THE CANADIAN MINERALOGIST

Journal of the Mineralogical Association of Canada

Volume 25 SEPTEMBER 1987 Part 3

Canadian Mineralogist
Vol. 25, pp. 381-392 (1987)

ELECTRONIC STRUCTURE AND THE CHEMICAL REACTIVITY OF THE SURFACE OF GALENA

JOHN A. TOSSELL
Department of Chemistry, University of Maryland, College Park, Maryland 20742, U.S.A.

DAVID J. VAUGHAN
Department of Geological Sciences, Aston University, Birmingham, England, B4 7ET

ABSTRACT

The geometry of the galena surface and the electronic structure of the surface region as compared to the bulk in PbS are discussed using literature data, along with new calculations and spectroscopic measurements. The latter include calculations on a PbS_6^{10-} cluster using the MS-Xα method, valence-region X-ray photoelectron spectra and sulfur LMM Auger spectra of galena crystals. The available evidence suggests a model involving little or no relaxation of surface atoms but a reduction in the band gap at the surface (from ~0.4 eV in the bulk to ~0.1 eV). Pb or S vacant sites may produce holes in the valence band and bound states below the conduction-band edge, respectively. The considerable number of studies of the reactivity of the galena surface (oxidation in air and in aqueous media) are reviewed in the light of the above models. Oxygen chemisorption at the galena surface, in which the oxygen behaves very similarly to sulfur, appears to be an important mechanism in galena oxidation, modifying the electronic structure of the valence band at the surface and affecting conductivities and reaction rates. Although a consistent picture of the geometry and electronic structure of the (100) surface of galena is emerging, and of the important effects caused by nonstoichiometry, further calculations involving adsorbed species will be needed for a more complete understanding.

Keywords: galena, surface, electronic structure, reactivity, nonstoichiometry, conduction-band edge, chemisorption of oxygen, mechanism of oxidation.

SOMMAIRE

Les aspects géométriques de la surface de la galène et la structure électronique de cette région, en comparaison des propriétés globales du PbS, font l'objet d'une discussion critique, à la lumière de calculs et de mesures spectroscopiques nouveaux. On présente les résultats de calculs pour le groupement PbS_6^{10-} par la méthode MS-Xα, par spectroscopie photoélectronique des rayons X pour la région des valences, et par spectroscopie Auger pour le soufre dans des cristaux de galène. Les données disponibles indiquent un modèle qui implique très peu ou pas de relaxation des atomes à la surface, mais par contre une diminution dans l'écart entre les bandes, d'environ 0.4 eV dans le volume de PbS à environ 0.1 eV. Les lacunes dans les sites Pb ou S pourraient induire des trous dans la bande de valence et dans les états en liaison en-dessous de la limite de la bande de conduction, respectivement. On passe en revue les études nombreuses de la réactivité de la surface de la galène (oxydation dans l'air et dans les milieux aqueux) à la lumière des modèles cités. La chimiosorption à la surface de l'oxygène, qui se comporte de façon très semblable au soufre, semble être un mécanisme important de l'oxydation de la galène, en modifiant la structure électronique de la bande des valences et en affectant à la fois conductivité et taux de réaction. Quoiqu'un consensus à propos de la géométrie et de la structure électronique de la surface (100) et des effets importants de la non-stoechiométrie est en train de se dégager, des calculs plus poussés seront nécessaires pour mieux comprendre ces phénomènes.

(Traduit par la Rédaction)

Mots-clés: galène, surface, structure électronique, non-stoechiométrie, écart des bandes électroniques, chimiosorption d'oxygène, mécanisme d'oxydation.

INTRODUCTION

Galena, the major ore mineral of lead, has been extensively studied with regards to electronic structure because of its importance as a detector of infrared radiation. There have also been extensive studies of its solution chemistry because of the importance of hydrometallurgical processing, and of surface alteration effects because of relevance to flotation methods of mineral extraction. However, little attempt has been made to examine the relationship between electronic structure and the surface properties of galena. It is, therefore, timely to consider the properties of galena that depend on surface behavior in the light of the most recent models of its electronic structure.

In this paper, experimental and theoretical evidence for the arrangement of atoms at the surface of galena, and for the electronic structure of PbS in bulk and at the surface, is presented and discussed. Experimental data on the reactivity of the galena surface exposed to oxidation in air and aqueous media are briefly reviewed and discussed in the light of current views on electronic structure. The aim is to present preliminary observations on this complex topic and to emphasize the importance of a unified approach.

GEOMETRY OF THE SURFACE OF GALENA

Galena has the cubic rocksalt structure, with Pb in perfect octahedral co-ordination to S. It has also perfect cubic cleavage {100}, along the planes that break the smallest number of cation–anion bonds. It can, therefore, be assumed (as a first approximation) that the crystallographic surface of galena most likely to be exposed to attack is this (100) surface (or the equivalents). A simple model of this surface is shown in Figure 1, based on the work of Henrich (1983). Here the surface cations have 5-fold co-ordination [whereas for (110) and (111) surfaces the cation co-ordination is 4- and 3-fold, respectively]. In presenting this model of the perfect surface of galena, we have assumed no relaxation of the surface atoms. On the basis of experimental evidence (Kahn 1983), this appears reasonable for the more "ionic" sulfides, but not for more covalent species, such as ZnS (Duke 1983a).

We can also explain the lack of relaxation in PbS compared to the substantial relaxation observed in

