METAL-SEMICONDUCTOR PHASE TRANSITION IN HYDRATED POWDERS OF VO$_2$ AS INFLUENCED BY ADSORBED WATER, POLYETHYLENE GLYCOL MEDIUM, AND TETRAETHYLAMMONIUM BROMIDE ADDITIVES

V.V. Turov[1], P.P. Gorbik[1], I.V. Laguta[1], O.V. Shulga[2], O.Yu. Semchuk[1], L.G. Grechko[1], V.M Ogenko[1], A.A. Chuiko[1], M. Willander[3], and M. Karlsteen[3]

[1]*Institute of Surface Chemistry, National Academy of Sciences, 17 Gen. Naumov str., 03164 Kyiv, UKRAINE; e-mail: user@surfchem.freenet.kiev.ua*
[2]*Department of Chemistry, The University of Toledo, Toledo OH 43606, USA*
[3]*Department of Physics, Chalmers University of Technology and Götenborg University, S-41296, Götenborg, SWEDEN*

Abstract

The opportunity of use of a ^{1}H NMR method for study of the performances of phase transition the metal - semiconductor in crystalline VO$_2$ is considered. The influence of the adsorbed water, polyethylene glycol medium and presence of the tetraethylammonium bromide additives on the phase transition performances is explored. The phenomenon of phase heterogeneity VO$_2$ is revealed which is exhibited as simultaneous existence of semiconductor and metal phases. Presumably this kind of heterogeneity is stipulated by an adsorption of bromide ions on a surface of particles VO$_2$.

Introduction

The metal-semiconductor phase transition (MSPT) in vanadium dioxide is a first-order phase transition (PT) and by this time it has been studied in more detail both for monocrystals and polycrystalline films [1]. However, up to the present the measurement of temperature parameters of PT in powders and suspensions of VO$_2$ has not been practically made, which is due to the difficulties encountered when measuring electrical conductivity under condition of a loose electric contact between material particles. Meanwhile, the properties of substance in disperse state may substantially differ from the bulk properties of the substance, which is of particular importance for the development of new composite materials [2,3].

When investigating phase transitions in solids, a wide use is made of the nuclear magnetic resonance spectroscopy [4]. This technique is contactless, which provides a number of advantages over standard measurement methods for electrical conductivity [5,6]. In particular, this technique allows one to study phase transitions in suspensions of solids with a low electrical conductivity of a dispersive medium, whereas other methods are practically untenable for such a study. The technique is based on the dependence of magnetic properties of nuclei on the phase state of a solid. By now, the researches of phase transitions by the NMR technique have been carried out predominantly by measuring temperature dependences of relaxation times of nuclei with a nonzero magnetic moment (^{93}Nb, ^{23}K, ^{14}N). As the temperature of a sample under study approaches the value characteristic of its phase transition, the curves of the temperature dependences of relaxation times show a clearly resolved inflection [4].

Today it is known that the MSPT temperature may change because of emergence of an electric charge on the VO_2 surface. Such a charge may appear during surface adsorption of some types of active molecules, in particular molecules of water and ammonia [7,8] as well as during interactions of VO_2 particles with a polymeric matrix [9,10]. These types of interactions can decrease the PT temperature down to 320 K. However, the search for new systems that would make it possible to vary the PT temperature sufficiently quickly and reversibly in a wider temperature interval remains an urgent problem.

According to a last investigations, researches into the properties of powders and suspensions of VO_2 can be carried out using a method of ^1H NMR spectroscopy of adsorbed molecules [11,12]. The method is based on the fact that spectral characteristics of a substance at the interface of disperse solids depend on the substrata material properties. In the presence of conducting materials the intensity of NMR signal for molecules of the material may be lower then in the case of diamagnetic media because of the partial absorption of the radio-frequency energy by the sample volume. Science the conductivity of VO_2 sharply increases at the temperature of MSPT (T_{MSPT}), one may expect a noticeable decrease in the NMR signal intensity in this temperature region. Free electrons are paramagnetic particles which bring about a fast nuclear spin relaxation of substance at the surface. Therefore an increase in the in the material conductivity must be accompanied by a NMR signal brooding [13]. In view of the fast molecular exchange, spectra display an averaged signal for adsorbate molecules contiguous to the surface and remote from it. The thicker is the adsorbed substance layer at the interface, the higher is the contribution to the mesured signal which is made by those molecules whose properties approach the adsorbate bulk properties, and the smaller is the experimentally measured width of the NMR signal.

