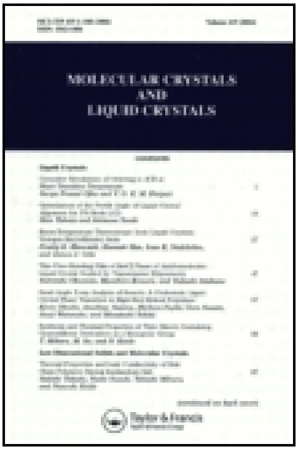

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Unusual Dielectric Behavior of Solid Cyclopentanol and Molecular Motion†

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Abstract—Dielectric and visual studies of cyclopentanol show the presence of a " rotational " form I stable from the melting point at −17.6 °C to a transition point at −37.5 °C, and a " rotational " form II from there to a second transition point at −72 °C. There are two " non-rotational " forms: form IV produced on quenching II with liquid nitrogen transforms upon warming to form III, which is the form usually produced when II is cooled, in the vicinity of −80 °C. The dielectric constant of form III is about 2.5 and does not change rapidly with temperature; that of form IV is consistently 1% below that of form III. The dielectric constant of I is about 30. That of II produced from I grown from the melt is variable and ranges as high as 80; but if II is produced from III, the dielectric constant will be only about 30. In both I and II there is an association of about three molecules in chains to produce the high dielectric constants. In I the chains are distributed isotropically; whereas, in II there is a preference, increasing at lower temperatures, to form chains so that the resultant dipole moment is oriented along the *c*-axis of the hexagonal crystal structure. Crystals of I tend to grow from the melt with their *c*-axes normal to surrounding surfaces. Since the transformation to II is barely first order and does not involve restructuring, the dielectric anisotropy of II results in abnormally high values of capacitance being measured. The randomly oriented crystallites of II produced from III result in the measurement of an average value.

1. Introduction

Highly unusual dielectric behavior for cyclopentanol was first observed by White and Bishop⁽¹⁾ and later confirmed by Corfield and Davies.⁽²⁾ When cyclopentanol is cooled from the melt, there is a small increase in dielectric constant upon freezing at the melting point

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‡ NDEA Title IV Fellow, 1967–70.

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of − 18 °C. Such behavior is not unexpected and has been frequently observed among members of the class of " plastic solids " having a permanent electric dipole moment. The usual explanation is that these are " rotator " solids in which molecules retain some degree of orientational freedom even while constituting a definite crystal lattice.(3) The truly anomalous dielectric behavior of cyclopentanol is seen when, upon further cooling, the solid undergoes a transformation at − 37.5 °C to produce a form whose dielectric constant increases greatly over that of the first solid produced. Still further cooling reveals a second transformation point at − 72 °C where a form is produced that has the normal low dielectric constant associated with non-rotational solids of the same type. If the sample is warmed, the transformation at − 72 °C reverses, but instead of returning to the anomalously high dielectric values observed during the cooling process, the dielectric constant rises to a value that is slightly less than that of the first solid formed. Corfield and Davies thought that there was only one solid form stable from the transition at − 72 °C to the melting point at − 18 °C, and that the abnormally high dielectric constant observed between − 37.5 °C and − 72 °C upon cooling was due to a metastable form. Corfield and Davies also discounted the idea of rotational freedom in any of the solid forms. Instead, they ascribed the high dielectric constant of the liquid and the first solids as being due to hydrogen-bonded chains. The abnormally high dielectric constant of the supposedly metastable form was thought to be due to longer chains.

We have restudied the dielectric properties of cyclopentanol and have come to rather different conclusions. In so doing, we have compared our findings to thermodynamic studies by Parks *et al.*(4) and by Adachi *et al.*(5) and to X-ray studies by Wheeler.(6) Our own direct visual observations of the solids formed and of their transformations were also of great importance in arriving at an understanding of the dielectric behavior. We have concluded that form I, the solid stable from the melting point to the transition point at − 37.5 °C, owes its high dielectric constant to the presence of hydrogen-bonded chains, but that the nearly complete orientational freedom of the molecules in the lattice results in a solid that is essentially isotropic in its dielectric constant. Form II, which is stable from the transition at − 37.5 °C to the lower transition at

– 72 °C, has a greatly decreased orientational freedom that results in the chains being formed predominantly in the *c*-direction of the crystals; consequently, the dielectric constant along the *c*-axis is much greater than that along the *a*- or *b*-axes. Because of the way the crystals happen to grow in the capacitors used for measuring dielectric constants, the crystals of I and of II formed from the melt are preferentially oriented with the *c*-axis normal to the electrodes. This results in an abnormally high value for the dielectric constant for form II. When the non-rotational form III is produced, there is a drastic restructuring that results in the formation of many small crystals. When these are transformed back to II or I upon reheating, their axes are randomly oriented. The averaged dielectric constant for II produced in this way is slightly lower than that for I.

In one sense, then, the anomalously high dielectric constant observed in form II is only an accident resulting from the method of measurement, and may represent a process that is unique to cyclopentanol. On the other hand, we have also obtained from the study of cyclopentanol insights into the behavior of molecules within the different structural modifications that may be applicable to a wide range of solids.

