RESULTS

Consideration of the Thermodynamic Stability of Transition Metal Sulfides

The stability of a catalyst under the reactor conditions employed is very important in any investigation into the development of a new catalyst system. Previous catalytic studies on alkali doped MoS_2 have shown that this catalyst is stable for long periods of time at pressures of 8.2 MPa and temperatures ranging from 250°C to 350°C [65]. However, knowledge about the stability of related transition metal disulfide systems is unavailable experimentally. For this reason an investigation of the thermodynamic properties of the third, fourth, and fifth period transition metal (T) disulfides, TS_2, has been carried out. In the reactor, H_2 gas is present as one of the reactants in the synthesis gas used for higher alcohol synthesis over these catalysts. The water gas shift (WGS) reaction and production of hydrocarbons from synthesis gas are both reactions that can produce H_2O (or consume H_2O in the case of the forward WGS reaction) in the reactor. For these reasons, the stability of the catalyst in a hydrogen environment towards its corresponding metal and most stable sulfide and oxide forms is valuable information. This information can be calculated from available thermodynamic data [84-86].

The overall reaction for the reduction of transition metal disulfides by H_2 is shown in Equation 13. Calculated Gibbs free energies at 298K and 0.1 MPa pressure are shown

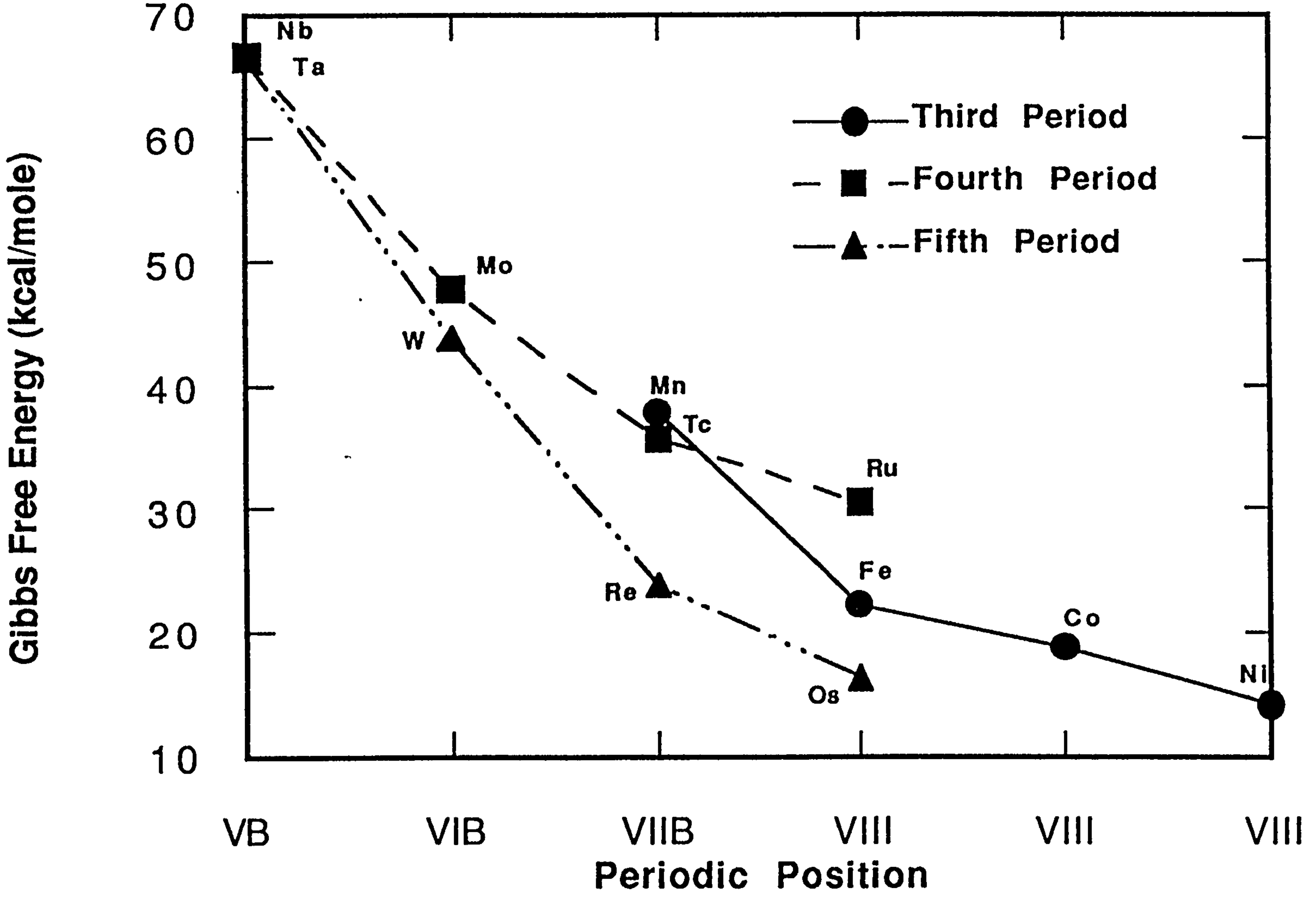
$$TS_2(s) + 2\ H_2(g) \rightarrow T(s) + 2\ H_2S(g) \qquad (13)$$

