Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **11**: 89–95, 1991.
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^{51}V NMR of Inclusion Compounds $H_2V_{12}O_{31-y} \cdot n\,H_2O$

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(Received: 13 February 1990; in final form: 29 October 1990)

Abstract. The parameters of hyperfine interactions on ^{51}V nuclei were determined on films of the inclusion compound $H_2V_{12}O_{31-y} \cdot n\,H_2O$ at different stages of hydration. It was established that the axial symmetry plane of the magnetic interaction tensor coincides with the film plane. The most probable direction (40° of the film plane) and the magnitude of the electric field gradient (EFG) on ^{51}V nuclei ($eqQ/h = 0.233$ MHz) were found for a completely dehydrated sample. An analysis of the line width angular dependences of satellites has shown the existence of a disorientation of the main EFG direction with a distribution width of about 50° in the film plane. The absence of satellites and the presence of an angular dependence of the ^{51}V NMR central signal of hydrated samples allowed the conclusion that the interaction of the V—O layer with molecules of water led to an increase in the disorientation of the film plane.

Key words. NMR, structure, xerogel, film.

1. Introduction

Xerogels of the inclusion compound $H_2V_{12}O_{31-y} \cdot n\,H_2O$ (polyvanadic acid) possess a number of interesting electrophysical properties determined by the large ionic and electronic components of the conductivity. Any understanding of electrotransfer mechanisms based on a separation of those contributions by means of electrophysical methods is difficult because dehydration processes and structural transformations begin to take place as early as at room temperature [1, 2]. The water content in the vanadium-oxygen monolayers should affect the electronic and crystalline structures of this compound, but up to now information about this relationship is not available. The nuclear magnetic resonance method is a powerful tool for solving this problem, since it is sensitive to the smallest change in crystalline and electronic structure of solids. The solution of this problem is facilitated by the fact that the thermodynamics of the dehydration process have been investigated in detail in [3, 4]. The two stages of the dehydration process are distinctly expressed in the thermogravimetric (TG) dehydration curve of polyvanadic acid xerogels. At the first stage zeolitic water is withdrawn from the interlayer space. This water does not have any direct contact with the vanadium–oxygen layers. The maximum of this effect occurred near 468 K. At the second stage the chemically bonded water was withdrawn. The effect attained a maximum at 553 K, and the effect observed at 620 K corresponded to the complete decomposition of the xerogel structure.

2. Experimental Procedures

The investigations were carried out on films of $H_2V_{12}O_{31-y}{\cdot}n\,H_2O$ ($n = 8.6$; $y = 0.3$) synthesized by conventional methods [5] on an organic glass substrate. In order to obtain monolytic samples, the films were cut into 4 × 4 mm squares which were stacked in a pile without change of orientation. The ^{51}V NMR was measured at 3.5, 15 and 20 MHz in the temperature range 77–400 K. In order to study the dehydration processes at higher temperatures the samples were calcined outside the spectrometer. The NMR spectra of the samples under study were recorded at room temperature in order to avoid undesirable effects involving water motion near the vanadium–oxygen layer. In order to prevent rehydration processes the samples were placed in hermetically sealed vessels. The chemical shifts of the ^{51}V NMR spectra were measured relative to a KVO_3/water solution. The ^1H NMR was measured at 54 MHz.

3. Results

The observed ^1H NMR lineshape in the NMR spectrum of $H_2V_{12}O_{31-y}{\cdot}n\,H_2O$ at 140 K was similar to that of the polycrystalline sample [1]. The shift of this line was independent of the film orientation in the magnetic field. At room temperature and above the ^1H NMR spectra were narrowed due to the active diffusion process and were also independent of the film orientation.

The ^{51}V NMR spectrum presented a narrow line with $\Delta H = 1.4$ Oe at 20 MHz. The signal shift showed an angular dependence the amplitude of which decreased with a lowering of the resonance frequency. This indicates that the observed shift is associated with the magnetic interaction. The maximum shift was observed at an H_0 direction normal to the film plane. The magnetic interaction had an axial symmetry plane which coincided with the film plane. No change in the ^{51}V NMR spectra was detected in the temperature range 140–400 K. After the sample was annealed at 450 K, the magnitudes of the magnetic interaction tensor components had changed. The results are presented in Table I where the b axis corresponds to the direction of H_0 (normal to the film plane), and the a and c axes lie in the film plane.

