Azimuthal anisotropy of thin films of a solution on the face of a single crystal

A. A. Chernov, V. V. Sipyagin, É. I. Fedin, and A. L. Blyumenfel'd

Crystallography Institute, USSR Academy of Sciences

(Submitted April 8, 1975; resubmitted May 13, 1975)
Pis'ma Zh. Eksp. Teor. Fiz. **22**, No. 5, 263-266 (5 September 1975)

Thin films (5–40 μ) of water and aqueous salt solutions adsorbed on the surfaces of faces of various single crystals, glass, and teflon were investigated by the NMR method. Anisotropy of the proton absorption spectrum, dependent on the azimuthal orientation of the film relative to the magnetic field, was observed for the adsorbed films on faces of noncubic crystals.

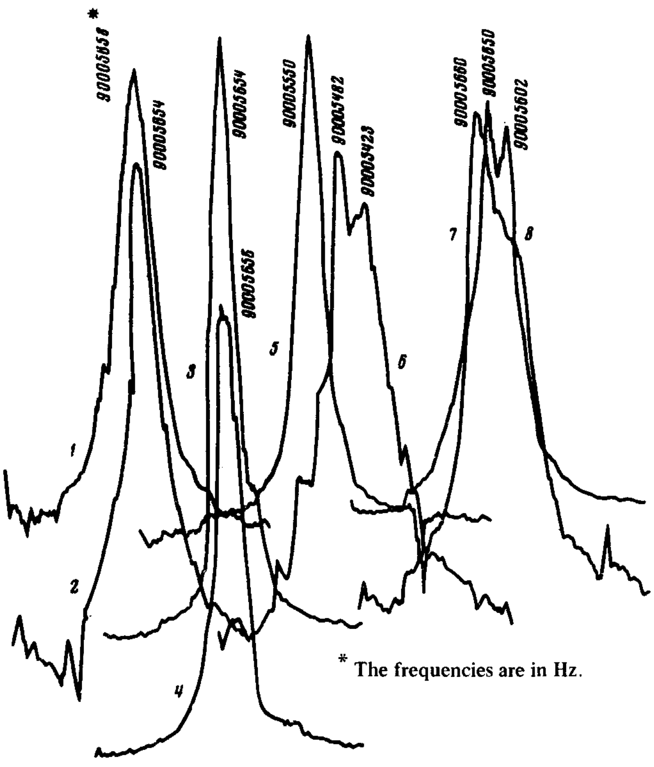
PACS numbers: 75.70., 61.16.H

It is known that the temperature dependences of the thermal conductivity of water,[1] of its compressibility,[2] electric conductivity,[3] ultrasound absorption,[4] and in particular surface properties[5] exhibit a nonmonotonic variation in the ranges 0–15 and 30–45 °C. In the same ranges, abrupt oscillations were observed in the rates of crystal growth from aqueous solutions.[6] Similar anomalies were observed in biological experiments.[7] These anomalies are usually attributed to transitions in the quasicrystal line structure of surface layers of water and solutions. Yet direct structure investigations of thin layers of the solutions were never carried out before. The present paper is devoted to results of such investigations by the NMR method.

The investigation was carried out with an SXP-4100 pulsed radiospectrometer (Bruker, West Germany) with working frequencies 90, 88, and 88.9 MHz, with external stabilization of the magnetic field and with the spectra recorded after Fourier transformation of the decrease in the free induction. The possibility of accumulating the signal in the spectrometer memory has made it possible to investigate individual films 5 to 40 μ thick.

The thickness of the solution film or water film was determined by introducing a measured amount of liquid through a capillary and determining the area of the sample. Round plate-like samples were placed in a glass ampule in such way that their planes were perpendicular to the axis of the ampule and parallel to the magnetic field of the spectrometer. By rotating the ampule in the field of the spectrometer it was possible to investigate the azimuthal dependence of the proton NMR spectra. All the measurements were performed at room temperature.

