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AN INVESTIGATION OF THE DYNAMICS OF THE MOTION OF TIN ATOMS ON A SILICA GEL SURFACE BY MEANS OF THE MÖSSBAUER EFFECT

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Nuclear gamma ray resonance (Mössbauer effect) is used to study the dynamics of the motion of tin atoms absorbed on a silica gel surface. The analysis of the experimental results indicates that the tin atoms exist on the surface in two states: one tetravalent and one divalent. The temperature dependence of the intensity of the Mössbauer effect shows that the tetravalent tin is attached to the surface by physical adsorption, whereas the divalent tin is held by chemisorption. A considerable asymmetry of the components of the doublet splitting is found in the spectrum of the tin adsorbed on the surface in the form of the compound SnO (surface chemisorption). The electric field gradient at the Sn^{119} nucleus in this compound increases with increasing temperature and is considerably larger than its value for crystalline SnO. Absolute values for the mean square displacement of the molecule $SnO_2 \cdot nH_2O$ on the surface, and of the tin atom within the molecule, are estimated from the experimental data as functions of the temperature. The experiments also led to estimates of the energy of the zero-point vibrations of tin atoms and molecules, the energy at which the binding between the molecule and the adsorption center on the surface vanishes, the absolute value of the mean square displacement of the tin atom within the SnO molecule normally and parallel to the surface, and the temperature dependence of these quantities.

A number of papers [1-4] have shown that it is promising to utilize the Mössbauer effect for the study of the dynamics of the motion of atoms on solid surfaces and the properties of the surface compounds. However, there are as yet few experimental papers in the literature which deal with this problem. In the present paper we study the dynamics of the motion of tin atoms adsorbed on a silica gel surface. For this purpose we chose a silica gel with a specific surface area of about 300 m^2/g and a particle diameter of about 100 Å. This was subjected successively to an ion exchange of the hydrogen atoms contained in the hydroxyl on the surface of the particles with Ca^{2+}, and then with Sn^{2+} [5,6]. In this way one obtained a system in which the tin was present as the SnO compound and formed a monolayer on the surface of the colloid particles. The replacement of hydrogen ions by Ca^{2+} was practically complete, but the subsequent replacement of Ca^{2+} by Sn^{2+} amounted to about 70%. The initial concentration of hydroxyl groups on the particle surface was 10 millimole/m^2. In the course of preparation part of the divalent tin ions which were adsorbed on the surface could change to the tetravalent state by acid hydrolysis.

A special cryostat was constructed for the temperature measurements, and could maintain any temperature between 90 and 300°K with an accuracy of 0.1°. The specimen temperature was determined from the resistance in the bridge of an electronic thermostat ÉT-6 connected to a platinum resistance thermometer. The electronic thermostat ÉT-6 automatically adjusted the current through the electric heater in the cryostat. The required dc current was taken from a UIP set. A supplementary temperature control was achieved by means of a differential thermocouple connected to a high-resistance dc potentiometer (type PPTV1) and a galvanometer of 0.05 degree/division sensitivity. One junction of the thermocouple was placed on the cooling tube near the specimen, the other on the edge of the liquid nitrogen reservoir. All measurements were carried out by means of the nuclear gamma-ray resonance spectrometer described earlier [7] and a source in the form of $Sn^{119*}O_2$.

Figure 1 shows the spectrum of one specimen, taken at T = 90°K. The spectrum consists of three lines (a singlet and a doublet) which suggest the distinction between tetravalent and divalent tin. The minimum on the left corresponds to tetravalent tin in the form $SnO_2 \cdot nH_2O$, and the other two minima correspond to SnO, as evidenced by the chemical

