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Fundamental Aspects of the Electronic Structure, Materials Properties, and Lubrication Performance of Sputtered MoS_2 Films

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An understanding of the fundamental properties of solid lubricants at the atomic level (e.g., crystallite structure and chemical bonding to substrates) and the ways in which those properties relate to tribological performance is essential for developing new lubricants to satisfy the demands of advanced mechanical technologies. Detailed measurements of the physical and chemical properties of both the surfaces of lubricant films and their substrates, and of the films' bulk crystalline and electronic structures, can be correlated with their friction, wear life, and resistance to reactive degradation. In this report are reviewed and discussed the experimental results of the electronic and crystal structures, film adhesion, and bulk friction of MoS_2 films that have been sputter-deposited. A model using a molecular orbital description of the electronic energy levels of MoS_2 is presented that can be used to interpret these data. The model also provides a rationale for the differences in lubrication effectiveness between $NbSe_2$ and MoS_2, and it can help in predicting means for improving the performance of MoS_2 films.

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PREFACE

Support for this work was provided by the U.S. Air Force Space Division and the Defense Advanced Research Projects Agency under Contract No. F04701-85-C-0086-P00016. Many thanks to Dr. P. A. Bertrand for her work on the MO model, to Drs. J. R. Lince and D. J. Carré for their work on surface bonding to MoS_2, to R. Bauer and P. M. Adams for the XRD and wear studies, and to Dr. H. K. A. Kan and all of the above for many useful discussions.

CONTENTS

FIGURES

I. INTRODUCTION

Layered transition metal dichalcogenide (LTMD) compounds constitute a class of materials with unique and unusual properties based on the extreme degree of anisotropy in their layered crystal structures. LTMDs are formed by stacking "sandwiches" consisting of a layer of transition metal between two layers of chalcogen. There is strong covalent bonding within the sandwiches but weak (van der Waals') bonding between them. Details of the exact crystal type within this general structure vary and result in some LTMDs being very good lubricants and others being poor lubricants or abrasives.[1,2] Coincidentally, the electrical properties vary greatly also, ranging from insulators to semiconductors, and finally to metals with evidence of superconductivity in some of the class members.[3-5] → 1073

Many empirical studies have investigated the lubrication properties of MoS_2 and some other LTMDs,[6,7] and considerable effort has been devoted to understanding the electronic structures of these materials.[8-11] In particular, numerous photoelectron spectroscopy, electron energy loss, and x-ray absorption/emission measurements have been correlated with various theoretical or semiempirical band structure or molecular orbital treatments of the electronic energy levels in order to describe the valence electronic structures of the layered compounds, especially for MoS_2. Until now, however, little effort has been devoted to exploiting the fundamental information on electronic structure to explain or predict the lubrication properties.

This report details the ways in which the electronic and chemical bonding properties of MoS_2 can provide a basis for explaining many of the lubrication properties of all LTMDs. In order to make the necessary correlations, the structural and chemical bonding properties of polycrystalline thin films, properties that make them good lubricants, are first reviewed; then ways in which electronic energy level data from single-crystal samples can be used to interpret these materials properties are described.

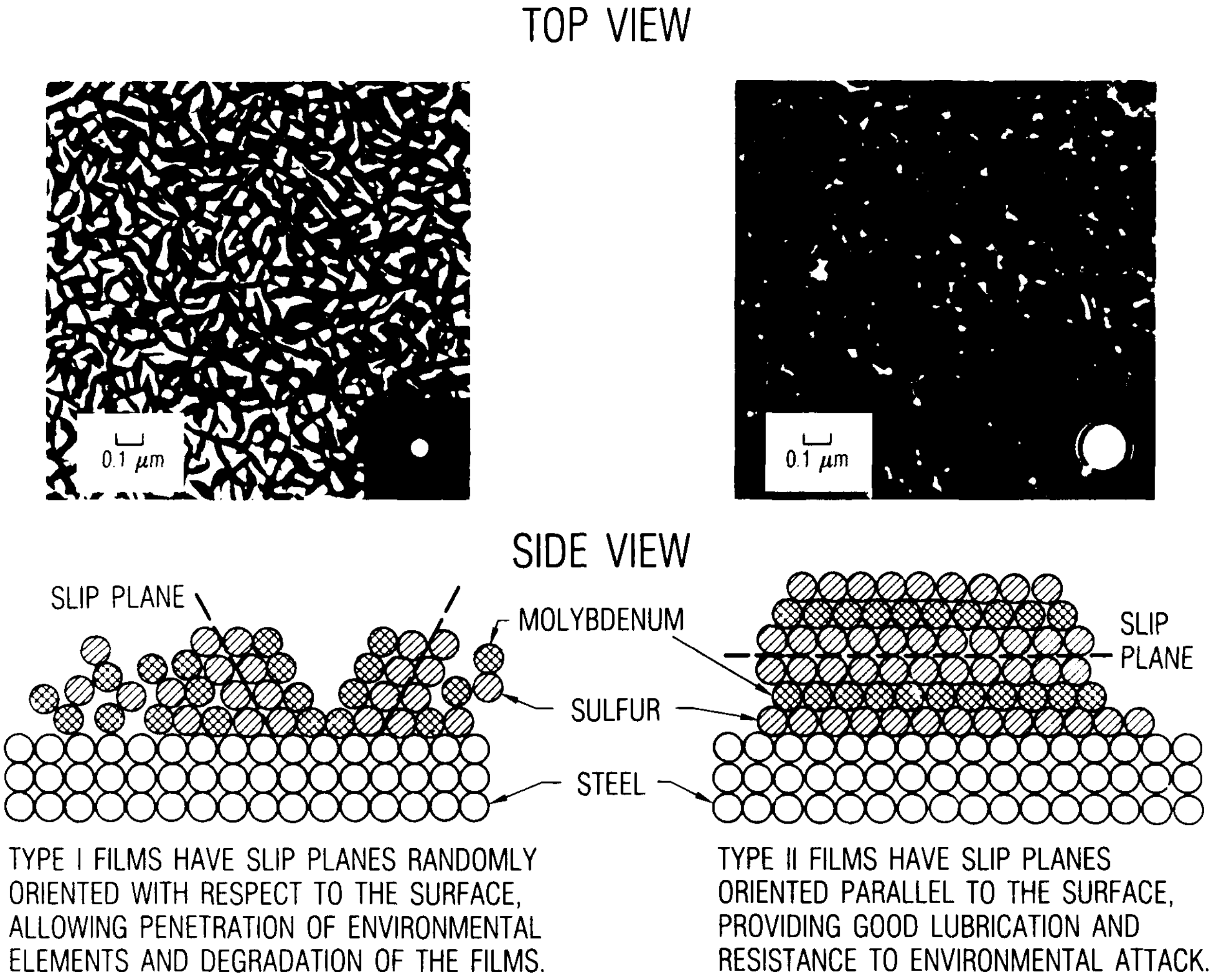
There exists considerable controversy over electronic structure models, mostly about whether the rigid-band model should be applied to describe the energy bands of MoS_2. Much of the difficulty appears to be that model's failure to include the presence of considerable covalent bonding within the S-Mo-S sandwiches.[8,12] Such bonding results in mixing of the metal s, p, and d orbitals with the sulfur p orbitals, and more recent studies have recognized the importance of such mixing.[9]

A relatively simple molecular orbital (MO) energy level model is described here. The MO model seems to fit most of the available experimental data, especially those related to lubrication. Admittedly, this schematic model needs refinement so that it can be extended to rigorously take into account the periodic properties of the layered crystals, but it does predict ways that MoS_2 and possibly other LTMDs can be modified to improve their lubrication performance.

