

THE INTERACTION OF OXYGEN WITH THE IRON (111) SURFACE: MAINLY STUDIED BY AES

By

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The cleaned surface was oxidized by means of pure oxygen at a pressure of 3×10^{-6} – 3×10^{-3} Pa and at temperatures of 300 K, 370 K and 620 K. The Auger peaks of high energy (for oxygen at 510 eV and for iron at 703 eV) were used for the quantitative determination of the oxygen coverage on the iron surface. The experimental results on the change of oxygen coverage as a function of the dose are interpreted by means of a theoretical model and provide definite information about the bonding state of the adsorbate. In the lower energy part of the Auger spectrum there appear peak shape modifications during oxidation. These observations allow us to assume that in the process of oxidation two kinds of chemical bond are formed between oxygen and iron, which differ regarding the density of states in the valence band.

1. Introduction

It is the aim of our investigations on the iron (111) surface by means of low energy electrons to contribute to the chemical and geometrical structural analysis of the clean and of the oxygen-covered surface of a typical transition metal, in order to understand the process of chemisorption quantitatively better. The present paper deals with the adsorption kinetics of oxygen and the effect related to changes in the density of states as resulting from chemical reaction between oxygen and iron studied by Auger electron spectroscopy.

The study of adsorbed layers and surface reactions on α -iron within atomic range was introduced by PIGNOCCO, PELLISSIER, SZOSTAK, MOLIÈRE, PORTELE and LÁZNIČKA [1 to 5]. Till now, some papers [6 to 10] on single crystals have been published in which the authors mainly derived statements concerning the growth of oxide layers on the (100) surface and on the most densely packed (110) surface. On the other hand, so far only few investigations have been made on the (111) surface [11 to 14], having the lowest density of iron surface atoms, though especially this surface is important for both adsorption and surface reaction in the sense of heterogeneous catalysis.

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2. Experimental

The (111) surface of iron was cleaned by in situ bombardment with argon ions and subsequent heating at 620 K under ultrahigh vacuum. Fig. 1 represents the Auger electron spectrum measured by means of a cylindrical mirror analyzer, for a surface after ion bombardment. Except for small amounts of oxygen, carbon, and argon, the surface may already be regarded as clean.

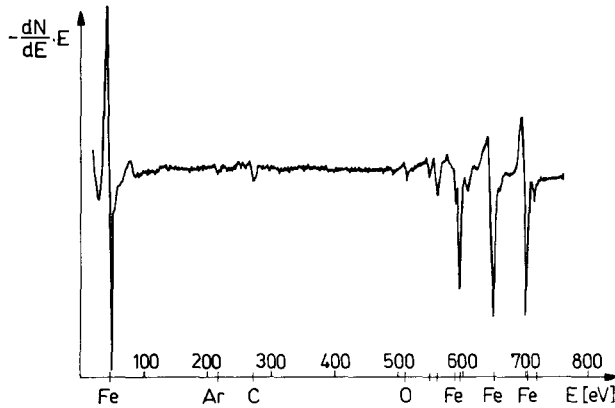


Fig. 1. Auger electron spectrum of the Fe (111) surface after bombardment with noble gas ions

By heating at 620 K, oxygen and carbon will desorb in the form of carbon monoxide, and after that argon is no longer detectable either.

The cleaned surface was oxidized by means of pure oxygen at a pressure of 3×10^{-6} Pa to 3×10^{-3} Pa and at temperatures of 300 K, 370 K and 620 K. After each oxygen exposure and pumping down to the vacuum of 10^{-8} Pa, Auger spectra were measured. In the same conditions, Auger spectra were taken on compressed pure magnetite and hematite powders. The Auger peaks of high energy (for oxygen at 510 eV and for iron at 703 eV) were used for the quantitative determination of the oxygen coverage on the iron surface, at 2,5 keV excitation energy.

3. Experimental results and discussion

3.1. Adsorption kinetics

In a first approximation, the oxygen coverage Θ may be determined according to the relation

$$\Theta = \tau_M \cos \alpha_0 \frac{(I_O/I_{Fe}) (\Phi_{Fe}/\Phi_O) (\gamma_{Fe}/\gamma_O)}{1 + (I_O/I_{Fe}) (\Phi_{Fe}/\Phi_O) (\gamma_{Fe}/\gamma_O)} \quad (1)$$

if in addition to the measured signal ratio I_O/I_{Fe} , the mean escape depth τ_M of the Auger electrons — measured in monolayers —, the entrance angle α_0 of the analyzer, and the ratios of the ionization cross section Φ and the emission probabilities γ are known.