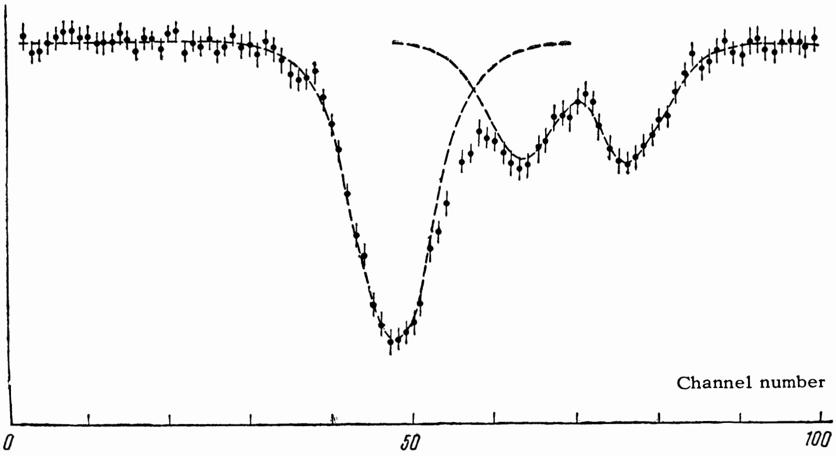

FIG. 1. The abscissae show the channel number. Each channel represents 0.13 mm/sec. The ordinates are the number of counts in each channel. The magnitude of the effect at maximum absorption is 12.8% for $SnO_2 \cdot nH_2O$ and 5% for SnO.

shift of the doublet (relative to SnO_2): $\delta = 2.70 \pm 0.07$ mm/sec. However, the quadrupole splitting $\Delta = 1.76 \pm 0.07$ mm/sec is substantially greater than the value $\Delta = 1.3$ mm/sec for ordinary crystalline SnO[8]. Δ increases from 1.76 ± 0.07 to 2.18 ± 0.07 mm/sec if the temperature is changed from 90 to 257°K. At the same time the chemical shift δ for SnO increases from 2.70 ± 0.07 to 2.94 ± 0.07 mm/sec while for $SnO_2 \cdot nH_2O$ $\delta = 0 \pm 0.07$ mm/sec in the same temperature range. At T = 213°K one finds an asymmetry of the doublet components, which belong to the tin nucleus in the compound SnO, whereas at T = 90°K no such asymmetry is observed. The nature of the temperature dependence of the magnitude of the effect df'/dT is appreciably different for SnO and $SnO_2 \cdot nH_2O$, as is easily seen from Fig. 2 (it is shown below that the amount of tin in these two compounds is about the same). This difference is due to the different nature of the adsorption of the divalent and tetravalent tin. As mentioned already, the SnO is formed on the particle surface by means of the substitution $H \rightarrow Ca \rightarrow Sn$, i.e., basically by chemisorption (forming a O–Sn–surface bond). The $SnO_2 \cdot nH_2O$ molecules, on the other hand, can be adsorbed on the silica gel particles only by Van-der-Waals forces, i.e., by physical adsorption. Hence the temperature dependence of the intensity of the Mössbauer effect for SnO should be weaker (because of the stronger binding) than for $SnO_2 \cdot nH_2O$. If the specimen is heated above 210°K the $SnO_2 \cdot nH_2O$ effect decreases even more rapidly, and disappears altogether at about 268°K.

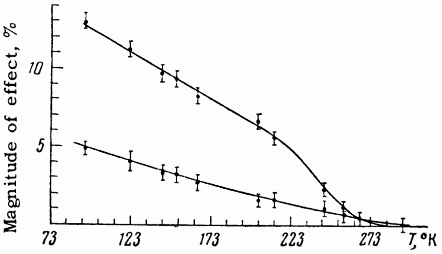

FIG. 2

From this temperature dependence of the intensity of the effect one can try to determine the temperature dependence of the absolute magnitude of the mean square displacement of Sn^{4+} on the surface. In the case of the physical adsorption of $SnO_2 \cdot nH_2O$, the intensity of the Mössbauer effect will depend on the displacement of each individual tin atom within the molecule and on the displacement of the whole $SnO_2 \cdot nH_2O$ molecule. By calculating the intensity of the Mössbauer effect $f' = f(T)$ one can therefore find $\langle x^2 \rangle_{Sn^{4+}} = f(T)$.