II. CRYSTALLITE ORIENTATION

Thin films of LTMDs, and in particular of MoS_2, are believed to be good lubricants because of their layered structure and because of the weak bonding between sandwich layers, which results in very low shear strengths (low friction) within the films in the direction of sliding.[6] This interpretation of lubrication action implies that in polycrystalline films that exhibit good lubrication the basal planes of their crystallites are parallel with the direction of sliding (i.e., parallel with the plane of the contacting surfaces). Experimental observations of film morphologies (electron microscopy) and crystallite orientations (x-ray diffraction) have shown these assumptions to be consistent, but not all films have the correct orientation in their as-prepared state.[13-20]

Sputter deposition is a convenient method for preparing lubricating films.[15,18-23] The resulting films function well in applications that require close tolerances in mechanical devices because they are thin (usually on the order of 1 μm thickness), and they generally adhere well to most surfaces. The actual lubrication performance (friction coefficients and durabilities) of these films, however, depends on minute variations in their crystallite structures and chemical compositions. Early work in our laboratory[20] demonstrated that sputtered films can be produced with two different morphologies, as shown in Fig. 1; more recent work, performed elsewhere, has provided empirical information about the sputtering conditions under which the different types of films are produced.[17,18,24] Studies of the reactivities of these two types of films in atmospheres of different relative humidities indicated that the crystallites within the films had different orientations with respect to the substrate plane.[20] On the basis of these reactivity studies and limited wear testing, a lubrication model was developed (see Fig. 2) that proposed that the best lubricating films would be those prepared initially in the coplanar (with substrate surface) orientation (type II films). Furthermore, that most type I (randomly oriented) films achieve orientation on burnishing (rubbing) does not mean that initially randomly oriented films will perform as



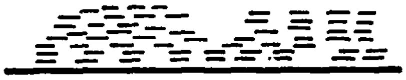
TYPE I FILMS HAVE SLIP PLANES RANDOMLY ORIENTED WITH RESPECT TO THE SURFACE, ALLOWING PENETRATION OF ENVIRONMENTAL ELEMENTS AND DEGRADATION OF THE FILMS.

TYPE II FILMS HAVE SLIP PLANES ORIENTED PARALLEL TO THE SURFACE, PROVIDING GOOD LUBRICATION AND RESISTANCE TO ENVIRONMENTAL ATTACK.

Fig. 1. Transmission electron micrographs and schematic drawings of types I and II sputter-deposited MoS_2 films. Films for transmission electron microscopy had an average thickness of approximately 75 nm.

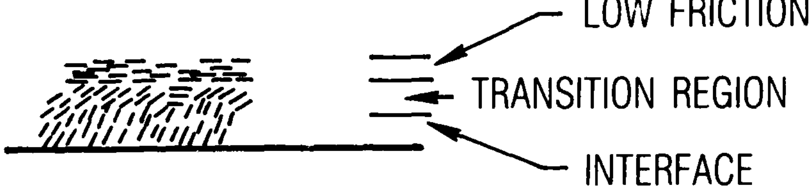
- PROPOSE THAT AS-PREPARED FILMS HAVE TWO DIFFERENT CRYSTALLITE ORIENTATIONS

TYPE I
EDGE PLANES EXPOSED



TYPE II
BASAL PLANES EXPOSED

- BURNISHED TYPE I WILL HAVE GOOD FRICTION BUT INFERIOR WEAR LIFE



- FOR BEST PERFORMANCE, PREPARE WITH PROPER INTERFACE ORIENTATION

Fig. 2. "Stick"-structure-performance model for sputter-deposited MoS_2 films.

well as type II films with use. It is proposed that there is always a zone of crystallites at the film-substrate interface that does not become properly oriented because of the strength of the chemical bonding between the MoS_2 edge-plane [e.g., (100)] atoms and the substrate atoms. Further, the plane representing the interface between crystallites of different orientations constitutes a region of failure during use.

The validity of the above hypothesis is demonstrated by the recent x-ray diffraction data in Fig. 3. These data represent high-resolution θ-2θ scans in the regions of the edge (100) and basal (001) plane reflections taken after the films had been rubbed (worn) for various times. The wear-test apparatus (described in detail in Ref. 25) consists of a mirror-flat 440C steel disk rubbing on the surface of a coated steel coupon at an average rotational speed of 33 mm s^{-1} under a load of 31 N. The detailed behaviors of the two different films represented in Fig. 3 are discussed in Ref. 26, but the general observation is that neither film is completely oriented during rubbing, even for wear times just prior to failure, which is defined by an abrupt increase in the friction between the two contacting surfaces. The data for the as-prepared films show that their crystallites are oriented with their basal planes perpendicular to the plane of the substrate surface; initially, there is no basal reflection. As rubbing commences, the crystallites reorient so that some of their basal planes become parallel to the substrate surface. However, this reorientation process appears to reach a steady-state level, and even after 100,000 revolutions of the disk, approximately 40% of the crystallites remain unoriented.

Since type I films cannot be oriented completely by rubbing, it is clearly necessary to prepare the films in the oriented configuration, i.e., as type II films. However, this requirement presents a paradox for layered materials: In order to achieve good adhesion of properly oriented films, strong bonds must form between the basal surfaces of the MoS_2 crystallites and the substrate, but these are the same low-energy (weakly bonding) surfaces that provide the film with the low shear properties required for good lubrication.

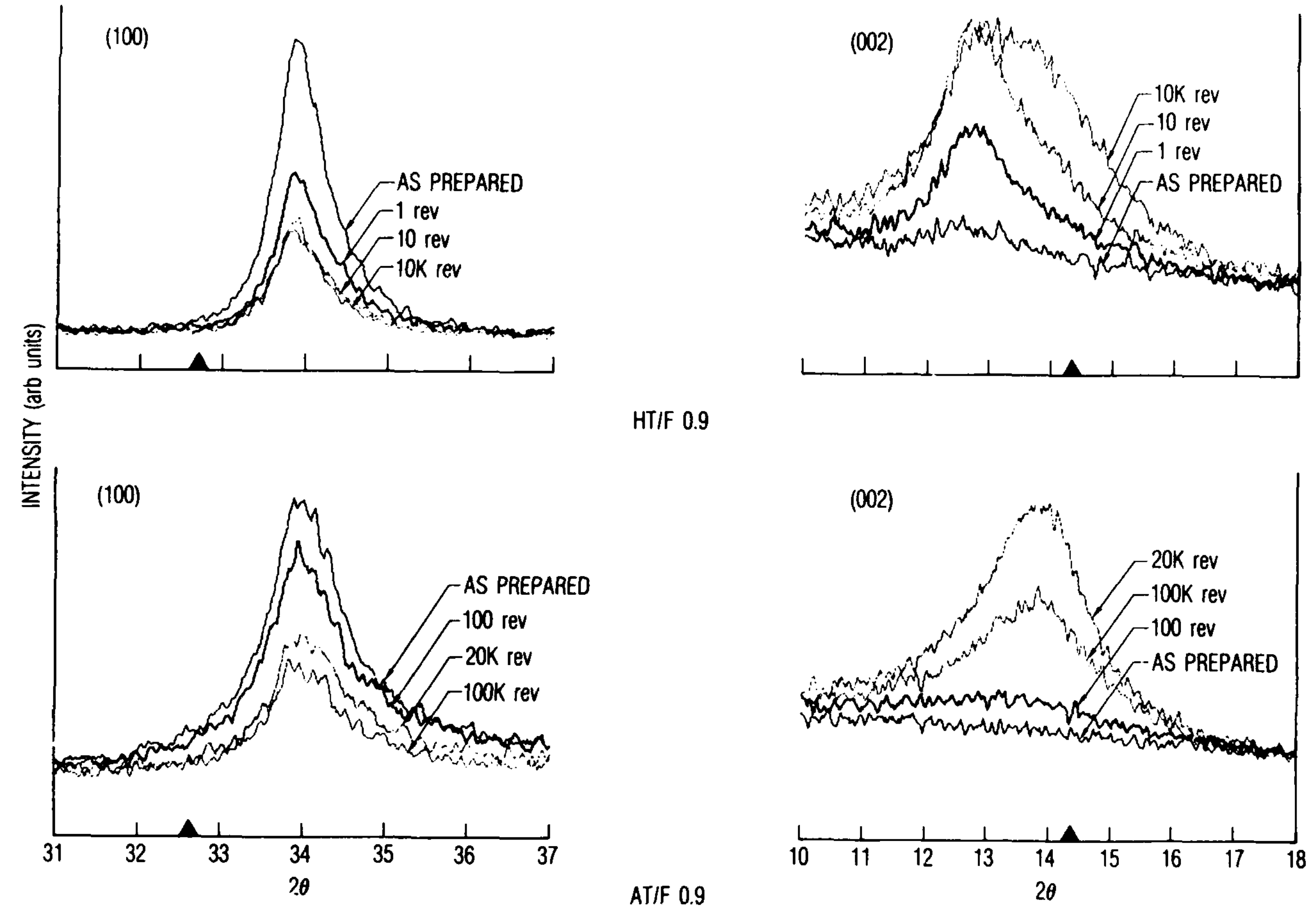


Fig. 3. X-ray diffraction peak changes for sputter-deposited MoS_2 films as a function of wear-test revolutions. HT and AT refer to films made with substrates at 230°C and ambient temperature (~ 70°C), respectively. F0.9 indicates that the mole fraction of MoS_2 in the films is > 0.9. ▲ denotes MoS_2 crystal.