The relation $(\Phi_O/\Phi_{Fe})(\gamma_O/\gamma_{Fe}) = 3.67$ has been experimentally obtained on the compact magnetite and hematite samples. By means of this value, the mean escape depth of the Auger electrons is then obtained for the energy

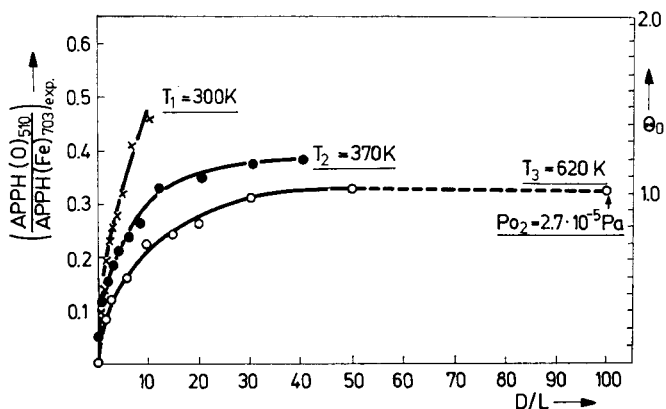


Fig. 2. Change of peak-height ratio and degree of coverage as a function of the dose for various temperatures ($p_{O_2} = 3 \times 10^{-6}$ Pa)

703 eV of the L_3VV transition, if, e. g. the signal ratio I_O/I_{Fe} is measured on a fully developed $p(1 \times 1) - O$ superstructure representing a coverage of $\Theta = 1$. The numerical value is 1.05 nm.

By means of this calibration it became possible to describe the kinetics of the initial step of the oxygen adsorption on the Fe(111) surface quantitatively. Fig. 2 shows the change of the Auger peak-height ratio of oxygen and iron and the coverage, respectively, as a function of the oxygen exposure at a constant pressure of 3×10^{-6} Pa for the temperatures 300 K, 370 K and 620 K. No pressure dependency could be stated in the range of 10^{-6} Pa.

The experimental curves may be described in good agreement by a theoretical model with a physisorption precursor state, which will not be dealt with in more detail. Accordingly, adsorption takes place dissociative, not activated, and immobile at two sites. On the assumption that the physisorbed molecules very quickly achieve a state of equilibrium and the desorption rate from the state of chemisorption can be neglected we have integrated the rate equations and obtained the solution

$$\Theta + \frac{K_D}{K_1} \left(1 - \frac{1}{z}\right) \left(\frac{1}{1-\Theta} - 1\right) - \frac{K_D}{K_1} \frac{1}{z} \ln(1-\Theta) = K_A p_{O_2} t, \quad (2)$$

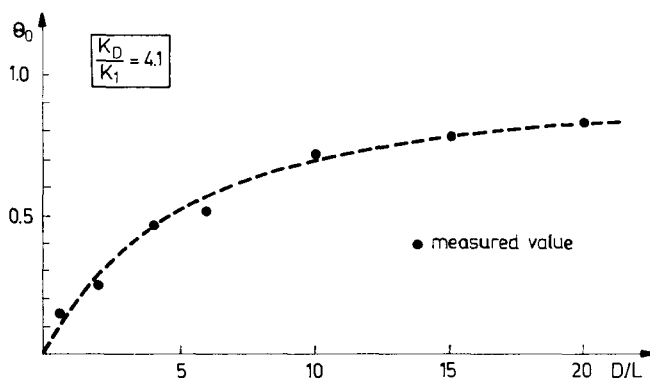


Fig. 3. Degree of coverage θ_0 of chemisorbed oxygen vs dose D ($T = 620$ K) calculated for immobile chemisorption complexes with $z = 3$

which is valid within the limits $0 \leq \theta < 1$. The best fitting of the theoretical function to the measured curve at 620 K can be obtained by assuming three nearest neighbours ($z = 3$) and choosing the quotient of rate constants for the desorption (K_D) and chemisorption (K_1) $K_D/K_1 = 4.1$ (Fig. 3). K_A is about $0.75 \times 10^4 \text{ Pa}^{-1} \text{ s}^{-1}$ for the Fe(111) surface, and $p_{\text{O}_2} t$ is the oxygen dose.