in Figure 15. The most stable TS_2 compounds will be the ones with the most positive ΔG values. As can be seen from the trends in Figure 15 the stability of the TS_2 toward its corresponding metal, T, decreases as one proceeds across each period. The most stable compound having a layered structure is NbS_2, while the most stable pyritic compound is

FIGURE 15

Stability of TS_2 Toward Reduction (T=298K, 1atm)

$TS_2(s) + 2H_2(g) \text{ -----> } T(s) + 2H_2S(g)$



RuS_2. In general, the thermodynamically most stable compounds are found in the fourth period.

When the stability of the TS_2 compounds are compared to the corresponding most stable oxide forms, the trend is markedly different. The general overall reaction for oxidation of the TS_2 compounds is shown in Equation 14. Calculated Gibbs free energies at

$$TS_2(s) + \left(\frac{y}{x}\right) H_2O(g) \rightarrow \left(\frac{1}{x}\right) M_xO_y(s) + 2\ H_2S(g) + \left(\frac{y}{x}-2\right) H_2(g) \qquad (14)$$

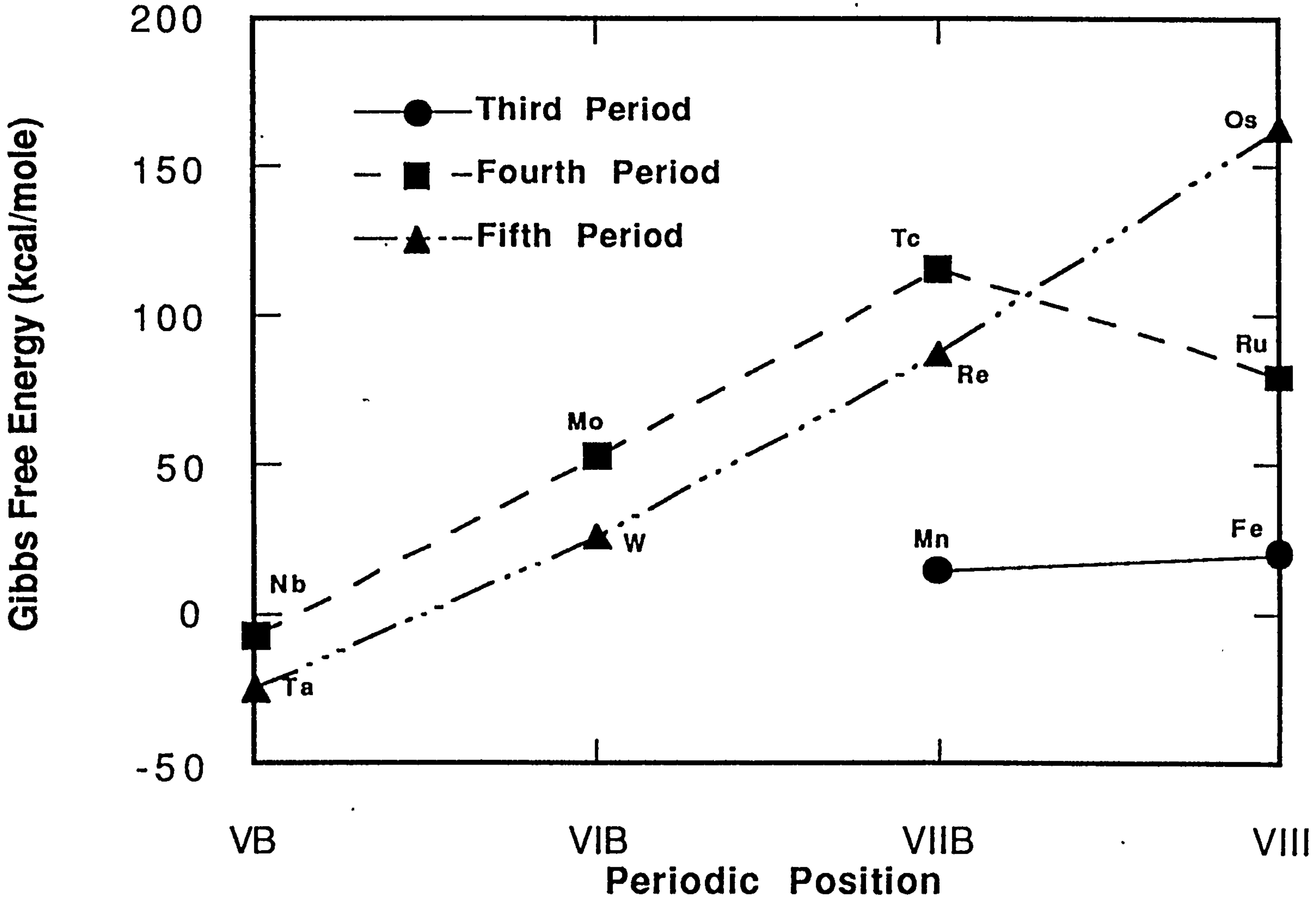
298K and 0.1 MPa pressure are shown in Figure 16. Again, the most stable TS_2 compounds will be the ones with the most positive ΔG values. As can be seen from Figure 16, the layered compounds NbS_2 and TaS_2 are very unstable toward oxidation to Nb_2O_5 and Ta_2O_5, respectively. Also, the third period TS_2 compounds are only moderately stable toward oxidation to Mn_3O_4 and Fe_3O_4(Fe_2O_3). As can be seen from the trends in Figure 16, the stability of the TS_2 compounds toward oxidation increases as one proceeds across each period. This trend is opposite to that found for reduction. Again, the fourth period TS_2 compounds are the most stable. Since the trends in stability are opposite for the two tests of reducibility and oxidizability, both stability criteria must be considered when choosing a catalyst. From this analysis, compounds with intermediate values of Gibbs free energy for both reduction and oxidation should be the most stable under the catalytic conditions employed. For example, the layered compounds MoS_2, WS_2, and ReS_2 and the pyritic compound RuS_2 should be the most stable compounds.

