STAT

ULTRASONIC WAVES AND THEIR APPLICATION

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A great deal of attention has been paid in the USSR during the last few years to the study of ultrasonics. The upper limit of the ultrasonic range has been considerably increased and has reached the order of 10^9 cycles [1]. Obtaining ultrasonic high frequencies opens up new possibilities for studying a whole series of physico-chemical processes. Ways have been discovered of making an ultrasonic microscope.

In a homogeneous elastic medium, as in monocrystals, the absorption of ultrasonic frequencies is slight, and is determined, basically, only by the coefficient of viscosity and of heat conduction. If the medium is not homogeneous, as in polycrystals, the coefficient of ultrasonic absorption is considerably increased and increases greatly in proportion to the lack of homogeneity.

Because of the small attenuation in monocrystals, there is observed a repeated reflection of ultrasonic frequencies from its facets. The number of these reflections is very great, several score, but they may even go up into the hundreds. For studying the extent of ultrasonic oscillations, ultrasonic impulses a microsecond in duration were used. These, being emitted in a crystal and reflected repeatedly from its facets, were registered on a cathode-ray oscillograph. When the repeated reflections ap-

peared on the screen of the oscillograph, there were seen a series of regular, equally spaced impulses.

In research on quartz monocrystals, which have internal homogeneity, ultrasonic impulses having a frequency of $f = 10^8$ cycles, being emitted in quartz, were reflected from two of its opposite facets several dozen times. If the quartz crystal possessed internal heterogeneity in the form of twinning, the oscillations were absorbed much more, and fewer impulses were reflected, the picture of the impulses obtained in this case was irregular, the impulses were located at unequal distances from each other.

Ultrasonic oscillations with a frequency of $f = 10^9$ cycles were successfully induced in quartz monocrystals. In Figure 1a are shown ultrasonic impulses with a frequency of $f = 10^8$ cycles, and in 1b are shown impulses with a frequency $f = 10^9$ cycles in the direction of the optic axis.

The Anisotropic Character of the Propagation of Ultrasonic Waves in a Piezoelectric Quartz-Crystal (1)

In studying the propagation of ultrasonic oscillations in quartz in the direction of the optic and electrical axes, anisotropic absorption of the ultrasonic waves was detected. The coefficient of ultrasound absorption had different values for these directions. A minimum absorption of ultrasonic waves was noticed in the direction of the optic axis. A maximum absorption was noticed in the direction of the electrical axis. Figure 1a shows a picture of the repeated reflection of impulses in a quartz sample

in the direction of the optic axis; Figure 2 - in the direction of the electrical axis. These illustrations clearly show a great difference in the coefficient of ultrasonic absorption in the directions indicated. A large number of quartz crystals were tested in this way, and in every case, anisotropic absorption of the ultrasonic waves was noticed.

Apparently the conclusion must be made that the coefficient of dissipation of an ultrasonic wave in piezoelectric crystals with anisotropic elastic properties has an anisotropic character. And the expression for the absorption coefficient of linear waves, derived for an isotropic medium [2]

$$\gamma_1 = \frac{\omega^2}{2\rho c_1^3}\left[\left(\frac{4}{3}\eta + \xi\right) + \frac{\times T\alpha^2\rho^3\left(c_1^2 - \frac{4}{3}c_1^2\right)}{c_p^2}\right]$$

should be noticeably different for an anisotropic medium (piezoelectrical crystals). Instead of the first and second coefficients of viscosity η and ξ, there should be the components of symmetrical tensor of viscosity η_{iklm} of the fourth order.

In a quartz crystal, ultrasonic oscillations of another type can be induced at the same time; they can be longitudinal, transverse and on the surface. Figure 3a is a photograph of repeated reflected impulses, showing simultaneous generation of longitudinal and transverse oscillations in the sample. The figure clearly shows the difference in the speed of propagation of longitudinal and transverse oscillations: $C_{\text{transverse}} < C_{\text{longitudinal}}$.

