

late that interstitial migration of impurities from the surface into the bulk proceeds along these channels. One might have expected the surface-region electrons to have more metallic character, and to have a far less corrugated charge distribution on the basis of Smoluchowski's smoothing argument.¹⁵ Bulk Si is fairly free-electron-like in the sense that the average gap is only $\frac{1}{4}$ of the appropriate free-electron Fermi energy, and the surface electrons experience even less ion potential. It is clear, however, that such arguments do not describe the results. One final point needs to be made. Note the prominent buildup of bond charge between Si atoms in the surface region in response to the attractive potential seen in Fig. 1. The charge density in the center of the band is almost twice what one would obtain from a superposition of pseudoatom charge densities. At the corresponding point above the surface atom, however, the charge is 20% lower than given by such a superposition. This latter effect arises because the dangling-bond surface-state band need be occupied by only $\frac{7}{10}$ of an electron per surface atom to neutralize the surface; as a consequence that bond is unsaturated and the site above the surface atom is expected to be chemically active. In this picture, then, chemically reactive sites are revealed as regions of attractive potential at which there has been incomplete charge buildup. Work is currently underway to study the bonding of ordered overlayers to this surface.

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Verification of the Metal-Rich Surface Model for the Oxidation of Sr, by Auger-Electron Spectroscopy*

C. R. Helms† and W. E. Spicer

Stanford Electronics Laboratories, Stanford, California 94305

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The oxidation of strontium has been studied by Auger-electron spectroscopy. It is found that the surface of Sr remains metallic during oxidation, in support of recent photoemission experiments. A model based on the large electrostatic or Madelung energy of "ionic" metal/adsorbate systems is suggested that explains the phenomena.

The kinetics of the oxygen adsorption/oxidation process for the alkaline-earth metals is of considerable interest because of the gettering capabilities¹⁻⁴ of these metals and the low work function of their oxides.⁵ Recently, the authors applied the technique of ultraviolet photoelectron spectroscopy (UPS) to a study of the oxidation of

Sr.⁶⁻⁸

In interpreting data from these studies we viewed the oxidation process, in a manner similar to that of a number of early workers,¹⁻⁴ as occurring in three states: first, oxygen chemisorption with rapid movement of the oxygen ions below the surface; second, oxide nucleation and

growth; and third, saturation with the formation of a semicontinuous oxide layer over the bulk metal. During all of these stages the UPS data⁶⁻⁸ indicate that the surface retains a metallic character even after many monolayers have been adsorbed, in agreement with the early work of Anderson and Hunt³ and Bloomer and Cox⁴ and with recent secondary-ion mass-spectrometry studies of Benninghover and Wiedmann⁹; the metallic surface layer can even persist after the formation of a continuous oxide layer over the bulk metal.

Recently Kress and Lapeyre,¹⁰ in UPS studies of the oxidation of Ba and Sr, have suggested an alternative model which neglects the diffusion of oxygen ions below the surface so that in their model "all the action" occurs on the surface rather than below the surface.

In this Letter we report on Auger-electron-spectroscopy (AES) studies of the oxidation of Sr, which clarify the situation and support our earlier interpretation of the UPS data. In addition, we give further theoretical justification for the retention of the metallic surface of Sr during oxidation.

The importance of this work is threefold. First, it resolves the discrepancy in the character of the surface between the two models mentioned above. Second, a theoretical framework is presented which predicts the metal-rich surface model for "ionic" metal-adsorbate systems. Third, it points out the utility of using both UPS and AES for studies where bulk and surface effects may be important.

The last point is particularly important for metal/metal-oxide systems since UPS, which may probe only a few angstroms below a metal's surface, normally probes much deeper in metal-oxide insulators if the threshold for electron-electron scattering via pair production is not exceeded by the excited electrons. One can guarantee that this condition is satisfied if $h\nu < 2E_g$, where E_g is the band gap of the insulator. AES, on the other hand, can be quite sensitive to the surface of an insulator since the hot-electron energy normally characteristic of AES is much greater than a typical band gap (the band gap of SrO is approximately 5.7 eV).

Of particular interest in the present work is the question of whether AES can distinguish between metallic Sr and a Sr ion as found in the oxide. In order to answer this question, we studied pure evaporated Sr and SrO films. These results, which are presented first, show that one can, indeed, distinguish between metallic Sr and

Sr⁺⁺ ions using AES. Having established this, results of the AES measurements during the oxidation of Sr will be discussed.

Finally, we will present a theoretical model for adsorption in metal-adsorbate systems which are highly "ionic" after reaction. This model, based on the difference in electrostatic or Madelung energy between adsorbed species on the surface and adsorbed species below the surface, predicts the occurrence of a metallic surface during adsorption as observed in the experiments.