III. INTERFACE BONDING

The above argument implies that strong chemical bonding between film and substrate atoms is a criterion for good film adhesion. However, the undisturbed basal plane surface of MoS_2 crystals has been shown to be inert by means of adsorption studies[27-29] and an analysis of the basal plane band-bending behavior evidenced by the photoelectron peak shifts produced by the deposition of a series of metals onto cleaved crystals.[30] Data from Ref. 30 are displayed in Figs. 4 and 5. Judging from the absence of peak shape changes for the molybdenum and sulfur core level transitions and from the linear dependence of peak shift on electronegativity of the deposited metal, it can be concluded that no specific bonding interactions occur between these metals and the MoS_2 basal surface. The large variation in band bending as different metals were deposited implies that the basal surface is completely "unpinned," a very unusual (perhaps unique) situation for a covalent semiconductor, and one that indicates a very inert surface.

How, then, can bonds be formed to this inert surface? One method is to take advantage of the tendency of LTMDs to form defects, specifically sulfur vacancies in MoS_2 within the basal plane or at step sites on the basal surface. The vacancies could act as anchor sites where substrate atoms bond directly, or they could serve as sites where atoms are substituted to form bridge bonds between substrate and film atoms.

The bombardment of the basal surface of MoS_2 crystals with ions in the 0.5- to 10-keV energy range produces sulfur vacancies, sometimes with molybdenum metal islands forming concurrently.[30-35] When combined with examination of the effects of metal deposition onto the bombarded surface, such studies provide information on the enhancement of the bonding processes of interest.[30] The slopes of the lines for plots such as those in Fig. 5 indicate the degree of surface pinning, which in the case of MoS_2 can be related to surface bonding. For the ion-bombarded surface, the slopes are reduced, and that for the Mo $3d_{5/2}$ peak binding energies is somewhat less than that for the S 2p peak, suggesting some tendency for bonds to form between the

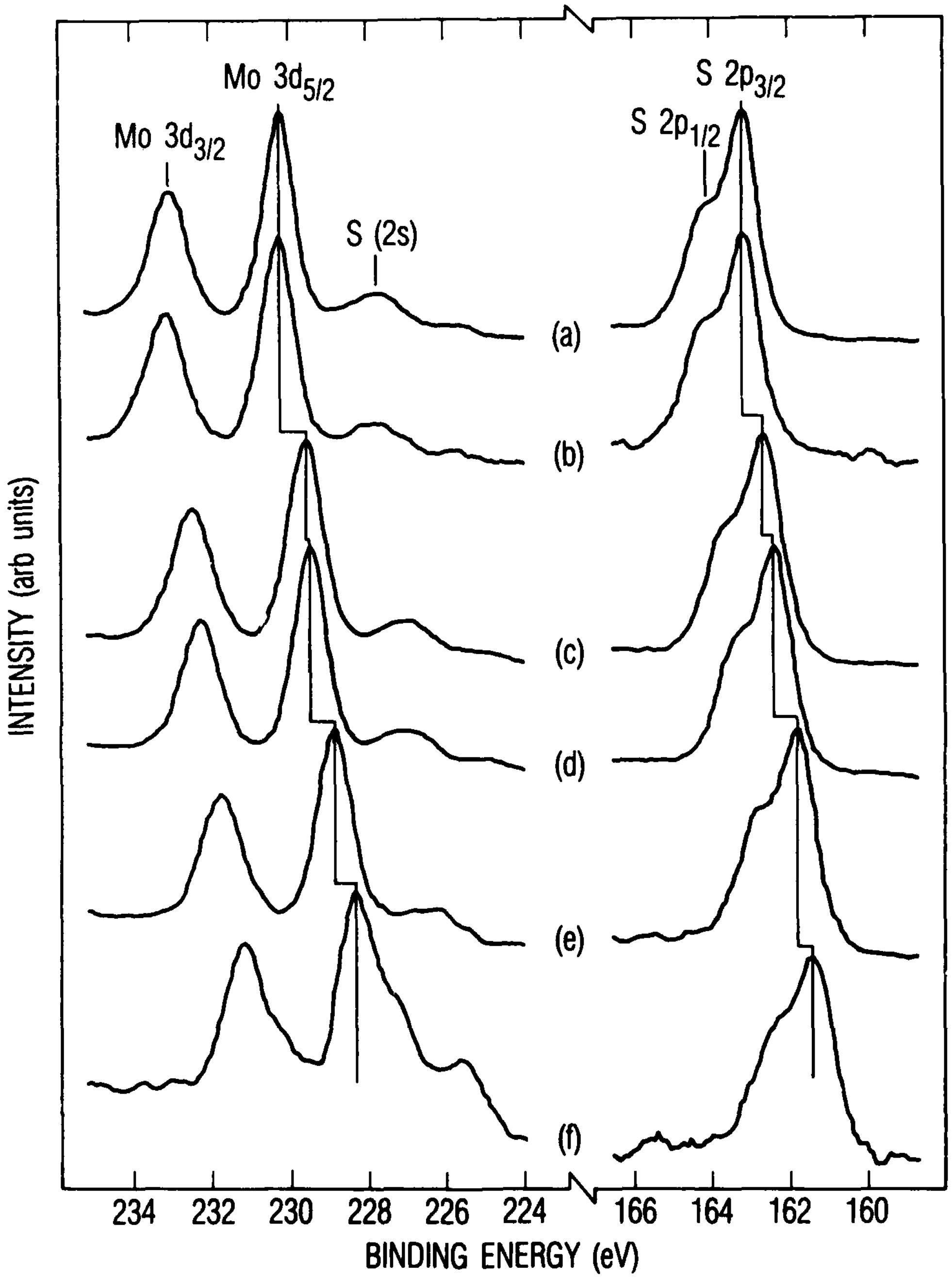


Fig. 4. X-ray photoelectron spectra of the {0001} surface of MoS_2 crystals (a) when freshly cleaved, and after deposition of (b) indium, (c) palladium, (d) iron, (e) aluminum, and (f) manganese. Note spectral peak shape changes for manganese deposition (see Ref. 30).

