Thiophene adsorption studies on clean and hydrogen-preadsorbed $MoS_2(100)$ surface

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It is known from temperature-programmed desorption studies that the binding energy of thiophene over Mo/γ-Al_2O_3 and Co–Mo/γ-Al_2O_3, hydrodesulfurization catalysts, is lower in the presence of hydrogen. The adsorption of thiophene on clean and hydrogen-adsorbed MoS_2 was modelled using extended Hückel tight binding band structure calculations. In the η^1 adsorption configuration the calculations show a lower binding energy for adsorption on the hydrogen-preadsorbed surface similar to that observed experimentally. The lowering is due to an increased occupancy of the Mo density of states in the presence of hydrogen.

Keywords: hydrodesulfurization catalysts, molybdenum disulfide, extended Hückel calculations

1. Introduction

The hydrodesulfurization (HDS) process over Co-promoted Mo/γ-Al_2O_3 catalysts is one of the most extensively investigated catalytic processes. In the active catalyst both Mo and Co are in the sulfided form. The Mo atoms are present in an environment very similar to that in bulk MoS_2. The relation of the sulfidized Co to any known bulk stoichiometric phase is doubtful. It has been proposed that Co atoms are adsorbed on the edges of MoS_2 forming a new so-called "Co–Mo–S" structure [1–12]. In a recent temperature-programmed desorption (TPD) and surface reaction (TPSR) study of thiophene over catalysts with varying Co to Mo ratios, it was found that the temperature of desorption as well as the heat of desorption of thiophene was identical for all catalysts [6,13]. It was concluded that thiophene was adsorbed on the "Mo–S" components of the catalyst and was unaffected by the presence of Co. The above observation is true whether the desorption experiments were carried out in the presence or absence of H_2. It was found, however, that the desorption temperature and heat of desorption of thiophene over Co–Mo/γ-Al_2O_3 were lower in the presence of hydrogen. In the presence of hydrogen the heat of desorption is 20.5 kcal/mol while in the absence of hydrogen it is 23.5 kcal/mol.

In order to understand the role of adsorbed hydrogen in lowering the heat of desorption or binding energy (BE) of thiophene, a semiempirical extended Hückel tight (EHT) binding band structrue calculation [14] for the adsorption of thiophene on a MoS_2 surface was carried out. Calculations indeed show lower binding energy for thiophene adsorption on the H_2-preadsorbed MoS_2 surface (3.67 eV) when compared to the clean surface (4.23 eV). The origin of this lowering is explained from an examination of the density of state (DOS).

Method of calculation

In the present study MoS_2 was chosen as the substrate, since desorption studies had shown that the heat of desorption of thiophene was invariant to the Co concentration and that the adsorption sites are on the "Mo–S" component of the catalyst [6]. The model surface chosen was the (100) edge plane of MoS_2. The edge sites on MoS_2 are the active sites on MoS_2. The model for the surface was identical to the one used by Zonnevylle et al. [15]. The energetics of thiophene adsorption on the clean as well as on the hydrogen-preadsorbed MoS_2 surface was calculated using the EHT band structure procedure. In order to avoid adsorbate–adsorbate interaction, the "large" or molecular unit cell approximation [16] was adopted.

The model surface was constructed by cutting a three-atom thick, one-dimensional, infinite ribbon from the basal sheet of MoS_2. Fig. 1 shows the basal plane structure of MoS_2; the thick dashed line shows the ribbon. The atoms which form the unit cell are numbered. It may be seen that for this model structure, Mo(1) and Mo(2) protrude in the y direction from the xz plane and are coordinatively unsaturated (coordination number $= 4$). These are assumed to be the active sites. For the bottom xz plane, it is the sulfur atoms which protrude. Mo(5) and Mo(6) are recessed and six-coordinate. The ribbon was generated by a one-dimensional translation in the xz plane. The translation vector is the thick line in fig. 1.

