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The value of charge of Fe atoms adsorbed on alpha-Al2O3(0001) surface α-$Al_2O_3(0001)$

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Studying the formation of submonolayer Fe films on the surface of 5 nm thick α-$Al_2O_3(0001)$ film, via the analysis of intensity ratio of Fe Auger LVV-triplet, it is found that the interface charge transfers from Fe to alumina, and the absolute values of charges acquired by Fe atoms in the coverage range from 0.12 to 0.96 monolayers are measured. Extrapolating the measured charge versus coverage plot to zero coverage the estimate value of charge of single Fe atom adsorbed on α-$Al_2O_3(0001)$ is determined, which is $+0.98e$ (in electron charge units)

Keywords: Surface, adsorption, thin films, metal/oxide systems, iron, aluminum oxide, surface analysis techniques.

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Systems representing metal atoms, clusters and films on the surface of metal oxides (metal-oxide systems) have been a field of increased focus of researchers for a number of years, mainly due to the wide practical application of such systems in various fields: from metal-ceramic technology to opto- and microelectronics and heterogeneous catalysis [1–4]. The unique properties of such systems are due to the specific features of the electronic state acquired by the metal atom on the oxide surface and the formed interfacial metal/oxide interface. Although considerable amount of material has been accumulated concerning the description of these features, no results have been reported so far on the measurement of the absolute value of the electronic charge acquired by the metal atom during its deposition on the surface of the oxide, except for a few calculations [5]. At the same time, this is what determines the physicochemical state of the deposited metal, the interfacial interface and the metal-oxide system as a whole. Therefore, the purpose of the present study was the experimental determination of the atomic charge for a special case of adsorption of Fe atoms on the surface of aluminum oxide α-$Al_2O_3(0001)$. Such metal-oxide system is typical, simulating the behavior of the systems, most widely used in real-case scenarios, based on transition metal and simple metal oxide.

To ensure the highest integrity of the experiment, the studies were carried out under ultrahigh vacuum conditions in the VGS Escalab MkII system by Auger electron spectroscopy (AES), low-energy ion backscattering spectroscopy (LEIBS), low energy electron diffraction (LEED), and contact potential difference in the Anderson variant to measure the work function. A single-stage cylindrical mirror electron energy analyzer with a coaxial electron gun with primary electron energy of 3 keV and current density of 10 mA/cm^2 was used for AES. The spectra were recorded as $dN(E)/dE$, generally taking the distance „from peak to peak" as the intensity (I) of the corresponding Auger transition. The atomic structure of surface was studied using LEED using four-grid electron optics with a Varian 981 coaxial electron gun. LEIBS spectra were recorded with a standard hemispherical analyzer of the Escalab system using He$^+$ ions with primary energy of 1 keV. The peculiarity of this method is its sensitivity to the uppermost atomic layer of the investigated object.

The aluminum oxide film α-$Al_2O_3(0001)$ of controlled thickness was formed on the surface of Mo(110) crystal using the well-known technique of reactive sputtering of Al atoms in the atmosphere of oxygen injected into the chamber of ultrahigh vacuum to a partial pressure of the order of 10^{-6} mbar, and subsequent thermal treatment [6]. Fe atoms were deposited on the surface of the aluminum oxide film by thermal sputtering from a Knudsen cell with the atom flux density controlled by a quartz resonator and verified by the substrate Auger signal attenuation and the concentration dependence of the work function of the Fe$-$Mo(110) system. The latter serves as an additional verification of the concentration of deposited Fe atoms because, as is well known, the concentration dependence of the work function of the Fe$-$Mo(110) system stabilizes at monolayer coating [7]. Considering that the surface concentration of Mo(110) facet atoms is $1.45 \cdot 10^{15}\,\mathrm{cm}^{-2}$, the number of Fe atoms corresponding to the coating (θ) in one monolayer (ML) is $1.55 \cdot 10^{15}\,\mathrm{cm}^{-2}$ $(\theta = 1\,\mathrm{ML})$. The same value of the concentration of Fe atoms also deposited on the surface α-$Al_2O_3(0001)$ was also taken as corresponding to one monolayer. This assumption seems to be justified since the LEIBS results below indicate the formation of a continuous coating on the aluminum oxide