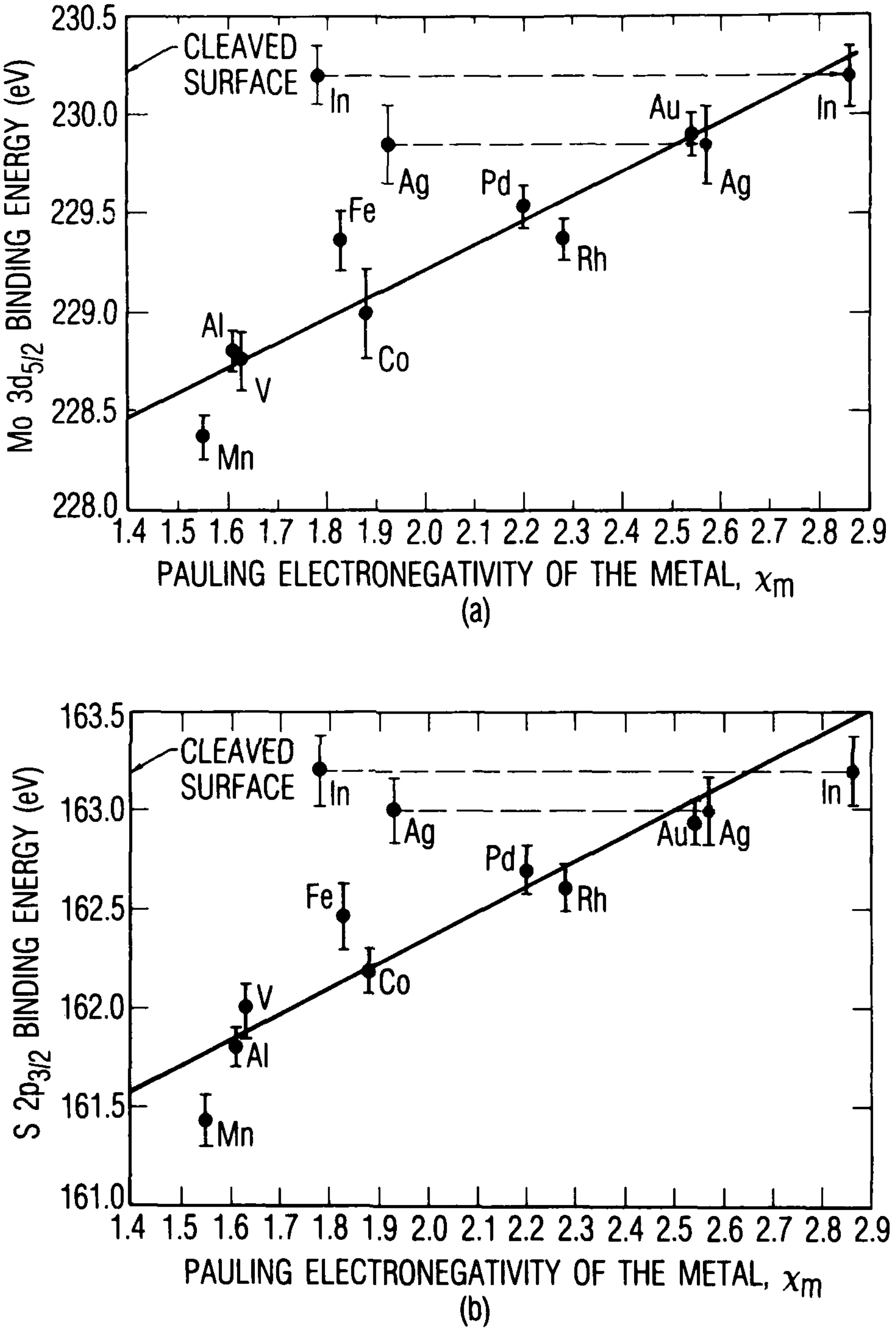


Fig. 5. XPS peak binding-energy changes for $MoS_2(0001)$ as a function of deposited metal electronegativity: (a) Mo $3d_{5/2}$ and (b) S $2p_{3/2}$. Corrected electronegativities for indium and silver are calculated using the Sanderson method (see Ref. 30).

deposited metal and the molybdenum atoms. However, the effects are very small and not conclusive. It may be that the creation of sulfur vacancies alone does not enhance adhesion of MoS_2 films to metal substrates, but further work is needed to determine whether this is true. Whether incorporation of appropriate bridge-bonding atoms into the sulfur vacancies will improve bonding and adhesion to the substrate must also be determined.

The type and degree of electron distribution changes within the energy states of the MoS_2 sandwiches produced by ion bombardment, reaction with adatoms, and metal deposition surely determine the tendencies of the crystal surfaces to form chemical bonds. The MO energy level diagram, developed in Section IV, provides a method for interpreting such electronic structure changes and for predicting the effects of substituting dopant atoms for sulfur atoms in the MoS_2 basal surface.

IV. MOLECULAR ORBITAL MODEL

Within the layered structure of MoS_2, the molybdenum atoms are surrounded by six sulfur atoms in the form of a trigonal prism (TP). Each sulfur atom is bonded to three molybdenum atoms with Mo-S-Mo bond angles of approximately 82° (Fig. 6). The molecular orbitals for the $Mo(S)_6$ units can be constructed according to the irreducible representations of group theory for the D_{3h} symmetry point group (i.e., the TP structure). The entire set of wave functions and a complete MO energy-level diagram for D_{3h} symmetry have been published[36] and can be applied to the MoS_2 system. However, in applying them, one must recognize a major difference between the bonding situation for a single molecule (i.e., ML_6) and that for a $Mo(S)_6$ group within a MoS_2 crystal, namely, the degree of involvement (if any) of π bonding orbitals.

Previous attempts at describing the electronic structure of TiS_2[3] and at interpreting the lubricant properties of LTMDs with MO theory[37] invoke S 3p-π orbitals that do not exist in these crystals because of the above-mentioned bonding of each sulfur to three (not one) metal atoms. The 82° Mo-S-Mo bond angles in MoS_2 are consistent with the involvement of essentially unhybridized S 3p orbitals in σ bonding to three molybdenum atoms within a sandwich. The energy-level diagram for the crystal is considerably more simplified than that of Ref. 36 (or Ref. 37) and is shown in Fig. 7. The ordering of levels in Fig. 7 is assigned on the basis of spectral data;[5,8-11,34,35] the correlation between both electron energy loss spectroscopy (EELS) and ultraviolet photoelectron spectroscopy (UPS) data and the MO energy levels is shown in Fig. 8. There are seven bonding or nonbonding MO energy levels that exactly accommodate the 14 valence electrons in the $Mo(S)_6$ unit within the crystal.

The significance of this MO interpretation is that, for MoS_2, all of the accessible orbitals for both molybdenum and sulfur are used in intralayer bonding, leaving only high-energy antibonding orbitals available for interlayer bonding or basal surface bonding as in adhesion to substrates. There are no dangling bonds (i.e., accessible orbitals) on either the molybdenum or