Precaution must be observed when analyzing the thermodynamic calculations presented in the preceding paragraphs. The calculations presented were obtained by using the thermodynamic values of bulk TS_2 compounds. However, the active portion of a catalyst

FIGURE 16

Stability of TS_2 Toward Oxidation (T=298K, 1atm)

$MS_2(s) + (y/x)H_2O$ -----> $(1/x)M_xO_y(s) + 2H_2S(g) + ([y/(x]-2))H_2(g)$



is actually the surface and not the bulk. The surface may consist of atoms with dangling bonds and unshared vacancies, and thus surface thermodynamics may be different from those of the bulk. However, to a first approximation the trends exhibited for the bulk can be assumed to be similar for the surface. An increase in pressure will not affect the reduction and oxidation reactions since the number of moles of reactant and product gases is equal.

Investigation of Electronic Structure

Theoretical calculations can provide insight into the electronic properties of materials that determine their experimental behavior. Investigations into the electronic structure of TS_2 compounds is important for an understanding of the catalytic mechanisms occurring at the surface. An understanding of the electronic structure at the catalyst surface is important when considering the interaction of an adsorbate with the catalyst surface. For example, in the formation of C_1-C_4 alcohols over Cs-doped MoS_2, the electronic interaction of H_2 with the surface of MoS_2 is an important issue. The Cs-doped MoS_2 system has been extensively studied in terms of catalytic activity but little is known about the method in which hydrogen is activated on the surface. Electronic studies characterizing the surface properties of MoS_2 may shed some light on the nature of hydrogen activation.