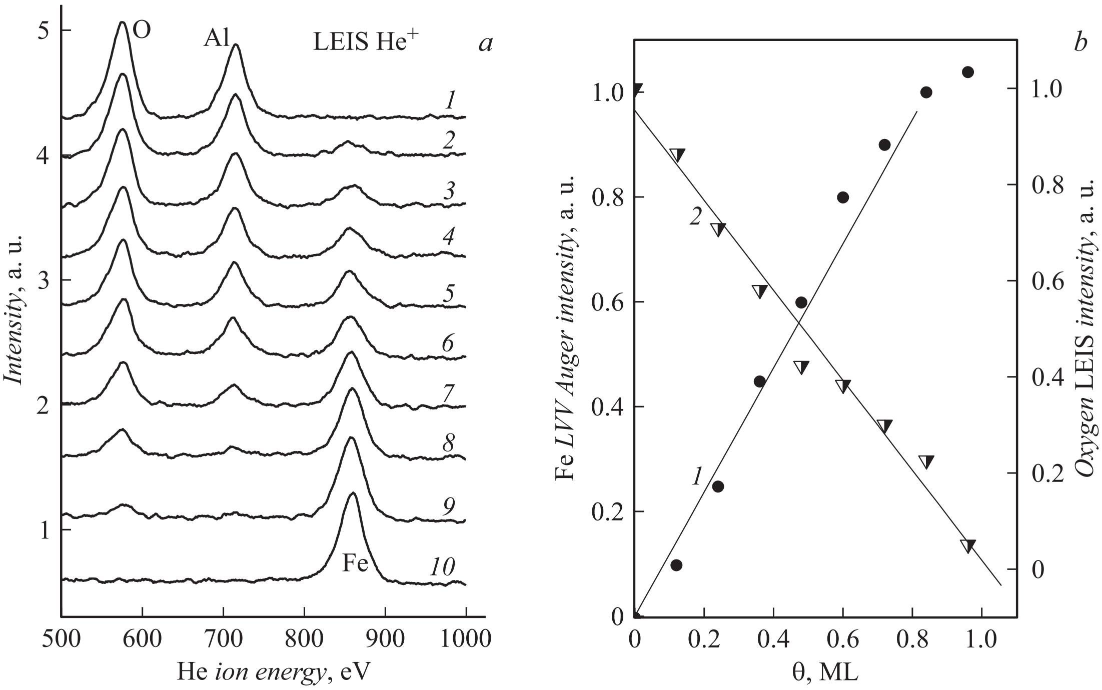

Figure 1. *a* — α-Al_2O_3(0001) surface. Fe coating, ML: *1* — 0, *2* — 0.1, *3* — 0.2, *4* — 0.3, *5* — 0.4, *6* — 0.5, *7* — 0.6, *8* — 0.8, *9* — 0.9, *10* — 1.0. *b* — dependence of the intensity of the Fe *LVV* (702 eV) Auger signal (*1*) and the intensity of ions backscattered from aluminum oxide oxygen *LVV* (702 eV) (*1*) α-Al_2O_3(0001) of He$^+$ (596 eV) (*2*) from the coating of Fe atoms on the surface of the α-Al_2O_3 (0001) film with a thickness of the order of 5 nm formed on Mo(110).

surface at monolayer Fe concentration. The experimental features have been described earlier in more detail [8–10].

As shown in [6,9], the formation of aluminum oxide film on the Mo(110) surface produces a well-ordered film starting from a thickness of the order of 1 nm, the structure of which corresponds to α-Al_2O_3(0001). The thickness of the aluminum oxide film used in the present study is of the order of 5 nm. When iron atoms are deposited on its surface, maintained at room temperature, there is a weakening of the intensity and smearing of the structural reflexes of the LEED pattern starting from submonolayer coatings and up to the studied coating value of the order of 2 ML, at which a diffuse background without clearly distinguishable superstructural diffraction reflexes is observed. This indicates that the Fe film formed on the surface of aluminum oxide is disordered at all studied coatings. To establish the film morphology, AES and LEIBS measurements were carried out. To record LEIBS spectra and Auger spectra, Fe/Al_2O_3 systems were formed separately in the range of coatings from 0.1 to 1.0 ML in the first case and in the range of coatings from 0.12 to 0.96 ML in the second case. The evolution of the LEIBS spectra during the growth of the Fe coating is shown in Fig. 1, *a*, and concentration dependences of the LEIBS signal intensity on oxygen (596 eV), a component of aluminum oxide, and the Fe *LVV* (702 eV) Auger signal intensity are shown in Fig. 1, *b*. The consistent linear course of these dependences and the almost zero intensity of the SORINE line in the Fe monolayer coating rather unambiguously indicate the formation of a two-dimensional iron film on the α-Al_2O_3(0001) surface, at least in the submonolayer region. This indicates the Fe ↔ Al_2O_3 chemisorption bond's dominance over Fe ↔ Felateral bonds.