It is seen from the figure that at different mutually perpendicular orientations the absorption spectra from distilled water placed between teflon surfaces (curves 1 and 2) and glass surfaces (curves 3 and 4) were the same, as expected. To the contrary, the absorption lines from the protons in the adsorbed films of a solution ~10 μ thick on the (100) faces of $NaNO_2$ and the



* The frequencies are in Hz.

NMR spectra of protons in thin films of water or solution between various surfaces: each pair of curves pertains to two mutually perpendicular azimuthal orientations in a magnetic field parallel to the film: 1, 2—water (thickness 20 μ) between teflon surfaces; 3, 4—the same between glass surfaces; 5, 6—KNO_3 solution (thickness 15—20 μ) between (010) faces of KNO_3; 7, 8—solution between (100) faces of $NaNO_2$.

(010) faces of KNO_3 (curves 5–8) had a different character and a different frequency shift at different field orientations. The observed anisotropy of the spectra cannot be the result of inhomogeneity of the field at the investigated part of the sample as a result of microscopic roughness of the face, since no such anisotropy was observed in special experiments with rough samples of teflon. Isotropic signals were also obtained from the adsorption films of the solution on the (100) faces of cubic crystals such as potassium-aluminum alum, hydrozin sulfate, although these crystals had natural step-like microrelief.

To verify the reproducibility we varied many times, during the course of the investigations, the samples of the single crystal plates, the thicknesses of the adsorption films, the setting of the instrument, and the working frequency of the pickup. Analogous results were obtained in all these experiments.

In estimates of the resonant frequencies (see the figure), account must be taken of only the difference between the frequencies of neighboring peaks (curves 5–8) on the resonance curves, which amounted to 48–59 Hz. The absolute resonance frequencies, depending on the tuning conditions and other factors indicated above, can differ for the same samples by several dozen hertz. At the same time, under the same conditions of the experiment, the scatter of the resonance frequencies when the samples are rotated about the vertical axis does not exceed 10 Hz, and the proper resolution of the apparatus is ± 5 Hz.

The anisotropic NMR spectra were obtained by us also for adsorbed films of the solution on the faces of single-crystal pentaerythrite, potassium biphthalate, and potassium-lithium sulfate, the anisotropy likewise being manifest in a splitting of the peaks at definite crystallographic orientations.

Similar experiments were performed also for films of nonpolar liquids (benzene and nitrobenzene) on the faces of the aforementioned noncubic crystals of pentaerythrite, KNO_3, and $NaNO_3$. In all these cases none of the above-noted splittings of the NMR lines were observed following azimuthal rotation. Nor was the effect present in experiments with water film on faces on a calcite rhombohedron, which was practically insoluble in water under the experimental conditions. Thus, anisotropy appears in thick near-surface liquid layers only in the case of a polar liquid (water) on the faces of crystals that are well dissolved in the liquid.

The structural ordering of the macroscopic adsorber layers can be naturally attributed to the influence of the crystal surface on the short-range order in concentrated saturated solutions.

[1] V. P. Frontas'ev, Dokl. Akad, Nauk SSSR **111**, 1014 (1956).
[2] M. Pena and M. L. McGlashen, Trans. Faraday Soc. **55**, 2018 (1959).
[3] K. Terao, Jpan J. Appl. Phys. **8**, 47 (1969).
[4] K. J. Taylor and P. D. Jarman, Brit. J. Appl. Phys. (J. Phys. D), Ser. 2, **1**, 653 (1968).
[5] W. Drost-Hansen, Chem. Phys. Lett. **2**, 647 (1968).
[6] V. V. Sipyagin and A. A. Chernov, Krystallografiya **17**, 1003 (1972) [Sov. Phys.-Crystallography **17**, 881 (1973)].
[7] H. K. Mitchell and M. B. Houlahan, Am. J. Botany **33**, 31 (1946).