The picture of the spacing of impulses, shown in Figure 3b, is very interesting. As can be seen in the figure, there are two groups of impulses [1].

The first group of impulses, which fit close together and are located in the left part of the figure, correspond to the longitudinal type of oscillations.

The second group of impulses, which are spaced much farther apart (about 4.5 times as much) apparently correspond to another type of oscillations, propagated with a speed approximately 4.5 times less.

Whether these oscillations should be taken as a new type, a new capillary type, propagated at a speed of approximately 1250 meters per second, or whether they should be explained as interferences phenomena, further experiments must determine.

Elastic heterogeneities occur in metals [3] along facets of contiguous crystals. Their value depends on the dimensions of the crystals and their orientation. In the propagation of ultrasonic waves on the contact faces of crystals, temperature fluctuations are formed, which lead to the formation of local heat currents. This increases the entropy of the oscillating body; that is, it increases the energy loss of the ultrasonic waves [4].

Since temperature properties depend on the dimensions of the crystals and their orientation, the energy losses of the ultrasonic waves which arise ΔE will also depend on the dimensions of the crystals and their orientation; that is, on the

structure of the medium. Thus

$$\Delta E = \varphi(d, a)$$

where d is the mean value of the granule and a is the parameter which determines the orientation of the granule.

The energy losses of the ultrasound depend also on the wavelength λ, more accurately on the parameter K, where

$$K = F\left(\frac{d}{\lambda}\right).$$

Experiments show that energy losses increase as the $\frac{d}{\lambda}$ relationship increases, and are more noticeable when $\frac{d}{\lambda} < 1$. If, however, $\frac{d}{\lambda} \gg 1$, an especially large absorption of the ultrasonic waves is observed, and the metal becomes "somewhat opaque". In this case the large absorption of the ultrasonic waves must be considered as the diffusive dissipation of waves, the propagation of which, in such a case, can be likened to the propagation of light in a turbid medium.

It should be noted here that ultrasonic x-raying of solids has found wide application in the defectoscope study of metals. Defectoscope analyses, based on this principle, permit metals to be x-rayed to a thickness of several meters and detect minute flaws and heterogeneities of local recrystallization.

The home of the ultrasonic defectoscope is the Soviet Union, where in 1927, S. Ya. Sokolov was the first to discover the fact that ultrasonic rays would penetrate metals and in 1928 [5] built the first model of the ultrasonic defectoscope.

Further development of ultrasonic defectoscope analysis [6] led to the idea of obtaining a visible representation of defects and heterogeneities, and later on — to making an ultrasonic microscope.

The Ultrasonic Microscope [7]

As has already been indicated above, at the present time there is a possibility of obtaining short ultrasonic waves of the order of long infrared waves and even visible light. This makes the ultrasonic microscope feasible, making it possible to see in a magnified fashion objects and heterogeneities found in media both transparent and non-transparent to light. Since almost all bodies in nature are transparent to ultrasonic waves, the ultrasonic microscope can find a wide application in different fields of science and industry.

The basic methods of obtaining a visible representation in the ultrasonic microscope have already been published by the author. Following are the essential elements:

1. Obtaining a visible representation by means of a revolving beam of a cathode tube similar to the method used in television [7].

2. Obtaining a visible representation in an ultrasonic microscope, which employes the methods used in electron microscopes, where a piezoelectric quartz plate serves as the photocathode of a vacuum tube — being under the influence of the ultrasonic waves from one side and illuminated from the other by a beam

of light. This causes secondary electrons to fly out [7] from the illuminated surface, which is covered by a photosensitive coating.

3. As in the preceding variations, a homogeneous beam of ultrasonic rays illuminates the object being examined or the heterogeneity in a liquid medium, and after passing through an ultrasonic lens, comes out on the surface where it produces the characteristics of the irregularities very accurately, thus giving a representation of the object being examined. By means of the beam of light, which falls at a certain angle, the representation is transferred either to a screen or is observed in a magnifier [8].

In the ultrasonic microscope, the resolving power, as in the optical microscope, depends on the wavelength of the ultrasonic waves λ and can be obtained close to the resolving power of the optical microscope.