A good experimental method of studying trends in the electronic structure of disulfide surfaces is by core level and valence band analysis *via* high resolution electron spectroscopy for chemical analysis (HR-ESCA), also called high resolution X-ray photoelectron spectroscopy, HR-XPS. HR-ESCA is a surface sensitive technique that can provide information on the oxidation state and chemical environment of surface species. Analysis of the valence bands *via* HR-ESCA can also lead to information on the highest occupied bands, which will most likely interact with specific adsorbates such as H_2. In general, since the TS_2 compounds are fairly covalent, the valence bands obtained *via* HR-ESCA are combinations of the atomic valence levels of sulfur and the transition metal. The experiment does not resolve the valence band into contributions due to the atomic valence levels from different atoms. Theoretically calculated valence bands can be used to interpret the HR-ESCA experimental results. A solid state adaptation of the extended Hückel theory is a very simple method that will calculate the density of states, as well as the contributions of the valence atomic orbitals to the density of states. As pointed out in the Experimental Section, the computational package used for these calculations was the "Extended Hückel Molecular, Crystal and Properties Package" [83]. This theory has been used to calculate the valence bands of representative transition metal disulfides, with some encouraging initial results. Thus, trends in the electronic structure of the disulfides can be studied in detail. Surface band structure can be theoretically investigated by setting up models with translational periodicity parallel to the surface, with the surface atoms in their regular or relaxed lattice positions, and the theory compared with experimentally determined band structures.

The computational program gives a density of states that cannot be compared directly to the valence band obtained *via* HR-ESCA. The ability of photoelectrons to be detected in the instrument depends on the incident X-ray energy and the atomic level and specific atom type from which the photoelectron originates. Thus, the experimental valence band could be considered to be a density of states modified by the photoelectron cross-sections of the atomic orbitals. Therefore, a theoretical valence band must be compared to the experimental valence band. A theoretical valence band can be obtained from the atomic orbital population (AOPOP) contributions to the density of states (DOS). These atomic orbital contributions (AOPOP's) are multiplied by their corresponding photoelectron cross-sections to obtain modified AOPOP's (MAOPOP). The modified AOPOP's are then summed at each energy to obtain the theoretical valence band that can be compared directly to experiment. In the case of MoS_2, the Mo 4d to S 3p photoelectron cross-section ratio is 4.08. Therefore, the Mo 4d AOPOP will be multiplied by a factor of 4.08 as compared to the S 3p AOPOP, resulting in a large contribution of the Mo 4d atomic orbitals to the valence band region.

The experimental HR-ESCA valence band regions of MoS_2 and NbS_2 are shown in Figure 17 and 18, respectively. The difference in the two disulfides can be seen immediately at the top of the valence band. The intensity of the peak at the top of the NbS_2 valence band relative to the rest of the valence band is less than in the case of MoS_2. NbS_2 (Nb^{+4}, d^1 system) is a metal and has the highest occupied crystal orbital (HOCO) only half-occupied. MoS_2 (Mo^{+4}, d^2 system) is a small band gap semiconductor and has the HOCO fully occupied by electrons. Theoretical valence bands that have been parametrized and modified by the photoelectron cross-sections are shown in Figure 19 and 20 for MoS_2 and NbS_2, respectively. The theoretical valence bands reproduce the experimental valence bands very well. The dispersion of the S 3s region is in good agreement between theory and experiment. The four-peaked nature and width of the upper portion of the valence band is reproduced theoretically. From experience manipulating the program, it has been found that the most important feature in obtaining an accurate description of the upper portion of the valence band is the radial extent of the S 3p atomic orbitals. If the S 3p Slater-type atomic orbitals are not highly diffuse, small overlap between the S 3p and Mo 4d atomic orbitals in the MoS_2 lattice will result in a 3-peaked valence band. However, more diffuse S 3p atomic orbitals produce the required overlap needed to give the valence band its 4-

FIGURE 17

Valence band region of polycrystalline MoS2 shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