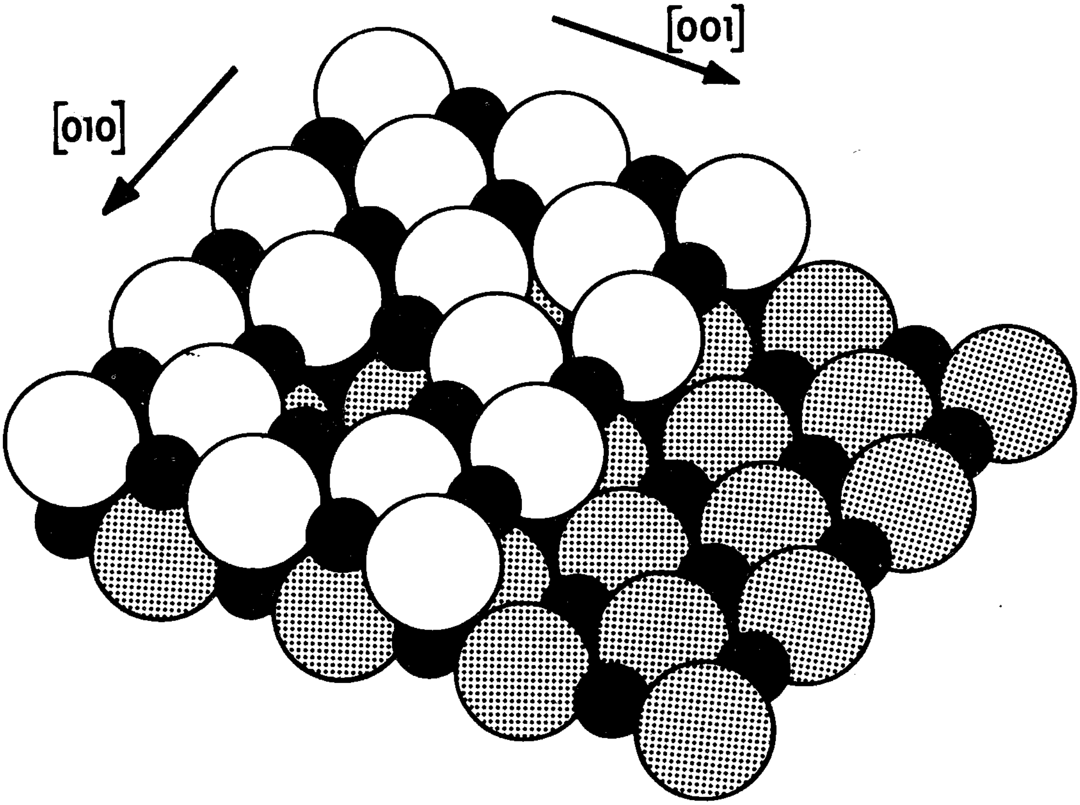

FIG. 1. Model of the galena (100) surface (after Henrich 1983). Large circles are S anions, and small circles are Pb cations. A {100} step to another (100) terrace is shown, as are both missing anion and missing cation point-defects.

ZnS (Duke 1983b) using qualitative molecular-orbital (MO) theory. In a covalent II–VI compound such as ZnS, the (110) surface is reconstructed with a movement of the Zn atoms inward (toward the bulk) and the S atoms outward. Harrison (1976, 1980) has explained this in terms of a conversion of half-occupied dangling-bond hybrid orbitals at both Zn and S on the reconstructed surface to a combination of a fully occupied bond-orbital on S and an unoccupied orbital on Zn for the reconstructed surface. The reconstruction stabilizes the orbital at S and converts it from sp^3 to s in type whereas the Zn orbital is destabilized and converted from sp^3 to sp^2. An equivalent description within the delocalized MO approach would relate the Zn site to a 6-valence electron AB_3 species, expected to be planar as in BH_3, and the S site to a 8-valence electron AB_3 species, expected to be pyramidal as in NH_3 (Burdett 1980, Tossell 1984). The degree of distortion will be dependent upon the change in energy of the surface orbital upon distortion in the angle B–A–B. This will depend partly upon the difference in electronegativity of the group-II and group-VI atoms, with a smaller electronegativity difference giving a larger degree of distortion from the unreconstructed geometry. Thus ZnS suffers a larger reconstruction than ZnO. This simple qualitative model is consistent with the results of accurate quantum-mechanical calculations (Swarts *et al.* 1980), which show for the GaAs surface a reconstruction that gives a geometry much like that of the corresponding trihydrides GaH_3 and AsH_3. An important aspect of this distortion is the stabilization of the A-centred highest occupied molecular-orbital (HOMO) of the electron-rich 8-electron AB_3 species by mixing with orbitals on B. If a geometrical reconstruction of the surface is unable to give this stabilization, then reconstruction will not be favored. For a sulfide with the rocksalt structure, we can con-

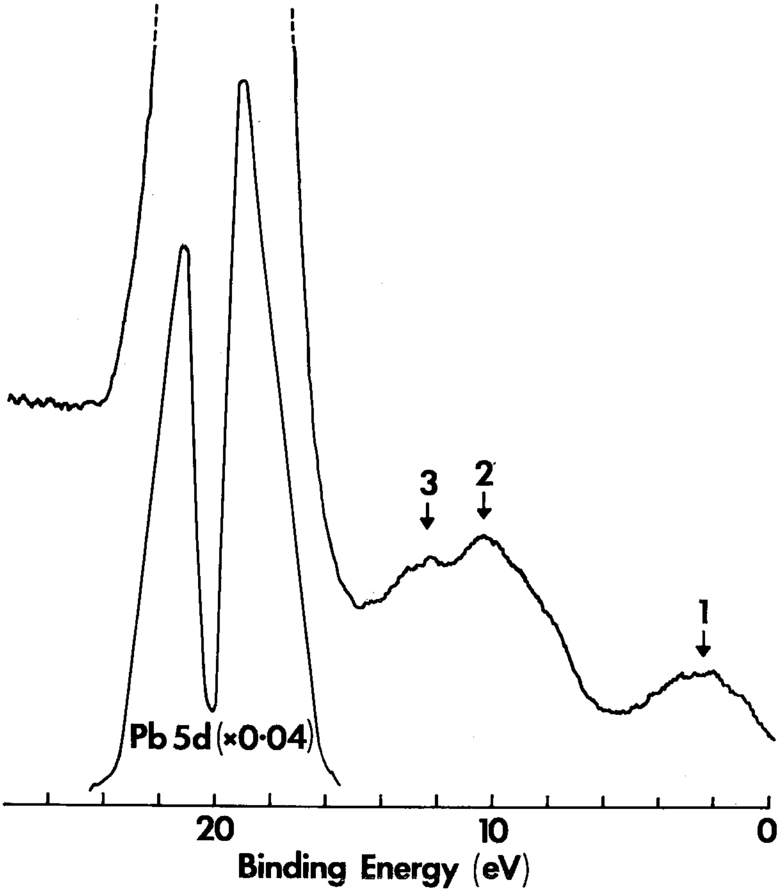

FIG. 2. X-ray photoelectron (XPS) spectrum of PbS obtained in the present study. Data were obtained from a natural crystal using a Kratos XSAM 800 instrument and Mg$K\alpha$ as the exciting radiation.

sider the geometry of S on the unreconstructed surface to be D_{4h} square pyramidal and consider the effect of moving the S inward to produce a D_{3h} trigonal bipyramid. Assuming a charge separation of M^+S^-, *i.e.*, converting the dangling bond-electrons on M and S into an empty orbital on M and a bond pair on S (as for ZnS above), we obtain the analogue of a 12-electron AH_5 species at S. However, such 12-electron AH_5 species are expected on qualitative MO grounds to be most stable in square-pyramidal geometries (Burdett 1980, p. 100-102). Thus covalent orbital mixing-factors do not favor reconstruction of the (100) surfaces of compounds having the NaCl structure, consistent with the lack of surface reconstruction in PbS.