By using ultrasonic oscillations in the future whose wavelengths are less than the wavelengths of light, we shall increase the resolving power of the microscope and make it greater than in the optical microscope. Use of the ultrasonic microscope will be greater when its resolving power is increased. We shall now give the results of several tests, carried out with an ultrasonic microscope.

To obtain a normal representation of the object viewed, it is necessary that the structure of the ultrasonic ray be homogeneous and be a regular flat wave; if not, the representation of the object will be distorted. Figure 4 is a representation of a metal wire,

placed in a homogeneous (a) and heterogeneous (b) ultrasonic field. As can be seen from the figure, the representation of the wire in the heterogeneous field is distorted. Figure 5 is a representation of the oscillating plate surface. The figure clearly shows that at various points the silver coating which covered the quartz plate surface, has been destroyed. It has been magnified 45 times.

The quality of the metal cover of the quartz plate surface can be very accurately determined this way. Figure 6 is an illustration of the border line between the twinning and the monocrystal fields on the quartz plate. By this means, it is possible to determine very accurately the elastic heterogeneities in various types of crystals which occur internally and cannot be discerned from the surface.

Figure 7 illustrates the process of dissolving crystal particles of citric acid in a liquid.

Figure 8a is a representation of a thin film of lacquer spreading in kerosene, magnified 33 times. Figure 8b is a representation of tiny defects in aluminum foil magnified 33 times.

From these experiments an idea can be obtained of how sensitive ultrasonic rays are to the smallest changes in the elastic properties of the medium. By means of the ultrasonic microscope it is possible to observe and study the formation of very minute air bubbles in a liquid medium (the appearance of cavitation, the development of chemical reactions, the lives of microorganisms, etc.)

Studying Physico-chemical Processes by Ultrasonic Waves

At the present time, measuring the speed of chemical reactions and observing the flow of chemical processes is done by methods usually only suited to a limited number of phenomena.

The proposed method using ultrasonic oscillations permits a large class of physico-chemical processes to be observed.

Following are the essential elements of the method: the medium in which the process to be investigated take place is "x-rayed" with ultrasonic rays. The speed of propagation of ultrasonic oscillations C and the coefficient of absorption α are measured throughout the whole process. Since the magnitudes of C and α vary as the process being studied develops, to a certain degree their change will characterize the process under investigation -- as for example, the time of its development. Thus, if the speed of sound propagation C and the coefficient of absorption α are recorded without interruption, we will obtain a curve of the magnitude of C or α measured in relation to the time of development of the process. By this curve, it is possible to judge the length of the phenomenon developing, the change of magnitude of the concentration of the substance investigated and other magnitudes.

It is possible by this method to measure very accurately the time of development of a chemical reaction regardless of how long the reaction goes on (ranging from several hours to microseconds).

The Quasi-Modulated Frequency Method

The essence of this method consists of the following: The frequency of the electric generator which excites a quartz crystal is changed by 5-10 percent by changing the capacitance or self-induction of the generator circuit. A high frequency generator is connected inductively with an electrical oscillator receiver. With such a hook-up, the receiver will be subject to the sum of the frequencies -- the frequency of the ultrasonic oscillations f_1 plus the frequency of the electric generator f_2. The sum is obtained from the time the ultrasonic oscillations act on the receiving quartz plate; the two frequencies f_1 and f_2 will act in the receiving setup in such a way that after the corresponding amplification and detecting, they will give the difference of the frequencies $f_1 - f_2 = \Omega$.

The difference of the frequencies Ω is recorded by an oscillograph, which has been plugged into the amplifier output. It is easy to see that the value of the frequency Ω is proportional to the length of the path of the ultrasonic ray ℓ and the diffusion speed of sound in the medium to be investigated. If the length of the path of the ultrasonic ray ℓ is set, the value Ω will be directly proportional to c. Consequently, changes of Ω will result from changes in the diffusion speed of the sound c. By this means, it is possible to record the smallest changes of diffusion speed of sound in a medium which changes its elastic properties during every step of the development of the chemical reaction.