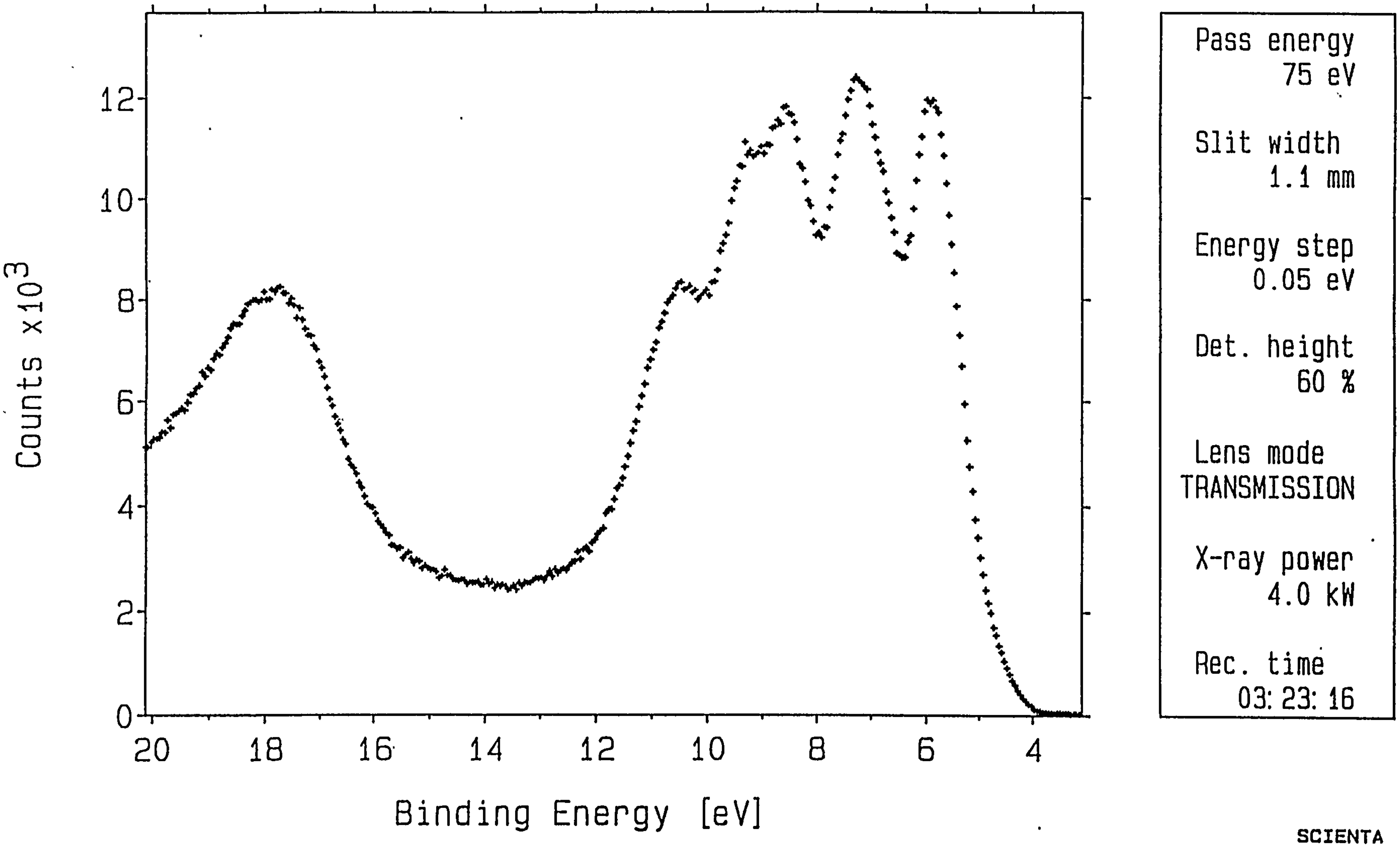


FIGURE 18

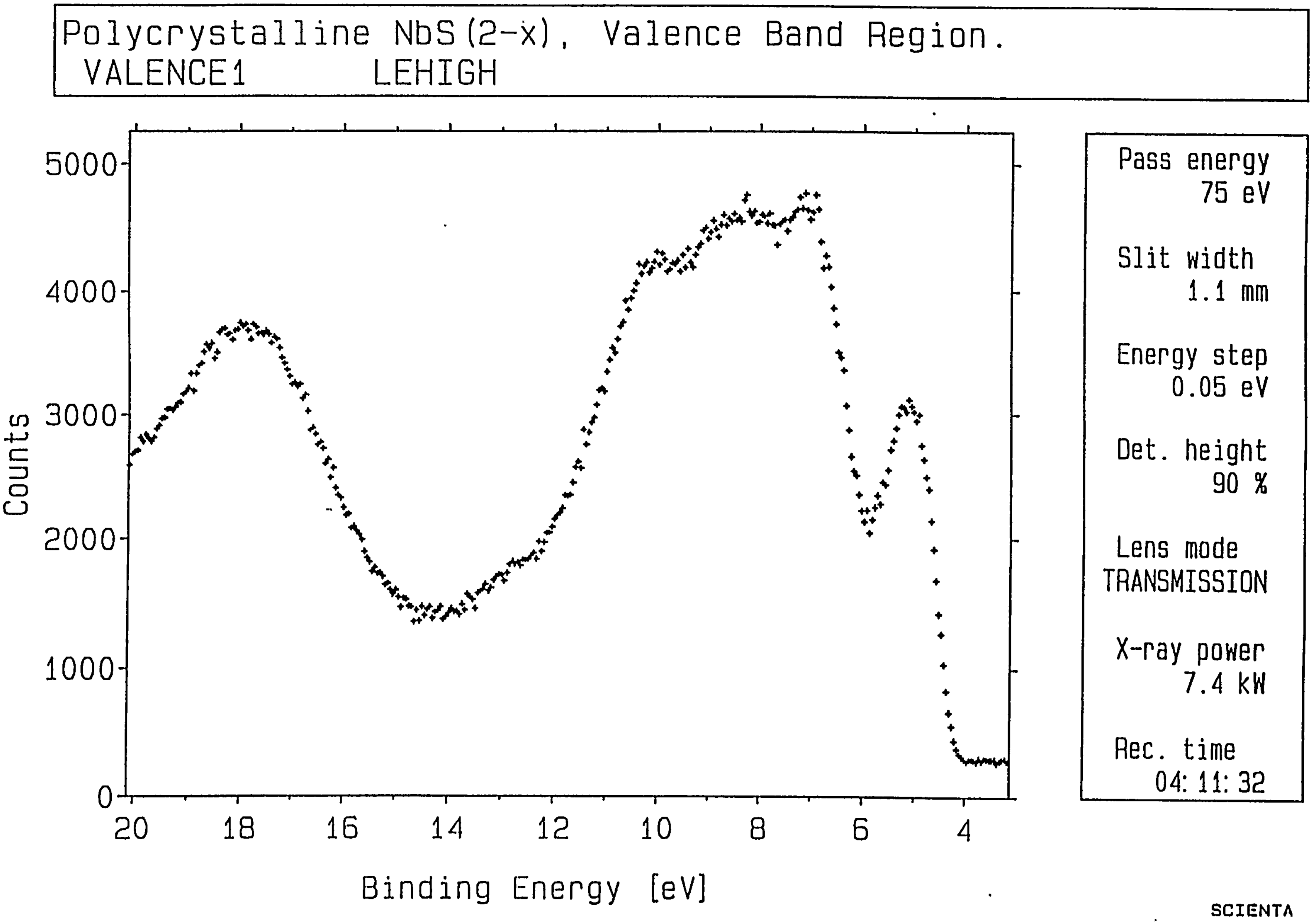

Polycrystalline NbS(2-x), Valence Band Region.
VALENCE1 LEHIGH
Counts
5000
4000
3000
2000
1000
0
20
18
16
14
12
10
8
6
4
Binding Energy [eV]
Pass energy 75 eV
Slit width 1.1 mm
Energy step 0.05 eV
Det. height 90 %
Lens mode TRANSMISSION
X-ray power 7.4 kW
Rec. time 04:11:32
SCIENTA

FIGURE 19

Valence band region of polycrystalline MoS2 shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