The adsorption of thiophene was carried out for the η^1-configuration wherein the thiophene molecule is

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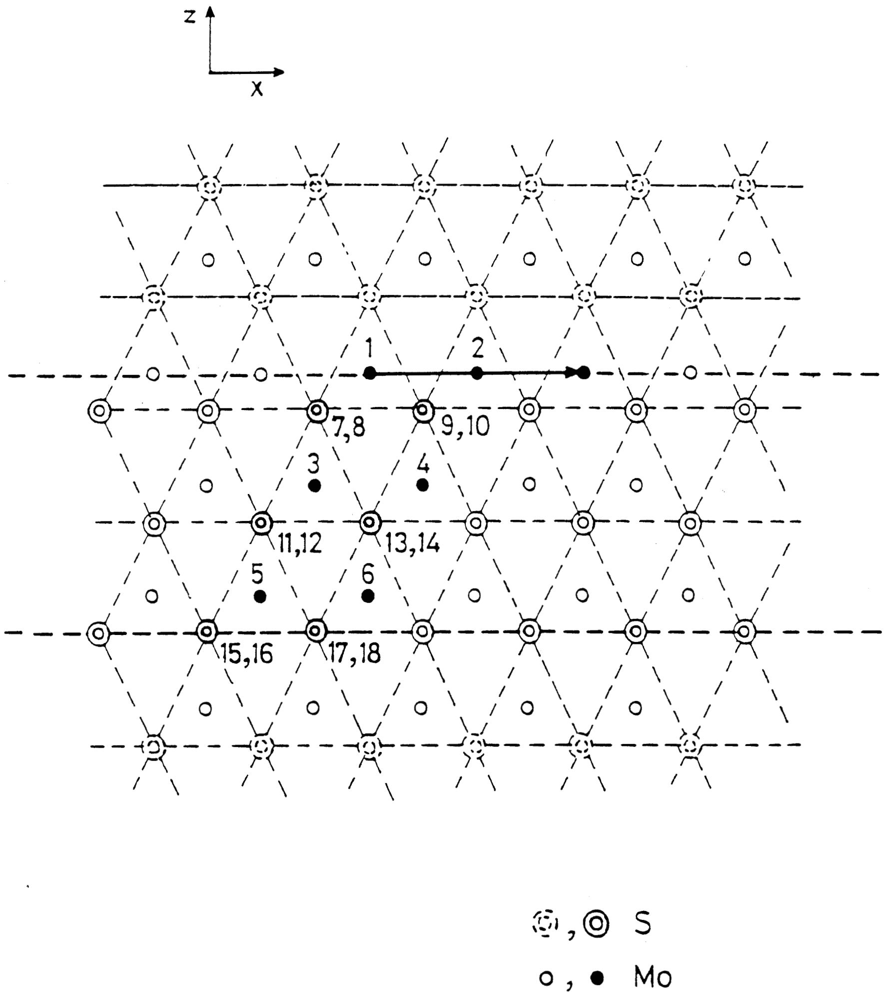


Fig. 1. Basal plane structure of MoS_2. The model surface was obtained by cutting the lattice along the thick dashed lines. The translation vector is shown as the solid arrow. The atoms which form part of the unit cell are numbered.

directly on top of Mo(2). The calculation was carried out for a fixed distance, 1.9 Å, between Mo(2) and the thiophene sulfur. This particular configuration was chosen since calculations by Zonnevylle et al. [15] had shown that the on-top η^1-configuration had a binding energy (BE) higher than the η^2- and η^5-configurations. It is known from inelastic neutron scattering experiments that chemisorption of hydrogen on MoS_2 occurs by homolytic dissociation forming S–H bonds [17]. The S–H bond was assumed to be perpendicular to the *xz* plane and the S–H distance kept fixed at 1.4 Å.

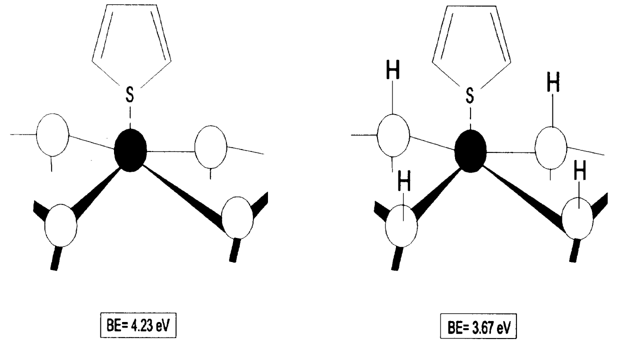
The band structure calculations were carried out using two translations of the unit cell and a cyclic boundary condition [18]. Since thiophene molecules are not adsorbed on Mo(1), thiophene molecule interactions on adjacent unit cells are negligible. The binding energy is defined as the difference in energy of the thiophene-adsorbed surface and the bare surface plus the energy for free thiophene.