The surface of the real material would contain numerous defect-sites and could never be modelled in detail. However, the simplest defects, namely those arising from removal of S or Pb atoms, can be considered. Removal of such surface atoms produces changes, for example in co-ordination and in the screening between cations, and in transfer of electrons to retain charge neutrality. A surface vacancy in an S site creates a symmetrical cluster of four four-fold co-ordinated cations in the surface plane below. A surface vacancy in a Pb site creates a symmetrical cluster of four sulfur anions in four-fold co-ordination to Pb and one again in five-fold co-ordination in the plane below (both kinds of defects are shown in Fig. 1).

Surface steps would be expected on cleaved surfaces of galena, and the most stable type would be a {100} step on the (100) surface as shown in Figure 1. The geometry of cations on the step edges is different from that on the perfect surface or at point defects. All step-edge cations have four-fold S co-ordination, but unlike the four-fold cations surrounding an S-vacancy, they are still well-screened from other cations. Similarly, of course, all step-edge anions are 4-co-ordinate.

ELECTRONIC STRUCTURE OF BULK PbS

The electronic structure of PbS in the bulk has been studied using a wide range of experimental techniques and theoretical models. Optical spectra were reported by Cardona & Greenaway (1964) and Schoolar & Dixon (1965), and high-resolution X-ray photoelectron spectra (XPS, which involves measuring the kinetic energies of electrons ejected by bombarding with monoenergetic X-rays), by McFeely *et al.* (1973). The theory and experimental methods of XPS have been extensively reviewed elsewhere (*e.g.*, Feuerbacher *et al.* 1978, Urch 1985). The XPS data obtained in the present study are shown in Figure 2. A Kratos XSAM 800 ESCA–Auger spectrometer was employed with Mg*K*α as the exciting radiation. The pressure inside the experimental chamber was $\sim 10^{-9}$ Torr. In line with the work of previous authors, the peak labeled 1 at the top of the valence band is interpreted to arise essentially from sulfur *p* orbital nonbonding molecular-orbitals. Below these lie the main bonding-orbitals of the system, which are chiefly lead 6*s*/sulfur 3*p* in character (peak 2); peak 3 represents sulfur 3*s* orbitals not involved in bonding. The intense (double) peak below this arises from the lead 5*d* orbitals.

In the present study, a calculation has been performed on a PbS_6^{-10} cluster unit using the MS–Xα method. This method, which has been applied to a variety of metal sulfide systems, has been well described with regards to general principles (Johnson 1973, Slater 1974) and applications to mineral systems (Vaughan *et al.* 1974, Sherman 1985). It involves selecting a "molecular" cluster unit (in this case Pb^{2+} surrounded by six S^{2-} at the corners of an octahedron); the space within and around the cluster then is geometrically partitioned into atomic sphere regions centred on the metal and anion nuclei, enclosed within an outer sphere, beyond which is an extramolecular region. Within the outer sphere but between atomic sphere regions is the interatomic region. The electrostatic potential of the remaining atoms in the crystal lattice is approximated by a spherical shell of positive charge (the Watson Sphere) passing through the anion nuclei. The potential energy in the various regions is evaluated electrostatically and then used to solve numerically the one-electron Schrödinger equation in each region. The resulting wave-functions and their first derivatives are joined continuously through the various regions using multiple-scattered-wave theory. From this result, the spatial distribution of electron density is calculated and used to generate a new potential for the next iteration. The entire procedure is repeated until self-consistency is attained; the result is a set of one-electron molecular orbitals characterized by their energies and distributions of electron density. The results of the calculation are shown in Figure 3 as an energy-level diagram. Here, molecular orbitals of the PbS_6^{10-} cluster are labeled according to the irreducible representations of the O_h symmetry group under which they transform. The (completely filled) lead 5*d* orbitals are calculated to lie ~21 eV below the valence band, in good agreement with the results of XPS studies. The orbitals with eigenvalues around −12 eV are essentially S 3*s* nonbonding orbitals. The main bonding-orbitals of the system with appreciable lead and sulfur character are the a_{1g}, t_{1u}, t_{2g} and e_g orbitals, which lie directly above these in energy. At the top of the valence band lie a group of orbitals of t_{2u}, t_{1u} and t_{1g} symmetry, closely spaced in energy, that are essentially S 3*p* nonbonding orbitals, with relatively little metallic character. However, the topmost filled orbital is antibonding and does have appreciable lead (Pb 6*s*) character.

The empty orbitals above this in energy (of t_{1u}, t_{2g} and a_{1g} symmetry) are antibonding orbitals with appreciable lead and sulfur character. The neglect of relativistic effects in this calculation leads to exaggeration of the separation between the topmost filled orbital and remaining filled orbitals, and of the stabilization of the Pb 5*d* levels. Relativistic effects can be estimated from calculations on the free lead atom, data for which are shown in Table 1. These will stabilize the a_{1g} highest occupied MO (predominantly Pb 6*s* in character) by about 2.86 eV, bringing it close to the e_g and t_{1g} occupied levels. The t_{2g} and e_g levels of Pb 5*d* character will be stabilized by about 4.1 eV.

Further improvement in the correspondence between calculated and measured energy-levels is achieved by making use of the transition-state procedure (Slater 1974), in which an electronic configuration halfway between the initial and final states is iterated to self-consistency. When this procedure, which takes into account any orbital relaxation that occurs during the transition, is utilized, the effect is to increase the relative ionization-potentials of highly contracted levels, such as the metal *d* levels, compared to less localized levels, such as the ligand *p* levels. Taking these considerations into account, the results of this calculation are generally in good agreement with the data from XPS studies outlined above.

