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INVESTIGATION OF THE ELECTRON STATE AND THE DYNAMICS OF MOTION OF TIN ATOMS ON THE SURFACE OF SILICA GELS AND ZEOLITE BY GAMMA-RESONANCE SPECTROSCOPY

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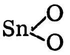
The nature of the vibrations and electron state of tin atoms on silica gel surfaces with various pore diameters (4–6, 140, and 270 Å) and on zeolite with channel diameters of 5–7 Å is investigated by gamma-resonance spectroscopy. The results of the experiments point to an increase of the isomer shift in zeolite compared to that in silica gel. The bonding of the tin to the surface becomes stronger with decrease of the pore diameter, down to dimensions close to molecular ones. A phase transition is observed for atoms on the surface of large-pore silica gel and is ascribed to a sharp drop of the probability of the Mossbauer effect and the increase of the line width. The activation energy for diffusion of $SnO_2 \cdot nH_2O$ over the surface of large-pore silica gel was estimated to be about 3 kcal/mole on the basis of the dependence of the line width on temperature. The temperature dependence of the quadrupole-splitting spectrum asymmetry is obtained by regarding the tin atom on the surface as harmonic oscillator. Comparison of the experimental results and the calculations yielded the value $\omega_1^{-2} - \omega_2^{-2} = 4.5 \times 10^{-27}$ sec for the difference between the inverse squares of the tin atom oscillation frequencies in a direction perpendicular to the surface and parallel to the surface. It is also found that the harmonic-oscillator approximation for tin atoms on the surface of silica gel is acceptable.

THE present paper is a continuation of the research on the dynamics of motion of tin atoms on the surface of solids, which we started earlier[1,2]. It is known that the dynamic characteristics of atoms on the surface and in the volume of a solid differ greatly (for example,[1-3]). It can be assumed that the dynamic characteristics of the atoms on the surface depend on the curvature of the surface. In order to verify this assumption, we have introduced the investigated atoms into the surfaces of pores of different dimensions. We took silica gels with pore diameter 270, 140, and ~4–6 Å and synthetic mordenite (a mineral from the zeolite group—porous alumosilicate crystals) with pore diameter ~6 Å. At a pore diameter 270 or 140 Å (large-pore samples), the surface is close to plane (the radius of curvature is two orders of magnitude larger than the dimension of the atom). Conversely, in small-pore samples, the pores (4–6 Å diameter) are so small that the atoms located on their surface are apparently under conditions intermediate between the surface and the volume of the solid.

EXPERIMENTAL PART

The tin atoms were placed on the surface of the investigated samples by ion exchange. Silica gel, as is well known, consists of globules of polysilicic acid, the surfaces of which are covered with silanol groups $\rightarrow$ Si-OH. The protons of these groups were first replaced by Ca^{2+} cations[4] which were then in turn replaced by Sn^{2+} ions. In the mordenite, the ions Sn^{2+} replaced the Na^+ ions situated in its pores and compensating the excess charge acquired by the zeolite lattice from the AlO_4^- tetrahedra.

Thus, the investigated silica gels and the zeolites contain divalent tin atoms chemically bonded to the surface atoms of the oxygen. In addition, there could appear on the surface also hydroxide forms of tetravalent tin ($SnO_2 \cdot nH_2O$), which was not bonded to the surface chemically, as a result of the hydrolysis of the  $\mathrm{Sn}\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$ bonds and subsequent oxidation of Sn^{II} into Sn^{IV}.

The γ-resonance spectra were obtained in the temperature interval 93–300°K with a setup using a $Sn^{119m}O_2$ source.

DISCUSSION OF RESULTS

Electronic state of the tin atoms on the surface. Figure 1 shows by way of an example the γ-resonance spectra of tin on the surface of silica gel (with pore diameter 140 Å) and zeolite. The spectra show the presence of tetravalent tin in the form $SnO_2 \cdot nH_2O$, sorbed on the surface, and of divalent tin chemically bonded with the surface oxygen atoms[1]. The isomer shift of $SnO_2 \cdot nH_2O$ is the same for all the investigated samples ($\delta E_I = 0 \pm 0.1$ mm/sec). The isomer shift of the divalent tin on the surface of the silica gels ($\delta E_1 = 2.7 \pm 0.1$ mm/sec) corresponds to the shift of SnO in the polycrystalline state, whereas in zeolite it increases noticeably ($\delta E_I = 3.4 \pm 0.1$ mm/sec); the quadrupole splitting of the SnO spectra is the same in both zeolite and in the silica gels and equals $\delta E_I = 2.1 \pm 0.1$ mm/sec (at 215°K). The large value of δE_I of the divalent tin in the zeolite is evidence of the larger ionicity of the bond of the tin cation with the zeolite frame compared with the silica gel. Indeed, since

$$\delta E_I \sim \frac{\Delta R}{R}\left[\,|\psi(0)|^2_{\text{absorber}} - |\psi(0)|^2_{\text{source}}\,\right]$$