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The Diffraction of Light Method in an Ultrasonic Field

In the propagation of ultrasonic waves in an elastic medium, concentrations and rarefactions are normally created. They are distributed and follow one after the other. The refractive index of the medium changes in accordance with the periodic distribution of concentrations and rarefactions. This takes place both for moving and for stationary waves. If the medium is x-rayed by a parallel beam of light, which passes perpendicular to the direction of the ultrasonic waves, the concentrations and rarefactions form an unusual "diffraction grating". The optic properties of such a grating change from point to point to the first approximation according to the sinusoidal law. The constant of the grating is equal to one-half the length of the ultrasonic wave. To obtain the diffraction picture, it is necessary that the length of the ultrasonic wave be rather small.

The phenomenon of the diffraction of light in such a grating can basically be likened to diffraction in the ordinary optic grating.

According to Debye's theory, the intensity of the spectra of the first order is proportional to the square of the amplitude of the ultrasonic wave. This relationship was confirmed experimentally for small amplitudes.

In an ultrasonic wave, the dielectric constant of the medium ε and the corresponding refraction index μ change periodically.

If we assume that the frequency of the ultrasound is considerably less than the frequency of light $\Omega \ll \omega$ -- that is, the change of density takes place very slowly when c is compared to the frequency of light ω; the formula for the diffraction field is:

$$E = \frac{\mu'}{\mu_c}\frac{K^2}{4\pi}\frac{x_o y_o z_o}{R_o} e^{i\left[(\omega \pm \Omega)t - (KR_o)\right]} \frac{\sin\left[\frac{\pi x_o}{\lambda}(\cos\phi - \cos\varphi)\right]}{\frac{\pi z_o}{\lambda}(\cos\phi - \cos\varphi)} X$$

$$X \frac{\sin\left[\frac{\pi x_o}{\lambda}\left(\sin\vartheta - \sin\varphi \pm \frac{\lambda}{\Lambda}\right)\right]}{\frac{\pi x_o}{\lambda}\left(\sin\vartheta - \sin\varphi \pm \frac{\lambda}{\Lambda}\right)} e^{\frac{iXz_o}{\lambda}(\cos\theta - \cos\varphi)} \qquad (1)$$

Here $K = \frac{2\pi}{\lambda}$; μ' - the change in refraction index; θ - the angle of refraction; φ - the angle of incidence of the beam of light; μ_c - the mean value of the refraction index; R_o - the radius vector of the point of observations; Z_o - the length of the path of light in the ultrasonic field; X_o - the width of the ultrasonic field.

The derivation gives a satisfactory description of the diffraction of light only for spectra of the first order.

Raman and Nagandra Nath [11] have assumed that the light ray, passing through an ultrasonic grating, preserves its rectilinearity. On the path between the planes $Z = 0$ and $Z = Z_o$, different rays pass a different optical depth and go out of the

ultrasonic wave field with different phases. As a result, the electrical field in the plane $Z = Z_0$, has a constant amplitude and is modulated only by phase. The assumption of phase modulation of the light rays explains the presence of spectra of higher orders. Their theory leads to the following conclusions:

1. The directions, which correspond to the main diffraction maximum, are defined by the expression

$$\sin\beta - \sin\varphi = \frac{n\lambda}{\Lambda}, \quad n = 0; \pm 1; \pm 2. \tag{2}$$