The AES measurements were made in a modified Varian low-energy electron-diffraction ultrahigh vacuum system with a four-grid energy analyzer. The base pressure in the system was 10^{-10} Torr or better. The experiments were performed on evaporated films of Sr prepared at pressures of (from 1.5 to 4) $\times 10^{-7}$ Torr, with ~ 5 -Å/sec deposition rates. The pressure dropped to 1×10^{-9} Torr within 1 min of the completion of the evaporation.

The bulk SrO was prepared by oxidizing the Sr films *in situ* at $\sim 200^\circ\text{C}$ at pressures ranging from 10^{-6} to 10^{-5} Torr. The oxidation of the clean Sr films at room temperature was performed by valving off the vacuum pumps and admitting oxygen at from 10^{-7} to 5×10^{-6} Torr, depending on the exposure desired. The Auger spectrum was then taken after each exposure.

The experimentally observed second-derivative Auger spectra for a clean Sr film are shown in Fig. 1(a). Four major transitions are observed: at 16.6 ± 0.1 , 66.4 ± 0.2 , 87.1 ± 0.2 , and 110.5 ± 0.5 eV. We identify these as due to the $N_{2,3}VV$, $M_{4,5}N_1N_{2,3}$, $M_{4,5}N_{2,3}N_{2,3}$, and $M_{4,5}N_{2,3}V$ transitions, respectively. Calculated values of these transitions by the method of Chung and Jenkins¹¹ are 17.2, 69.7, 88.5, and 109.9 eV, respectively. No structure was observed in the spectra of Fig. 1(a) indicative of impurities present, up to transition energies of 1000 eV.

The experimentally observed spectrum from SrO prepared as described above is shown in Fig. 1(b). The oxygen triplet at ~ 500 eV is obviously present for the SrO case with the major transition occurring at 510 eV, and the spectrum due to the Sr transitions in SrO is significantly different from that obtained from pure Sr. For SrO, strong transitions at 64.5 ± 0.2 , 85 ± 0.2 , and 104.5 ± 0.5 eV are observed. The transition observed at 16.5 eV for pure Sr is completely absent, although a new transition of much smaller intensity at 22.5 ± 0.1 eV is observed.

The shift observed in the $M_{4,5}N_1N_{2,3}$ transition

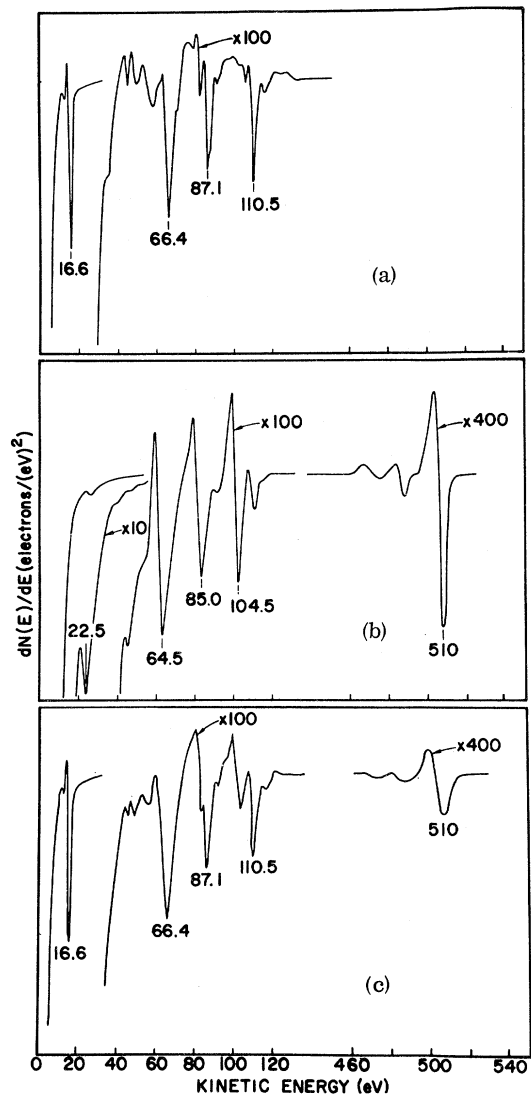


FIG. 1. Auger spectra of (a) clean Sr, (b) SrO, and (c) Sr after exposure to 5000 L of O_2 .

from 66.4 to 64.5 eV and the shift observed in the $N_{4,5}N_{2,3}N_{2,3}$ transition from 87.1 to 85.0 eV are caused by the chemical shift of the Sr core levels due to the ionic nature of the Sr atoms.¹²⁻¹⁴ The shifts are approximately 1.9 ± 0.3 and 2.1 ± 0.3 eV, respectively, to lower energy.