The densities of states (DOS) were calculated over ten equally spaced *k* points in the one-dimensional Brillouin zone. The projected density of states was calculated using the Mulliken overlap population analysis [19]. In the Mulliken analysis the overlap population, $2c_ic_jS_{ij}$, is divided equally between the two centres. The population of electrons in the *i*th orbital is given by $\sum_j c_i^2 + c_ic_jS_{ij}$, where c_i and c_j are the coefficients of the wave function, and S_{ij} is the overlap integral.

The bonding and antibonding contributions to the projected density of states of a bond may be separated by the crystal orbital overlap population (COOP) analysis [19]. In the COOP analysis, the Mulliken overlap projected density of states between orbitals *i* and *j*, $c_ic_jS_{ij}$, is calculated and separated into bonding density of states, c_i and c_j having the same sign, and antibonding density of states, c_i and c_j having different signs.

2. Results and discussion

Extended Hückel band structure calculations were carried out for thiophene adsorbed in the η^1-configuration on the exposed Mo atom of the edge plane of the MoS_2 structure (Mo(2) in fig. 1). The calculations were



Scheme 1.

carried out for both the clean as well as the hydrogen-preadsorbed MoS_2 surface. The binding energies are determined as 4.23 eV for thiophene adsorbed on the clean surface and 3.67 eV for adsorption on the hydrogen-preadsorbed surface (scheme 1). The calculations show the same trend as the experimental results on the HDS catalysts, i.e. a lowering of the heat of desorption of thiophene in the presence of hydrogen.

In order to understand the origin of this lowering in BE, the change in the electronic density of state (DOS) was examined. Figs. 2a and 2b show the total DOS for bare and hydrogen-covered MoS_2. The two DOS are almost identical except for the feature at −17 eV in fig. 2b. The DOS of "clean" MoS_2 is identical to that previously reported [14]. There are essentially four regions in the DOS. The sulfur "s" states contribution to the total DOS is predominantly in the −24 to −18 eV region. The sulfur "p" states with some admixture of the Mo "d" states appear between −17 and −12 eV while the Mo "4d" appear between −12 and −7 eV in the DOS. The Mo "5s" and "5p" contribute to the DOS above −11 eV. The features at −15 eV and −8 eV are due to orbitals of $d_{x^2-y^2}$ symmetry. These orbitals interact strongly with the S atoms since they point towards the sulfur. Part of the $d_{x^2-y^2}$ levels are pulled into the s and p block to form

