Low Frequency Dispersion of a Molecular Crystal

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(Z. Naturforsch. **32 a**, 515–516 [1977]; received January 29, 1977)

The dielectric behaviour of solid 1,4-Butandiol has been studied. A region of low frequency dispersion has been observed. In a crystalline sample treated to have more lattice faults, the losses were increased. The effect is attributed to a dielectric relaxation process existing in connection with the lattice defects.

It is well known that many physical properties of crystals dependent upon the previous history of the specimen, the presence of impurities and other structural defects [1]. In ionic crystals that have been treated to obtain a relatively large number of lattice defects, small dielectric loss maxima have been observed in the kilocycle region [2, 3]. The effect was attributed to pairs of associated lattice defects considered as dipoles.

In this paper we have studied the dielectric properties of a solid consisting of polar molecules in their dependence on structural faults. As an example we have chosen 1,4-Butandiol.

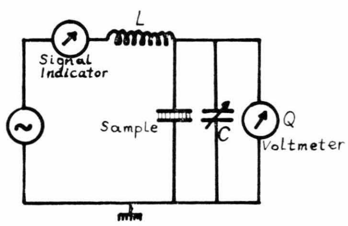

Fig. 1. The apparatus.

Experimental

The real part ε' of the complex dielectric constant $\varepsilon^* = \varepsilon' - j\,\varepsilon''$ and the loss tangent $\tan\delta = \varepsilon''/\varepsilon'$ were determined in the frequency region 10^3 to 10^6 Hz, using a Q-Meter (Figure 1). The apparatus is equiped with a variable frequency oscillator and a series-resonant circuit the L and C elements of which are also variable. The Q-Meter is well suited to capacitance measurements at high frequency by means of the substitution method. In addition the range of measurements can be extended down to very low frequencies through use of an external L.F. oscillator in place of the oscillator of the Q-Meter. The measuring equipment also includes a set of calibrated coils, a peak voltmeter and a micrometer capacitor.

The measuring cell functions as a capacitor connected in parallel across the variable capacitor of the Q-Meter. With the addition of one of the calibrated coils the system forms a series resonant circuit. The Q factor and the tuning capacitance of this circuit are first measured with the empty cell (Q_0, C_0) and then with the dielectric added to the cell (Q, C). ε' and the loss tangent of the sample have been calculated by means of the formulas:

$$\varepsilon' = 1 + \Delta C / C_a \,, \qquad (1)$$

$$\tan\delta = \frac{C_0}{Q \cdot Q_0} \, \frac{\Delta Q}{\Delta C + C_a} \qquad (2)$$

where $\Delta C = C - C_0$, $\Delta Q = Q - Q_0$, $C_0 = 1/4\,\pi^2 f^2 L$, f = the frequency, L = the inductance of the coil used and C_a = the active capacitance of the measuring cell ($C_a = 1$ pF).

The cell was calibrated with liquids of known dielectric constant and the temperature controled by a LAUDA thermostatic circulator, with control accuracy ± 0.2 °C.

The accuracy of the measurements was 2% for ε' and about 3% for the loss tangent.

The substance under investigation (1,4-Butandiol) was obtained from Fluka Company with a purity better than 99% by weight. 1,4-Butandiol solidifies at about 5 °C and the measurements were taken for each frequency from higher to lower temperatures.

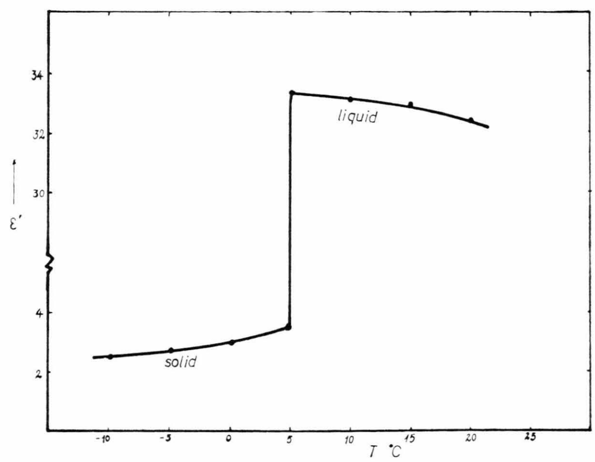

Fig. 2. Variation of ε' with temperature of 1,4-Butandiol at 100 kHz.