3.2. Chemical changes

For the quantitative chemical analysis up to now we have only used the intensity of the Auger electron signals in the derivative mode. A possible fine structure in the peak form that refers to a splitting of core levels or re-

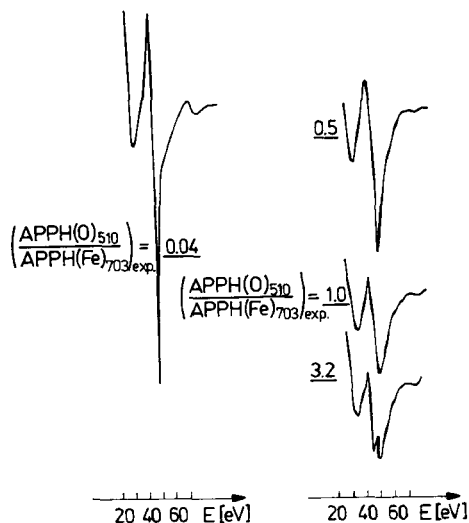


Fig. 4. Changes of Auger electron spectrum by oxidation at room temperature

flects the density of states in a bond has not been taken into account. Both effects are dominantly produced by chemical surface reactions.

In the low energy part of the Auger spectrum of pure iron (Fig. 1) there appears a peak at 47 eV corresponding to a $M_{2,3}VV$ electron transition of the Auger process. As a result of the oxidation of the iron surface at room temperature, it is observed that increasing oxygen coverage on the surface, the peak height decreases; also splitting is successively observed, as already known from literature [15 to 17], in peaks at 44 eV and 51 eV (Fig. 4). SAVTCHENKO [15] assigned the corresponding Auger electron transitions to $3p_{Fe} 2p_O 2p_O$ and $3p_{Fe} 3d_{Fe} 3d_{Fe}$ where the iron energy level $3p$ was shifted from 56 eV in pure iron to 58 eV in Fe_2O_3 below the Fermi level. In the valence band two maxima are found, one at 5 eV associated mainly with electrons from the $2p$ oxygen level, and the second at 1.5 eV associated with electrons from the $3d$ iron level (Fig. 5).

In Fig. 6, the peak heights at 44 eV and 51 eV in the Auger spectrum are shown, obtained on magnetite, hematite and a thin layer of oxygen on the iron surface, the Auger spectrum remaining unchanged by the further oxidation process. The comparison of the relative heights of those peaks shows that on the oxidized iron surface a thin oxide layer is formed of a composition approaching Fe_3O_4 . The ratio of the peak height at 44 eV to that at 51 eV