Amongst other calculations of the electronic structure of PbS in bulk can be mentioned the band-structure calculations of Herman *et al.* (1968) and of Tung & Cohen (1969), which are based on the OPW method, and the larger MS–Xα cluster calculations of Hemstreet (1975). The overall electronic structure of bulk PbS based on these calculations (and on experimental data) is illustrated in Figure 4. It again shows that in PbS, a topmost (filled) band in the valence region is dominantly S 3*p* nonbonding in character and lies above a band comprised of the main bonding-orbitals of the system, with Pb 6*s*–S 3*p* character. More deeply buried are the nonbonding S 3*s* levels and (at ~20 eV binding energy) the Pb 5*d* orbitals. A gap of around 0.4 eV separates the top of the valence band from the conduction band of largely Pb 6*s* – S 3*p* antibonding character.

ELECTRONIC STRUCTURE OF PbS SURFACES

Several spectroscopic studies have been undertaken that provide information on the electronic structure of a "clean" cleavage-surface of PbS. Grandke & Cardona (1980) studied the UV photoemission of a (100) surface of both *n*- and *p*-type PbS, and Grandke *et al.* (1979) used angle-resolved UV photoemission to study temperature effects on the valence-band levels in PbS. Both UV and soft X-ray photoemission were used to examine core and valence-band spectra by Hagström & Fahlman (1978).

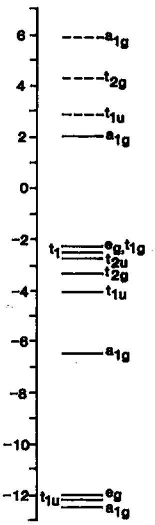

FIG. 3. Molecular orbital energy-levels calculated for a PbS_6^{10-} cluster using the MS–Xα method. Molecular orbitals are labeled according to the irreducible representations of the O_h symmetry group with filled orbital energy-levels shown as solid lines, empty as dashed lines.

Auger electron spectroscopy is one of the most widely employed spectroscopic methods in surface studies (e.g., Carlson 1975, Lichtman *et al.* 1981). It involves the decay of an initial core-orbital hole (formed by X-ray bombardment) by a process in which a higher-energy electron drops into the core hole, and the resultant energy, rather than being emitted as X-rays (as in X-ray emission spectroscopy), is transferred to a second higher-energy electron, the Auger electron, which is ejected. In the present work, the S_{LMM} Auger spectra of clean surfaces of galena have been examined. In Figure 5 are shown the differentiated spectrum and a computer fit of three peaks of the undifferentiated spectrum, at kinetic energies of 140, 145.2 and 145.9 eV, respectively. The widths and normalized intensities of these features are also given in Figure 5. Comparison with the X-ray photoelectron spectrum (Fig. 2) and the results of calculations described and illustrated above (Figs. 3, 4) suggest that the peaks at 149.5, 145.2 and 140 eV arise from the sulfur 3*p* nonbonding orbitals, lead 6*s* – sulfur 3*p* bonding orbitals and the dominantly sulfur 3*s* nonbonding orbitals, respectively.

In his review of transition-metal-oxide surfaces, Henrich (1983) noted, on the basis of experimental evidence and calculations, that the electronic structure of five-fold co-ordinated surface cations is very similar to that of bulk cations in $SrTiO_3$ and TiO_2. Comparison of the spectroscopic evidence noted above with calculations of the electronic structure of bulk PbS also suggests that the changes are small.

TABLE 1. RELATIVISTIC EFFECTS ON THE ATOMIC ORBITAL ENERGIES OF THE FREE LEAD ATOM

Pb Atomic orbital	Nonrelativistic[a]	Relativistic (average)[b]	Difference
5p	98.33	103.50	5.17
5d	33.32	29.24	-4.08
6s	12.51	15.37	2.86

a. Data from Mann (1967).
b. Data from Desclaux (1973).

However, calculations by Tsukada *et al.* (1983) using the DV-Xα cluster method to model the electronic structure of the surface of MgO (a phase isostructural with PbS) did show some significant differences (see Fig. 6). Compared with an $(MgO_6)^{10-}$ cluster used to model the electronic structure of bulk MgO, the five-co-ordinate surface-species cluster $(MgO_5)^{8-}$ showed the (full) valence-region levels (largely O 2*p* in character) to be shifted to higher energy and substantial shifts to occur in the (largely Mg 3*s*, 3*p*) empty levels, which overlie them. The remarkable lowering of the 11_{a1} level can be explained by the distortion due to the surface field. Because of the field normal to the surface, the Mg 3*s* and 3*p* orbitals are admixed to form the $(3s + 3p_z)$-like 11_{a1} level and the $(3s-3p_z)$-like 12_{a1} levels. Since the potential decreases toward vacuum, the energy of the 11_{a1} level is considerably depressed, and that of 12_{a1}, raised. The effect is, therefore, to substantially reduce (by ~2 eV) the gap between highest-energy filled and lowest-energy empty levels. This prediction for the electronic structure of a clean MgO (100) surface is supported by experimental evidence from electron-energy-loss spectroscopy (see Tsukada *et al.* 1983).

By analogy of the work done on MgO (100) surfaces, the electronic structure of the perfect PbS (100) surface might be expected to show similar differences to that of the bulk. Hence the dominantly Pb 6*s*, 6*p* conduction levels would be expected to be lowered in energy relative to the top of the valence band, leading to a reduction of the band gap. This is also in accordance with arguments put forward by Levine & Mark (1966) on electrostatic grounds, which predict a narrowing of the gap at the surface in such compounds.

Experimental evidence bearing on differences in the electronic structure of bulk and (100) surfaces of PbS is provided by Grandke & Cardona (1980). From the study of the binding energies of core levels using UV photoemission spectroscopy, they have suggested a reduction in the band gap from 0.4 eV in the bulk to less than 0.1 eV at the surface for freshly cleaved specimens examined in vacuum. These authors also observed changes in the spectra of PbS held under vacuum for 3 hours; they attributed these changes to the development of a sur-