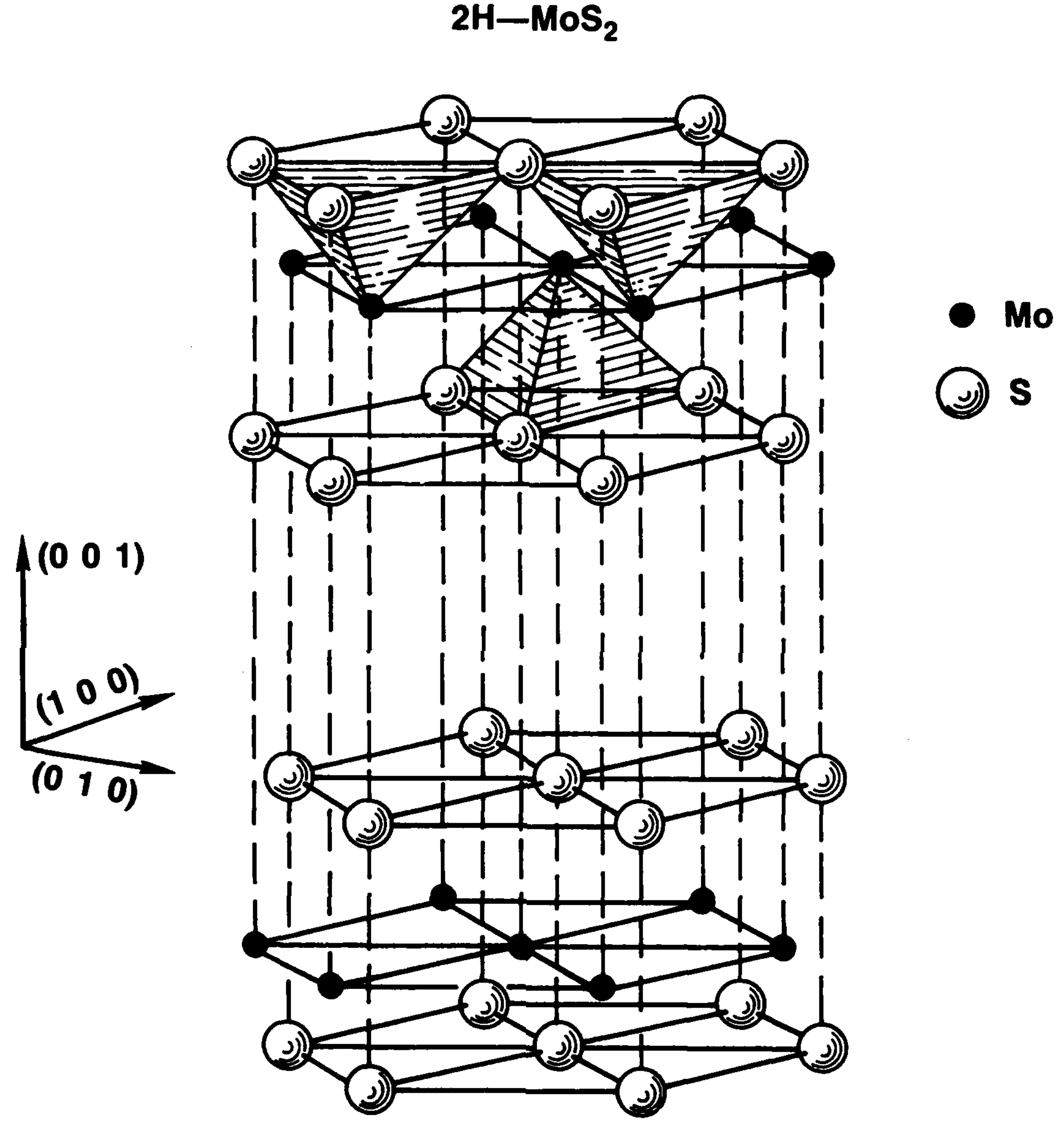


Fig. 6. Crystal structure of MoS_2.

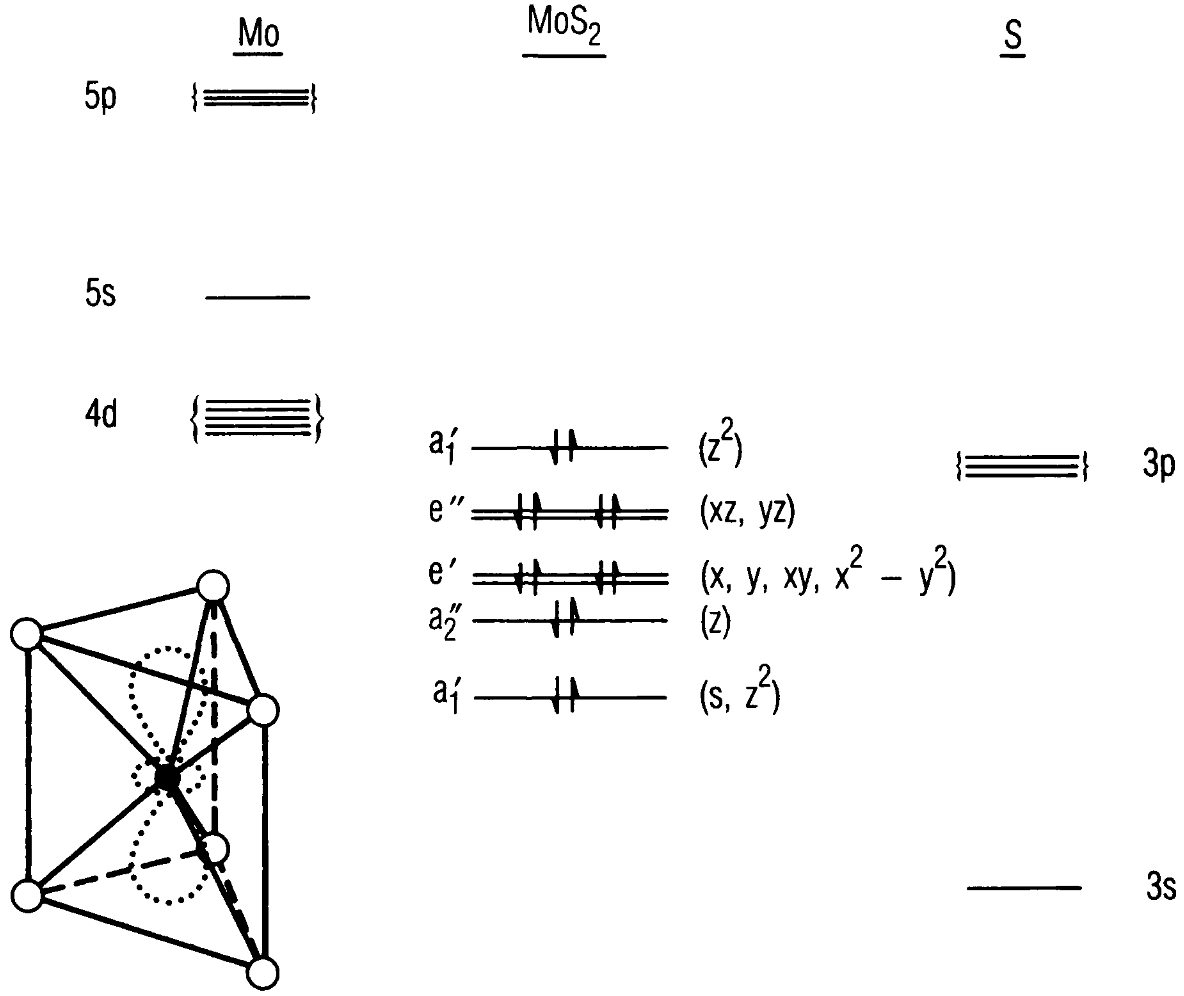


Fig. 7. MO energy-level scheme for MoS_2. See text for explanation of the ordering of the levels.