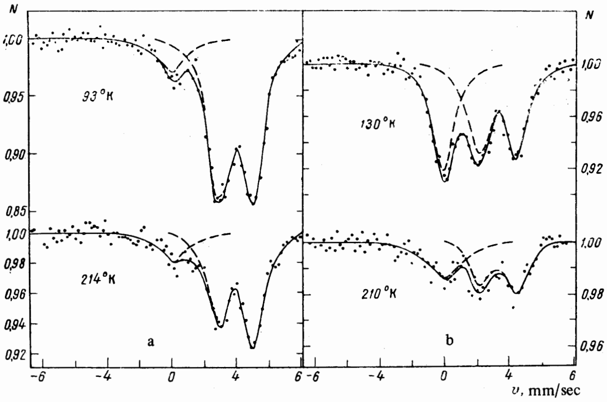


FIG. 1. γ-resonance spectra of tin atoms on the surface of zeolite and silica gel at different temperatures: a—tin atoms on surface of mordenite; b—tin atoms of the surface of silica gel with pore diameter 140 Å.

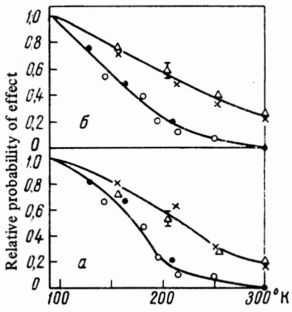


FIG. 2

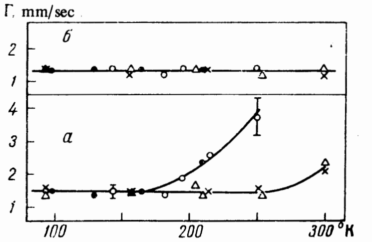


FIG. 3

FIG. 2. Temperature dependence of the relative probability of the effect for tin atoms on the surface of silica gels and zeolite: a—temperature dependence for tin atoms in the form $SnO_2 \cdot nH_2O$; b—temperature dependence for tin atoms in the form of SnO. The experimental points X and Δ correspond everywhere to mordenite and to small-pore silica gel, while the experimental points ● and ○ correspond to large-pore gel with pore diameters 140 and 270 Å, respectively.

FIG. 3. Temperature dependence of the γ-resonance line widths for $SnO_2 \cdot nH_2O$(a) and SnO(b). The experimental points are marked as in Fig. 2.

and $\Delta R/R > 0$, the removal of the bond-producing p-electrons from the tin (that is, the increase in the ionicity of the bond) leads to an increase of $|\psi(0)|^2$ from the s-electrons due to the decrease of the screening by the p-electrons, and consequently to an increase of δE_I.

The quadrupole splitting of the spectrum remains unchanged in this case. This is apparently connected with the fact that the value of ΔE_Q is governed by the action of both the unbalance of the p-electrons and by the action of the crystal field, the two factors having opposite signs. In this case the large value of δE_I for Sn in the form of SnO in zeolite offers evidence of the weakening of the influence of the crystal field, which mixes the s- and p-states in the ordinary polycrystalline SnO sample[5]; this also leads to an increase of the s-density on the nucleus. Thus, a decrease in the influence of the crystal field takes place in zeolite simultaneously with the decrease of the unbalance of the p-electrons, and the value of ΔE_Q remains unchanged compared with the value of ΔE_Q for SnO in the silica gel.

It should be noted that for ions of divalent iron in zeolites we have previously also observed an isomer shift $\delta E_I = 1.5$ mm/sec, which is close to the possible maximum[6]. This agrees with the result obtained for the tin ions in the present paper (on iron, $\Delta R/R > 0$, but the bond is effected essentially by the s-electrons, and therefore the increase of δE_I is also evidence of the increased ionicity of the bond).