1. Experimental

Disperse powders of VO_2 were produced by solid-phase synthesis method [2]. The V_2O_5 powder ultrahigh purity grade was used as a starting material. At first, vanadium oxide V_2O_3 was prepared through the direct reduction with hydrogen of high purity. VO_2 was synthesized from a stoichiometric mixture of V_2O_3 and V_2O_5 by the reaction:

$$V_2O_3 + V_2O_5 \rightarrow 4VO_2$$
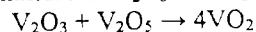
NMR spectra were registered with a high-resolution spectrometer WP-100 SY (Bruker, Germany). Temperature within the detector was maintained constant with the aid of a thermal device B-VT-1000 accurate to ±1 degree. During the process of the temperature setting departures from a predetermined value did not exceed 2,5 degrees. The signal integration accuracy was ±15 %. The dosing of the water adsorbed on VO_2 powder samples was effected with a microdoser by the injection of fixed portion of H_2O into a measuring ampule to stand for 8 days for the adsorption equilibrium to be established The water content of samples was determined by measurement of the ^1H NMR signal intensity at 293 K.

Polyethylene glycol (Ferak) with a molecular mass of 1500 was chosen as a polymeric matrix. The melting temperature of this substance is 315 K, therefore at temperatures near to the PT temperature for VO_2 its state is close to that of a very viscous liquid. PEG is able to absorb a considerable amount of water. Besides, it can dissolve many organic compounds. A use was made of the chemically pure TEABr. The test samples were prepared in the following way. At room temperature 1 part of TEABr, 10 parts of PEG, and 20 parts of VO_2 were grounded in a porcelain mortar, following which the homogenized mixture was placed into a measurement ampule and heated in it at a temperature close to the boiling temperature of PEG for 0.5 – 1.0 min.

2. Results and discussion

Figure 1a shows the temperature dependence of the ^1H NMR spectrum for VO_2 samples containing 5 % (by weight) of adsorbed H_2O. The spectrum consist of a single peak whose shape is close to a Gaussian, and whose width varies from 7 kHz (at $T < T_{MSPT}$) to 12 - 14 kHz (at $T > T_{MSPT}$). The adsorbed water signal intensity at the phase transition decreases approximately by a factor of 2, which allows us to make a reliable record of absorbing properties variations for samples. The changes of the adsorbed water intensity with temperature in the interval of $200 < T < 250$ K are

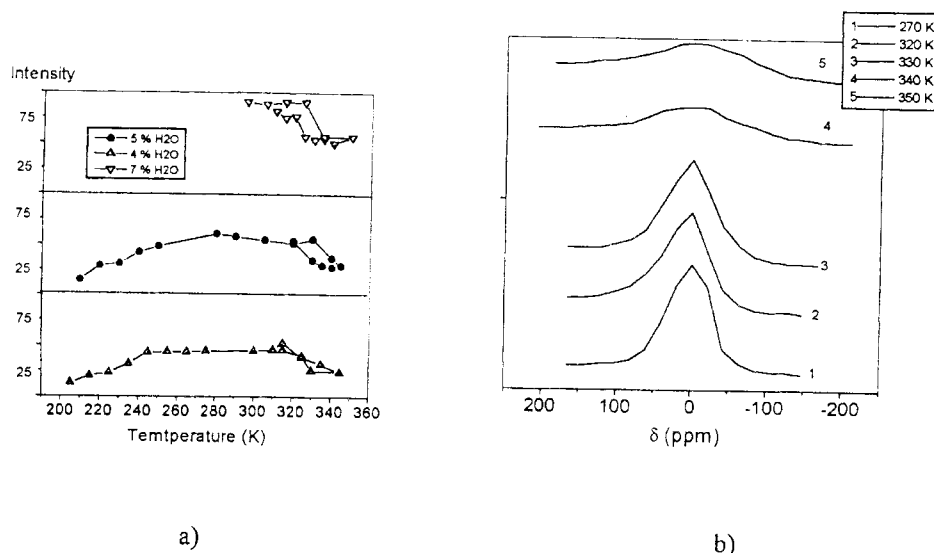shown in the fig. 1b. The level of hydration for samples was 4, 5 and 7 % wt. of H_2O (curves 1 - 3 respectively