It should be noted that we did not find any satellite transitions at the first stage of the dehydration though the occurrence of an EFG on vanadium nuclei (^{51}V) with spin $I = 7/2$ is possible due to the low dimensionality of this system. Satellite transitions appeared after the complete dehydration of a xerogel at 640 K when,

Table I. Values of magnetic interaction tensor components of xerogel films and single crystal V_2O_5

Composition	T, K	$\sigma_a \times 10$	$\sigma_b \times 10$	$\sigma_c \times 10$
$H_2V_{12}O_{31-y}{\cdot}n\,H_2O$	<400	−0.67	1.2	−0.67
$H_2V_{12}O_{31-y}{\cdot}n\,H_2O$	450	−0.95	1.5	−0.95
V_2O_5 film	640	−0.55	1.2	−0.55
V_2O_5 single crystal*	–	−2.8	7.1	−1.7

*The data are taken from [8]

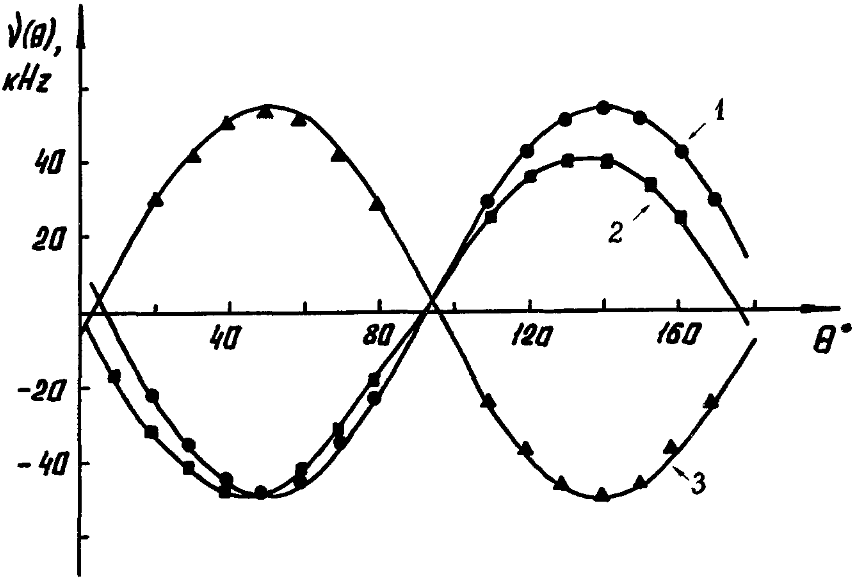

Fig. 1. Angular dependences of distance between satellites obtained by V_2O_5 film rotation around: (1) a' axis, (2) b axis, (3) c' axis.

according to the X-ray data, it had been transformed into a textured film of V_2O_5. The angular dependences of distances between the satellites corresponding to the $(3/2 \leftrightarrow -1/2)$ and $(3/2 \leftrightarrow 1/2)$ transitions are presented in Figure 1. They are described by the expression:

$$\nu_a = 2.(5) + 51.(9)\cos 2(\Phi + 40) \qquad (1)$$

$$\nu_b = -5.(1) + 45.(4)\cos 2(\Phi + 45) \qquad (2)$$

$$\nu_c = 2.(5) + 51.(9)\cos 2(\Phi - 50) \qquad (3)$$

were ν_i is the distance between satellite transitions in KHz and i indicates the rotation axis. The values of the main components of the EFG tensor and their eigenvectors were found in the laboratory coordinate system (LSC) (a', b, c') by the methods described in [6]. Within experimental errors $V_{XX} = V_{yy} = 116$ KHz and $V_{zz} = 233$ KHz. Coordinates of the EFG eigenvectors in the LSC are presented in Table II. Unlike a single crystal of V_2O_5 the V_2O_5 film posesses strong angular dependence of the satellite line width, particularly with sample rotation around the b axis (Figure 2).

4. Discussion

The absence of any angular dependence of the ^{1}H NMR spectra of the hydrated films served as evidence for the random distribution of the oxygen–proton groups in the interlayer space of the $H_2V_{12}O_{31-y} \cdot n\, H_2O$ xerogel. The results of the ^{51}V NMR indicate that the first stage of the dehydration up to a temperature of 450 K was not accompanied by pronounced changes in the ^{51}V NMR spectra, i.e.

Table II. Eigenvectors of EFG of V_2O_5 films in LCS.