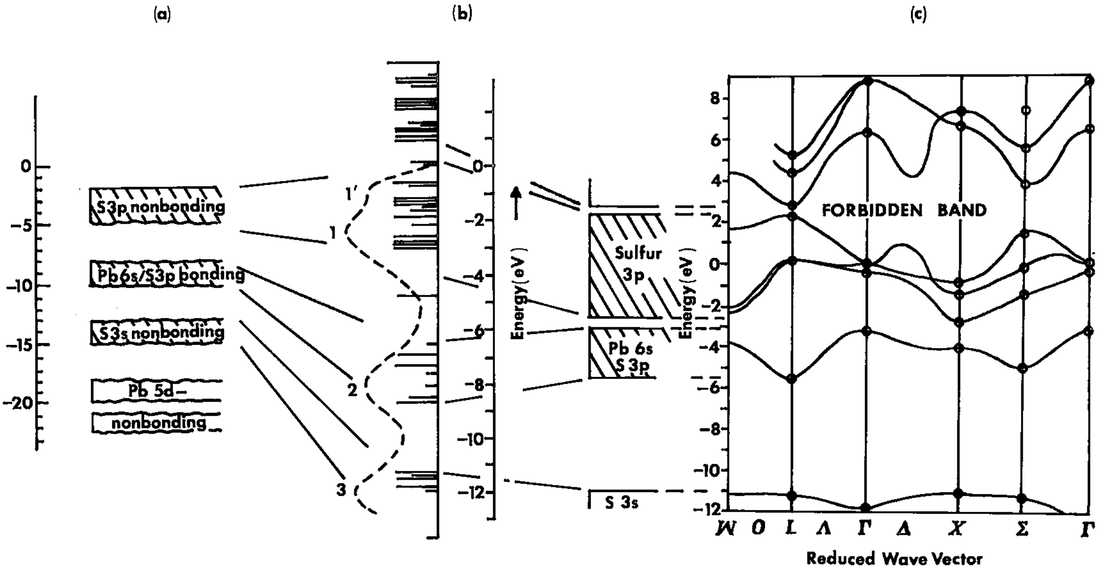

FIG. 4. Electronic structure models for galena: (a) simplistic band-structure representation based on spectroscopic data; (b) molecular orbital energy-levels calculated for a $SPb_6S_{12}Pb_8$ cluster using the MS-Xα method (after Hemstreet 1975) and with features from the X-ray photoelectron spectrum of PbS superimposed; (c) band-structure model for PbS calculated by the OPW method (after Tung & Cohen 1969).

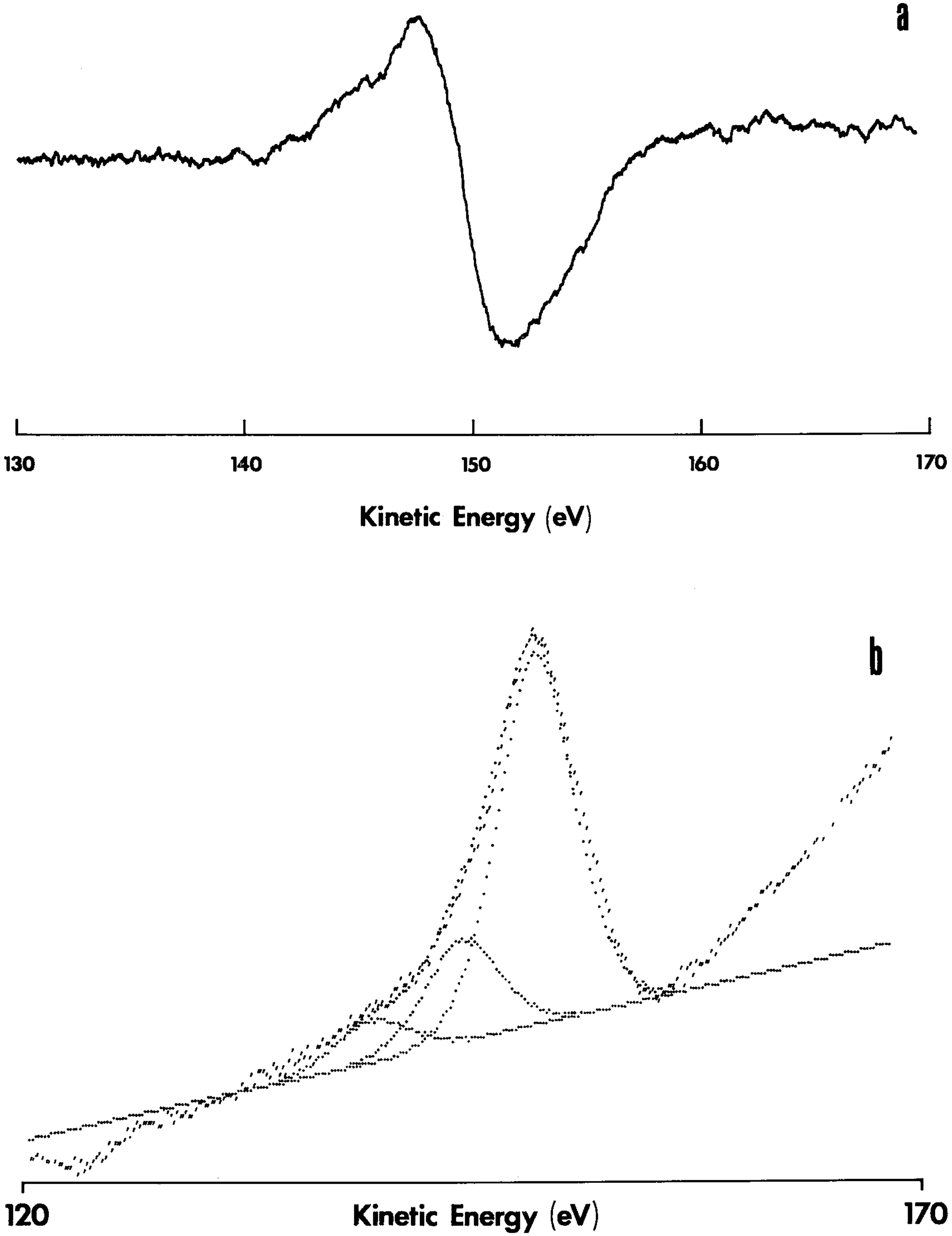

FIG. 5. Sulfur LMM Auger electron spectra of PbS obtained from a natural specimen of high purity: (a) differentiated spectrum; (b) undifferentiated spectrum showing computer fit of the data points (dashes) to three-component peaks (dots) at 140, 145.2 and 149.5 eV, respectively. Data were obtained using a Kratos XSAM 800 instrument.