a)   b)

Fig.1. a) Temperature-induced variations of ^1H NMR spectra of water adsorbed on VO_2 powders: (water concentration 5% wt.).

b) Temperature dependencies of the ^1H NMR signal intensity for water absorbed on the VO_2 powders surface at different levels of sample hydration.

As it is seen from this figures, all the samples display temperature hysteresis whose loop area increases with the sample humidity. The onset of MSPT is shifted to a region of low temperatures as it is the case for polycrystalline films of VO_2 [1]. However, the temperature of the phase transition onset is somewhat lower then for these films and amount to 315 K for a sample containing 4 % wt. Of H_2O (fig. 1b, curve 1). The decrease in the signal intensity occurs in concord with the increase in its width which gives reason to infer a symbatic variation of the material absorbing properties and the free carriers concentration at the solid body-adsorbed water interface.

The measurements were made in the region of high levels of surface hydration when at the interface of disperse VO_2 particles there is a multilayer film of adsorbed water. In this case one can schematically distinguish between tightly and weakly bond waters [14]. The tightly bound water is usually referred to as that part of the superficially adsorbed water whose energy of the interaction with the surface is muck higher then the energy of the interaction between molecules in the bulk of the liquid. Such a water does not go from a

liquid state to a solid phase of ice at $T < 273$ K and freezes at significantly lower temperatures. Such properties are characteristic of surface adsorption films whose thickness is 2 – 4 molecular diameters. But if such a film has a greater thickness, in the process of cooling a weakly bond water freezes. As a result, spectra of the high-resolution ^{1}H NMR bring out a decrease in the water signal intensity since the solid water is not observed in these spectra due to vary small times (down to 10^{-6} s) of the transverse relaxation of nuclear spins.

The approach described was taken by us to the identification of that type of water which is responsible for the changes in parameters of the temperature hysteresis at MSPT in VO_2. Figure 1b (curves 1,2) shows the temperature dependence of the water signal intensity when freezing samples. As is seen from this figure, in the case of the sample containing 4 % wt. of water the decrease in the water signal intensity is observed only at the temperature $T < 240$ K, i.e., the main amount of water is a tightly bound water. As the level of hydration increases to 5 % wt. the fraction of the weakly bond water increases, and its freezing occurs at temperature close to 273 K. Thus, the experimental data give evidence that it is the increase of the amount of weakly bond water which leads to an increase in the width of the temperature hysteresis loop at MSPT.

The occurrence of hysteresis phenomena in processes proceeding at first-order phase transitions is attributed to the existence of the rearrangement activation energy for a substance (solid adsorbent in our case) at a phase transition and should not depend on the availability of adsorbed water molecules distant from the surface. The regularity discovered seems to be caused by the fact that disperse particles of VO_2 are complex aggregates (formed from primary microcrystals in the process of the synthesis) whose surface has a high affinity to water molecules. The water penetrating into gaps between microcrystals exerts a wedging pressure on them [8] and, thereby, varies the properties of disperse particles weacening the bonding between them. It hinders a coordinated rearrangement of extended material domains at MSPT, and, as a consequence, the energy which is necessary for a phase transition to occur increases.