LCS \ EFG axes	x	y	z
a'	0.71	0.54	−0.45
b	0.00	0.65	0.76
c'	0.71	−0.54	0.45

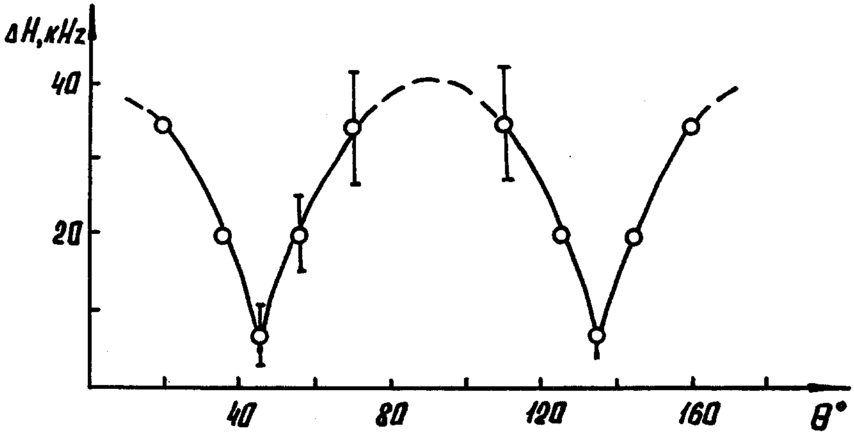

Fig. 2. Angular dependence of $-3/2 \leftrightarrow -1/2$ transition linewidth, obtained by V_2O_5 film rotation around b axis.

the hypothesis that water has no direct interactions with the vanadiun–oxygen layer can be ignored.

The isotropic shift $K_{\mathrm{iso}} = 1/3\Sigma\sigma_i < 0$. It is equal to the sum of three contributions $(-K_{\mathrm{H}} + K_{\mathrm{p}}^{\mathrm{c.s.}} + K_{\mathrm{d}}^{\mathrm{c.s.}})$, where K_{H} is the Knight shift proportional to the density of states at the Fermi level and $K_{\mathrm{p}}^{\mathrm{c.s.}}$ is the paramagnetic term of the chemical shift. Its value depends on the distribution of the electron density in the crystal. The third term, $K_{\mathrm{d}}^{\mathrm{c.s.}}$, depends only on the ground state of the molecule. It is weakly affected by distortions of the structure and changes of the composition and therefore $K_{\mathrm{d}}^{\mathrm{c.s.}}$ will not be discussed below. The existence of the marked negative shift suggests that the Knight shift contribution is dominant, and the stability of K_{iso} with temperature increase up to 400 K suggests the absence of changes in the electron structure of the xerogel. In particular, this indicates that the maximum of electroresistance near 370 K [2, 3] is certainly associated only with the change of the ionic component of the conductivity. The increase of the isotropic shift after the first stage of the dehydration ($T \sim 450$ K) may be connected with the K_{H} increase or the $K_{\mathrm{p}}^{\mathrm{c.s.}}$ decrease.

It is possible qualitatively to separate the contribution due to the isotropic shift by analysis of K_{iso} together with $K^{\mathrm{ax}} = (2\sigma_b - \sigma_{a'} - \sigma_{c'})/6$. The K^{ax} dependence on the symmetry of the spin density distribution around the resonating nucleus and the Knight shift is not included in K^{ax}. In the molecular orbital approximation [6]

K^{ax} and $K_p^{c.s.}$ may be expressed through the bond population P_i of the V_2O_5 compound.

$$K_p^{c.s.} \simeq (P_x + P_y + P_z) - (P_xP_y + P_yP_z + + P_xP_z)/2 \tag{4}$$

$$K^{ax} \simeq (2P_x + P_y + P_z) - (2P_xP_z + P_yP_z + P_xP_y)/2 \tag{5}$$

As it has been established by experiment, $K^{ax} > 0$ and it increases after the first stage of dehydration. It was reasonable to suppose that the bond population P_z increases and the P_x decreases. As can be seen from Equation (4), such changes of the populations lead to an increase of $K_p^{c.s.}$ and, consequently, to a decrease of K_{iso}. Thus the K_{iso} decrease must be associated with the predominant increase of the Knight shift K_H. In other words, the break-away of the water molecules from the vanadium–oxygen layer leads to an increase in the density of states in the conduction zone.

After complete dehydration ($T > 640$ K) the isotropic shift rises above zero. The magnitude of K^{ax} decreased, but remained positive. According to these results the value of the Knight shift of the dehydrated film decreased and consequently the density of states in the conduction zone decreased.

It is interesting to note that quadrupole effects were not observed for compounds with a large water content. The appearance of satellite transitions was observed only after the disturbance of the xerogel structure, the satellite widths depending on the angle. The presence of the angular dependences of the satellite transitions indicates the spread of the EFG tensor components. The most probable direction of the tensor components and their magnitudes were determined by angular dependences of the satellite shift. The EFG direction was described by a matrix (Table II). Unlike the V_2O_5 single crystal [8], the vector V_{zz} of the V_2O_5 films did not coincide with the (a', b') plane. This was determined by a random choice of the a' and c' axes and their noncoincidence with the crystallographic a and c axes. If the space group of the symmetry of the closest vanadium environment is *Pmnm* then the crystallographic c axis should coincide with the Z axis of the EFG tensor component. Thus, in order to obtain the direction of the tensor, it is necessary to convert the LCS into a CCS (crystal coordinate system). For this purpose the a' and c' axes should be rotated around b to align the c' axis with the direction of one of the EFG axes. According to Table II the coincidence of the X and c' axes was achieved only by a rotation of 45°. Then the Y and Z axes were placed in the (a, c) plane as it should be in the case of *Pmnn* symmetry. In the new coordinate system the (CCS) tensor of the eigenvectors was described in the form presented in the Table III.