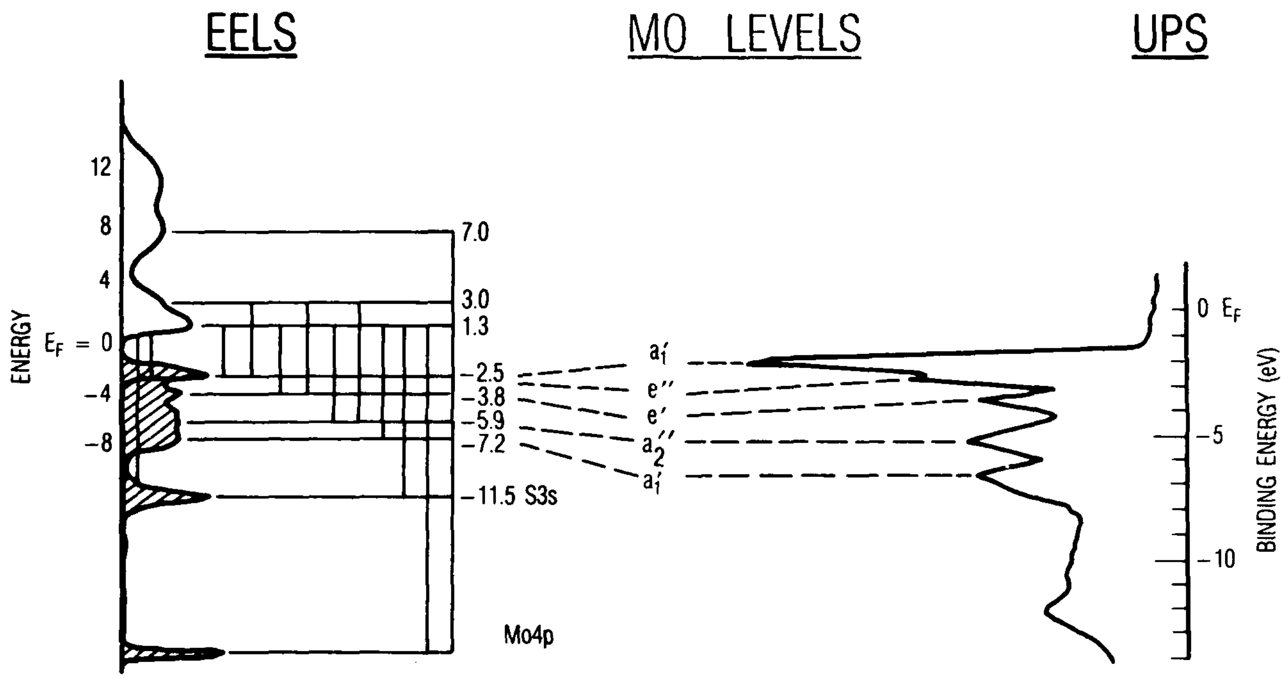


Fig. 8. Assignment of EELS and UPS peaks for $MoS_2(0001)$ with MO energy levels. The EELS diagram is of the density of states, from Ref. 11. The UPS spectrum, for He I excitation, is from Ref. 35.

sulfur surface atoms; the "lone pairs" of S 3s electrons occupy very stable orbitals and would not interact with adatoms. It is now obvious that the undisturbed {0001} basal surface of MoS_2 cannot form bonds or react unless its molecular orbital scheme is altered by physical or chemical manipulation.

One such manipulation is the creation of sulfur vacancies by ion bombardment. The MO model helps to understand the effects of ion bombardment and to predict the effects of other surface modifications as follows. First, the excellent correlation of the MO energy levels with the UPS-EELS data means that such spectroscopic measurements can be used to establish changes in the occupation of the MO levels. For example, if a sulfur atom were removed from the $Mo(S)_6$ trigonal prism and a sulfur vacancy created without the remaining $Mo(S)_5$ unit being reorganized (into another symmetry group), the net effect would be to remove electrons from the a_1' (essentially Mo d_z2) level. (The initial removal of sulfur valence electrons would be from lower bonding levels, but relaxation of these excited states then results in the holes being in the nonbonding a_1' level.) The requirement that the D_{3h} symmetry be maintained is easily met since the $Mo(S)_5$ unit is still part of the MoS_2 crystal. Depletion of electron density from the a_1' level then produces a preferential decrease in intensity of the uppermost peak in the UPS or EELS spectra. The results of ion bombardment of MoS_2(0001) as measured by EELS[32] and by UPS[35] are shown in Figs. 9 and 10, respectively. The relative intensities of the peaks, assigned as excitation of electrons from the a_1' level, decrease sharply when sulfur vacancies are created.

Adsorption of O_2 on a lightly bombarded surface further decreases the relative intensity of the a_1' peak in the UPS spectrum, whereas adsorption on the as-cleaved {0001} surface has no effect.[35] This result is similar to those reported in Ref. 38 for "poorly crystallized" MoS_2; Liang et al. interpret the decreased UPS peak intensity as being due to depletion of d_z2 electrons by the adsorbed O_2. Evidently, the d_z2 orbitals in the undisturbed surface of MoS_2 are shielded by the S atoms so that the O_2 molecules cannot withdraw the d electrons. The creation of defects, either by intentionally forming poor-quality crystals or by bombardment, provides sites where O_2 has access to these electrons. The adsorption of O_2 has relatively little effect

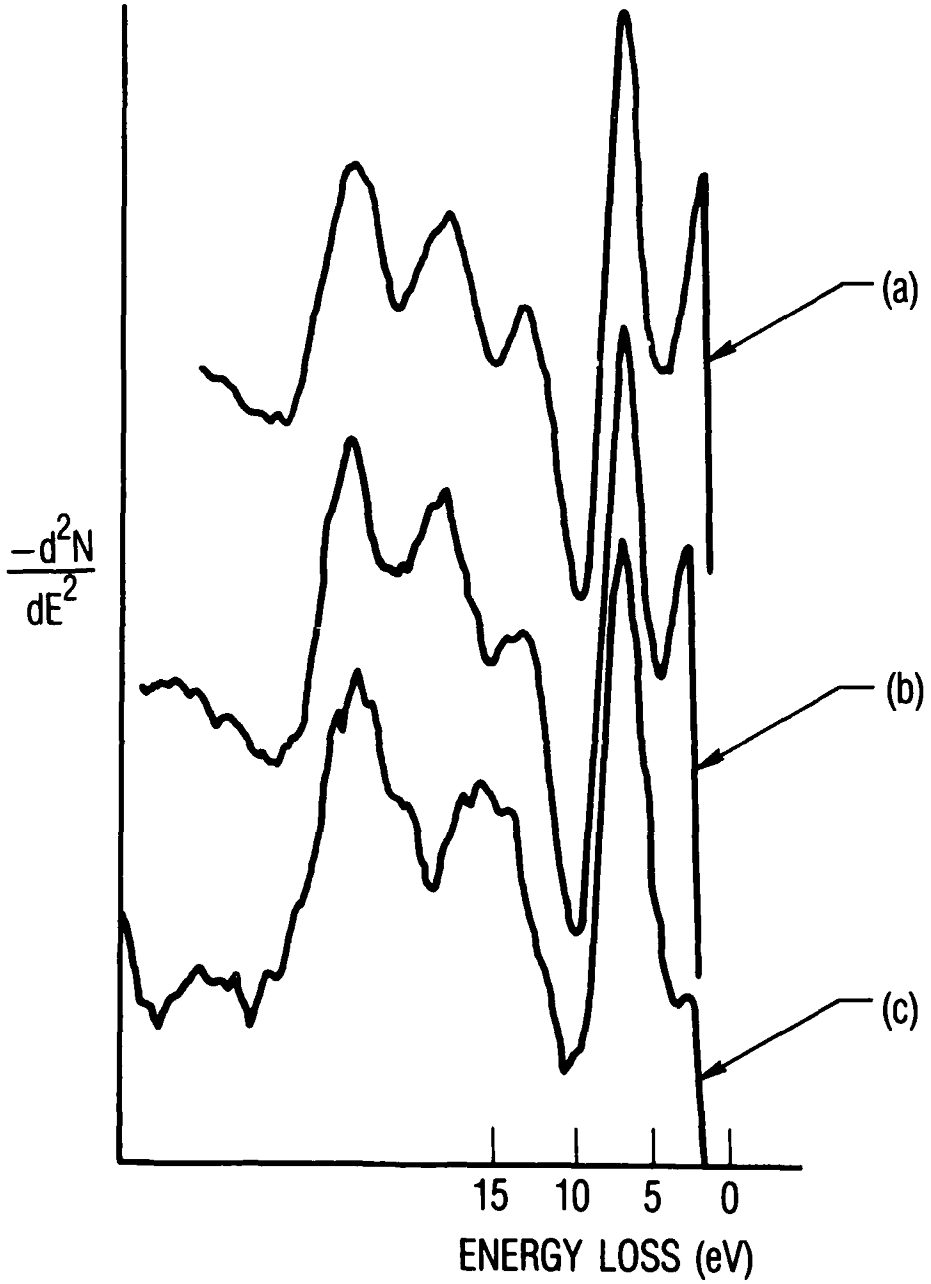


Fig. 9. Changes in EELS spectrum (primary electron beam energy, 500 eV) of $MoS_2(0001)$ as a function of Ne^+ ion (1 keV) bombardment (after Ref. 32): (a) initial cleaved surface, (b) 2×10^{14} ions cm^{-2}, (c) 1×10^{17} ions cm^{-2}.