The validity of the hypothesis about the mechanism described is substantiated by the fact that the introduction of VO_2 powders into an aqueous medium leads to their dispersion and formation of stable suspensions whose particle size is by 1 - 2 orders of magnitude smaller then in the case of starting powders. Solid particles in such suspensions do not settle out in the course of several days, which corresponds to particle sizes smaller then 0.1 mm.

The temperature dependencies of the ^{1}H NMR signal intensity in suspensions differ in many respects from the hydrated powders described above. Figure 2 displays the temperature-induced variations of NMR spectra and water signal intensity in water suspensions of VO_2. We investigated suspensions whose solid phase concentration were 60 % wt. (Fig. 2a, b, curve 2) and 7 % wt. (Fig. 2b, curve 1). From the juxtaposition of the data in Fig. 1 and Fig. 2 it follows that the temperature interval of MSPT in water suspensions is broader then in hydrated powders. The transition onset is observed at a temperature close to room temperature. The thermal hysteresis loop are decreases, and in the case of dilute solutions heating curves display a negative hysteresis. The distinction in the properties of hydrated powders and suspensions of VO_2 may be attributed both to change of the substance grain size distribution and to an effect of the dispersive medium. In order to make a choice between those factors we looked for a liquid which when mixed with water in any would not cause the dispersion of VO_2 powders. One of such media turned out to be dimethylsulfoxide (DMSO) Figure 3 illustrates temperature variation of the shape of NMR spectra and the intensity of signals for a suspension of VO_2 in DMSO (fig 3a, curve 2) and in a mixture of H_2O + DMSO in the 1:1 proportion (fig 3b, curve 1).
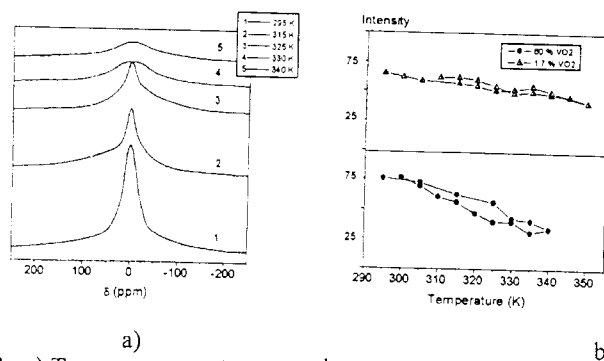
Fig. 2. a) Temperature variations of ^{1}H NMR spectrum shape for water in 60 wt % aqueous suspensions of VO_2; b) Effect of temperature on ^{1}H NMR water signal intensity for water concentration.

The concentration of the solid phase was about 80 % wt., which corresponds to settled suspensions. The spectra present the overall signal of proton of water and DMSO molecules.

Comparing the data of figs. 2b (curve 1) and 3b (curves 1,2) makes it possible to conclude that the shapes of temperature dependencies for a dilute water suspension and concentrated suspensions of VO_2 in DMSO and its mixture with water are practically identical. Thus, the experimental date corroborate the conclusion that in this case the dispersive medium exerts a more profound effect on characteristics of MSPT in VO2 than the change of its dispersity does.

One of the distinctive feature of suspensions on the basis of DMSO is a temperature dependence of a line shape in NMR spectra (fig. 3a). While the signal intensity decreases monotonously the signal width makes a rapid leap at temperatures in a range of $325 < T < 330$) K as it is the case in hydrated powders (fig 1a). As it has been mentioned above, an increase in the line width in ^{1}H NMR spectra in the region of MSPT for VO_2 is attributed to an increase in the concentration of free electrons in the solid give rise to a paramagnetic relaxation of nuclear spin of H_2O molecules contiguous to the VO_2 surface. At the same time the signal intensity decrease is
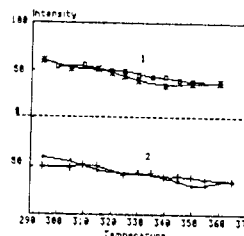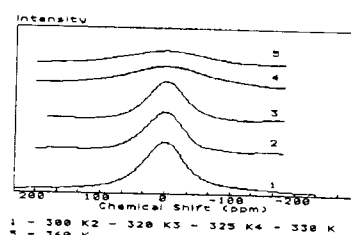