2. Experimental Details

The capacitor used for most of the dielectric work was a three-terminal cylindrical capacitor made of brass with an inner radius of 1.351 cm, an outer radius of 1.500 cm, and an effective length of 12.65 cm. The measuring circuits included a General Radio Type 1615-A capacitance bridge, a tuned amplifier and detector, several oscillators, and a crystal mixer. Most measurements of capacitance were made at a frequency of 1 kc/s. For measurements of dielectric dispersion frequencies up to 4 Mc/s were used.

In order to verify the suspected effects of the growth habit of cyclopentanol on the measured dielectric constant, a special capacitor was constructed. The electrodes were 30 cm by 10 cm and had a separation of 2 cm. The electrodes were grooved so that 150 1-mm glass slides could be inserted between the electrodes. The 1-mm spaces between the slides could then be filled with cyclopentanol. This special capacitor was also constructed as a three-terminal capacitor both for accuracy and also to simplify calibration and interpretation of measured capacitances in terms of an effective dielectric constant for the solid cyclopentanol.

Visual observations were accomplished by containing a sample within a holder made from two $3\frac{1}{2} \times 4$-inch glass lantern slides cemented together on three sides with 1-mm glass spacers. Because of the hygroscopic nature of cyclopentanol, provisions were made for sealing the holder with a gasket after the sample had been inserted. Similar provisions were also made for the capacitors.

All measurements were made by placing the capacitors and sample holder inside a Conrad environmental chamber that cools to -70 °C by mechanical refrigeration and to lower temperatures by liquid nitrogen. The temperature within the chamber is steady to within 1 °C for any length of time needed. The actual sample temperatures were monitored by a copper-constantan thermocouple attached to the capacitor or sample holder. The chamber was constructed to allow direct viewing so that lighting from the rear could be produced by an external projector whose beam passed through a heat filter (copper sulfate solution) and a polarizing plate. Inside the chamber a diffusing plate just behind the sample holder produced even illumination over most of the sample. The sample could then be viewed directly or photographs could be taken through the front part of the chamber. Photographs were taken with Mamiya-Sekor and Alpa 35 mm cameras using Kodachrome II professional film. Many photographs were also taken through a travelling microscope that could be mounted in front of the chamber. The sample was usually viewed or photographed through a crossed analyzing polaroid as an aid to distinguishing crystal boundaries and grain structure.

The cyclopentanol was obtained from Eastman practical grade by several fractional distillations over sodium metal. All samples used had melting points of -17.6 °C except for one run with the capacitor with the glass slides in which part of the material had a melting point of -18 °C.

3. Results

(A) VISUAL OBSERVATIONS

Cyclopentanol freezes from the melt into phase I in the form of translucent crystals that are of the order of 1 cm across (Plate I). A hexagonal crystal form is evident for a majority of the crystals as they are growing. It is also clear that most of the nucleation must have taken place on the surfaces of the glass lantern slides rather than within the liquid. Because of the interference in growth occurring when two independently growing crystals meet, the hexagonal structure is not so evident when the entire sample has become frozen. A few of the growing crystals display a rectangular growth pattern. When the crystals are viewed through crossed polaroids, weak colours are observed for most of the crystals except for a few that show the hexagonal growth pattern. From the number and size of the crystals formed, it is clear that the process is growth-dominated with only a few centers of nucleation. Cyclopentanol does not supercool to any appreciable degree, and attempts to produce a larger number of smaller crystals by rapid cooling were not very successful.

Because of the difficulty of nucleation and because of the fact that what nucleation there is appears to take place at the glass surfaces, we believe that the crystals of cyclopentanol I formed from the melt are strongly disposed to grow with their *c*-axis perpendicular to the surface on which nucleation occurs, be it the glass plate of the sample holder or the electrodes of the cylindrical capacitor. We infer that the hexagonal crystal structure, which was also obtained by Wheeler in his X-ray studies, results in an optical anisotropy that gives the weak color effects between crossed polaroids when the *c*-axis is not exactly directed along the path of the transmitted light.

Cyclopentanol I transforms to II at the transition temperature of -37.5 °C. The transformation proceeds with no visible changes in the sample except for a slow, gradual and uniform clearing of the crystals over a period of a few hours. Cycling back and forth between I and II produces no changes in the visible crystal patterns except for the slight haziness of form I (Plates II and III).

From -72 to -75 °C, form II transforms to form III by spherulitic growth of a few nuclei over times of several hours. Below this, much heavier nucleation and faster growth completes the transformation in a few minutes (Plate IV). The transformation to III clearly involves a complete structural reordering in which the large crystals of I-II break up into much smaller fragments. On trans-

