following time translation:

$$c_{l,\sigma}{}^{\dagger}(t)=c_{l,\sigma}{}^{\dagger}\exp\{-i[\epsilon_l(\langle\tau\rangle)-\mu]t\}. \tag{12}$$

Using the Kubo-Martin-Schwinger boundary condition[6] it follows that

$$\langle c_{l,\sigma}{}^{\dagger}c_{l,\sigma}\rangle=\left(1+\exp\{\beta[\epsilon_l(\langle\tau\rangle)-\mu]\}\right)^{-1}. \tag{13}$$

The temperature dependence of $\langle\tau\rangle$ is determined by[7]

$$\lim_{\Omega\to\infty}\left[H_N-\mu N_e,\frac{b^{\dagger}}{\sqrt{\Omega}}\right]=0=\hbar\omega s+\frac{\gamma^{1/2}}{\Omega}\sum_{n,\sigma}\frac{d\epsilon_n(\langle\tau\rangle)}{d\langle\tau\rangle}c_{n,\sigma}{}^{\dagger}c_{n,\sigma}. \tag{14}$$

Because the state is assumed to be homogeneous and extremal invariant for space translations, the operator

$$\lim_{\Omega\to\infty}\frac{1}{\Omega}\sum_{n,\sigma}\frac{d\epsilon_n(\langle\tau\rangle)}{d\langle\tau\rangle}c_{n,\sigma}{}^{\dagger}c_{n,\sigma}$$

is also a c number. After some trivial calculations it follows that relation (14) is the same as relation (4), which was obtained by the minimization procedure. The conclusion is obvious; The dynamic model is equivalent to the static model in the thermodynamic limit for the case that the state of the system is assumed to be homogeneous and extremal invariant for space translations. This results from the fact that both sublattices become infinitely heavy in the thermodynamic limit.

Although only a one-dimensional model is considered in this paper, the last result holds also for higher dimensional models. Further details concerning the calculations and the extension to higher dimensionality will be presented in a forthcoming paper.

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Photoemission Studies of the Oxidation of Strontium*

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The oxidation of strontium has been studied by ultraviolet photoelectron spectroscopy. Minimal oxidation produces a relatively sharp peak (width about 0.5 eV) in the energy distribution curves originating from a state 5.0 eV below the Fermi level; this state is seen to broaden strongly into a band as the O^{--} concentration increases and O^{--}-O^{--} overlap occurs. The metallic component of the emission appears to originate from a thin layer near the surface and is little affected by the oxidation.

It is well known that the alkaline-earth metals such as Sr react readily with gases such as oxygen, forming quite stable compounds.[1] The surfaces of these metals do not passivate as do those of metals such as Al, and complete oxidation of typical samples occurs in air in relatively short times.[1] In this Letter we report on the study of changes in electronic structure of an Sr film during oxidation.

The technique used in this study was photoelectron-emission spectroscopy. The photoemission technique has proven a powerful tool for studying the electronic structure of many materials. More recently the technique has been extended to the study of surface states on semiconductors[2] and absorbed gases on clean metal surfaces.[3] Other techniques for studying absorbed gases on metals, such as ion-neutralization spectroscopy[4] and field-emission spectroscopy,[5] are limited to probing the electronic structure only for very short distances below the surfaces of the materials of interest. The photoemission technique on the other hand can provide information on the electronic structure much deeper into solids. This makes the photoemission technique particularly well suited for this study since the oxidation process is strongly a bulk rather than simply a surface effect.

As will become apparent in this Letter, Sr was as exceedingly fortunate choice for the study of oxidation. The Sr Fermi energy is relatively small, about 3.5 eV, and the O^{--} state lies about 5 eV below the Sr Fermi level. Because of this separation in energy, one can examine rather independently the metallic Sr states and O^{--} energy levels as the oxidation proceeds.