Fig 3. a) Temperature variations of ^{1}H NMR spectrum shape for an average signal of water and dimethylsulfoxide in 80 wt % VO_2 suspensions containing 5% wt. of H_2O.

b) Effect of temperature on ^{1}H NMR signal intensities for suspensions of VO_2 whose liquid phase contains 95 % wt. DMSO (1) and 50% DMSO (2), and the concentration of the solid phase in 80% wt.

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determined by the increase of the absorbing capacity of the whole sample volume. Then the observed uncoordinated variations of the signal intensity and width may be attributed to the difference in the PT temperature on the periphery and in the bulk of VO_2 particles. The existence of a negative temperature hysteresis in suspensions gives reason to believe that the mechanism of the dispersive medium effect on MSPT parameters is a rather and requires further studies.

Fig. 4 illustrates the temperature-induced variations of the ^1H NMR spectra for VO_2 in PEG as well as the temperature dependence of the proton signal intensity (I).
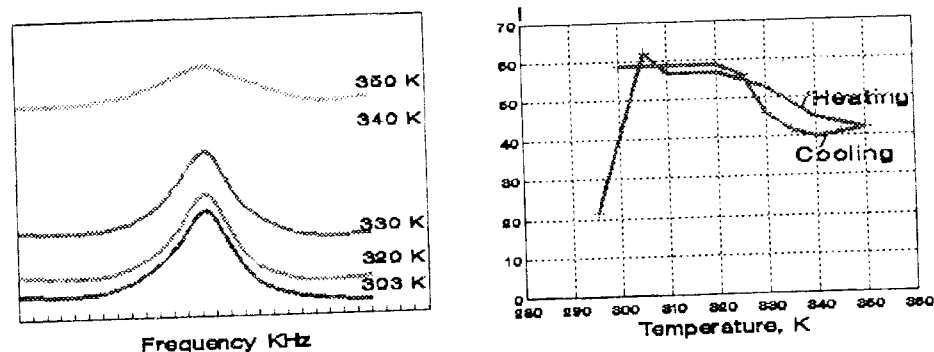

Fig. 4. Temperature-induced variations of the ^1H NMR spectra shape and signal intensity for protons in VO_2 powders in a PEG matrix.

In these spectra there is a broad single peak that is an averaged signal for protons of CH and OH groups of PEG and of impurity water molecules adsorbed on the VO_2 surface and in the bulk of PEG. As the temperature approaches the PT temperature value, the width of the signal sharply increases, and its intensity decreases by about 40 %, which allows reliable recordings of the PT occurrence in the system. The PT parameters for a VO_2 powder in a PEG matrix are close to the parameters that earlier were observed in hydrated VO_2 powders in the case of low concentrations of adsorbed water.

At temperatures $T < 305$ K the relationship $I = f(T)$ displays a decrease in the ^1H NMR signal intensity, which is attributed to a partial crystallization of PEG. At the crystallization temperature the polymer portion
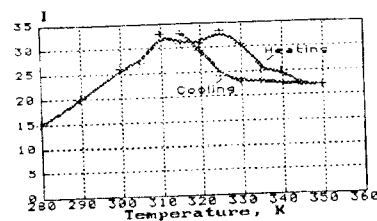

Fig. 5. Temperature dependence of variations of the ^1H NMR signal intensity for a sample of VO_2 in a PEG medium containing 10 wt.% of water.

