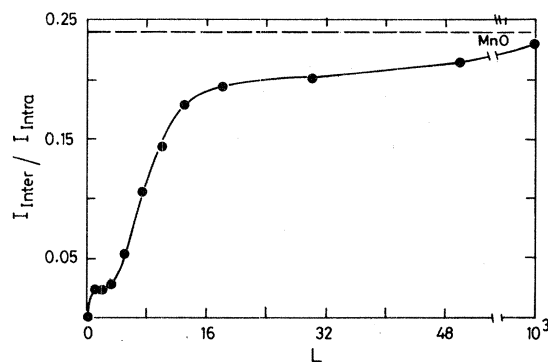tomic LVV Auger transitions of Mn oxides should

FIG. 4. Plot of the ratio of interatomic and intra-
atomic LVV Auger intensities in the $Mn+O_2$ system
against oxygen exposure.

really be ascribed to a process where the final state
has two holes in the bonding levels of MnO_n^{m-}
clusters and the intra-atomic transition to a process
that leads to two holes in the antibonding levels.
The bonding orbitals are mainly contributed by the
ligand orbitals while the antibonding orbitals are
mainly $M\,3d$ in character, although there is consid-
erable mixing of the metal orbitals with those of
the ligand. In the presence of considerable mixing
of orbitals, it is somewhat artificial to maintain the
distinction of interatomic and intra-atomic Auger
processes, since both the transitions involve molec-
ular orbitals arising from the overlap of the metal
and the ligand orbitals. Whenever this mixing is
greater (or the compound is more covalent), we
would expect greater intensity of "interatomic"
transitions. We see weak shoulders corresponding
to the so-called "intra-atomic" transitions in d^0 ox-
ides like V_2O_5 which may arise from a small ener-
gy gap between the bonding levels (t_{2g} and e_g).
Further studies on the Auger spectra of metal-
oxygen systems are now in progress.

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