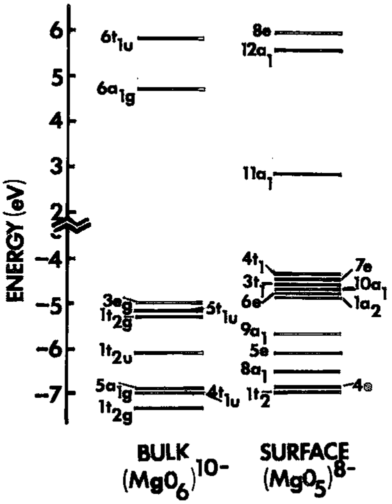

FIG. 6. Energy levels for MgO_6^{10-} and MgO_5^{8-} clusters from DV–Xα calculations (after Tsukada *et al.* 1983).

face showing *n*-type conduction, in turn attributed to loss of sulfur from the surface and a resulting excess of lead atoms.

With regards to the more complex questions of the electronic structure associated with defects, and in particular with Pb or S vacant sites, the calculations of Hemstreet (1975) provide some information of relevance. In the case of a lead vacancy, each vacancy produces two holes in the valence band, producing a *p*-type sample; there appears to be no localization of charge about the vacancy site. A sulfur vacancy, according to the work of Hemstreet (1975), produces a bound state below the conduction-band edge, the two electrons associated with the sulfur vacancy being localized to within a lattice constant or so of the defect site.

REACTIVITY OF THE GALENA SURFACE

A large number of studies of reactions at the surface of galena has been undertaken, most notably of oxidation in air and in aqueous media, because of its relevance to extraction methods involving flotation and leaching. The results of these studies are summarized in Table 2; the discrepancies arise partly from the problems of accurately characterizing small quantities of surface species (particularly in the early work) and possible variability of the stoichiometry of the galena.

However, particularly bearing in mind the greater sensitivity of the modern methods of surface analysis, certain conclusions can be drawn. The first is that the major product of the oxidation of galena in air (at lower temperatures) and in aqueous media is $PbSO_4$ (Steger & Desjardins 1980, Manocha & Park 1977). There is evidence, however, that the initial step of oxidation may differ from the major step and involve the formation of PbO and S. Manocha & Park (1977) concluded that lead-rich sulfides initially undergo oxidation of Pb and PbO through chemisorption of oxygen (followed by slow adsorption of hydroxyl ions from the atmospheric environment). As also found in the work of Eadington & Prosser (1969), oxidation was initially much slower in lead-rich samples than in sulfur-rich samples of galena.

In the X-ray and UV photoelectron spectroscopic studies of Evans & Raftery (1982), involving both reactive oxygen species and normal air as media, it was concluded that oxygen atoms attack (100) surfaces of galena at Pb and probably also at S sites (and not only at defects). PbO species then form, whilst substantial quantities of S are lost from the surface, but some elemental S remains trapped at the interface between the PbS and its oxidation products. Sulfate species are also formed, and the sulfate and oxide coexist in an unstructured layer (which may also contain other species such as hydroxide). Oxidation in air was found to give similar products, but at much slower rates of reaction. There was no evidence for thiosulfate formation under any of the conditions studied.

Buckley & Woods (1984a, b) used X-ray photoelectron spectroscopy to study the oxidation of galena and also reviewed some of the earlier spectroscopic studies of galena oxidation. As well as confirming that lead sulfate is the product of exposure of galena to air for extended periods, they noted other changes during the first few days of exposure. It was proposed that air-oxidation results initially in lead becoming concentrated at the surface, where it is present as lead oxide and hydroxide (and subsequently as carbonate, basic sulfate and sulfate). Formation of the oxides, it was concluded, must be associated with the development of a metal-deficient layer of lead sulfide.

In their detailed study of the oxidation of PbS in aqueous media, Eadington & Prosser (1969) proposed an electrochemical model for the oxidation of galena in aqueous suspensions, with anodic reaction of the lead sulfide:

$$PbS \rightarrow Pb^{2+} + S + 2e^-$$

and a corresponding cathodic reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

This pair of reactions was determined as the major step in the reaction and was preceded by an induction period, during which oxygen is rapidly chemisorbed from solution, with transfer of electrons

TABLE 2. STUDIES ON THE OXIDATION OF PbS

Medium and Conditions	Oxidation Products	Method of Characterization	Reference
Air; 200°C	$PbSO_4$	Electron Diffraction	Hagihara (1952)
Air	PbO+S	Chemical + X-ray	Reuter & Stein (1957)
Moist Air	$PbS_2O_3.PbO$		
Air; 100-400°C	$PbSO_4$		
Air; 400°C	$PbSO_4.PbO$		
Air	$\underline{PbSO_4} + PbSO_3 + PbS_4O_6$	Infrared	Greenler (1962)
Air	PbS_2O_3	Infrared	Poling & Leja (1963)
Acid aqueous	$\underline{S} + PbSO_4$	Wet chemical analysis	Eadington & Prosser (1969)
Neutral aqueous	$S + \underline{PbSO_4}$		
Alkaline aqueous	$\underline{PbS_2O_3} + PbSO_4 + PbS_4O_6$		
Air and aqueous media (varying pH)	$\underline{PbSO_4}$ + minor S initially; Pb-rich PbS gives some PbO	XPS	Manocha & Park (1977)
Neutral or Alkaline aqueous	PbO + S (also some thiosulfate from the S)	Electrochemical	Gardner & Woods (1979)
Moist air	$PbSO_4$	Wet chemical analysis	Steger & Desjardins (1980)
Air	$PbSO_4$	XPS	Brion (1980)
Reactive oxygen (also air)	PbO + S + $PbSO_4$	XPS	Evans & Raftery (1982)
Air (ambient temp. and humidity)	Initially PbO, $Pb(OH)_2$ then $PbCO_3$, $PbSO_4$, $PbsQ_4$ Ultimately $PbSO_4$	XPS	Buckley & Woods (1984a,b)
Air-saturated acetic acid	Evidence observed for metal polysulfides	XPS	Buckley & Woods (1984a,b)
Aqueous [$+H_2O_2$]	Initially $Pb_{1-x}S$ [$+H_2O_2$ decomposition — elemental S] $PbSO_4$. Minor elements conc. at surface	XPS	Buckley & Woods (1984a,b)
Anodic oxidation	Initially $Pb_{1-x}S$ At low pH lead hydroxide — elemental S and S-oxygen species	Electrochemical and XPS	Buckley et al. (1985)

from the PbS. In the overall reaction described above, transfer of electrons from the PbS leaves (positive) holes; this also corresponds to the breaking of a Pb–S bond and results in S remaining at the surface, with Pb^{2+} going into solution. It can also be regarded as development of a *p*-type surface on the galena. The subsequent reactions leading to the final products of oxidation (Table 2) depend on the pH of the solution, with major sulfur plus sulfate under acid conditions, sulfate and some sulfur at neutral pH, and formation of thiosulfates under alkaline conditions.