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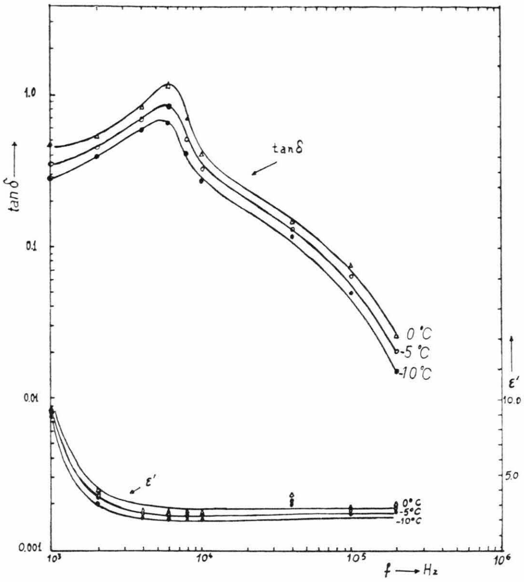

Fig. 3. Dependence of ε' and $\tan\delta$ upon frequency (solid 1,4-Butandiol).

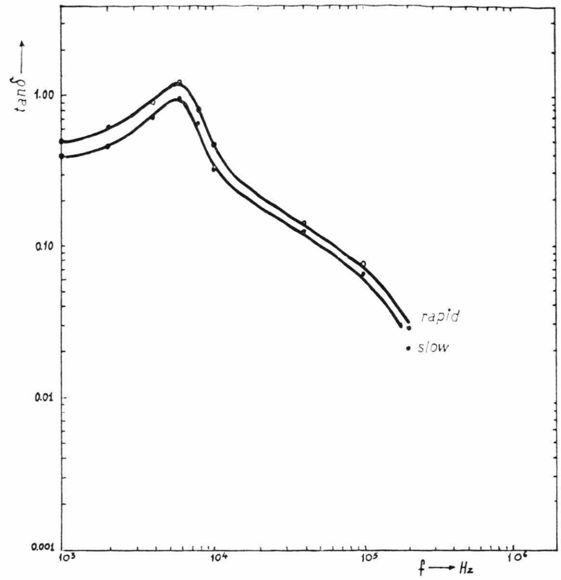

Fig. 4. Dependence of dielectric loss upon the rate of solidification (solid 1,4-Butandiol at 0 °C).

In the solid state the material was frozen between the fixed plates of the measuring cell, so that the amount of material between the plates did not change with temperature (density).

Results and Discussion

The results of the measurements are shown in Figs. 2, 3 and 4. The great change of ε' at the melting point (Fig. 2) shows that 1,4-Butandiol is a polar molecule which aquires freedom of rotation on melting.

The maximum of $\tan\delta$ and accompanying decrease of ε' at 6 kHz (Fig. 3) indicates the existence of a dielectric relaxation process. From Fig. 4 it is clear that the dielectric loss increases with the rate of solidification and consequently with the number of structural faults in the solid.

The loss maximum may be used to determine the activation energy for the mechanism of polarization by means of the simple formula [4]

$$2\pi\nu\cdot\tau_0 = \exp\{-U/kT\}$$

where ν is the frequency at maximum loss, τ_0 the time constant of the lattice vibrations (the order of 10^{-13} sec) and U the activation energy of the process. The value of U thus calculated is 0.36 eV.

It seems likely that the polarising units of the low frequency dispersion are some of the existing electric dipoles with a freedom of orientation as a consequence of lattice deformations.

[1] C. P. Smyth, Dielectric Behavior and Structure, McGraw-Hill, New York 1955, Chapter V.

[2] R. G. Breckenridge, J. Chem. Phys. **18**, 913 [1950].

[3] G. Arlt et al., Phys. Stat. Sol. (a) **3**, k 243 [1970].

[4] S. Glasstone, K. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York 1941, Chapter IX.