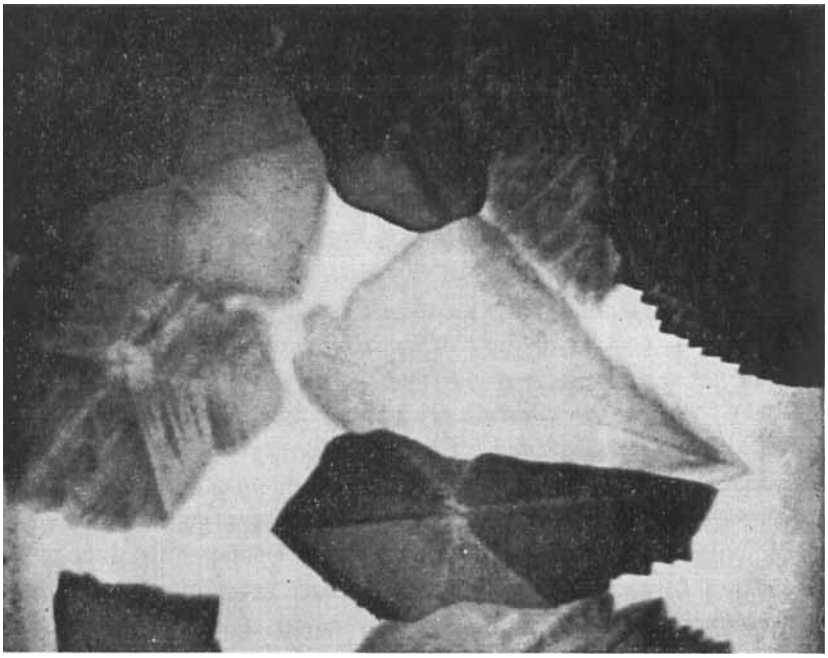

Plate I. Cyclopentanol freezing at about −18 °C showing hexagonal growth patterns. Through crossed polaroids, magnification × 2.

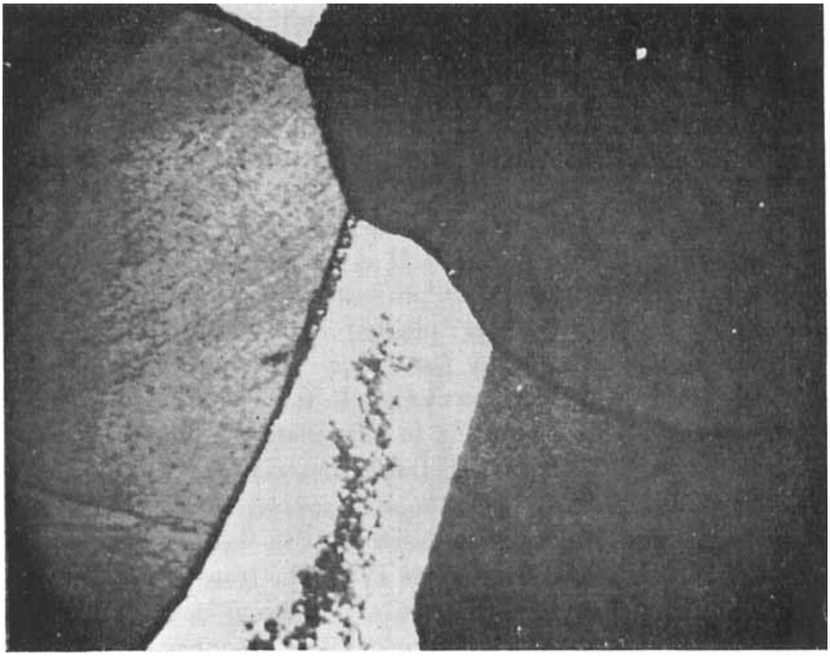

Plate II. Cyclopentanol in form I at −30.0 °C. Through crossed polaroids, magnification × 16.

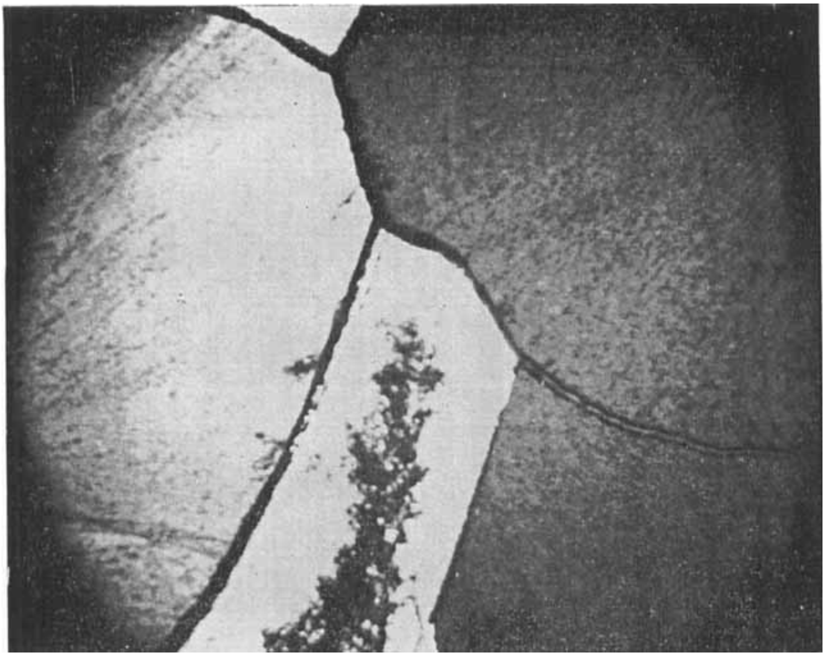

PLATE III. Cyclopentanol in form II at –41.2 °C. Through crossed polaroids, magnification × 16.