The large shift of 6.0 ± 0.7 eV of the $M_{4,5}N_{2,3}V$ transition from 110.5 to 104.5 eV is due primarily to the energy shift of the valence electrons in going from Sr to SrO. The complete loss of the $N_{2,3}VV$ transition in SrO can also be explained in terms of difference in the valence bands between Sr and SrO.^{8,14}

The appearance of the transition at 22.5 eV is

difficult to explain. There is no Auger transition whose calculated energy lies close enough to this energy to be assigned. Other workers have observed a transition similar to this one for various oxides, the transition being absent in the case of pure metal. Various arguments have been used to justify the transition. It is felt, however, that irrespective of the mechanism of the transition, it is definitely associated with the oxide rather than with the pure metal.

The large differences we have observed in the Auger spectra between metallic Sr and a Sr ion in SrO make it possible to determine the chemical environment, i.e., metallic versus ionic, of a Sr atom at the surface during oxidation.

We will now examine the Auger spectra of Sr during oxidation at room temperature. Data were taken after 25-, 50-, 75-, 100-, 250-, 500-, 750-, 1000-, 2500-, and 5000-L (Langmuirs) exposures to O_2 ($1 \text{ L} \equiv 10^{-6} \text{ Torr sec}$). The data in all cases showed very little change from those obtained for clean Sr. A typical Auger spectrum from Sr during oxidation is shown in Fig. 1(c) after 5000 L exposure. The Auger peak positions due to the Sr transitions are at the same energies as those observed for pure Sr. The signal from the oxygen-derived transition is also noticeably smaller than for the SrO case. After this level of exposure, it is estimated from UPS data and the work of others^{1,2,4} that an ~ 50 -Å-thick continuous film has formed between the bulk Sr and metallic surface.

The weakness of the oxygen Auger signal coupled with the unchanging Sr spectra support our original model for the oxidation kinetics of Sr. That is, a chemically metallic layer remains at the surface even after large quantities of oxygen have been absorbed, and even after a continuous oxide layer is present.

We believe that this metallic layer is responsible for the emission from initial states near the Fermi level observed in the UPS work.⁶⁻⁸ It can, however, be argued that even though there exists a metallic layer at the surface, the emission from the metalliclike states may originate from the metal below the oxide. Two factors argue against this interpretation. (a) Studies of the oxidation of other metals⁷ indicate that oxidation brings on large changes in the photoemission spectra from metalliclike states even for very thin oxides. (b) Even at approximately 10 eV where the UPS experiments were performed, Sr has a very short electron escape depth^{7,8} (a monolayer or less); thus emission from even a very

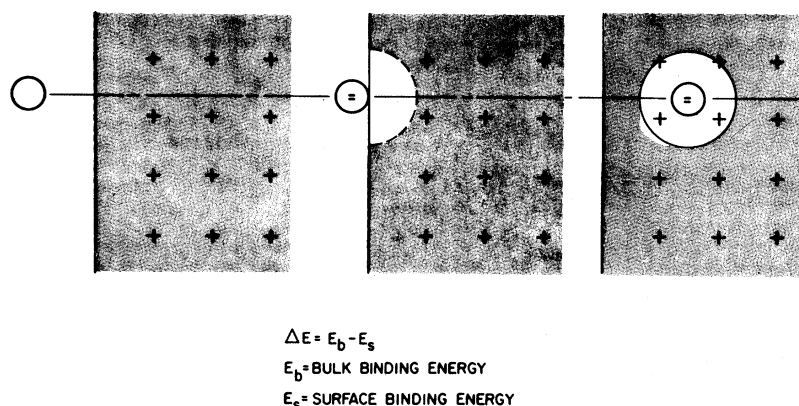


FIG. 2. Schematic diagram of adsorption and absorption for highly "ionic" systems.

thin layer of metal on the oxide would appear similar to emission from a bulk metallic sample.

The question that must be asked now is this: What is the driving force that causes the surface of Sr to remain metallic during oxidation? We believe that this driving force comes from the "ionic" nature of the strontium-oxygen system after reaction. By ionic, we mean that the ground state is derived from an O^{2-} ion and that the wave function of the O^{2-} ion does not overlap significantly with the remaining electronic wave function of the metal. Evidence for the correctness of this picture has been given previously and is based on the narrow width of emission from the oxygen-derived $2p$ levels in a UPS experiment on the Sr/O system.

The description of the model for the surface composition for highly ionic metal/oxygen systems given below will be divided into two sections: (i) The difference between the binding energy of an adsorbate at a clean metal surface and one absorbed in the bulk will be discussed for highly "ionic" metal-adsorbate systems. (ii) We will extend the arguments used for the adsorbate/clean-metal case to determine the binding energy of an anion at the surface of an ionic crystal. For both cases it will be shown that the surface can retain a metallic character.