Photoemission measurements at energies below 11.7 eV were made in an ultra-high vacuum system described elsewhere.[6] Typical base pressures for the system are 5×10^{-11} Torr or better. The experiments were performed on evaporated films of Sr prepared at pressures of approximately 10^{-8} Torr, with approximately 100 Å/sec deposition rates. The pressure dropped to 5×10^{-10} within 1 min of the completion of the evaporations.

The films were oxidized by allowing oxygen into the vacuum system at pressures of 10^{-8} Torr and less, depending upon the exposure desired. The electron distribution curves (EDC's) were measured after each exposure at pressures of 10^{-10} Torr or better. In this way the equilibrium configuration of the partially oxidized Sr was studied. It should be stressed that the data presented here were not taken during the oxidation but after the oxygen had been turned off and approximate equilibrium reached.

Some experimentally measured EDC's for a 2000-Å film of Sr at low photon energies are shown in Fig. 1(a). These curves are plotted against the electron's final-state energy; $E_{\mathrm{final}} = E + \Phi$, where E is the kinetic energy of the excited electrons and Φ is the work function; the Fermi level has been taken as the zero of energy. All EDC's presented here have been normalized so that the area under a curve is proportional to the yield in electrons per absorbed photon. As photon energy is increased, a sharp peak emerges at the high-energy edge of the EDC's. We identify this leading peak as due to unscattered primary electrons from the s-d conduction-band states. The Fermi energy in Sr is about 3.5 eV so that all primary electrons from the metallic Sr must be emitted within this energy of the EDC leading edge. The height of this peak is a strong function of photon energy, having a maximum at 6.2 eV.

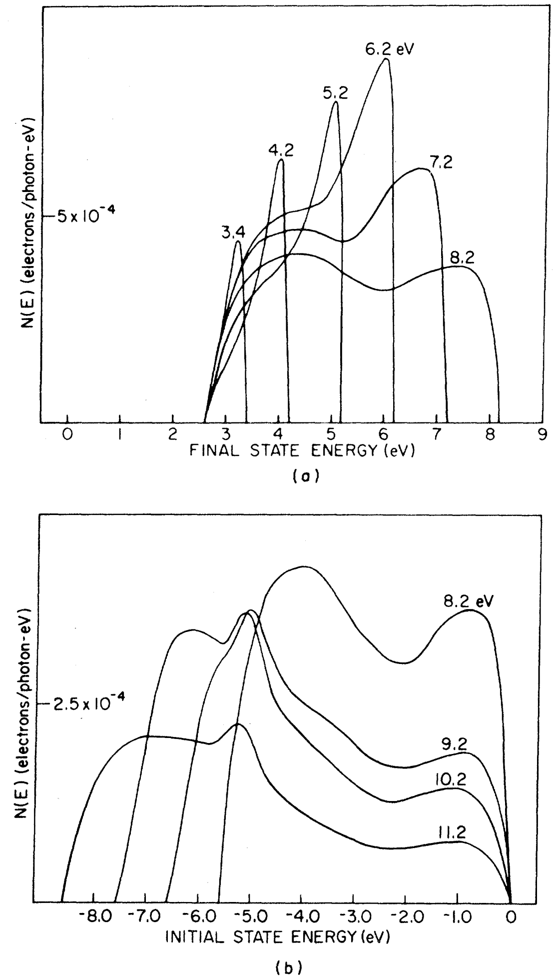

FIG. 1. (a) EDC's for Sr taken at low photon energies are plotted against the final-state energy of the emitted electron. The curves are normalized to the absorbed photon flux, so that the area under each curve is proportional to the quantum yield at that photon energy. (b) EDC's for Sr taken at high photon energies plotted against the electron's initial-state energy and normalized to absorbed photon flux.

