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exercises on the disk. To do this, the constraints of the disk are given the form of elastic cantilevers which yield immediately to the action and thereby measure, and record as functions of time, the *torque* and the *axial force*, that is, the moment about the axis, and the force perpendicular to the plane of the disk. As the yield of the cantilevers changes the dimensions of the gap, it is necessary to prevent these changes from becoming large enough to disturb the time effects significantly, and to use combinations of mechanical and optical lever systems (not shown in the figure) with a sensitivity of about  $10^{-6}$  cm.

The experimental results are conveniently expressed by three graphs in which are plotted, against time, the angular velocity of the cone and the torque and axial force on the disk, each quantity being expressed in percentage of its maximum value. Assume the material to be incompressible, and the motion one of laminar shear throughout the gap. The torque, T, and the axial force, F, are then related to the stress components tangential and normal to the plane of the disk by a purely geometrical factor, and as this factor is independent of time, it cancels out when the percentage values are considered as functions of time. Explicitly, introducing cylindrical co-ordinates, we find that in a differential cell at a point  $(r, \varphi, z)$ the stress, P, has in the plane of the disk the tangential and normal components

 $P_{\varphi z} = P'_{\varphi z}$  and  $P_{zz} = - P'_{\varphi \varphi} \log R/r$ ,

whence integrating over the area of the disk we deduce

$$T = rac{2}{3}\pi \ R^3 \ P'_{\, arphi z} \ ext{and} \ F = rac{\pi}{2} \ R^2 \ P'_{\, arphi arphi},$$

where the indices attached to P indicate the coordinates involved and the dash denotes the value at a point of the rim of the gap (r = R).

For such an ideal case the three graphs obtained for the macroscopic development in time must be identical with those obtained in every differential cell of the material for the percentages respectively of the strain velocity, and of the stress components tangential and normal to the plane of the disk. (The height of the gap is chosen sufficiently small to make the forces of inertia negligible under the motions of the material here considered.)

In one type of experiment we used visco-elastic liquids ; solids are more troublesome for this type of experiments, since in the build-up period they tend to break under the large strains required, and in the relaxation period show inconveniently slow changes of stress. We were concerned with the time effects encountered in the build-up, and in the relaxation of the various components of stress during periods of stationary rates of laminar shearing displacements. It might appear that during these periods any liquid would run out of the gap. However, in the conditions of shear considered, the viscoelastic liquids used here develop hoop-stresses sufficiently strong to form a cylindrical free boundary, and prevent the running out. At first the material was in its ground-state, and the cone and disk were at rest. Next we started a period of build-up of stress by keeping the disk at rest and suddenly imparting to the cone a rotation with an angular velocity that was maintained throughout the period at a constant level sufficiently high to bring about measurable torques and axial forces on the disk. Finally we proceeded to a period of relaxation of stress by suddenly arresting the motion of the cone and keeping the cone and the disk at rest henceforth. Both periods were covered

by a photographic record, and a typical set of results is shown on the right-hand side of the figure in the three graphs. The actions applied to the cone are seen in the graph of the angular velocity, and the anisotropic time effects in the differences between the graphs of the torque and axial force. Interpreting the graphs for every differential cell of the material, we find that the strain velocity is exactly synchronized with the action on the cone, while the stress components are delayed, and show anisotropic time effects, the percentage rates of build-up and relaxation being different as between the components tangential and normal to the plane of the disk.

In a second type of experiment we used viscoelastic materials, both liquid and solid, and proceeded as in the first type, except that the shearing displacement imposed by the rotation of the cone was now varied harmonically in time, with a frequency and amplitude chosen sufficiently high to give measurable torques and axial forces. The results obtained so far showed that, in this case, the torque, and the tangential component of stress, varied around a mean value of zero with the same frequency as the imposed displacement, while the axial force and the normal component varied around a mean value different from zero with twice that frequency. The phase and amplitude relations are still being investigated.

The experiments thus show that anisotropic time effects are produced even in isotropic materials during transitions between shear-free and sheared states, and that in the case of laminar shearing displacements the tangential and normal components of stress conform to the theory, showing simultaneously different times of build-up under a stationary rate of displacement, different times of relaxation under constantly maintained displacement, and different frequencies of vibrations under harmonically varying displacements.

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<sup>1</sup> Weissenberg, K., Arch. Sci. Phys. et Nat., 17, 1 (1934); Nature, 159, 310 (1947).

<sup>2</sup> Weissenberg, K., Conf. British Rheologists' Club, London, 1946.