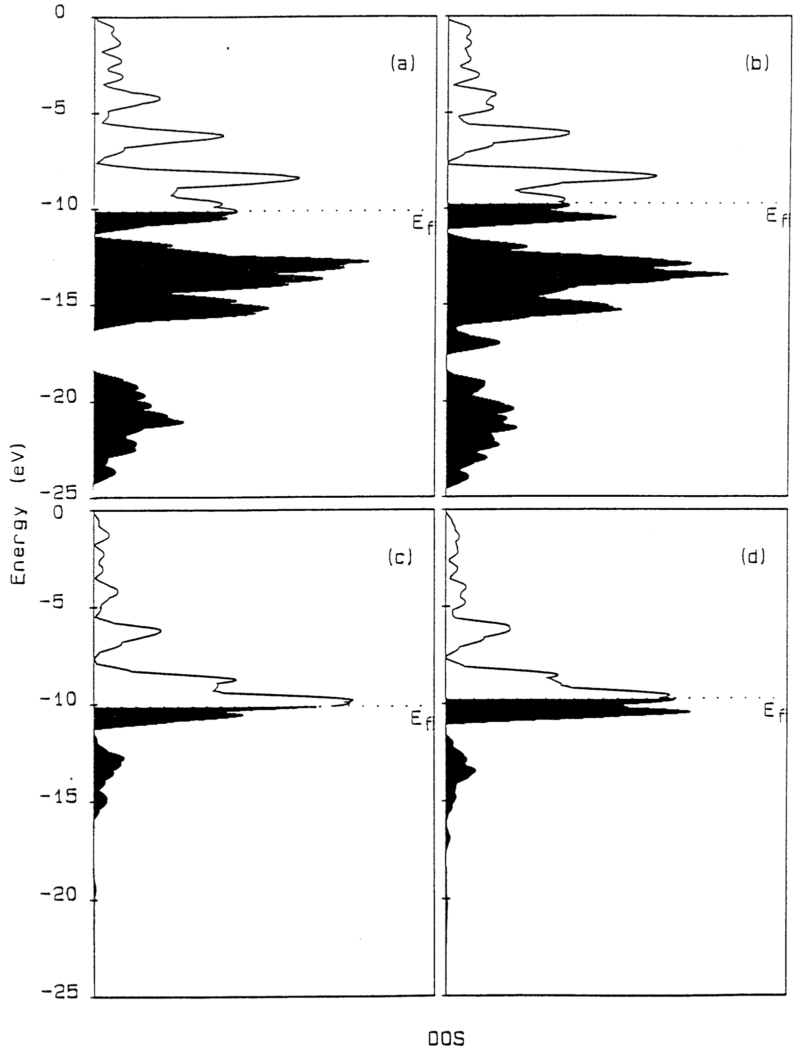


Fig. 2. Total DOS for (a) clean and (b) hydrogen-preadsorbed MoS_2 surfaces. (c) and (d) are the projected densities of "d" states of the protruding Mo(2).

the Mo–S bond and their antibonding counterpart pushed above the main Mo d block which lies between −12 and −8 eV. Although MoS_2 is a semiconductor, the calculations do not show a gap at the Fermi level due to the presence of the coordinatively unsaturated Mo edge atoms. The projected density of "d" states of the exposed Mo atom shows a large contribution at E_f (figs. 2c and 2d).

It may be seen that for the hydrogen-covered surface, in addition to the feature at −17 eV due to the formation of the S–H bond, the Fermi level, E_f (HOMO), is pushed up in energy. The E_f for the bare surface is −10.14 eV and for the hydrogen-covered surface −9.97 eV. There is an increased electron density on the Mo atom. This may be clearly seen from the comparison of the projected DOS of d states of the exposed Mo atom, Mo(2), in figs. 2c and 2d.

The chemisorption bond relies on a combination of electron donation from an occupied adsorbate orbital to the surface, and back-donation from the surface to an empty adsorbate level. In the present case, the acceptor level of thiophene would be the empty $3b_1$ and the donor orbitals are the sulfur lone pairs. These are the $2b_1$ orbital perpendicular to the ring and $9a_1$ orbital tangential to the ring of the two sulfur lone pairs. Of the two thiophene sulfur lone pairs, the most effective donor is the one best able to interact with the Mo orbitals. For the on-top site, the bonding between Mo yz and the thiophene $2b_1$ MO will be π-type. The $9a_1$ thiophene MO will interact with metal orbitals of d_{z^2} symmetry to form a σ-bond.

It was at first thought that the increase in electron density on the Mo atom may lead to a stronger back-donation to the antibonding $3b_1$ thiophene orbitals, and hence give rise to a stronger chemisorptive bond and consequently "activating" the thiophene by weakening the C–S bond. This, however, is not the case, as may be seen from the crystal orbital overlap population (COOP) curves of C–S bond of thiophene adsorbed on the bare and hydrogen-preadsorbed surfaces. It may be seen that both COOP curves (figs. 3c and 3d) are identi-