Table III. Eigenvectors of EFG of V_2O_5 films in CCS.

CCS \ EFG axes	x	y	z
a	0.00	0.76	−0.65
b	0.00	0.65	0.76
c	1.00	0.00	0.00

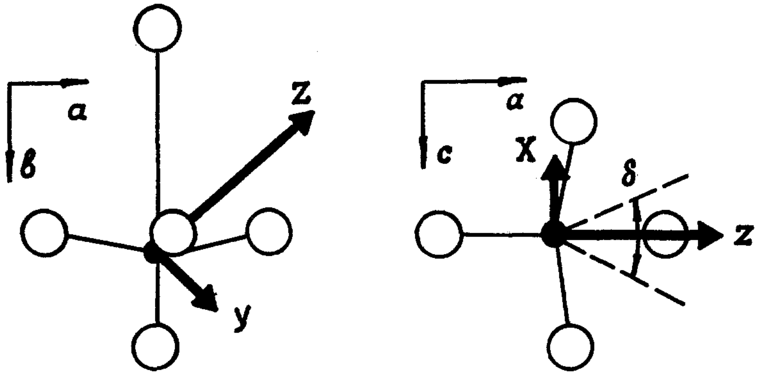

Fig. 3. Projection of oxygen environment of vanadium and EFG components (*xyz*) in (*a*, *b*) and (*a*, *c*) planes.

For the single crystal V_2O_5 and the V_2O_5 film the angle between the main direction Z of the EFG tensor and the a axis was 40°. This is probably caused by a deformation of the vanadium nuclei nearest neighborhoods (Figure 3).

Information about the disorientation of the EFG tensor components can be obtained from the angular dependence of the satellite transition line widths (Figure 2). According to [9] the $3/2 \leftrightarrow 1/2$ transition line width is presented as

$$\Delta H = [(\partial \nu / \partial \theta^2|_{\theta_0} \sigma_\theta^2 + (\partial \nu / \partial q^2|_{q_0} \sigma_q^2]^{1/2} \qquad (6)$$

where σ_θ^2 and σ_q^2 are an angle and magnitude root-mean-square deviations of EFG, respectively. The fact that in the region of extrema of the $\nu(\theta)$ dependences, ΔH had a value close to the only dipole width, and the maximal broadening was observed at the angle at which $\nu(\theta) = 0$, suggested that $\sigma_q^2 = 0$. The value of $\sigma_\theta^2 = 0.16$ was defined by the optimization of the $H(0)$ dependence. If we consider that the angle distribution was random (Gaussian), we obtain the distribution width $\delta \sim 50°$ in the (*a*, *c*) plane (Figure 3).

The disappearance of the satellite transitions upon the interaction of the vanadium–oxygen layer with water indicated that a significant disorientation of the EFG tensor components had taken place. The cause of this phenomenon is probably the formation of an irregular state in which the vanadium atoms are not in the minima of the potential, the profile of which is determined by the oxygen skeleton structure. This state is possible due to an irregular polarization or deformation of the V—O layer by the oxygen–proton groups and, according to the data, does not affect the magnetic interaction tensor.

Thus it is possible to conclude that the irregular state is formed due to a random deformation which leads to a rotation of the EFG tensor and the magnetic interactions in the (*a*, *c*) plane. The width of the disorientation function of angle was 50° in the dehydrated V_2O_5 film. In the hydrated film $H_2V_{12}O_{31-y} \cdot n\ H_2O$ the interaction of the vanadium–oxygen layers with the molecules of water leads to an increase of the disorientation resulting from the satellite transitions, which was unobservable. Since the magnetic interaction tensor in the (*a*, *c*) plane was axial, this rotation did not lead to a change of the $(1/2 \leftrightarrow -1/2)$ transition in the ^{51}V NMR spectra.

The stability of the magnetic interaction tensor for the film dehydrated up to 450 K suggests that the sharp change of the electroresistance at 370 K was connected with specific features of proton diffusion. The changes of the electron component of the conductivity should be expected at the second stage of the dehydration when withdrawal of the oxygen–proton groups directly bonded with the vanadium–oxygen layer takes place.

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