To estimate the absolute value of charge transfer during the formation of chemisorption bonds (the charge of the Fe adatom), one can use well established patterns relating the probability of Auger and photoelectron transitions to the charge value at the corresponding levels of the atom [11,12]. In particular, for the dependence of the intensity (I) of the signals *LVV* of the Auger triplet 3*d*-metals on the charge (q) there is a ratio $R = I(LVV)/I(LMM) = Cq(q-1)$ on their valence shell (R). In case the Fe atom forms a chemisorption bond with the surface of aluminum oxide with charge transfer of $\pm\Delta q$ value to/from the metal atom, this ratio will be rewritten as $R = C(q+\Delta q)(q+\Delta q-1)$. Based on measuring the intensity ratio of *LVV* and *LMM* signals during the evolution of spectra as the surface concentration of Fe atoms on the surface increases α-Al_2O_3(0001)(Fig. 2), the charge magnitude (Δq) of the chemisorbed Fe atom at different surface concentrations can be estimated. The corresponding dependence of $\Delta q(\theta)$ in the range of coatings from 0.12 to 0.96 ML is shown in Fig. 3. The obtained values of $\Delta q(\theta)$ are rather accurately approximated by a nonlinear dependence (curve *1*). It can be seen that as the Fe coverage increases, the charge of the adatom decreases naturally, reaching a value close to that characteristic of a neutral atom ($\Delta q \approx 0$). Extrapolation of this dependence to $\theta \to 0$ allows estimating the value of the

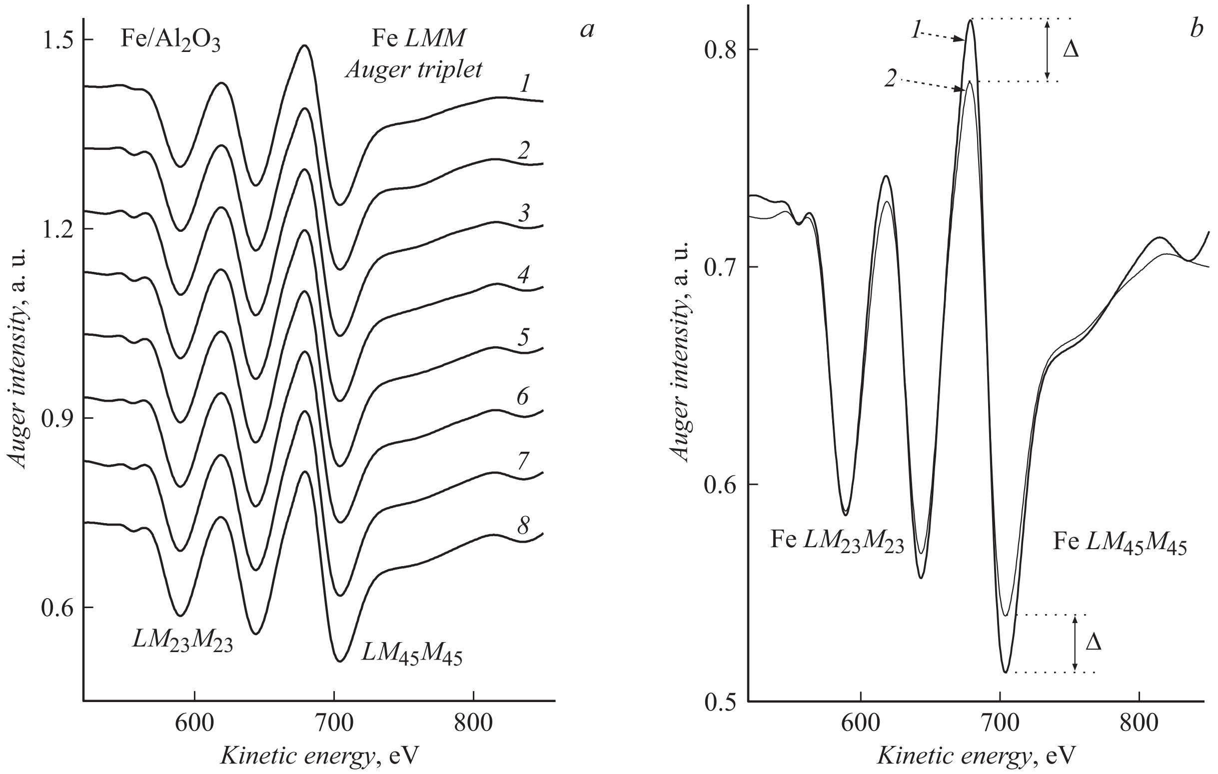

Figure 2. *a* — Fe *LMM* Auger spectra during the growth of the Fe coating on the α-Al$_2$O$_3$(0001) surface. Fe coating, ML: *1* — 0.12, *2* — 0.24, *3* — 0.36, *4* — 0.48, *5* — 0.60, *6* — 0.72, *7* — 0.84, *8* — 0.96. *b* — comparison of Auger spectra at Fe 0.96 (*1*) and 0.12 ML (*2*) coatings. The spectra were normalized by the intensity of the low-energy triplet component $LM_{23}M_{23}$ to better represent the relative change in intensity (Δ) of the high-energy component $LM_{45}M_{45}$ with changing coverage.