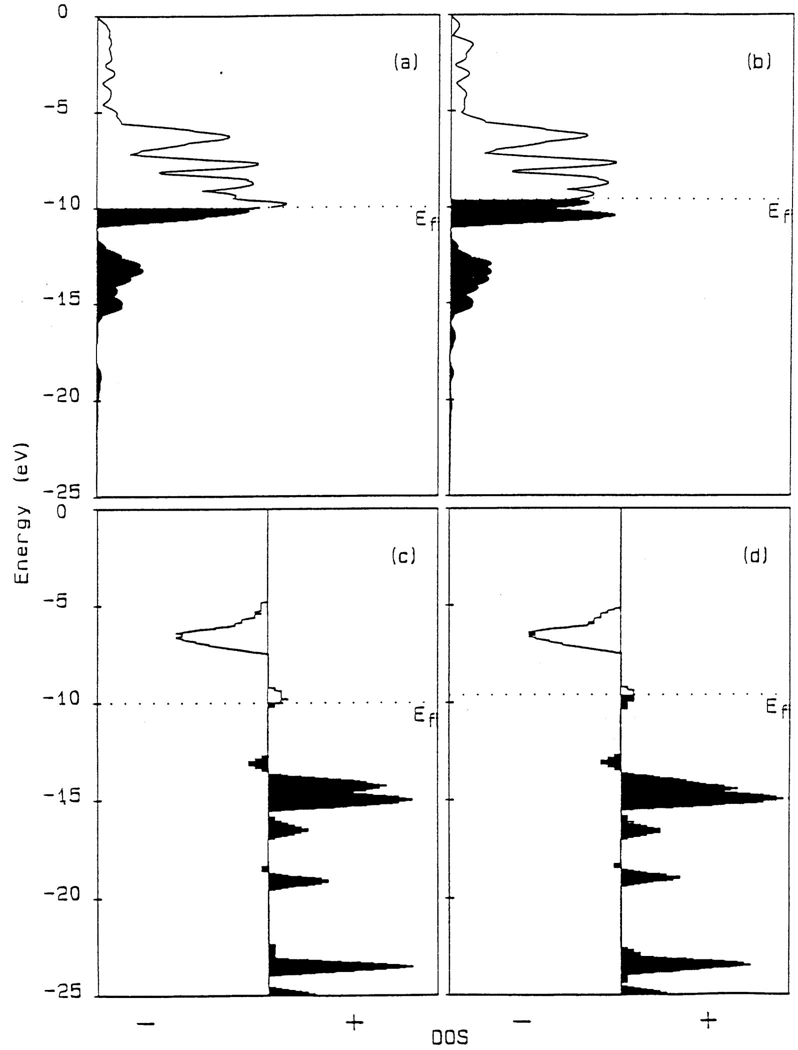


Fig. 3. Projected density of states of Mo(2) after adsorption of thiophene on the (a) clean and (b) hydrogen-preadsorbed MoS_2 surface. (c) and (d) are the COOP curves of the C–S bond of thiophene adsorbed on (c) the clean and (d) hydrogen-preadsorbed MoS_2 surfaces.

cal, implying that there is no increase in electron density on the $3b_1$ antibonding thiophene MO, in the presence of hydrogen. Any increase in the occupation of the $3b_1$ orbital would have shown up as an increase in the antibonding density in fig. 3. The possible reason for the noninteraction may be that the orbitals do not have the right symmetry to interact. This result is in agreement with the TPSR results. The TPSR of thiophene over Co–Mo/γ-Al_2O_3 HDS catalysts had established that the thiophene with $\Delta H_{\mathrm{des}} = 20.5$ kcal/mol is unlikely to be the active species; it desorbs much before the HDS reaction commences.

The increased electron density on Mo, on the other hand, makes the donation of electrons from thiophene to MoS_2 energetically more expensive, since the transferred electrons would have to occupy levels with higher energy as compared to that for bare MoS_2. Figs. 3a and 3b show the projected density of "d" states of Mo(2) for thiophene adsorbed on MoS_2 and for the thiophene adsorbed on the hydrogen-covered MoS_2. For the latter, on adsorption of thiophene, the Fermi level is pushed up by 0.145 eV, from −10.145 to −10.000 eV. For the hydrogen-covered surface, the E_f is pushed up by 0.17 eV, from −9.77 to −9.60 eV. This large increase in E_f, 0.17 eV as compared to 0.145 eV, would itself account for a difference of 0.6 kcal/mol in the binding energies. It may be seen from the projected density of states that for the bare surface the adsorption of thiophene causes an increase in occupation of the DOS, in the region lying between −11 and −10 eV. For the hydrogen-covered surface, this region already has an increased density (due to transfer of electron from hydrogen) even prior to the adsorption of thiophene. Thus when thiophene is adsorbed, the transferred electrons are forced to occupy states of higher energy (−10 to −9 eV). The lowering in BE of thiophene in the presence of hydrogen is consequently due to the comparatively larger increase in the E_f along with an increase in the DOS in this region.