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that does not interact with the surface (bulk component) solidifies and is not registered any more in the spectra due to a considerably lower time of transverse relaxation of protons in solids in comparison with that in liquids. The spectra register only the PEG molecules whose free energy has been lowered by the adsorption interactions with the surface. Such molecules can pass into the solid phase of PEG only at a temperature that is lower than the temperature of crystallization of PEG in the bulk of the liquid. The stronger are the adsorption interactions, the lower are the temperatures at which the crystallization of a substance is possible.

The parameters of MSPT in disperse VO_2 may substantially vary when the moisture content of a sample increases. On the one hand, this variation is caused by the formation of an electric charge on the surface, which is induced by the electron density transfer from VO_2 to unshared electron pairs of oxygen atoms of adsorbed water molecules,[14] and, on the other hand, it is due to changes in the interactions between microcrystals (which form VO_2 particles) owing to wedging pressure of adsorbed water.

Fig. 5 shows the temperature dependence of the ${}^1H$ NMR signal intensity for VO_2 in a PEG matrix whose water content is 10 wt.%. A comparison between the data of Figs. 5 and 1b permits us to infer that, in contrast to the case of hydrated VO_2 powders, the temperature of MSPT in a PEG medium vary slightly, when the moisture content of a sample increases. It is attributed to the fact that molecules of PEG interact with molecules of water through formation of hydrogen-bonded associates. As they penetrate into the bulk of the polymer, molecules of water do not adsorb on the VO_2 particle surface but reside within the polymeric matrix.

In the capacity of a modifying dopant capable of exerting an effect on the VO_2 surface we have tested a quaternary ammonium salt TEABr, Some media with a low dielectric permitivity, which include polyethylene glycol, can carry quaternary ammonium salts in the form of tight ionic pairs. Because of the great difference in sizes of anionic and cationic components of a molecule their mobilities differ considerably. In the viscous PEG medium this difference should be even greater on account of the strong dispersion interaction between ethyl groups of the $(C_2H_5)_4N^+$ cation and molecules of the polymer. In view of this, it could be expected that cationic and anionic components of TEABr molecules would interact with the VO_2 surface in different ways and give rise to its polarization.

Fig. 6 displays temperature variations of the ${}^1H$ NMR spectra for VO_2 in the PEG medium containing small (< 1 wt.%) additives of TEABr.
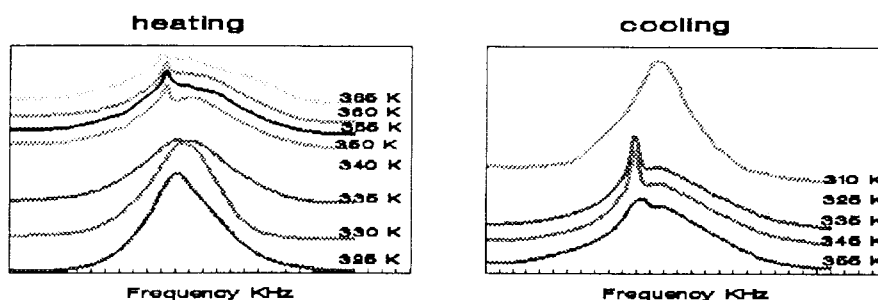

heating   **cooling**

Fig. 6. Temperature-induced variations of the ${}^1H$ NMR spectra shape for a sample of VO_2 in a PEG matrix containing an additive of tetraethylammonium bromide.

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As is evident from the figure, at heating up to temperatures lower than the MSPT temperature the shape of the spectrum peaks is similar to that of the spectrum in Fig. 4. One can see that at a temperature 335 K there occurs a phase transition. It manifests itself in a broadening of the signal width and lowering of its intensity. At the same time, however, in the background of the main signal there appears a signal of a lower intensity whose width is substantially smaller than that of the main signal. The width of this signal does not practically vary in the temperature interval $340 < T < 360$ K. At higher temperatures its width increases. The presence of the second signal in the spectra is observed even more distinctly under cooling of a sample. In this case the second signal in the spectra is not detected only at temperatures of $T \leq 310$ K.