Eadington & Prosser (1969) also studied the effects of varying extent of nonstoichiometry on the aqueous oxidation of PbS and the action of light on reaction rates. The oxidation of sulfur-rich galena was found to take place more rapidly than that of lead-rich samples, which was in turn a more rapid reaction than for stoichiometric PbS. Visible light had the effect of reducing the steady rate of oxidation but had no effect on the induction period or products of reaction. The leaching of galena by nitric acid, on the other hand (Eadington 1973), was enhanced during the initial stages by the action of UV–visible light.

Studies of chemisorption, particularly of oxygen, on the surface of PbS are clearly of interest with regards to an understanding of surface reactivity. Hagström & Fahlman (1978) studied the interaction of oxygen with the lead chalcogenides using UV and

X-ray photoelectron spectroscopy. They proposed that oxygen exposed in moderate amounts (as O_2 gas) to the PbS surface interacted only weakly with that surface, being "physisorbed" rather than chemisorbed. They further suggested a relationship between surface reactivity and the "ionicity" of the material, with the most ionic phase (PbS) showing the least reactivity, and PbSe and PbTe surfaces being successively more reactive.

Grandke & Cardona (1980), in their UV-photoelectron studies of the position of the Fermi level at the (100) surface of *n*- and *p*-type PbS, claimed to have a more sensitive technique for determining changes in surface chemistry than that used by Hagström & Fahlman (1978). They interpreted measured shifts in the Fermi level as due to oxygen atoms occupying vacancies in the surface layer left by evaporation of sulfur atoms, a process that occurs under vacuum and leads to an *n*-type surface. These oxygen atoms, therefore, restore the surface to a quasi-stoichiometric state and appear to be about as tightly bound as the sulfur atoms at the surface.

DISCUSSION

It has been suggested here that the surface geometry of a cleavage face of PbS can, for an ideal crystal, be modeled in a simple way without recourse to deformation of the surface atoms due to relaxation. The predominantly occuring 5-fold co-ordination site would nevertheless lead to a reduction in the band gap at the surface of the galena; this is supported by experimental evidence (Grandke & Cardona 1980), evidence that also lends support to this simple general model of surface geometry.

Oxidation studies, both in air and in aqueous solution, provide evidence for the occurrence of oxygen chemisorption onto the surface of galena. Spectroscopic evidence suggests that oxygen at the surface behaves very similarly to sulfur (Grandke & Cardona 1980). The transfer of electrons, which would be associated with oxygen chemisorption, should generate positive holes in the valence band (*i.e.*, *p*-type conduction and, hence, a *p*-type surface). Calculations (Hemstreet 1975) suggest that these holes are delocalized and would enhance conductivities, and therefore reaction rates, in the essentially electrochemical process of oxidation in aqueous solution. This delocalization also accounts for the more rapid rate of reaction for S-rich galena observed in experimental systems (Eadington & Prosser 1969). The sulfur vacancies present at the surface of Pb-rich galena apparently produce localized electron-states (Hemstreet 1975) not conducive to rapid rates of reaction. Presumably the vacant sites would also become occupied by oxygen chemisorbed into them and thereby approach the more stable quasi-stoichiometric condition (and also the least reactive state).

The action of visible light on the system would cause a change in the electron–hole distribution, which may also be akin to producing a quasi-stoichiometric condition (Eadington & Prosser 1969), and hence its effect in slowing down the oxidation reaction. The opposite effect, that of enhancing reactivities, which was observed in the leaching of illuminated lead sulfide with nitric acid (Eadington 1973), must again arise from changes in the electron-hole distribution in the valence-band region.

Thus a consistent picture is emerging of the geometry and electronic structure of the (100) surface of galena and of the overall effects produced by nonstoichiometry. Certain of the controls influencing the nature and rate of surface oxidation are evident. A more complete picture will depend upon further calculations involving distorted clusters and absorbed species.

ACKNOWLEDGEMENTS

This work was undertaken with the support of NATO (Research Grant No. 833/83). Mr. J. Sullivan and Mr. A. Abbott (Dept. of Mathematics and Physics, Aston University) are thanked for help and advice in obtaining XPS and Auger spectra. Mrs. C. Gee and Ms. S. Knox are thanked for help in preparation of the manuscript and illustrations.

REFERENCES

BRION, D. (1980): Photoelectron spectroscopic study of the surface degradation of pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS) in air and water. *Applic. Surf. Sci.* **5**, 133-152.

BUCKLEY, A.N., HAMILTON, I.C. & WOODS, R. (1985): Investigation of the surface oxidation of sulfide minerals by linear potential sweep voltammetry and X-ray photoelectron spectroscopy. *Dev. Mineral Processing* **6**, 41-60.

______ & WOODS, R. (1984a): An X-ray photoelectron spectroscopic study of the oxidation of galena. *Applic. Surf. Sci.* **17**, 401-414.

______ & ______ (1984b): An X-ray photoelectron spectroscopic investigation of the surface oxidation of sulfide minerals. *Proc. Electrochem. Soc.* **84**, 286-302.

BURDETT, J.K. (1980): *Molecular Shapes: Theoretical Models of Inorganic Stereochemistry.* Wiley-Interscience, New York.

CARDONA, M. & GREENAWAY, D.L. (1964): Optical properties and band structure of Group IV–VI and Group V materials. *Phys. Rev.* **A133**, 1685-1697.

CARSLON, T.A. (1975): *Photoelectron and Auger Spectroscopy*. Plenum Press, New York.

DESCLAUX, J.P. (1973): Relativistic Dirac-Fock expectation values for atoms with Z = 1 to Z = 120. *Atomic Data and Nuclear Tables* **12**, 311-406.

DUKE, C.B. (1983a): Structural chemistry of the cleavage faces of compound semiconductors. *J. Vac. Sci. Tech.* **B1**, 732-735.

______ (1983b): Atomic geometries of semiconductor surfaces: determination and relation to chemical bonding. *Adv. Ceram.* **6**, 1-14.

EADINGTON, P. (1973): Leaching of illuminated lead sulphide with nitric acid as a function of the solid state electronic properties. *Trans. Inst. Mining Metall.* **C82**, 158-161.