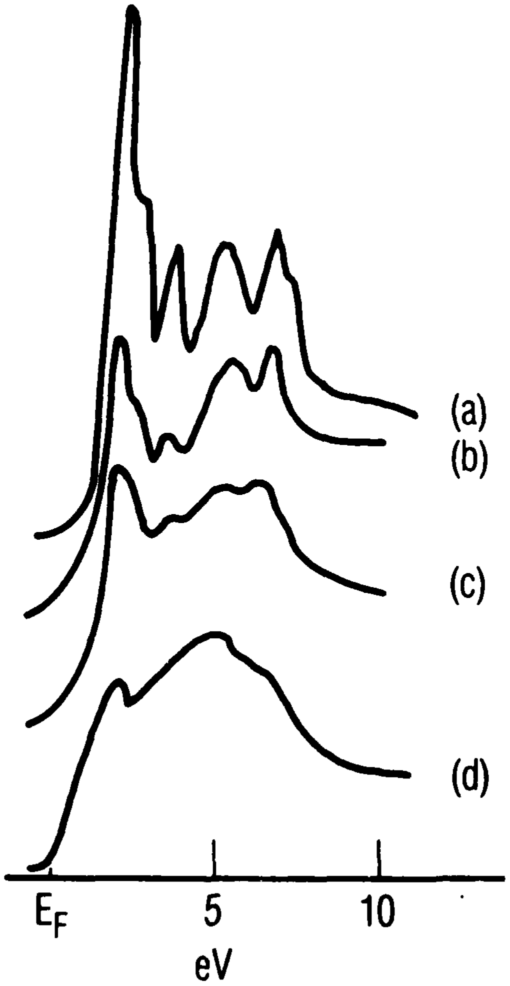


Fig. 10. Changes in UPS spectrum of $MoS_2(0001)$ as a function of N^+ ion (0.5 keV) bombardment (after Ref. 35; ion flux not given): (a) initial cleaved surface, (b) bombardment for 5 s, (c) bombardment for 10 s, (d) bombardment for 300 s.

on the primarily S 3p electrons that constitute the e' and a_2'' bonding MO levels.[35,38]

If the above results are to aid in designing interfaces to enhance adhesion between the MoS_2 {0001} surface and appropriate substrates, then perhaps bridge-bonding atoms must be incorporated into the MoS_2 plane; such atoms will interact with the Mo through the a_1' level but will not significantly disturb the surrounding sulfur atoms and related MO levels. The deposition of metals onto ion-bombarded MoS_2 {0001}, discussed earlier,[30,31] had a greater effect on the Mo 3d core levels than on the S 2p levels. Although UPS data are not yet available for metal deposition, the similarities among the earlier results suggest that metal atoms within the film-substrate interface region may provide the type of electronic interactions required to facilitate bonding. It would be intriguing to interpret the observed improvement in lubrication behavior of MoS_2 when various metals are deposited onto steel substrates prior to film growth[39] as being due to such bonding, but such an extrapolation is premature until specific interface studies are conducted.

The incorporation of substituent elements such as phosphorus or arsenic into the sulfur vacancies may benefit adhesion. Those elements have one less p electron in their valence shells compared to sulfur, providing holes in the a_1' MO level similar to those described below for $NbSe_2$ compounds. If substrate metal atoms donated electrons into the a_1' level through attachment to the phosphorus or arsenic substituents, improved film adhesion would result. (Incidentally, there appears to be no available data on the relative adhesive strengths of $NbSe_2$ and MoS_2 films, but an alternative method of improving MoS_2 adhesion may be to have an intervening layer of NbS_2.)

V. LUBRICATION PROPERTIES

The MO model can also be used to interpret differences in the effectiveness of various LTMDs as solid lubricants. $NbSe_2$, an LTMD with the 2H TP structure, is a poor lubricant in the pure state. It is converted into a good lubricant by intercalation with coinage metals.[2] The intercalates probably donate valence electrons into the orbital structure of the $NbSe_2$. Such intercalation reduces the conductivity of the host and eventually causes a change from semimetallic to semiconducting character.[40] In the context of the MO-level scheme, the pure $NbSe_2$ has a half-filled a_1' level that becomes filled on intercalation. Figure 11 depicts the influence of the half-filled d_z2 orbital on the registry and interlayer interactions of $NbSe_2$ and presents a diagram of MoS_2 with completely full MO levels for comparison. Even though $NbSe_2$ has the 2H TP structure, like MoS_2, the niobium atoms are aligned one over the other in adjacent sandwiches, whereas molybdenum atoms are aligned opposite sulfur atoms. The $NbSe_2$ alignment could either result from or provide for long-range interactions between the metal atoms, through the partially filled d_z2 orbitals; such interactions would increase the resistance toward sliding of adjacent sandwich layers (i.e., raise friction). Intercalation and filling of the orbitals converts the registry of the crystal into that of MoS_2 and also facilitates sliding, thus reducing friction.

The $NbSe_2$ example shows how a poor lubricant can be converted into a good one by having its electronic structure altered. The properties of an admittedly good lubricant, MoS_2, can also be manipulated by similar alterations. Possible effects on adhesion have already been discussed. The influence of electronic structure on both the crystal structure and friction of MoS_2 films can be determined from XRD data of the type shown in Fig. 3. The positions of the diffraction peaks provide a measure of the d-spacing between the planes of the crystal in a given crystallographic direction (see Fig. 6). Smaller diffraction angles correspond to larger d-spacings and vice versa. Sputter-deposited films are compressed in the edge directions, but they are expanded in the basal direction.[26]