The samples under investigation contains not only molecules of PEG but also molecules of TEABr (up to 10 wt.%), therefore the second signal can be attributed both to protons of molecules of PEG and to protons of dissolved TEABr. Since such a sample was prepared by homogenization in the solid state, it is possible to assume that during the course of melting of the sample TEABr is dissolved in the liquid polymer, and ethyl groups of TEABr manifest themselves by a narrow component of the signal. In this case, however, one should expect that with increasing temperature the intensity of the second component would increase (due to additional dissolution of TEABr), which does not agree with the data presented in Fig. 6. Then, it is most likely that the observed narrow signal (as well as the broad one) is a signal from protons of PEG molecules, but the properties of the surface of nearby VO_2 particles differ from those that give rise to the broad signal component.

Fig. 7 presents curves of relationship $I=f(T)$ for a sample containing a TEABr additive. In comparison with the dependence plotted in Fig. 4 this relationship exhibits several particularities. One of them is the appearance of practically horizontal segments in the temperature interval $335 < T < 345$ K. Such segments are observed on the curves both at cooling and heating of samples. It should be noted that it is in this temperature interval that the intensity of the second signal has the maximum value (Fig. 6).

The results achieved can be interpreted as follows. In the case of disperse VO_2 powders the presence of TEABr in a PEG matrix causes formation of sections on the VO_2 particle surface, where the MSPT temperature is shifted into a higher temperature region. Within these zones the metal-semiconductor phase transition is observed only when the temperature reaches the value of $T=365$ K. The phenomenon detected is the first example of the increase in the MSPT temperature under the action of external factors.

Fig. 7. Temperature dependence of variations of the ^1H NMR signal intensity for a powder of VO_2 in a PEG matrix with an additive of TEABr.

As it was mentioned, the cause for changes in the MSPT temperature may be emergence of an electric field near the surface, that is assigned to polarization of molecules of an adsorbed substance. In particular, at surface adsorption of electron-donating molecules of ammonia and water the VO_2 surface acquires a positive charge whose value increases
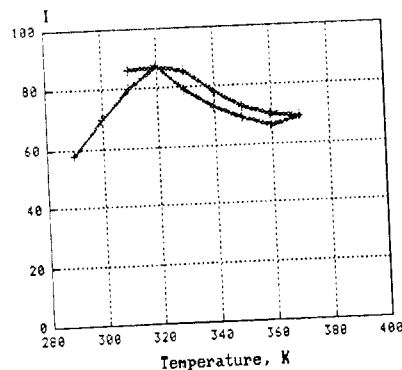
proportionally with concentration of adsorbed substances. For the material in question, i.e. the system of disperse VO_2 in a PEG matrix with additives of TEABr, one can expect the appearance of charges of opposite signs on the VO_2 particle surface. Actually, negatively charged ions of bromine are a more mobile type of ions. These ions can diffuse to the VO_2 surface. In this case, near the surface one can observe the emergence of electric fields between negatively charged VO_2 particles and $(C_2H_5)_4N^+$ cations that are located within the polymeric matrix. Since the solubility of TEABr in PEG is low, tetraethylammonium ions are located only near a small zone of the surface of VO_2 particles, which accounts for simultaneous existence of the semiconducting and metallic phases of VO_2 in a wide temperature region (340 - 365 K). It should be noted that in this temperature interval the width of the second signal is considerably smaller than that of the first one. So far as the signal width in the ^1H NMR spectra increases with increasing concentrations of free electrons, the smaller width of the signal of polyethylene glycol molecules adsorbed on the VO_2 surface may be attributed to decreasing in conductivity of the VO_2 surface zones responsible for the appearance of this signal.

In cases where the proposed approach is valid, it is possible to expect that a time dependence will appear for the ratio of concentrations of VO_2 portions which have a semiconducting or metallic phase. This dependence is assigned to the fact that, as bromine ions undergo reduction and chemisorption on the VO_2/PEG interface, new molecules of TEABr (that is present in excess) may enter the volume occupied by PEG. In this case, one should expect an increase in the intensity of signals that are caused by the substance located near the surface of VO_2 particles with semiconducting properties.