Temperature dependence of the probability of the effect. Figure 2 shows the temperature dependence of the relative area under the resonance curves for surface atoms of tetravalent (2) and divalent (b) tin. The figure shows clearly that for small-pore samples (the points X and Δ, pore diameter ~5—7 and ~4—6 Å) the temperature dependence differs noticeably from that for large-pore samples (points ● and ○, pore diameter 140 and 270 Å). It follows from these data that the tin atoms are much more strongly bonded on the surface of a pore with dimensions 4—7 Å than on the "plane" surface of a large pore. Such a result is well known for molecules of adsorbed gases and vapors, but it has apparently been obtained for the first time for atoms that are chemically bonded to the surface of the solid.

Figure 3 shows the temperature dependence of the line width of Sn^{IV}(a) and Sn^{II}(b). The line width of Sn^{2+} ion which is chemically bonded to the surface is the same for all samples and does not depend on the temperature, thus pointing to the localization of the ion in the crystal lattice. In the case of $SnO_2 \cdot nH_2O$, to the contrary, the line begins to broaden with increasing temperature, and in this respect there is again observed a sharp difference between the large-pore and small-pore samples. In the case of large pores, the broadening begins with 190°K and reaches a rather large value already at 250°K. In the case of small pores, a slight broadening is observed only at 300°K. The resonance-absorption line broadening of the tin atoms with increasing temperature can be connected in this case with the diffusion of the atoms[7]. If it is assumed that the diffusion is via jumping from one localized position to another (which is perfectly natural for such a nonvolatile insoluble compound as SnO_2), then the time of stay of the molecule in the localized position can be determined from the expression $\tau = 2\hbar/\Delta\epsilon$, where $\Delta\epsilon$ is the experimental broadening of the γ-resonance line[7]. Recognizing that the time of stay of the particle in the localized position on the surface is determined[8] by the expression $\tau = \tau_0 \exp(Q/RT)$, where Q is the height of the potential barrier separating the localization centers, we can obtain Q from the experimental relation $\ln \tau = f(1/T)$. In our case, for the surfaces of large pores, this value turned out to be ~3 kcal/mole.

In our earlier paper[1] we estimated the height of the potential barrier for the surface diffusion as being simply equal to the energy kT corresponding to the temperature at which the line intensity decreases abruptly. However, such an estimate is less accurate and may not correspond to the real height of the barrier for surface diffusion, since a sharp increase in the line intensity can be connected with the phase transition on the surface or with the breaking of the bonds of the surface molecules with one another.

It should be noted that in large-pore samples, the start of the broadening of the Sn^{IV} line and the sharpest decrease in the magnitude of the effect for Sn^{IV} take place in the same temperature region—approximately 200°K. This allows us to assume that a phase transition in the adsorption layer is realized in the indicated temperature interval and leads to an increase in the mobility of $SnO_2 \cdot nH_2O$. The fact that the broadening begins at higher temperatures in small-pore samples indicates that diffusion in small pores is hindered.

The assumption that the surface compound $SnO_2 \cdot nH_2O$ (unlike the surface atoms Sn^{II}) is connected with the surface by Van der Waals forces[1] was based on the fact that the effect has a steeper temperature dependence for $SnO_2 \cdot nH_2O$. The data obtained in the present paper on the line broadening with increasing temperature essentially confirm this assumption. We note, however, that another explanation of the broadening of the line of the surface SnO_2. is also possible (and in our opinion is of low probability). If we assume that the oxidation of the surface Sn^{II} atoms occurs with only one of the chemical bonds of these atoms to the surface broken, then the broadening of the line may be attributed, generally speaking, to the freeing of the rotational motion with increasing temperature, if the rotation axis passes through the Sn atom. In this case the activation energy of the line broadening corresponds as before to the potential barrier separating the resonance-atom localization centers, and the difference of the temperatures of the start of line broadening in the large-pore and small-pore samples can be connected with the difficulty of rotation in the thin pores.

Temperature dependence of the asymmetry of the γ-resonance spectra of Sn^{2+}. As is clear from Fig. 1, the spectra of Sn^{2+} in silica gel have an integral asymmetry (that is, the areas of the two components of the quadrupole splitting of the line differ in magnitude). The appearance of such an asymmetry of the quadrupole splitting of the spectra of polycrystals as a consequence of the anisotropy of the Debye-Waller factor for the corresponding single crystals is called in the literature the Gol'danskiĭ-Karyagin effect[9,10]. A characteristic property of the asymmetry of the lines in this effect is its intensification with increasing temperature, due to the oscillation frequency of the atoms. Since the oscillations of the adsorbed atoms along the surface of the adsorbent are not equal to the oscillations normal to it, the Gol'danskiĭ-Karyagin effect is quite clearly pronounced for surface layers.