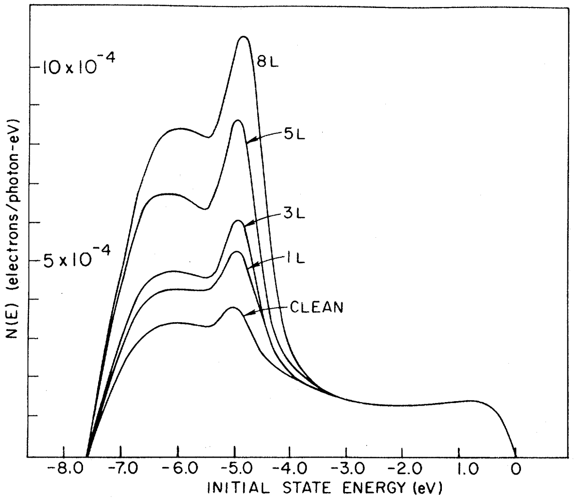

FIG. 2. EDC's for lightly oxidized Sr taken at 10.2 eV, normalized to incident photon flux. The lower curve was taken from a "clean" surface; the others were taken after 1, 3, 5, and 8 L of oxygen exposure, respectively.

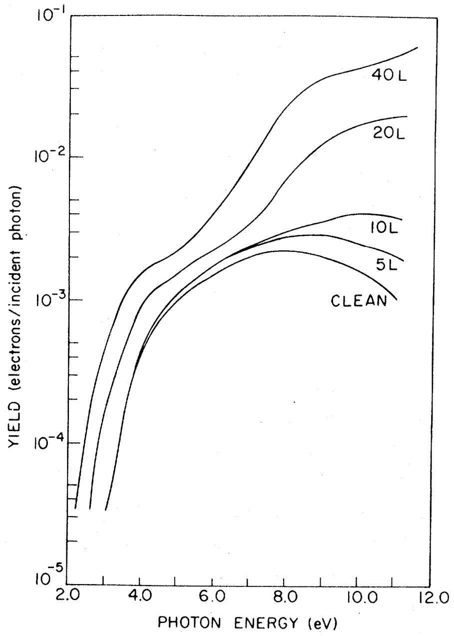

FIG. 3. The yield for oxidized Sr plotted against the photon energy. The curves were measured on films after the oxygen exposure indicated.

The modulation of the height in this way can be understood in terms of the transport and surface properties of Sr and will be discussed in more detail elsewhere.[7]

Figure 1(b) shows normalized EDC's from the same film taken at higher photon energies. In contrast to Fig. 1(a), these curves are plotted against the electron's initial-state energy; $E_{\text{initial}} = E + \Phi - h\nu$. The striking feature of these EDC's is the sharp peak originating from an initial state 5.0 eV below the Fermi level. We identify this peak as emission from an O^{--} $2p$ state, in the Sr matrix, formed by the chemisorption of oxygen during or after deposition of the film. The large peak that appears at low kinetic energies is characteristic of emission due to electron-electron scattering.

Some EDC's taken at 10.2 eV for a 500-Å film of partially oxidized Sr are shown in Fig. 2. These curves are plotted against the electron's initial-state energy as in Fig. 1(b), and have also been normalized to the yield (using the data of Fig. 3) so that the area under each curve is proportional to the respective yield in emitted electrons per incident photon. The lower curve is for a "clean film" prepared as indicated above; the other curves were taken at pressures of 10^{-10} Torr or better, after 1, 3, 5, and 8 L (Langmuirs) of oxygen exposure, respectively; (1 L $\equiv 10^{-6}$ Torr sec).

The EDC's of Fig. 2 can be divided into two parts. For $E_{\text{initial}} < -3.5$ eV, there is virtually no change with increasing oxidation. As mentioned earlier, the Fermi energy of Sr is 3.5 eV and, therefore, the emission of unscattered primary electrons originating from the metallic Sr must fall in the range $-3.5 < E_{\text{initial}} < 0$. It thus appears that emission from the metallic Sr in this range of oxidation is virtually unaffected by the oxygen. For $E_{\text{initial}} < -3.5$ eV, the magnitude of the emission spectra increases by about a factor of 3 as the oxidation proceeds. This increased emission is clearly due to the presence of the O^{--} ions in the film. It includes the sharp resonance peak we have previously associated with emission from the O^{--} $2p$ states plus the broad structure extending from the low-energy cutoff through the resonance peak. The shape and position of this peak suggest that it is due to inelastically scattered electrons, possibly scattered from the excited electrons in the sharp resonance peak. The peak may also be due to emission from a broader O^{--} band similar to the bands observed by Eastman and Cashion in oxidized Ni.[3] In any case it is remarkable how well the peak's growth follows the growth of the O^{--}.