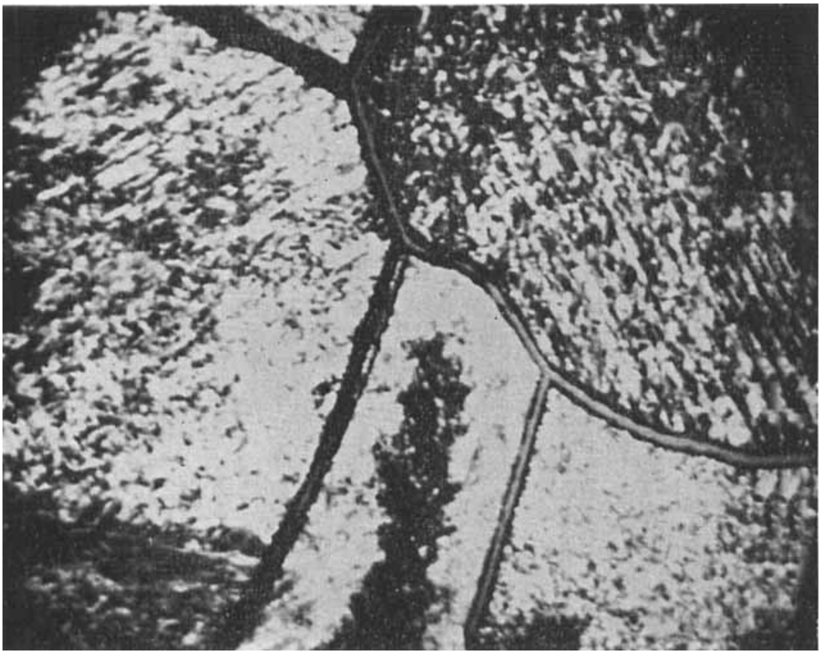

PLATE IV. Cyclopentanol in form II nucleating and transforming to forms III at –85 °C. Through crossed polaroids, magnification × 16.

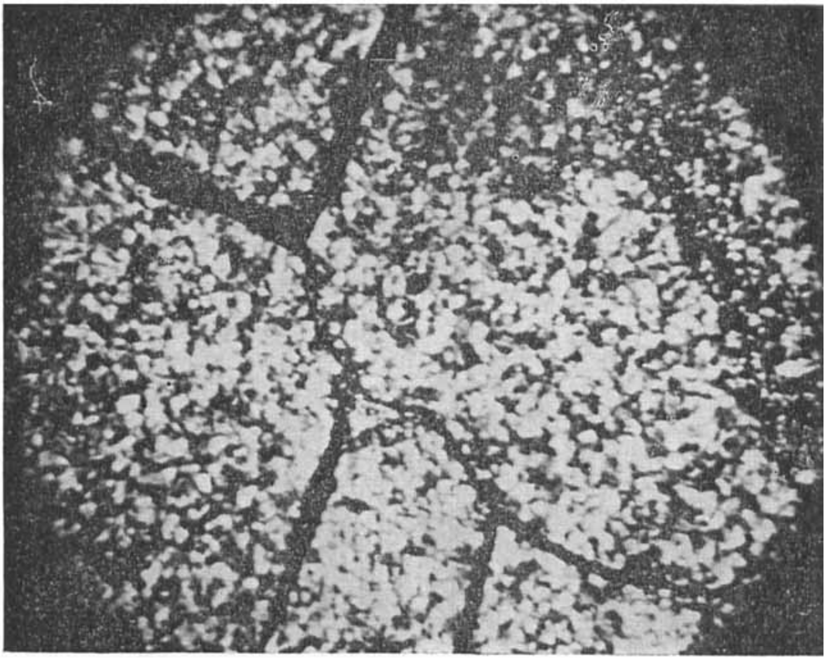

Plate V. Cyclopentanol in form II′ at −62 °C after having been cycled through the transition at −37.5 °C three times. Through crossed polaroids, magnification × 16.