Indeed, regarding the tin atom on the surface as a harmonic oscillator, we obtain[1]:

$$\langle x^2\rangle = \frac{\hbar}{2M\omega^2}\operatorname{cth}\frac{\hbar\omega}{2kT}.$$

The temperatures kT larger than $k\Theta/2$ (where Θ is the Debye temperature), and consequently larger than $\hbar\omega/2$, this expression can be approximately written in the form $\langle x^2\rangle \approx kT/M\omega^2$. For tin atoms on a surface, this formula is suitable for temperatures higher than 80–100°K (for example, for β-Sn the Debye temperature is $\Theta = 140$°K, and for surface atoms the effective Debye temperature is even lower[2]).

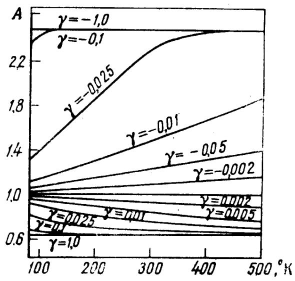


FIG. 4

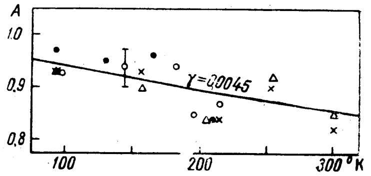


FIG. 5

FIG. 4. Calculated dependence of the asymmetry of the quadrupole-spectrum lines as a function of the temperature.

FIG. 5. Experimental results A = f(T) for all the silica gels in zeolite. The experimental points are designated in exactly the same manner as in Fig. 2 and 3. For comparison we give the calculated curve $A_{theor} = f(T)$ with parameter $\gamma = 0.0045$.

We now write the general expression for the asymmetry of the lines of the quadrupole spectrum[11] in the case of disordered orientation of the surfaces:

$$A = \left\{\int_0^\pi (5/3 - \cos^2\theta)\exp(-\varkappa^2\langle x^2\rangle)\sin\theta\, d\theta\right\}^{-1} \times\left\{\int_0^\pi (1+\cos^2\theta)\exp(-\varkappa^2\langle x^2\rangle)\sin\theta\, d\theta\right\},$$

where θ is the angle between the direction of the γ-quantum beam and the electric field gradient, and κ is the wave vector of the γ radiation. Substituting here the expression for $\langle x^2\rangle = f(T)$ and putting $\cos\theta = u$, we arrive at the expression

$$A = \left\{\int_0^1 (5/3 - u^2)\exp\left[-\frac{\varkappa^2 kT}{M}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right)u^2\right]du\right\}^{-1} \times\left\{\int_0^1 (1+u^2)\exp\left[-\frac{\varkappa^2 kT}{M}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right)u^2\right]du\right\}.$$

We have assumed here that $\omega_1 \neq \omega_2 = \omega_3$; ω_3 is the frequency of oscillations along the axis of the electric-field gradient (that is, under certain assumptions, perpendicular to the surface), and ω_2 and ω_3 are the frequencies of the oscillations perpendicular to the axis of the electric field gradient (that is, along the surface).

Introducing the parameter

$$\gamma = \frac{\varkappa^2 k}{M}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right)$$

we obtain, after numerically calculating the ratio of these integrals, a network of plots of $A = f(T, \gamma)$ (Fig. 4). Knowing the experimental $A = f(T)$ dependence, we can choose γ and thus calculate the difference of inverse squares of the frequencies for the inverse force constants

$$\gamma = \frac{\varkappa^2 k}{M}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right) = \varkappa^2 4\pi^2 k\left(\frac{1}{\nu_1} - \frac{1}{\nu_2}\right).$$

Figure 5 shows the experimental temperature dependence of the asymmetry of the quadrupole spectra of the surface ions Sn^{2+} (calculated under the assumption that the gradient of the electric field on the nucleus is positive[1]) for all silica gels and zeolite, which corresponds within the limits of error to the theoretical relation with a parameter $\gamma = 0.0045\ \mathrm{deg}^{-1}$. The numerical calculations yield

$$\frac{1}{\omega_1^2}-\frac{1}{\omega_2^2}=4{,}5\cdot 10^{-27}\ \text{sec}^{-2},\quad \frac{1}{\nu_1}-\frac{1}{\nu_2}=5{,}8\cdot 10^{-7}\ \text{dyne/cm}.$$

The agreement between the theoretical $A = f(T)$ dependence with the experimental data offers evidence that the divalent tin ion on the surface of the silica gel and zeolite can be regarded as a harmonic oscillator.

In conclusion, the authors are grateful to V. I. Gol'danskiĭ for valuable discussions.

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