Figure 4 shows EDC's at 11.2 eV after 5, 10, 20, and 40 L of oxygen exposure, respectively. The curves are again normalized to incident pho-

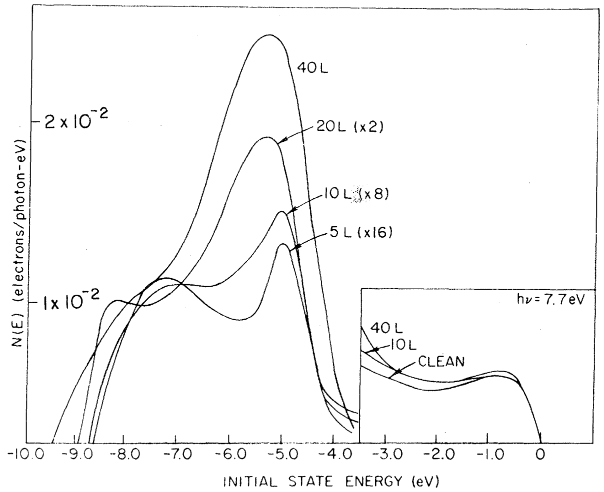

FIG. 4. EDC's for heavily oxidized Sr taken at 11.2 eV, normalized to incident photon flux. The curves were taken after the oxygen exposures indicated. The heights of the 20-, 10-, and 5-L curves are multiplied by 2, 8, and 16, respectively. The insert shows EDC's taken on the same films at 7.7 eV. They are normalized, and plotted on the same horizontal axis as the 11.2-eV curves.

ton flux. The magnitude of the structure originating from the oxygen states is seen to increase dramatically with oxygen exposure. We attribute this large increase in emission to the bulk nature of the oxidation process and thus the bulk nature of the optical absorption and photoemission process. For exposures of 10 L and larger the width of the -5-eV peak gradually increases. By 40 L it has increased in width about a factor of five and is approaching the width one might expect from oxygen states in pure SrO.[8]

We suggest that the width of the -5-eV peak at low oxygen exposures is characteristic of an isolated O^{--} ion that has diffused into the Sr matrix. When the O^{--} concentration becomes large enough so that overlap due to O^{--} ions starts to be come important, the width increases. (Note that since the bottom of the Sr valence band lies well above -5 eV, the O^{--} states will not be degenerate in energy with the Sr states.) Another remarkable thing is that the emission associated with the O^{--} increases by 2 orders of magnitude, while the emission due to Sr is almost unchanged (normalized EDC's for $E_{\text{initial}} > -3.5$ eV taken at 7.7 eV are shown in the insert in Fig. 4). This is consistent with a model[9,10] which assumes that the O^{--} emission comes from ions which diffuse into the bulk, whereas the Sr photoemission (i.e., that for $E_{\text{initial}} > -3.5$ eV) comes from a thin layer of metal that remains at the surface (experiments on very thin films of Sr support this assumption). The metallic layer at the surface appears to remain despite the heavy oxidation. The behavior of the work function also supports this model; the work function is observed to change from 2.6 eV for a clean surface to 1.7 eV after a 40-L exposure. This behavior suggests that the O^{--} below the surface form a dipole layer with a metal-rich region at the surface-vacuum interface, thus lowering the work function.

Thus, as Sr oxidizes, the surface appears to create a chemical potential which draws O^{--} ions away from the surface and/or Sr-metal atoms to the surface, so that a very strongly reducing, i.e., metal-rich, surface is retained as long as appreciable Sr remains within the bulk[11] (for our purposes here we associate something like the first 1000 Å of Sr with the bulk). This helps explain the difference between the oxidation processes in Sr and, for example, Al. It is consistent with the successful use of Sr and similar materials as chemical getters.