3. Conclusions

The adsorption of thiophene on clean and hydrogen-adsorbed MoS_2 was modelled using a semiempirical extended Hückel tight binding band structure calculation. It was found that the binding energy of thiophene on the hydrogen-preadsorbed MoS_2 was lower than that on clean MoS_2. The results are in agreement with the experimental temperature-programmed desorption which showed a lower heat of desorption for thiophene over hydrodesulfurization catalysts, in the presence of H_2. This is attributed to the increased electron density of states on the Mo atoms which forces the electrons donated from thiophene, during chemisorption, to occupy energetically higher levels of the density of states.

Table 1
Extended Hückel parameters

Orbital		H_{ii} (eV)	ξ_1	ξ_2	c_1 [a]	c_2 [a]
Mo	5s	−8.34	1.96			
	5p	−5.24	1.90			
	5d	−10.50	4.54	1.9	0.5899	0.5899
S	3s	−20.00	1.82			
	3p	−13.30	1.82			
C	2s	−21.40	1.63			
	2p	−11.40	1.63			
H	1s	−13.60	1.30			

[a] Contraction coefficients used in double-ξ expansion orbital ionization potentials, and the orbital exponents are taken from the work of Zonnevylle et al. [15].

Appendix

Band structure calculations were performed using the extended Hückel (EHT) tight binding method [14,20,21]. The H_{ii} are taken from the work of Zonnevylle et al. [15] and are given in table 1. The MoS_2 model surface was constructed from the crystal structure of Wyckoff [22]. The geometry of the thiophene molecule is taken from the work of Bak [23]. The densities of states (DOS) were calculated over ten equally spaced k points in one-dimensional Brillouin zone. The projected densities of states were calculated using the Mulliken overlap population analysis [19].

References

[1] R. Prins, V.H.J. de Beer and G.A. Somorjai, Catal. Rev. Sci. Eng. 31 (1989) 1.
[2] B. Delmon, *Proc. Climax 3rd Int. Conf. on the Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.H. Mitchell (Climax Molybdenum Company, Ann Arbor, 1979) p. 73.
[3] P. Ratnasamy and S. Sivasankar, Catal. Rev. Sci. Eng. 22 (1980) 401.
[4] H. Topsøe and B.S. Clausen, Catal. Rev. Sci. Eng. 26 (1984) 395.
[5] R.R. Chianelli, Catal. Rev. Sci. Eng. 26 (1984) 361.
[6] M. Jayamurthy and S. Vasudevan, J. Phys. Chem. 98 (1994) 6777.
[7] G. Sankar, S. Vasudevan and C.N.R. Rao, J. Phys. Chem. 91 (1987) 2011.
[8] B.S. Clausen, H. Topsøe, R. Candia, J. Villadsen and B. Lengellar, J. Phys. Chem. 85 (1981) 3868.
[9] T.G. Parham and R.P. Merill, J. Catal. 85 (1984) 295.
[10] H. Topsøe and B. Clausen, Appl. Catal. 25 (1986) 273.
[11] S.M.A.M. Bouwens, J.A.R. van Veen, D.C. Koningsberger, V.H.J. de Beer and R. Prins, J. Phys. Chem. 95 (1991) 123.
[12] G.U. Kulkarni and C.N.R. Rao, Catal. Lett. 9 (1991) 427.
[13] M. Jayamurthy and S. Vasudevan, Catal. Lett. 23 (1994) 49.
[14] M.-H. Whanbo and R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 6093.
[15] M.C. Zonnevylle, R. Hoffmann and S. Harris, Surf. Sci. 199 (1988) 320.
[16] H. Kobayashi, S. Yoshida, H. Kato, K. Fukui and K. Tarama, Surf. Sci. 79 (1979) 189.

[17] C. Sampson, J.M. Thomas, S. Vasudevan and C.J. Wright, Bull. Soc. Chim. Belg. 90 (1981) 1215.

[18] R.P. Messmer, B. McCarroll and C.M. Singal, J. Vac. Sci. Technol. 9 (1972) 891.

[19] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (VCH, New York, 1988).

[20] R. Hoffmann, J. Chem. Phys. 39 (1963) 1397.

[21] J.H. Ammeter, H.-B. Burgi J.C. Thibeault and R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 3686.

[22] R.W.G. Wyckoff, *Crystal Structure*, Vol.1 (Wiley, New York, 1963) p. 280.

[23] B. Bak, D. Christensen, J.R. Andersen and E. Tannenbaum, J. Chem. Phys. 25 (1956) 890.