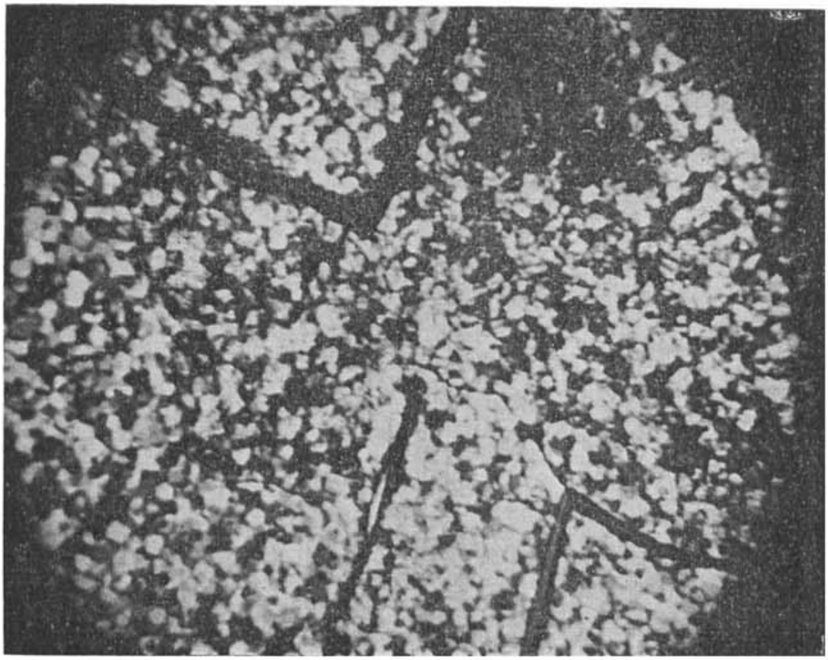

Plate VI. Cyclopentanol in form I′ at −35 °C after having been cycled through the transition at −37.5 °C three times. Through crossed polaroids, magnification × 16.

forming back to II′,† we find an entirely different appearance than that associated with the original form II. The same is true for the form I′ obtained from form II′ by warming the sample above the upper transformation temperature. The sample in forms I′ and II′ is clear, as contrasted with the opaque appearance of form III, and shows color effects with crossed polaroids; however, the scale of the crystals is much smaller. Evidence of the original boundaries between the large crystals formed from the melt remains, but the original regions are fractured into many crystallites with varying orientations. Cycling between I′ and II′ results in a small amount of annealing growth, but the crystallites remain with dimensions of the order of 0.1 to 1 mm as compared to dimensions of the order of centimetres for the original forms I and II (Plates V and VI).

(B) Dielectric Studies

The original dielectric studies on cyclopentanol were performed in these laboratories by Griffith(7); these have since been confirmed and extended. Figures 1 and 2 show the results of two runs that are characteristic of the dielectric behavior of cyclopentanol as obtained from the three-terminal cylindrical capacitor. It should be noted that the data points are obtained from measurements made after equilibrium had been achieved following each change in temperature. On cooling from the melt, we obtain the same dielectric constant for I regardless of the freezing time. The dielectric constant obtained after the sample has been transformed to II by cooling below the transition temperature of −37.5 °C, however, varies from run to run, with the dielectric behavior in Fig. 2 representative of the highest values ever obtained. Even though the behavior is different from one run to another, once the sample has been frozen, its dielectric behavior is fixed. On a given run, cycling back and forth between I and II only reproduces the particular dielectric curve. White and Bishop(1) reported a variation of 5% in the dielectric

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† Because of the difference in dielectric behavior, we have labeled forms I and II that were obtained from form III with a prime. This is not intended to imply that we are dealing with a different structural form, but is to indicate that because of the difference in thermal history there will be differences in macroscopic properties. Forms I and II obtained directly from the melt are written without primes.

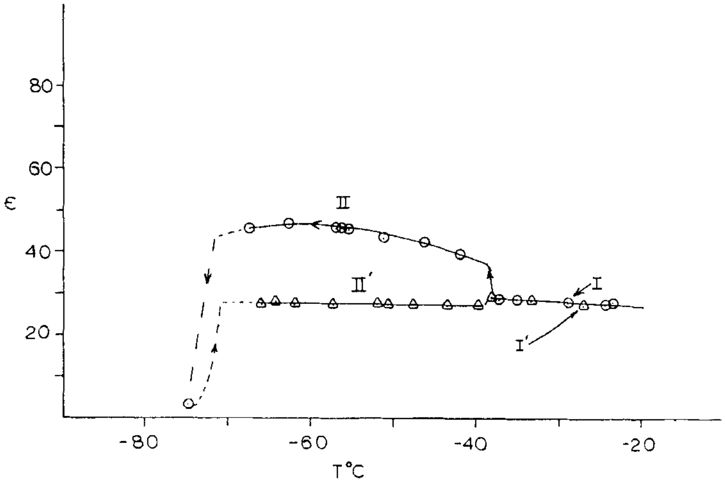

Figure 1. Typical dielectric curve for cyclopentanol.

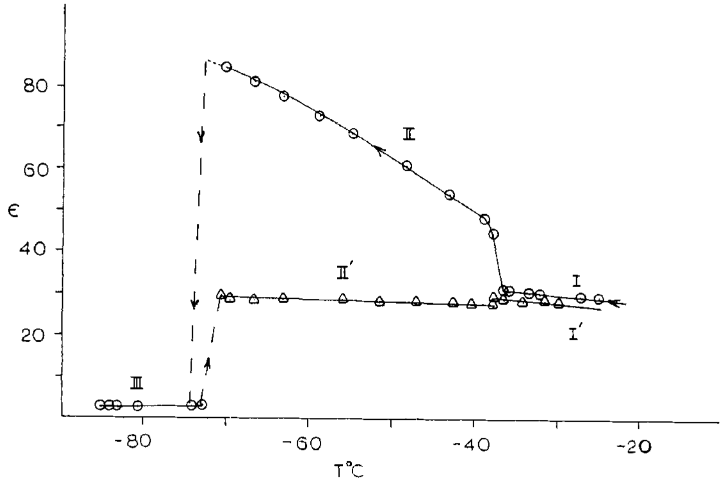

Figure 2. Dielectric curve for cyclopentanol showing the highest values observed for form II.

constant of II and attributed this to variability in the formation of voids. We cannot agree with this conclusion because the similarity in crystal form between I and II would lead one to expect similar effects in the dielectric constant of I, but such effects are not observed.