The adsorption process for an "ionic" system of the type discussed above is illustrated in Fig. 2. Adsorption for a highly ionic metal-adsorbate system will be accompanied by charge transfer forming a negatively charged adsorbate ion at the surface and a net positive region in the metal near the adsorbed ion. This charge transfer will give rise to an electrostatic dipole tending to drive the adsorbate anion into the bulk. If the oxygen ion resides away from the surface in the bulk,

it will be surrounded by this positive charge. Thus the energy of the oxygen ion in the bulk E_B will be lower than the ion's surface energy E_S . If the metal-oxygen bond is of a more covalent nature, however, the problem is much more complicated and great care must be taken.

The same framework can be applied when considering the surfaces of highly ionic compounds as well. This would correspond to the stage in the oxidation process where an oxide layer has grown over the bulk metal. For highly ionic compounds, the cohesive properties are determined primarily by the Madelung energy of the crystal. The Madelung energy at the surface, however, is different from that in the bulk. In Table I reductions in the Madelung constant accompanying the formation of various surfaces for the NaCl structure are listed.¹⁵ A typical highly ionic oxide such as SrO has a Madelung energy of ~ 30 eV and a cohesive energy of ~ 6 eV. The formation of (100), (110), and (111) surfaces would create a reduction in the Madelung energy of 1.2, 4.2, and 15 eV, respectively. For the (100) and (110) surfaces, despite the reduction, there is still cohesion. For the (111) surface, however,

TABLE I. Difference in Madelung constant for various surfaces for a NaCl structure (Ref. 15).

Surface	Ratio of Madelung constant to that of the bulk
(100)	0.96
(110)	0.86
(211)	0.60
(111) ^a	0.50

^aRef. 16.

the ionic nature of the surface atoms is no longer favored because of the energy required to form the ions. Neutral atoms will be formed and desorption of the gaseous constituent can occur, leaving a metallic surface. One would thus expect the (100) and possibly (110) surfaces to be stoichiometric, whereas the (111) surface should be metallic.¹⁷

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†IBM Postdoctoral Fellow.

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Internal-Displacement Order Parameter below the 151-K Phase Transition in PrAlO₃

E. Cohen,* M. D. Sturge,† R. J. Birgeneau, E. I. Blount, and L. G. Van Uitert
Bell Laboratories, Murray Hill, New Jersey 07974

and

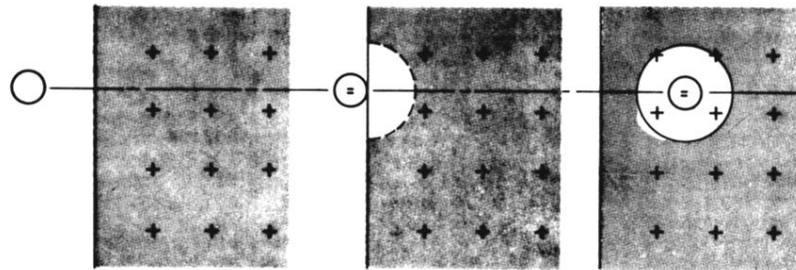
J. K. Kjems

Brookhaven National Laboratory, ‡ Upton, New York 11973
(Received 14 November 1973)

EPR measurements of Gd³⁺ impurities in PrAlO₃ show that the direction of maximum electric field gradient at the Pr³⁺ site rotates continuously from the [101] to [001] perovskite axis below 151 K. This angle gives a direct measure of the displacement associated with the optical phonon mode participating in the Jahn-Teller transition; the angle is found to vary as $(T_c - T)^{1/2}$ near T_c .

Recently, considerable attention has been directed toward systems exhibiting structural phase transitions driven by the cooperative Jahn-Teller effect.¹ A striking example of this has been discovered in the perovskite PrAlO₃.²⁻⁴ In this system there are phase transitions at 1320, 205, and 151 K which are, respectively, second, first, and second order. Harley *et al.*³ have noted that the characteristic feature of each of

these transitions is that upon completion the AlO₆ octahedra are rotated in a staggered sense about the [111], [101], and [001] perovskite axes, respectively, and they have postulated that the latter two transitions are driven by the coupling between the Pr³⁺ electronic levels and the AlO₆ rotary modes. In particular, there is a competition between the cubic anharmonic lattice interactions which prefer a [111] rotation axis and the



$$\Delta E = E_b - E_s$$

E_b = BULK BINDING ENERGY
 E_s = SURFACE BINDING ENERGY

FIG. 2. Schematic diagram of adsorption and absorption for highly "ionic" systems.