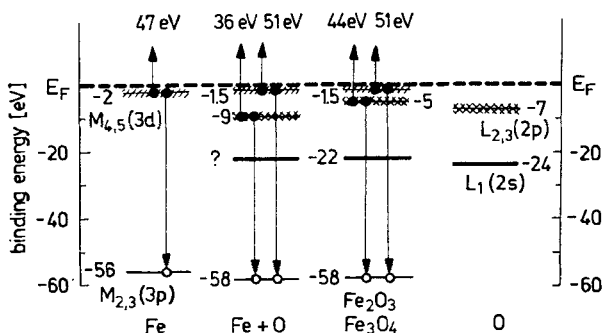


Fig. 5. Simplified schemes of energy levels

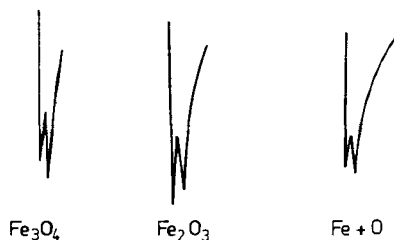
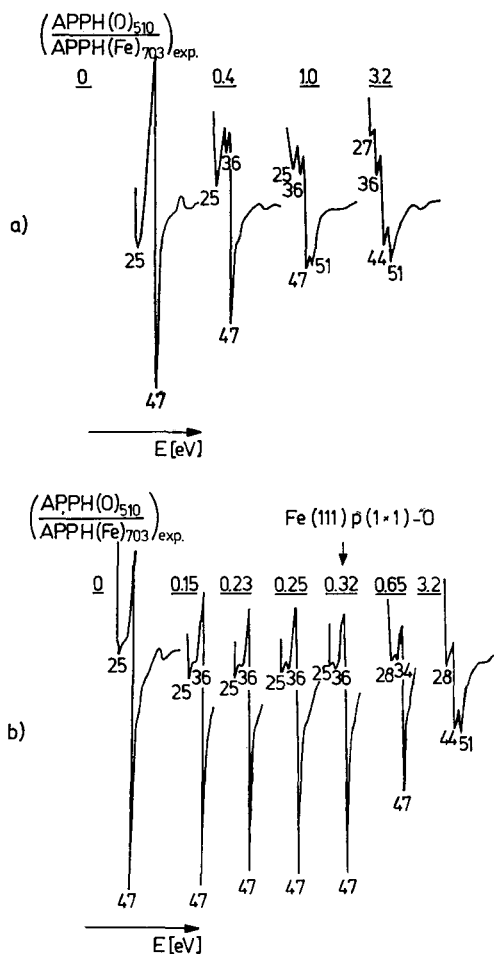


Fig. 6. Auger peaks at 44 eV and 51 eV

in hematite is higher than in magnetite. This fact confirms the contribution the cross-transition $3p_{Fe} 2p_O 2p_O$ to the peak at 44 eV, because, with increasing oxygen concentration in iron oxides, the electron density increases on the $2p$ level. The probability of the Auger transitions is enhanced with these electrons contributing.

While oxidizing iron at temperatures of 370 K and 620 K, new features were observed in the Auger spectrum (Fig. 7). At a small coverage of the iron surface with oxygen, a peak is appearing at 34 eV to 36 eV. Simultaneously, at 51 eV a well defined peak is being formed that becomes clearer with progressing oxidation. As a consequence of progressing oxidation in the Auger spectrum a total decline at 47 eV peak and a simultaneous appearance of a



Figs. 7. Changes of Auger electron spectrum by oxygen adsorption at 370 K (a) and 620 K (b)

44 eV peak are observed while a 36 eV peak is present (see oxidation at 370 K in Fig. 7a). It proved to be practicable to determine the 36 eV peak shape during the oxidation process at 620 K (Fig. 7b), well defined at a coverage on the iron surface equal to one. 7×10^{18} atoms/m² correspond to the structure Fe(111) $p(1 \times 1) - O$, the existence of which was stated by the method of low energy electron diffraction (LEED) [18].

Similar changes in the Auger spectrum, but in reverse order have been observed during the reduction of the iron surface oxidized at room temperature, as resulting from step by step heating (Fig. 8). By the LEED method

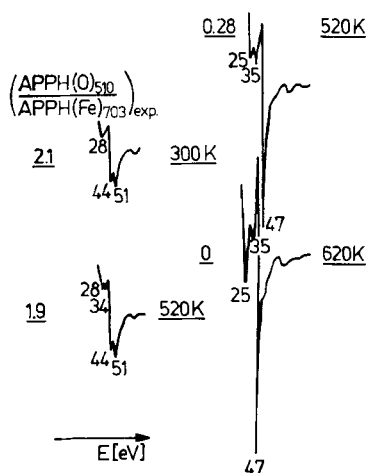
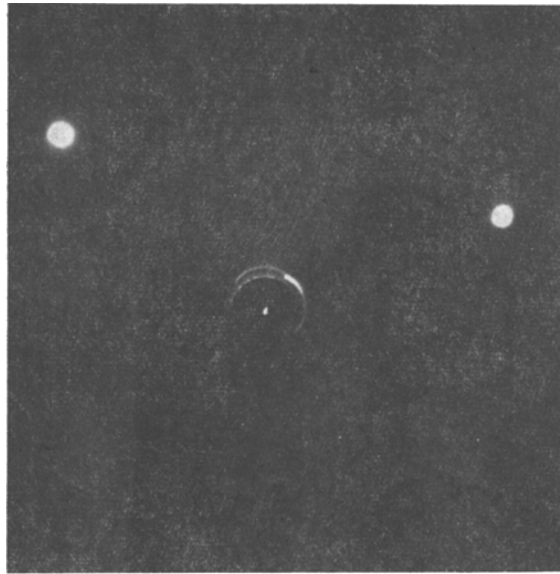