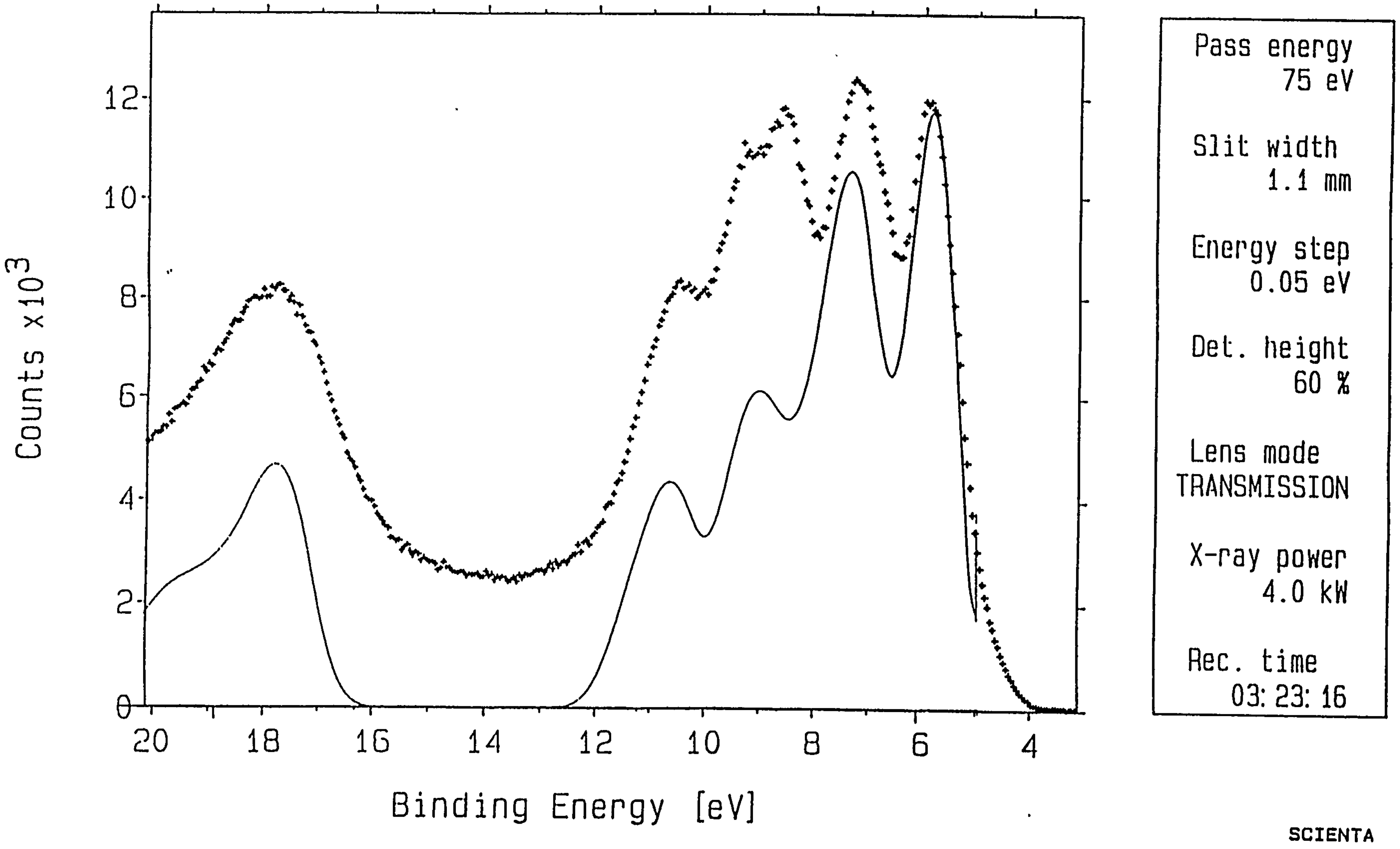
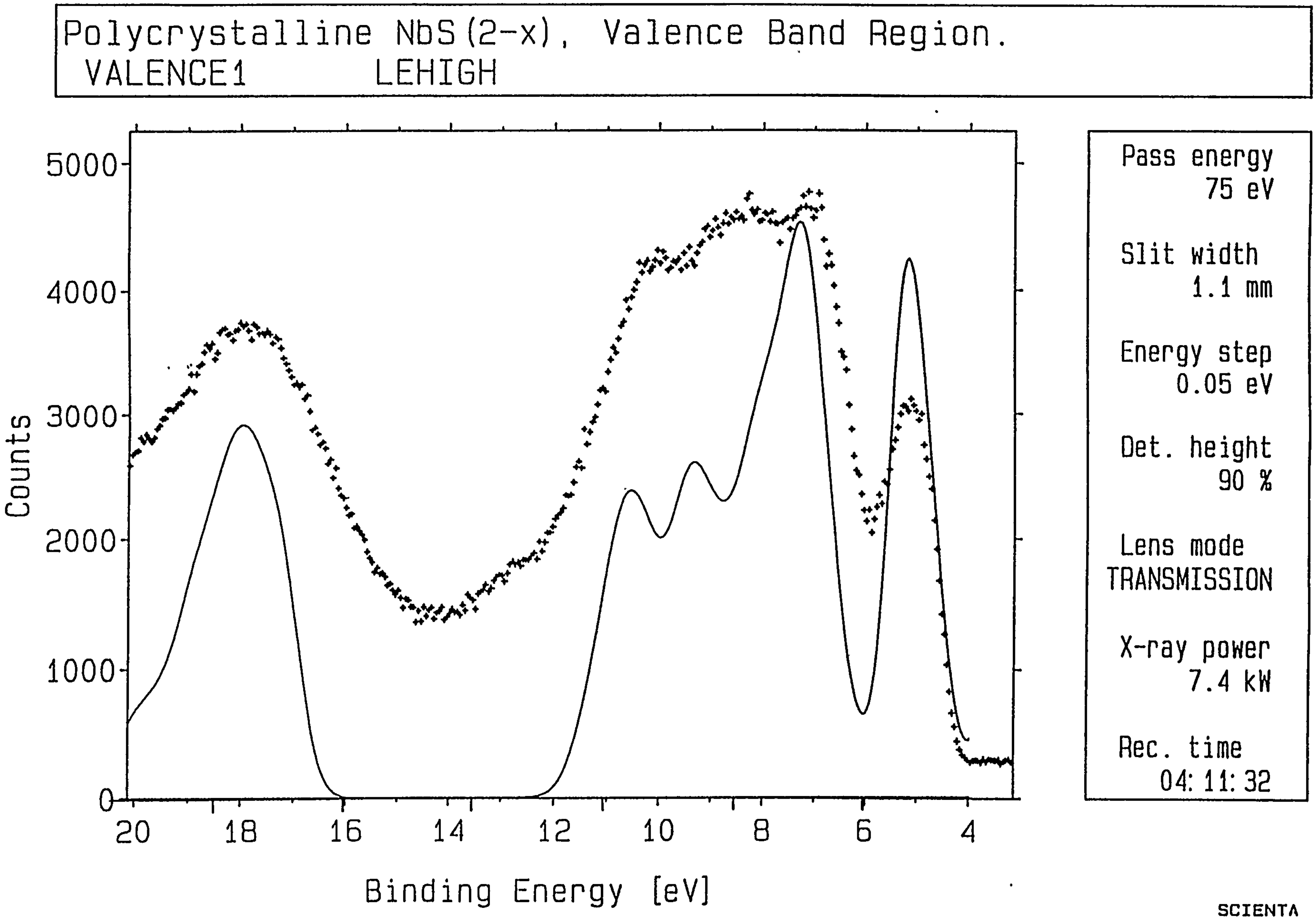