The times needed for the transformations I→II and II→I are less than a few minutes. Because of the fact that the sample containers are cooled (or heated) only by forced air convection within the environmental chambers, there is a lower limit to meaningful measurements that can be made on times of transformation. We were thus also not able to achieve any appreciable degree of supercooling of I in going to II.

When the sample in form II is cooled to temperatures in the vicinity of −76 °C, it transforms within a few minutes to form III. The dielectric constant of III is 2.51 at −130 °C. If the sample of II is cooled rapidly by liquid nitrogen to −150 °C or so, a different non-rotational form IV results whose dielectric constant is consistently lower than that of III by 1% at equal temperatures. When IV is warmed slowly, it transforms to III in the vicinity of −80 °C in agreement with the thermal studies of Adachi *et al.*⁽⁵⁾ We have never observed III transform into IV.

On warming III above the transition temperature of −72 °C, we find the dielectric constant increases to values characteristic of form II′ that are markedly lower than the values found earlier for form II before it had passed through form III. Further warming produces a small but definite increase in dielectric constant at −37.5 °C marking the transformation to form I′. If forms I′ and II′ are cycled repeatedly, there is a very slight lowering of the dielectric constants until the final stable values shown in Figs. 1 and 2 are reached. These final values are not only reproducible upon further cycling within a given run, but they are also consistent from run to run.

Because of the amount of orientational freedom that the cyclopentanol molecules must possess in both forms I and II, it is not unreasonable to apply the Onsager equation(8) to learn something about the degree of association indicated by the abnormally high dielectric constants. It is clear that even in the liquid complete orientational freedom is not sufficient to account for the high dielectric constant of a substance for which the molecular dipole moment μ_0 is only 1.72 D[9]. Taking $\epsilon_\infty = 2.69$, a value characteristic of III just below the transition temperature, we calculate the effective number of associated molecules n_e from

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}\,\frac{4\pi N_a\rho}{9MkT}\,n_e\mu_0^2. \qquad (1)$$

The curves of Fig. 3 were obtained from (1) using the high values for ϵ_{II}. We believe that the association indicated from use of the Onsager equation comes about through the formation of chains of molecules by hydrogen bonding in agreement with the earlier ideas of Corfield and Davies. It must be remembered, however, that because of the experimental arrangement, the dielectric constant measured in the cylindrical capacitor is appropriate to the crystal direction that happens to be normal to the electrodes of the capacitor. An increase in effective chain length between two different forms of a compound could be brought about by (1) an actual increase in the length of the chains in an isotropic or nonisotropic solid, or (2) an increase in the degree of orientation of the chains in the direction of

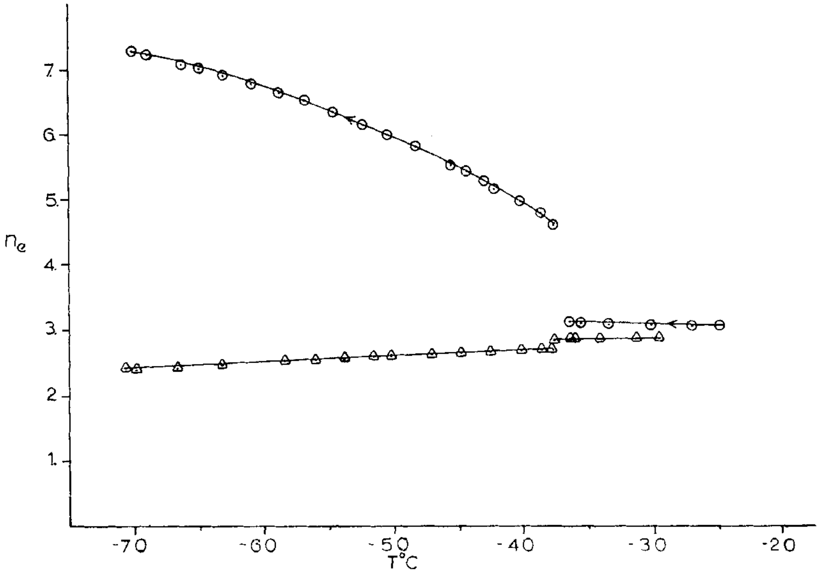

Figure 3. Effective number of associated molecules in cyclopentanol obtained by direct application of the Onsager equation.

measurement in a nonisotropic solid. In the second case, if the amount of ordering is governed somewhat by chance, one would expect to find a range of values, as is observed in practice, for the dielectric constant of form II. We shall return to this point in Sec. 4.