charge of a single Fe atom chemisorbed on the surfaceα-Al$_2$O$_3$(0001), which is$+0.98e$ (in units of electron charge).

This value is significantly higher than that for the previously studied case of Fe adsorption on the Mo(110) surface: $+0.15e$ [10], indicating a greater degree of polarization of the chemisorption bond Fe $\rightarrow$ Al$_2$O$_3$(0001). Moreover, the difference is that in the case of the metal adsorbent the concentration dependence of the adatom charge has a linear character, while in the considered case the dependence is nonlinear. The nonlinear character of this dependence is qualitatively indicated by the results of theoretical calculations, which testify to a sharp transition of the adatom state on theα-Al$_2$O$_3$(0001) surface from the ionic form to the neutral one at the coating exceeding 0.33 ML [13], schematically represented by the curve *2* in Fig. 3 for convenience of comparison. These two circumstances indicate different adsorption and transformation mechanism of chemisorption bond with the coating of metal atoms on the surface of metal and oxide substrate. According to the calculation results [13], in contrast to metal substrates, on the surface of which hybridization of orbitals of the corresponding symmetry of the adatom and adsorbent occurs, on the surface of the oxide at small coatings there is a Madelung potential-induced polarization of the adatom charge. As the coating increases, the electrostatic interaction decreases due to the formation of lateral bonds between adatoms, and weaker polarization interaction forces become predominant. Knowledge of the absolute value of the atom charge on the oxide surface contributes to a more complete understanding of the specific features of the corresponding metal-oxide system, and the possibility of varying this value due to the coating allows controlled tuning of the system parameters for those or other practical applications. Furthermore, the possibility of comparing this value with the calculation results can contribute to a more complete justification and selection of appropriate theoretical models.

The results of this study show that the deposition of Fe atoms on the surface of aluminum oxide α-Al$_2$O$_3$(0001) under ultrahigh vacuum conditions leads to the formation of a two-dimensional metal film within the first monoatomic layer. The Fe film thus formed lacks long-range structural order for all coatings in the submonolayer region. By analyzing the ratio of the intensities of the Fe *LVV* Auger triplet components during film growth, it is shown that charge transfer from Fe to aluminum oxide occurs. The dependence of the value of the acquired charge of Fe adatoms on their coverage has been determined. The value of the charge of a single Fe atom adsorbed on the surface α-Al$_2$O$_3$(0001), which is $+0.98e$ (in units of electron charge), has been estimated. Knowledge of this value is of both applied and fundamental importance, in particular from the

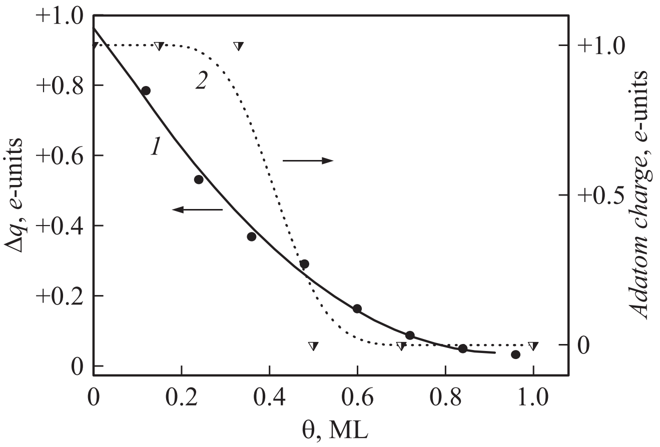

Figure 3. Dependence of the charge value of Fe adatoms on their coating on the surface α-Al$_2$O$_3$(0001) (*1*). For convenience of comparison, the results of [13] (*2*), indicating the transition of transition metal adatoms from the ionic ($\theta < 0.33$ ML) to the neutral state as their coating on the α-Al$_2$O$_3$(0001) surface grows, are plotted in comparable coordinates.

point of view of adjusting the corresponding theoretical models.

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Conflict of interest

The authors declare that they have no conflict of interest.

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