______ & PROSSER, A.P. (1969): Oxidation of lead sulphide in aqueous suspensions. *Trans. Inst. Mining Metall.* **C78**, 74-82.

EVANS, S. & RAFTERY, E. (1982): Electron spectroscopic studies of galena and its oxidation by microwave-generated oxygen species and by air. *J. Chem. Soc., Faraday Trans.* **I 78**, 3545-3560.

FEUERBACHER, B., FITTON, B. & WILLIS, R.F. (1978): *Photoemission and the Electronic Properties of Surfaces*. Wiley-Interscience, Chichester, England.

GARDNER, J.R. & WOODS, R. (1979): A study of the surface oxidation of galena using cyclic voltammetry. *J. Electroanal. Chem. Interfacial Electrochem.* **100**, 447-459.

GRANDKE, T. & CARDONA, M. (1980): Electronic properties of clean and oxygen covered (100) cleaved surfaces of PbS. *Surf. Sci.* **92**, 385-392.

______, ______ & LEY, L. (1979): Temperature effects on valence bands in semiconducting lead chalcogenides. *Solid State Comm.* **32**, 353-356.

GREENLER, R.G. (1962): An infrared investigation of xanthate absorption by lead sulfide. *J. Phys. Chem.* **66**, 879-883.

HAGIHARA, J. (1952): Surface oxidation of galena in relation to its flotation as revealed by electron diffraction. *J. Phys. Chem.* **56**, 610-615.

HAGSTRÖM, A.L. & FAHLMAN, A. (1978): The interaction between oxygen and the lead chalcogenides at room temperature studied by photoelectron spectroscopy. *Applic. Surf. Sci.* **1**, 455-470.

HARRISON, W.A. (1976): Surface reconstruction on semiconductors. *Surf. Sci.* **55**, 1-19.

______ (1980): *Electronic Structure and the Properties of Solids*. W.H. Freeman & Co., San Francisco, California.

HEMSTREET, L.A., JR. (1975): Cluster calculations of the effects of single vacancies on the electronic properties of PbS. *Phys. Rev.* **B11**, 2260-2270.

HENRICH, V.E. (1983): The nature of transition-metal oxide surfaces. *Prog. Surf. Sci.* **14**, 175-200.

HERMAN, F., KORTUM, R.L., OUTENBURGER, I.B. & VAN DYKE, J.P. (1968): Relativistic band structures of GeTe, SnTe, PbTe, PbSe and PbS. *J. Phys. (Paris)* **29**, C4, 62-77.

JOHNSON, K.H. (1973): Scattered wave theory of the chemical bond. *Adv. Quantum Chem.* **7**, 143-185.

KAHN, A. (1983): Semiconductor surface structures. *Surf. Sci. Rep.* **3**, 193-300.

LEVINE, J.D. & MARK, P. (1966): Theory and observation of intrinsic surface states on ionic crystals. *Phys. Rev.* **144**, 751-763.

LICHTMAN, D., CRAIG, J.H., JR., SAILER, V. & DRINKWINE, M. (1981): AES and XPS spectra of sulfur in sulfur compounds. *Applic. Surf. Sci.* **7**, 325-331.

MANN, J.B. (1967): Atomic structure calculations. I. Hartree-Fock energy results for the elements hydrogen to lawrencium. *Los Alamos Sci. Lab., Rep.* **LA-3690**.

MANOCHA, A.S. & PARK, R.L. (1977): Flotation related ESCA studies on PbS surfaces. *Applic. Surf. Sci.* **1**, 129-141.

MCFEELY, F.R., KOWALCZYK, S., LEY, L., POLLAK, R.A. & SHIRLEY, D.A. (1973): High-resolution X-ray-photoemission spectra of PbS, PbSe, and PbTe valence bands. *Phys. Rev.* **B7**, 5228-5237.

POLING, G.W. & LEJA, J. (1963): Infrared study of xanthate adsorption on vacuum deposited films of lead sulfide and metallic copper under conditions of controlled oxidation. *J. Phys. Chem.* **67**, 2121-2126.

REUTER, B. & STEIN, R. (1957): Die Oxydation von Bleisulfid bei niederen Temperaturen. *Z. Elektrochem.* **61**, 440-454.

SCHOOLAR, R.B. & DIXON, J.R. (1965): Optical constants of lead sulfide in the fundamental absorption edge region. *Phys. Rev.* **A137**, 667-670.

SHERMAN, D.M. (1985): The electronic structures of Fe^{3+} coordination sites in iron oxides; applications to spectra, bonding and magnetism. *Phys. Chem. Minerals* **12**, 161-175.

SLATER, J.C. (1974): *The Self Consistent Field Method for Atoms, Molecules and Solids*. McGraw-Hill, New York.

STEGER, H.F. & DESJARDINS, L.E. (1980): Oxidation of sulfide minerals. V. Galena, sphalerite and chalcocite. *Can. Mineral.* **18**, 365-372.

SWARTS, C.A., GODDARD, W.A. III & MCGILL, T.C. (1980): Theoretical studies of the reconstruction of the (110) surface of III–IV and II–VI semiconductor compounds. *J. Vac. Sci. Tech.* **17**, 982-986.

TOSSELL, J.A. (1984): A qualitative MO model for bridging bond angle variations in minerals. *Phys. Chem. Minerals* **11**, 81-84.

TSUKADA, M., ADACHI, H. & SATOKO, C. (1983): Theory of electronic structure of oxide surfaces. *Prog. Surf. Sci.* **14(2)**, 113-173.

TUNG, Y.W. & COHEN, M.L. (1969): Relativistic band structure and electronic properties of SnTe, GeTe, and PbTe. *Phys. Rev.* **180**, 823-826.

URCH, D.S. (1985): X-ray spectroscopy and chemical bonding in minerals. *In* Chemical Bonding and Spectroscopy in Mineral Chemistry (F.J. Berry & D.J. Vaughan, eds.). Chapman and Hall, London.

VAUGHAN, D.J., TOSSELL, J.A. & JOHNSON, K.H. (1974): The bonding of ferrous iron to sulfur and oxygen in tetrahedral coordination: a comparative study using SCF–Xα scattered wave molecular orbital calculations. *Geochim. Cosmochim. Acta* **38**, 993-1005.

Received October 23, 1985, revised manuscript accepted September 22, 1986.