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Lett. 30A, 322 (1969); T. H. DiStefano, thesis, Stanford University, 1970 (unpublished)]. In all cases the width of the EDC's from the valence bands of these materials were much larger than the O^{--} widths found here for $L < 10$ L, whereas, the widths for 20 and 40 L were consistent with the widths found in the alkali halides.

[9] An alternate model might involve the formation of islands of SrO on the Sr surface similar to the formation of AgS on Ag, described by H. E. Bennett, R. L. Peck, D. K. Burge, and J. M. Bennett, J. Appl. Phys. 40, 3351 (1969). Since in this case the islands are made up entirely of the compound, one would expect little dependence of the EDC width on concentration, in contradiction to experiment. It should also be noted that AgS is quite covalent and Bennett *et al.* attribute the formation of AgS islands to the small attractive forces between the AgS covalent molecule and free Ag. The situation will be very different for SrO because of the ionic nature of the molecule. Here the O^{--} ion will seek as many Sr neighbors as possible, since the Coulombic repulsive forces between two neighboring O^{--} ions would be quite large. Since a Sr film will oxidize quickly and to completion at room temperature, it is clear that diffusion of the oxide through the film takes place rapidly, which is not the case for AgS on Ag. Certainly the getter action of Sr argues strongly against an SrO island-formation model. Thus it appears that such a model can be rejected.

[10] Bennett, Peck, Burge, and Bennett, Ref. 9.

[11] If the oxidation rates are large enough and the diffusion coefficient into the bulk small enough, the surface can saturate with O^{--}. In the present experiments the maximum rates were approximately 10^{-2} monolayer per second and the exposure times relatively short, so that appreciable saturation would not occur. The concept of a metal-rich surface would therefore only strictly be correct when the oxygen pressure is zero at the metal vacuum interface.

Energy Dependence of Quasifree Scattering in Deuteron Breakup under α-Particle Bombardment from 30 to 80 MeV

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α-particle–induced quasifree scattering in deuteron breakup exhibits no difference between kinematically equivalent α-p and α-n channels, in contrast to previously measured proton-induced breakup. This supports the hypothesis that spin and statistics play a dominant role in deuteron breakup reactions and that previously postulated charge and final-state effects cannot explain the proton data.

Recently a large and as yet unexplained difference in the quasifree scattering (QFS) cross section for the two kinematically equivalent modes of deuteron breakup under proton bombardment has been observed.[1] The ratio of the two cross sections is strongly energy dependent, being as large as 5 around 20 MeV. In a simple impulse approximation (SIA) calculation the only difference between the $D(p,pp)n$ and $D(p,pn)p$ QFS is in the free (p,p) and (p,n) scattering cross section. This difference in free scattering cross sections is, however, much too small to explain the observed ratio. The measured peak cross sections can be explained by a modified impulse approximation with energy-dependent cutoff radii that are different for the two breakup channels.[2] However, even the introduction of cutoff radii will not explain the observed angular variation.[3] Final-state interaction (FSI) as well as Coulomb effects have been postulated as possible causes for the observed large difference in cross section for the two deuteron breakup channels. It has been shown[3] that FSI effects alone cannot, in any simple manner, explain the angular variation. Bassel and Langworthy[4] have developed a semiphenomenological theory, based on distorted wave methods, which treats the spin of the three-body system exactly. Since one of the QFS channels has two identical particles (protons) interacting, spin and statistics considerations break the SIA amplitude into several terms which are different for the (p,p) or (p,n) QFS, thus predicting a branching difference. A branching difference is predicted only for the case in which there are two identical particles in the exit channel. Similar conclusions regarding the importance of the Pauli exclusion principle in deuteron breakup have been reached by Cahill.[5] His approach is based on the Amado[6] model, ignoring Coulomb effects. No complete calculations of the Coulomb effects over the entire range of bombarding energies exist, even though some $D(p,$