It is however obvious that the calculation of the quantity $f'_{SnO_2 \cdot nH_2O}$ from the experimental data requires a knowledge of the absolute amount of tin atoms in the tetravalent state. In one of the specimens all the adsorbed tin was transformed into the tetravalent state by means of acid hydrolysis. As a result the SnO spectrum disappeared and observations of the $SnO_2 \cdot nH_2O$ spectrum at various temperatures showed that the temperature dependence of the effect was the same as in other specimens. From the known number of tin atoms on the surface, and from the area under the experimental absorption curve for $SnO_2 \cdot nH_2O$, we could determine the quantity $f'_{SnO_2 \cdot nH_2O}$. By the same method, an absolute calibration point was found for $\langle x^2 \rangle_{Sn^{4+}}$. Using the knowledge of the quantity $f'_{SnO_2 \cdot nH_2O}$, one can now find the numbers of tin atoms in the tetravalent and divalent states in each specimen, which turned out to be about the same, and hence the absolute value of f'_{SnO}.

Figure 3 shows the absolute magnitude of the mean square displacement $\langle x^2 \rangle_{Sn^{4+}}$ against temperature. The curve shows a steep rise of $\langle x^2 \rangle_{Sn^{4+}}$

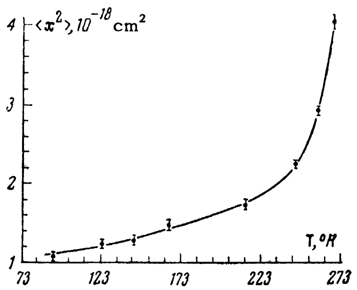

FIG. 3.

in the temperature range 210—268°K. As mentioned above, the tin atom performs two types of vibration: intramolecular vibrations, and vibrations together with the whole $SnO_2 \cdot nH_2O$ molecule. If we remember that in the quantum case (in the harmonic approximation) the probability of various values of the normal coordinate of the oscillator is given by the distribution*

$$dw_q = \left(\frac{\omega}{\pi\hbar}\operatorname{th}\frac{\hbar\omega}{2kT}\right)^{1/2}\exp\left(-q^2\frac{\omega}{\hbar}\operatorname{th}\frac{\hbar\omega}{2kT}\right)dq$$

(see e.g.[9]), we find

$$\langle x^2\rangle_{Sn^{4+}}(T) = \langle x^2\rangle_{01}\operatorname{cth}\frac{\alpha_1}{T} + \langle x^2\rangle_{02}\operatorname{cth}\frac{\alpha_2}{T}, \qquad (1)^\dagger$$

where the first term gives the mean square displacement of the molecule as a whole, and the second the mean square displacement of the tin atom within the molecule. In the range between 93 and 230°K, the curve of Fig. 3 is well approximated by the formula (1) with

$$\langle x^2\rangle_{01} = 0.15\cdot 10^{-18}\text{ cm}^2,\quad \langle x^2\rangle_{02} = 0.55\cdot 10^{-18}\text{ cm}^2,$$
$$\alpha_1 = 30^\circ\text{ K},\quad \alpha_2 = 220^\circ\text{ K}.$$

Using the values of α_1 and α_2 we can estimate the zero-point energy of a $SnO_2 \cdot nH_2O$ molecule physically adsorbed on a silica gel surface and of the tin atom within the molecule. A theoretical estimate of the quantities $\langle x^2\rangle_{01}$ and $\langle x^2\rangle_{02}$ with due allowance for the coefficients of the mass tensor confirms this deduction.

$$E_{0\,\text{mol}} = 0.26\cdot 10^{-2}\text{eV},\quad E_{0\,\text{at}} = 1.9\cdot 10^{-2}\text{eV}.$$

Hence, whereas at T = 0°K the Mössbauer effect depends mainly on the vibrations of the atom in the molecule, at higher temperatures the vibrations of the whole molecule play a leading part. Above 230°K the amplitude of the vibrations of the molecule rises sharply and at T = 263°K the molecule is practically free. From this result we find that when the molecule is dissociated from the adsorption center its mean kinetic energy is

$$E \approx 0.022\text{ eV}.$$

This value is a few times less than the energy required to separate the molecule from the surface (of the order of 0.1—0.05 eV)[10].

It appears therefore that there are two potential wells for physical adsorption. When $T < 300$°K there exists a radial potential which binds the molecule to the adsorption center on the particle surface, and when $T > 300$°K the molecule begins to move freely on the particle surface under the influence of a Lennard-Jones potential[11].