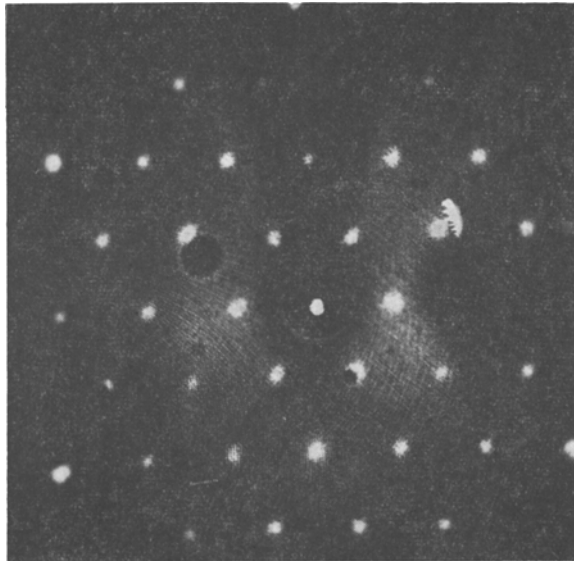
Fig. 8. Changes in the Auger electron spectrum of a sample oxidized at room temperature during a heat treatment to 620 K

it was stated that by heating the oxidized iron surface above 520 K, a two-dimensional structure Fe(111) $(2\sqrt{3} \times 2\sqrt{3}) - 30^\circ - O$ will be formed on the surface [19]. In Fig. 9b the LEED pattern represents this superlattice at 34 eV and, for comparison, that of the clean Fe(111) surface at 30 eV is shown in Fig. 9a. The high value of the period length of this structure indicates that the diffraction pattern may not be assigned to a single substance but to a coincidence lattice of the substrate and the surface layer of FeO with the orientation (111). Thus, by means of diffusion, the most iron-rich oxide phase is developed.

The Auger spectra obtained on the iron surface after its correspondingly long oxidation within the studied range of temperatures and a pressure up to 10^{-3} Pa exhibit a similar character proving the identical chemical composition of the thin oxide surface layers.



a)



b)

Fig. 9. LEED pattern a) of the clean Fe (111) surface ($E = 30$ eV); b) of the Fe (111) $(2\sqrt{3} \times 2\sqrt{3})-30^\circ-0$ superstructure ($E = 34$ eV)

4. Conclusions

The observations described above allow us to assume that in the process of oxidation two kinds of chemical bond of oxygen with iron are formed which differ regarding the density of states in the valence band as shown in our diagram (Fig. 5). One kind is characteristic for iron oxides, the second occurs at the first stage of oxidation and is associated with chemisorbed oxygen. In both cases, the position of maxima in the density of states related to iron was assumed to be equal which is proved by the existence, in all Auger spectra, of the 51 eV peak, corresponding to the transition $3p_{\text{Fe}}3d_{\text{Fe}}3d_{\text{Fe}}$.

The 36 eV peak is attributed to "cross-transition" between oxygen and iron with participation of levels 3p iron and 2p chemisorbed oxygen with the maximum in the density of states located about 9 eV below the Fermi level.

As it now appears from these scattered investigations, the presence of chemisorbed oxygen on the iron surface depends on temperature and thickness of the magnetite film. At room temperature, we do not observe the peak at 36 eV in the Auger spectrum, indicating the absence of bound oxygen on the iron surface, which may be due to the fast transition of chemisorbed oxygen into oxides. This is indicated by new spots in the LEED pattern already appearing at the exposure of about 10 L oxygen.

The presence of chemisorbed oxygen is observed at higher temperatures of oxidation and reduction, respectively, when oxygen forms regular two-dimensional structures on the iron surface, also when the thin oxide layer is surely thicker than the magnitude of the escape depth of 703 eV electrons, i. e. thicker than 1.05 nm. This is proved by the 36 eV peak appearing in the Auger spectrum, when the ratio of the peak heights of oxygen to iron reaches the maximum value. From the last observation, something more may be concluded, namely that oxygen bound with iron is located at the boundary of phases:

- oxygen gas (during the measurement — the vacuum) and
- the thin oxide layer.

Finally, on the thin passive oxide layer no chemisorption of oxygen is taking place under the conditions of measurement.

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