## DIELECTRIC CONSTANT AND PIEZO-ELECTRIC RESONANCE OF BARIUM TITANATE CRYSTALS

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THE growth of barium titanate single crystals and the ferro-electric behaviour of their pseudocubic modification have been described earlier<sup>1,2</sup>, and more detailed data can now be given.

There can be obtained at least four modifications of barium titanium compounds, among which the hexagonal and the pseudocubic ones definitely are stoichiometrically BaTiO<sub>3</sub><sup>1,2,3</sup>. The dielectric constant of the hexagonal modification is comparatively low, namely, between 100 and 200. The temperature characteristic shows two small peaks near 0° C. and 100° C., at which points maxima of the dielectric constant for the pseudocubic crystals have been found<sup>3</sup>.



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Crystals of the pseudocubic modification grown from alkali carbonates or barium chloride show a discoloration which ranges from yellow to clear red. Spectroscopic investigation confirmed that this colour is mainly due to dissolved platinum. Colourless crystals were obtained by using carbon crucibles.

The dielectric constant and the piezo-electric resonance frequency have now been measured as a function of temperature, parallel to the three crystallographic directions of the same crystal, that is, along its cube edges. The electric field strength was less than 1 volt per cm. at a frequency of 1 kc. The Miller indices on the graphs serve merely to distinguish the three directions in which the electric field was applied to the cube. The crystals usually are twinned with respect to the 011 and  $01\overline{1}$  planes<sup>4</sup>.

Dielectric hysteresis characteristics have been observed in all three directions and show that the hysteresis disappears only above 100° C. (Slight deviations in temperature from values observed by other authors are probably due to impurities.) Therefore, this temperature represents the only Curie point in contrast to the peaks around 5° C. and -70° C., as already shown in previous measurements<sup>2,3,6</sup>. The course of the piezo-electric resonance indicates some kind of a transition at these temperatures<sup>5</sup>, but more investigation is necessary to reveal its nature.



The thermal hysteresis is considerable and has to be attributed to the existence of large (about 1-2mm.) spontaneously polarized domains. which are easily visible7.

From the crystallographic point of view, the present situation is different from that of Rochelle salt or the di-hydrogenphosphates in that barium titanate is a new type of ferro-electric in which all the three crystallographic axes seem to show a similar behaviour. The twinning might give some erroneous results for the absolute value of the dielectric constant; but as microscopic observations with a heating stage show, the twinning should only affect the 010 and 001 results, since here the different axes might overlap one another. That there is virtually no twinning perpendicular to 100 confirms the fact that the ferro-electric behaviour of barium titanate is much less anisotropic than that of the above-named salts, and much more similar to the ferro-magnetics. Considerable progress has been made in obtaining untwinned crystals, and more conclusive results will be given shortly?.



Whether the crystals in the Curie range really are tetragonal seems doubtful. Observations with polarized light, made by Prof. Fairbairn of this Institute, give no evidence whatsoever for a tetragonal structure, but point to optical biaxiality. More complete optical data would be desirable and will be obtained when larger unstrained crystal sections become available.

From the dielectric and piezo-electric behaviour of single crystals given above, the peculiar piezo-electric property of barium titanate ceramics<sup>8</sup> may be perhaps interpreted similarly to the quadratic magnetostrictive effects in polycrystalline iron.

- <sup>1</sup> Blattner, H., Matthias, B., and Merz, W., Helv. Phys. Acta, 20, 225 (1947).
- <sup>2</sup> Blattner, H., Matthias, B., Merz, W., and Scherrer, P., Experientia, 3, No. 4 (1947).
- <sup>3</sup> Matthias, B. T., Breckenridge, R. G., and Beaumont, D. W., *Phys. Rev.*, **72**, 532 (1947). <sup>4</sup> Kay, H. R., and Rhodes, R. B., Nature, 160, 127 (1947).
- <sup>5</sup> Matthias, B., Helv. Phys. Acta, 16, 209 (1943).
- <sup>6</sup> von Hippel, A., Breckenridge, R. G., Chesley, F. G., and Tisza, Laszlo, *Ind. and Eng. Chem.*, 38, 1097 (November 1946).
  <sup>7</sup> Data presented at the meeting of the National Research Council in Cambridge, Massachusetts, September 26, 1947. A paper by B. T. Matthias and A. von Hippel is in preparation.
  <sup>8</sup> Roberts, Shephard, *Phys. Rev.*, 17, 12, 890 (1947).

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