The chemical shift for the molecule $SnO_2 \cdot nH_2O$ does not change with increasing temperature, and this shows that the electronic state of the tin atom does not change in the process.

As already mentioned, Sn^{2+} is adsorbed on the particle surface by chemisorption, in the form of the compound SnO. One would expect the degree of symmetry of the SnO compound on the surface to be less than in the tetragonal crystal. (The surface compound SnO should, because of the conditions for adsorption on the surface of silica gel, have a structure identical with the low-temperature modification of SnO and not with the high-temperature ortho-rhombic modification.) This should lead to an increase of the electric field gradient at the tin nucleus. Indeed the surface form of SnO has a splitting $\Delta = 1.72 \pm 0.07$ mm/sec at T = 93°K ($\Delta = 1.3 \pm 0.02$ for crystalline SnO). At 257°K the quadrupole interaction for the surface form rises to $\Delta = 2.18 \pm 0.07$ mm/sec, whereas in the crystalline form the value of Δ does not change. The fairly strong dependence of Δ on temperature can be explained as follows. With rising temperature the mean distance between the oxygen atoms sticking out from the particle surface increases because of the thermal expansion. As a result the overlap integral of the p orbit of oxygen with the p orbit of tin may tend to increase and this leads to a decrease of the contribution of the p electrons of tin to the molecular orbital of the Sn–O bond and therefore to an increase of the electric field gradient at the tin nucleus. This is also confirmed by the observed increase in the chemical shift, which is a typical feature of divalent tin compounds in cases when the ionic character of the bond decreases[10,12]. We note that the thermal shift of the line is unobservably small even for crystalline SnO, and it was shown in [13] that the thermal shift for surface atoms must be less than inside the crystal.

From the general expressions derived in [14,15], the asymmetry of the components of the quadrupole

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*th ≡ tanh.

†cth ≡ coth.