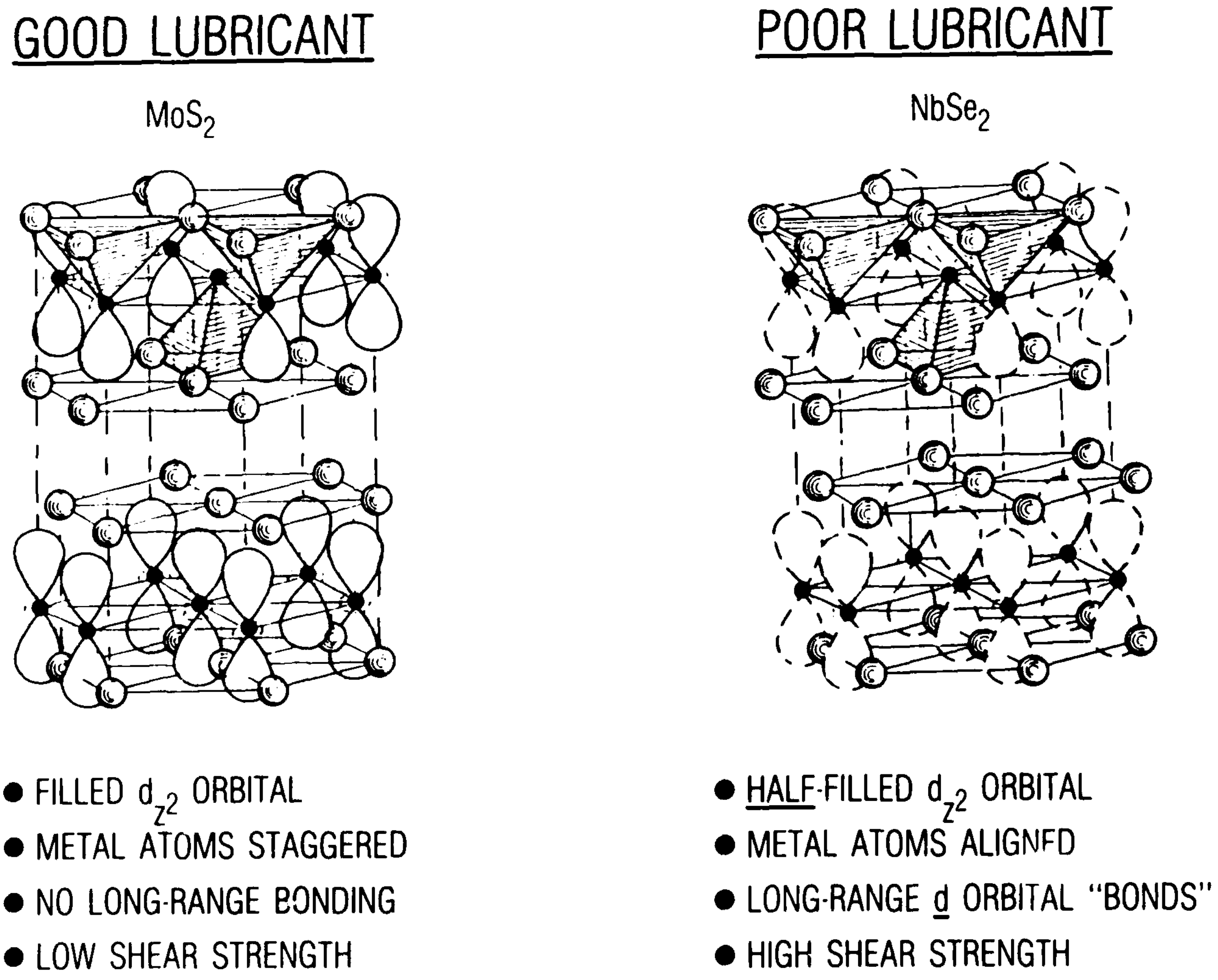


Fig. 11. Influence of d_{z^2} orbital (a_1' MO level) filling for MoS_2 and $NbSe_2$ on their structures and lubrication properties.

Partial oxidation of sputter-deposited MoS_2 to form Mo(VI), detected in XPS, causes the changes in the MoS_2 d-spacings, depicted in Fig. 12, for the <100> direction. The line through the open circles refers to films that are partially oxidized throughout their bulk during deposition, whereas the horizontal line represents films for which only surface oxidation occurred during storage in a humid atmosphere.

Oxidation of MoS_2 removes electron density from the molybdenum atoms and, specifically, from the a_1' MO level in Fig. 7. Depletion of electron density from this essentially nonbonding level, composed primarily of the Mo d_{z^2} orbital that protrudes between sulfur atoms, reduces repulsion within the sulfur atom plane so that the Mo-S-Mo bond angles become slightly smaller and the crystal contracts along the edge [<100> or <110>] directions. Such atom movement might simultaneously increase the spacing in the <001> direction, but confirming measurements have not been made except after the films have been rubbed. Expansion in the <001> direction of other LTMDs has been correlated with decreasing friction,[2] so one would expect that partially oxidized MoS_2 films would have slightly lower friction than very pure films, and there is some evidence that this is true.[41] Surface oxidation of MoS_2 films has little or no effect on their d-spacing or friction properties because the bulk layers are not affected.[42]

The above arguments pertaining to electron-density changes and atom movement when MoS_2 films are oxidized are exactly analogous to an explanation of the effect of intercalation of $NbSe_2$ with rubidium atoms as studied by extended x-ray absorption fine structure (EXAFS).[43] The intercalated material, wherein electrons were donated into the a_1' level, was observed to be compressed in the <001> direction and expanded in the <100> direction. There were no measurable changes in the Nb-S bond lengths, only variations in bond angles and in Nb-Nb separations. This is the exact reverse of the process described above, a fact that provides one with some confidence in our interpretations of lubrication behavior based on electronic structure arguments.

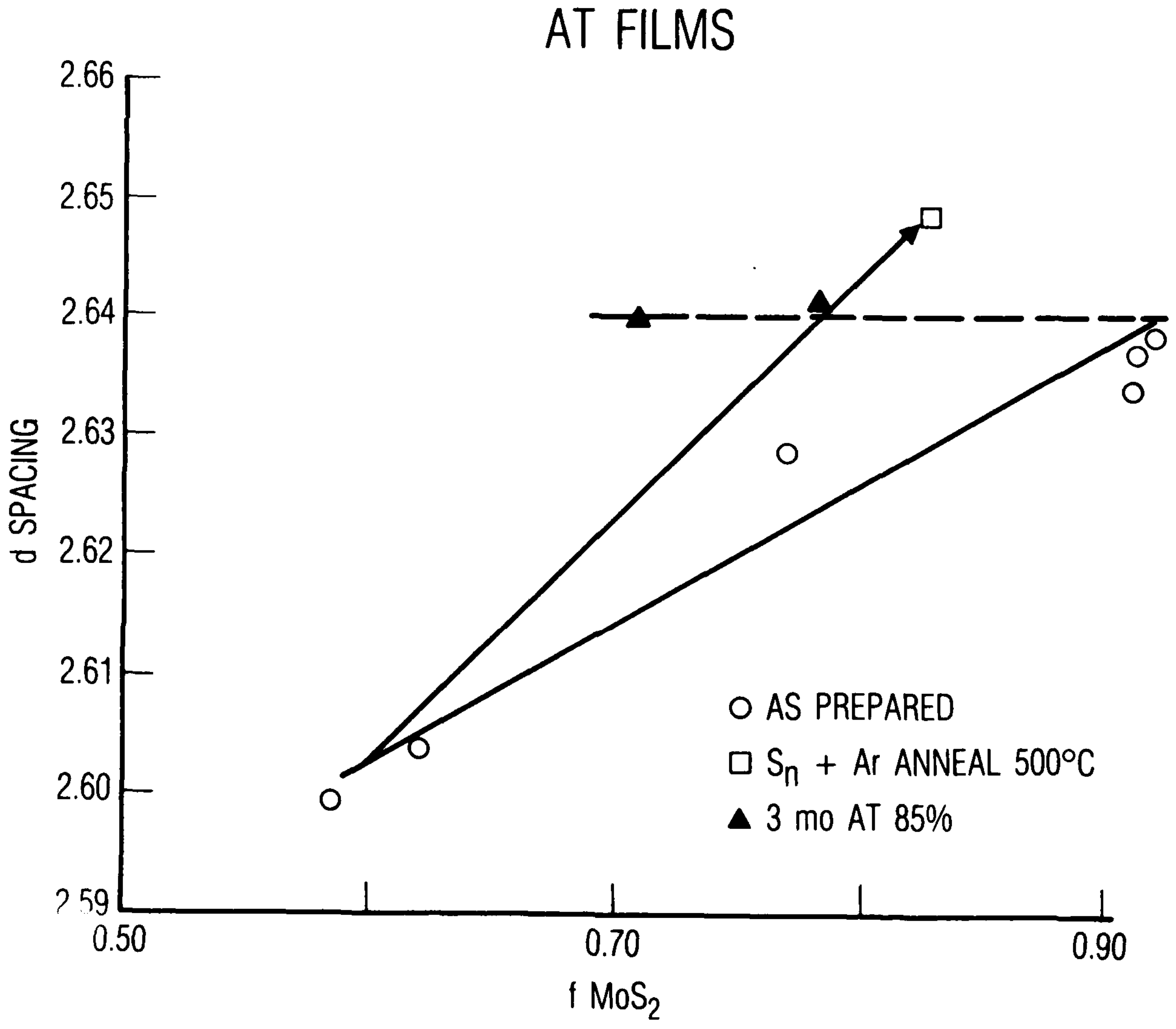


Fig. 12. Variation in crystallite d-spacing in the <100> direction for sputter-deposited MoS_2 films with the mole fraction of sulfide for a sulfide-oxide mixture: ○, as-prepared films that were oxidized through the bulk; ▲, surface-oxidized films; and □, bulk-oxidized film that was annealed in sulfur-argon gas.

VI. CONCLUSIONS

A schematic molecular orbital description of LTMDs has been detailed. It realizes the effect of the absence of π orbitals on the sulfur atoms and can be used to explain the available data on electronic transitions, variations in lubrication effectiveness of different LTMDs, and chemical and structural modifications to MoS_2 that alter the adhesion and friction properties of MoS_2. This model succeeds where rigid-band models have failed because it recognizes implicitly the covalent bonding within the sandwich layers of the LTMDs. The results of valence electron spectra measurements for MoS_2 agree excellently with the MO model predictions, thus providing a convenient means of checking further predictions. We propose that further refinement and application of this model will result in the ability to conduct materials engineering studies of LTMDs, and specifically of MoS_2, and will provide more effective lubrication performance for future demanding applications.

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