A study of dielectric dispersion was also made on forms II and II′ in which ϵ' and ϵ'' were measured at temperatures from −43.5 °C to −67.6 °C and for frequencies up to 4 Mc/s. A plot of the logarithm of the relaxation times so obtained is given in Fig. 4 as a function of

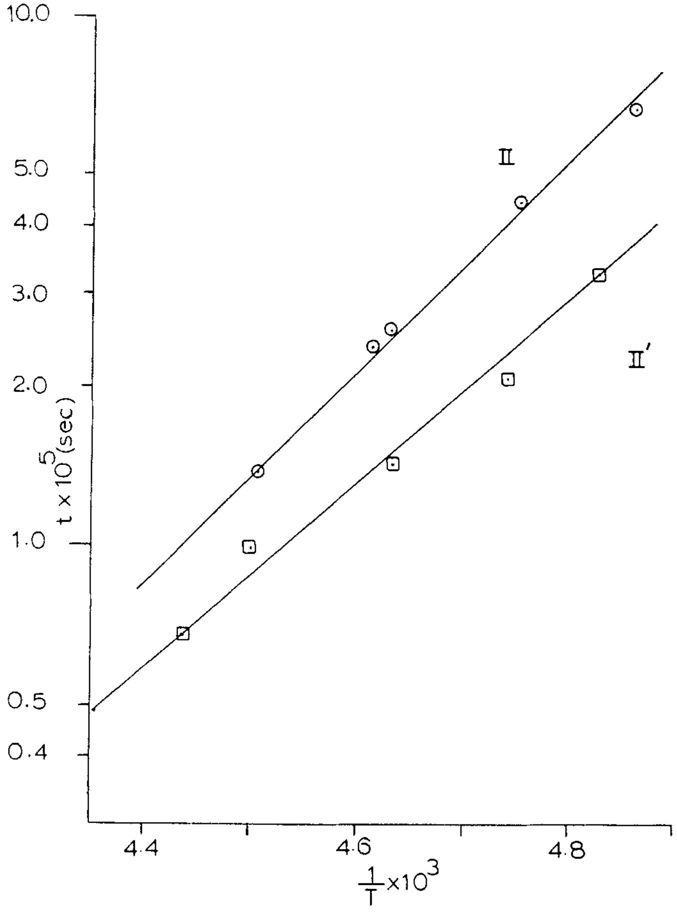

Figure 4. Logarithm of the relaxation time as a function of the inverse temperature for cyclopentanol in forms II and II′.

the inverse temperature. The slopes of these two curves give the heats of activation for what would correspond to dipole reorientation in simpler systems. These are found to be 10.0 ± 0.4 Kcal/mol for form II and 9.2 ± 0.3 Kcal/mol for form II′.

(C) X-RAY STUDIES

At this point it is necessary to review briefly some of the results of Wheeler's X-ray studies on cyclopentanol.(6) The structures proposed by Wheeler for two of the forms of cyclopentanol are shown in Fig. 5. At −30 °C form I is hexagonal with two molecules per cell and with lattice constants $a = 5.88$ Å and $c = 9.45$ Å for a close-packed structure. Wheeler was able to obtain theoretical agreement with the observed ratio of line intensities by placing the two molecules at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) with the assumption that the molecules were rotating with spherical symmetry.

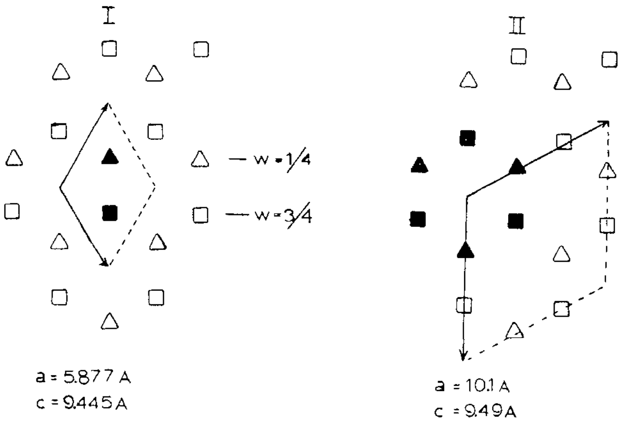

Figure 5. Crystal structures proposed for cyclopentanol forms I and II by Wheeler.(6)

The unit cell for form II at −56 °C is also hexagonal, but with cell constants $a = 10.1$ Å and $c = 9.49$ Å. This structure keeps the molecules at the same positions as in form I, but requires that the orientational freedom be reduced. The transformation from I to II would then be nonreconstructive as suggested by the thermal data of Parks *et al.* Despite the large number of parameters that can be adjusted, we have as yet been unable to find a pattern of orientational freedom for the molecules in form II that will give agreement with the observed intensities.