The phase heterogeneity of disperse VO_2 in a PEG matrix decreases sharply, when PEG absorbs a small amount of water. Thus, absorption of 5 wt.% of water by the polymeric matrix leads to the practically complete disappearance of the narrow signal component (Fig. 8).
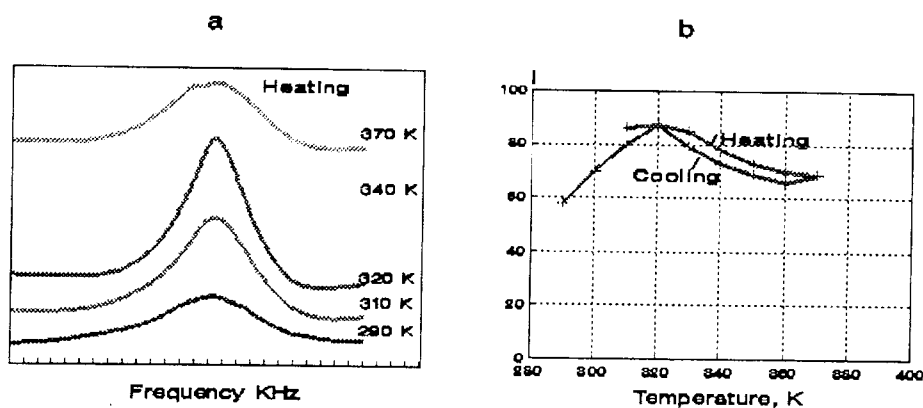

Fig. 8. Temperature-induced variations of the ^1H NMR spectra (a) and signal intensity (b) for a sample of VO_2 in a PEG matrix doped with TEABr and containing 5 wt.% of water.

Such a behaviour of the system is evidently caused by an increase in the mobility of TEABr cations in the polymeric matrix containing water. Moreover, under the action of the strong electric field that exists between the TEABr cations and negatively charged surface of VO_2 particles these cations move towards the surface. The local electric field is confined within the gap between the TEABr cations and VO_2 particle surface, and in terms of its geometry it is analogous to an electric field between a point charge and conducting surface. The migration of the cations towards the surface leads to a decrease in the VO_2 particle surface portion that is subjected to the action of the local electric fields.

3. Conclusion

From the results of this study it is possible to conclude that the method of the ^1H NMR spectroscopy of adsorbed molecules may be efficiently applied to researches into peculiarity of the MSPT dynamics in solvates and suspensions. In the case of hydrated powders of VO_2 the metal- semiconductor phase transition region is in a temperature range of $315 < T < 340$ K and depends on the surface hydration level. The temperature intensity curves display a hysteresis whose loop with increases with the sample hydration level. Most likely it occurs owing to the penetration of water molecules into gaps between microcrystals making disperse VO_2 particles. The validity of this statement is substantiated by the dispersion of powders which leads to the formation of stable colloids. The ^1H NMR signal intensity in suspensions varies continuously in a temperature interval $295 < T < 340$ K; besides, a negative temperature hysteresis is observed.

Small concentrations of TEABr in a PEG matrix can exert a strong effect on the electronic structure of disperse VO_2 particles. This is accompanied by the appearance of phase heterogeneity of VO_2, which manifests itself in the fact that with the onset of MSPT with increasing temperature one portion of the substance passes to the metallic state, and the other remains in the semiconducting state. The heterogeneity of a sample is observed in the wide temperature interval $305 < T < 390$ K. One of the probable causes of the observed phenomenon is a strong bonding of TEABr cations with the polymeric matrix, while bromine anions diffuse to the VO_2 surface where they lose their charge in the process of chemisorption. As a result, an electric field sets up, and the field lines are directed from cations localized in the polymer matrix to the VO_2 particle surface

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