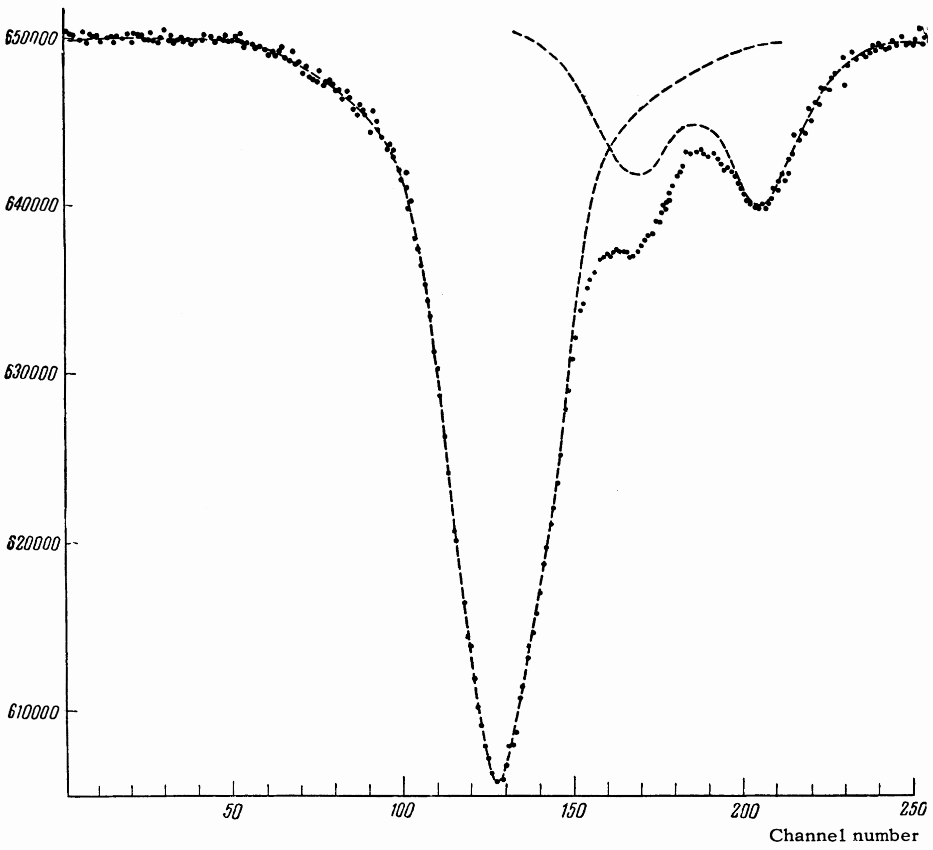

FIG. 4. The abscissae show the channel number. Each channel represents 0.052 mm/sec. The ordinates show the number of counts in each channel.

splitting can give evidence of a difference between the mean square displacements of the atoms in a direction normal to the surface (i.e., parallel to the electric field gradient) and parallel to the surface. Such an evaluation for iron atoms adsorbed on a silica gel surface was first carried out by Flinn et al.[3] It is obvious from the spectrum in Fig. 4 that in our case there is a considerable asymmetry of the components of the SnO doublet. The spectrum obtained at 213° was analyzed with an M-20 electronic computer.

For SnO on the surface, the electric field gradient $\partial^2\varphi/\partial z^2$ is axially symmetric and positive as a result of the lack of electrons on the z-axis. It is known that the quadrupole moment Q of the excited state of the nucleus Sn^{119*} is negative[16]. The sign of the quadrupole interaction therefore becomes negative, i.e., the nuclear level with spin $^3/_2$ lies below the level with spin $^1/_2$. Using an expression derived in [3] it can be shown that

$$\frac{I_\pi}{I_\sigma} = \int_0^1 (1+u^2)\exp(-\varepsilon u^2)\,du \Big/ \int_0^1 (^5/_3 - u^2)\exp(-\varepsilon u^2)\,du, \tag{2}$$

where $u = \cos\theta$ (θ is the angle between the wave vector and the direction of the electric field gradient); $\epsilon = k^2(\langle z^2\rangle - \langle x^2\rangle)$ (it is assumed that the atomic vibrations in the xy plane have equal components along the x and y axes).

From the observed ratio of the areas under the peaks for the π and σ transitions, which in our case is $I_\pi/I_\sigma = 0.80 \pm 0.08$, and from the numerical values of the ratio of the integrals in [2], which are tabulated for various ϵ in [3], we find

$$(\langle z^2\rangle - \langle x^2\rangle)_{\mathrm{SnO}} = 1.3\cdot 10^{-18}\ \mathrm{cm}^2.$$

Hence the mean square displacement of the tin atom in the surface compound SnO is greater in the z direction (i.e., normal to the particle surface) than in the xy plane.

The absolute determination of the values of the mean square components of the atomic displacements requires, as already mentioned, a knowledge of the absolute magnitude of f′. Using the known number of tin atoms contained as SnO and the observed resonance absorption, we find two equations

$$\langle z^2\rangle - \langle x^2\rangle = 1.3\cdot 10^{-18}\ \mathrm{cm}^2,$$

$$\langle z^2\rangle + 2\langle x^2\rangle = 2.67\cdot 10^{-18}\ \mathrm{cm}^2, \tag{3}$$

therefore

$$\langle x^2\rangle = 0.46\cdot 10^{-18}\ \mathrm{cm}^2,$$

$$\langle z^2\rangle = 1.76\cdot 10^{-18}\ \mathrm{cm}^2. \tag{4}$$

We see from (4) that at 213°K the rms displacement of the tin atom in SnO normal to the surface amounts to 0.13 Å, and is roughly twice the rms displacement parallel to the surface. At 93°K we see from Fig. 3 that the difference between $\langle x^2 \rangle$ and $\langle z^2 \rangle$ vanishes.

It is evidently possible to determine similarly the absolute magnitude of the mean square displacements as functions of the temperature, and to extrapolate these values to absolute zero. This makes it possible to estimate the corresponding vibration frequencies. The temperature dependence of $\langle \mathbf{x}^2 \rangle$ which we obtained for the physical adsorption allows us in principle to find the form of the potential well for the adsorbed atoms or molecules. This problem will be considered in subsequent papers.

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180