FIGURE 20


Polycrystalline NbS(2-x), Valence Band Region.
VALENCE1 LEHIGH
Counts
5000
4000
3000
2000
1000
0
20
18
16
14
12
10
8
6
4
Binding Energy [eV]
Pass energy
75 eV
Slit width
1.1 mm
Energy step
0.05 eV
Det. height
90 %
Lens mode
TRANSMISSION
X-ray power
7.4 kW
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peaked nature. On comparison of the theoretical valence bands of MoS_2 and NbS_2 a question might arise as to the difference in the dispersion of the S 3s region. In MoS_2, the theoretical dispersion is greater because of the smaller lattice constant, 3.16 Å, that separates the sulfur atoms within each S atomic layer. In NbS_2, the theoretical dispersion is smaller because of the larger lattice constant, 3.31 Å, that separates the sulfur atoms within each S atomic layer.

A better understanding of the experimental valence band can be achieved by analysis of the theoretical MAOPOP's. Shown in Figure 21 are the modified AOPOP's (Mo 4d, S 3s, and S 3p) for MoS_2. Thus, the S 3s atomic orbitals are mainly the cause of the dispersion of the peak located at approximately 17.8 Ev. The top of the valence band and (HOCO) located at approximately 6.0 Ev is made up mainly of Mo 4d character. This character is usually referred to as d_z2. However, an analysis of the atomic orbital coefficients that make up the crystal orbitals shows that the Mo 4d AOPOP consists of a considerable amount of $d_x2_{-y}2$ and d_{xy} as well as d_z2 character. The covalent nature of MoS_2 can be seen in the large amount of mixing in the remainder of the valence band between the S 3p and Mo 4d atomic orbitals.

Now that the electronic structure of the bare MoS_2 surface has been investigated theoretically, predictions as to probable adsorption sites can be made. Studies under way at this time involve the adsorption of hydrogen on the MoS_2 surface both theoretically and experimentally. The latter studies are centered on HR-XPS, and TPD studies should also be carried out. Theory, when compared to experiment, will lead to the identification of catalytic activation sites and insight into the mechanism of hydrogen adsorption. Subsequent studies are needed on the alteration of the electronic properties of MoS_2 upon surface doping with alkali and the influence that this has on the adsorption of CO.

FIGURE 21

Theoretical Valence Band
2-D MoS_2 (#171 kp)