2. The intensity of the n spectrum during diffraction in a moving wave is proportional to

$$J_n^2\left[\frac{2\pi\Delta}{\lambda\cos\varphi}\sin\left(\frac{\pi z_0}{\Lambda}\operatorname{tg}\varphi\right)\right]; \quad \Delta = \frac{\mu'}{\mu_0}, \tag{3}$$

where J_n is a function of the n order; in case of normal incidence, the intensity is proportional to

$$J_n^2\left(\frac{2\pi\Delta z_0}{\lambda}\right).$$

3. The diffracted beams are monochromatic, and the frequency of the n spectrum is equal to

$$\omega_n = \omega + n\Omega$$

From (3), it can be seen that energy is symmetrically distributed in the spectra. However, the symmetry of the diffraction picture regarding the spectrum of zero order is not confirmed by experiment. As a more precise examination indicates, the theory of Raman and Nagandra Nath is to be applied only in case of long ultrasonic waves which satisfy the condition

$$\frac{\lambda z_0}{\Lambda} \ll 1.$$

Rytov [2] studied instances of small angles of incidence. He pointed out that as the wave length of the ultrasonic waves diminishes, the diffraction picture comes closer to the Bragg-Wolf condition and corresponds to selective reflection. By changing the distance between diffraction spectra, we can measure the speed of sound propagation.

If the medium under investigation is x-rayed by ultrasonic rays in 3 mutually perpendicular directions, it is possible to obtain on the screen a 3-dimensional spectrum, which can give an idea about the development of the chemical reaction in this medium not only in time but in space.

The Method of Ultrasonic Impulses

In this method, just as explained before, short ultrasonic impulses are emitted in the medium to be tested and are received on the opposite side of the vessel, which contains the liquid to be tested, or they are reflected from the opposite sides of the vessel and are received on the quartz plate, which emits them.

The distance between impulses on the screen of the oscillograph is a measurement of the length of the path of the ray in the liquid to be tested. To make measurements more accurate, it is necessary to increase the rectification of the cathode oscillograph to the point where the impulse structure is a block of sinusoidal curves (Figure 9).

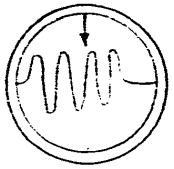

Figure 9.

If a fixed point is put on the sine wave of the impulse by a permanent mark on the oscillograph, the smallest displacements of the impulse from the starting position will be noticed. Knowing the part of the sine wave where the impulse was displaced, and the frequency of emission, it is easy to compute the angle of lead or delay of the ultrasonic beam, if the medium changes its elastic properties. Thus, if the length of the path of the ultrasonic waves in the liquid, the oscillation frequency and the magnitude of the ultrasonic impulse displacement be known, it is easy to find the magnitude of the change in the speed of sound propagation in the medium. Just as in the preceding cases, it is possible to judge the physical or chemical process which occurred in the medium to be examined by the change in the speed of the propagating sound. This method is especially suitable for measuring concentrations

of one medium in another, for measuring low-temperature fluctuations of the medium and for determining the development of diffusion. In all cases, to generate the ultrasonic impulses we used a complex quartz emitter, consisting of a thin quartz plate on the surface of which were attached steel coverings from 1 to 3 millimeters in thickness. A quartz plate is most suitable in this system and emits more effectively. Such an emitter assures the emissions of a large quantity of higher components. When on the basic frequency and also while oscillating, one-half the wave length is fixed along the thickness of the simple quartz plate. Figure 10 shows the setup of a complex emitter.

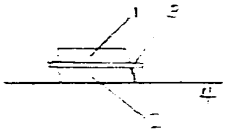

Figure 10. 1 and 2 - steel plates 1 - 3 mm in thickness 3 - quartz plate 0.1 - 0.2 mm in thickness
4 - metal

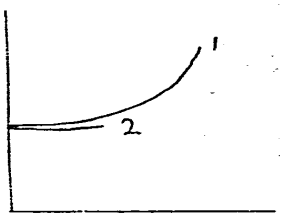

Figure 11. 1 - for methocrylic ether 2 - for cane sugar

The following reactions were tested by the methods set forth above:

1. Polymerization of methacrylic ~~ether~~ ester under the influence

of a catalyst (benzoyl peroxide). The reaction occurred at a temperature of 50 degrees Centigrade, the amount of polymerizing substance taken was 100 cubic centimeter.

2. Inversions of can sugar.

Figure 11 shows curves of the change of speed of propagation of sound during the 1st and 2nd reactions. It is possible to determine the speed of the reaction by these curves.

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