(D) THE GLASS PLATE CAPACITOR

It began to seem likely that effects of preferential orientation were involved to produce the anomalous dielectric behavior of form II. In the visual observations we noted that nucleation was scanty and occurred on the glass surfaces and also that while they were growing from the melt, most of the crystals displayed a hexagonal pattern. In view of the crystal structure of cyclopentanol as given by the X-ray studies, it is to be expected that since form I is indeed a hexagonal close-packed structure and since nucleation does occur on the boundary surfaces, the growth would be preferentially oriented with the c-axis normal to the surface. This is primarily because of the fact that the crystal plane perpendicular to the c-axis contains the maximum density of molecules. In view of this, we would then expect that the cylindrical capacitor, which has essentially the same geometry because of its dimensions as the visual sample holder, would measure an effective dielectric constant primarily along the c-axis of the crystals. Because of the spherically symmetric orientational freedom of form I, this would have no special effect; however, in the case of the more restricted orientational freedom in form II, we might well anticipate that the crystal would be strongly anisotropic dielectrically. Since the transformation from I to II is nonreconstructive, the crystals of form II would also be preferentially oriented with their c-axes normal to the electrodes. Because of the hexagonal symmetry, it is necessary in any case that $\epsilon_a = \epsilon_b$. If in addition $\epsilon_c > \epsilon_a$, the preferred orientation of the crystals would result in the abnormally high effective dielectric constant observed. Chance variations in the orientations produced when form I first freezes would account for the variations in dielectric constant observed for form II, while that for form I would not be affected. The transformation to form III and the reformation of II′ from III, however, will result in many small, randomly oriented crystallites; consequently, a smaller dielectric constant nearer in value to that of I should be observed.

It was to test this hypothesis that we constructed the glass plate capacitor. The glass plates had 1-mm spacing, close to that of the electrodes in the cylindrical capacitor; but they were inserted normal to the electrodes so that if form I were indeed to grow preferentially with the *c*-axis normal to the surrounding surfaces, the crystals would grow so that the effective dielectric constant measured would be that for the equivalent *a*- and *b*-axes. A typical run produced the dielectric curve shown in Fig. 6. The dielectric constant in form II, produced from form I frozen from the melt, shows a clear, although small, drop in value from that of form I. When the sample is transformed to III and then back to II′, the dielectric constant is higher than in form II, but agrees with the dielectric constant measured for form II′ in the cylindrical capacitor. This is exactly the behavior to be expected on the basis of our hypotheses.

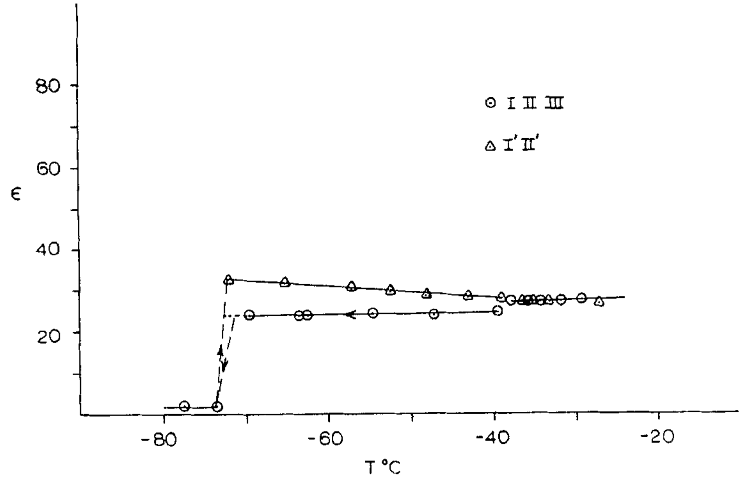

Figure 6. Dielectric curve for cyclopentanol obtained with the glass plate capacitor that was especially designed to test for effects of orientation of growth.

4. Development of the Model

To investigate these effects quantitatively, let us assume that the run in which form II displayed the highest values for the dielectric constant was indeed a fortuitous case in which all of the crystals happened to grow with their c-axes normal to the electrodes. These results would then give us values for ϵ_c. We can now use the regularly reproducible values for form II′ to obtain ϵ_a in the following way. Because of the small size of the crystallites formed in II′, even though the spacing of electrodes in the cylindrical capacitor is small, we know that we would traverse a fairly large number of randomly oriented crystallites in going from one electrode to the other. If the space between the plates be divided into n layers of equal thickness, the effective dielectric constant for the series combination is given by

$$\bar{\epsilon} = \frac{1}{(1/n)\sum\limits_i (1/\epsilon_i)} \tag{2}$$

where ϵ_i is the dielectric constant for the ith layer in which the field direction makes direction cosines l, m, n with the principal axes of the crystallite and is given by

$$\epsilon_i = l^2\epsilon_x + m^2\epsilon_y + n^2\epsilon_z, \tag{3}$$

ϵ_x, ϵ_y, ϵ_z being the values of the dielectric constant along the principal axes.(10) Because of the symmetry of the hexagonal structure, we can take $\epsilon_x = \epsilon_y = \epsilon_a$ and $\epsilon_z = \epsilon_c$. The denominator in the expression for $\bar{\epsilon}$ can be approximated by the average calculated for an infinite number of layers of isotropically oriented crystallites. That is, since

$$n^2 = \cos^2\theta \quad \text{and} \quad l^2 + m^2 = 1 - n^2 \tag{4}$$

we can approximate

$$(1/n)\sum_i (1/\epsilon_i) \rightarrow \int_0^\pi \frac{\frac{1}{2}\sin\theta\, d\theta}{\epsilon_a + (\epsilon_c - \epsilon_a)\cos^2\theta}. \tag{5}$$

We thus obtain for the effective dielectric constant for the randomly oriented crystallites of II′ the expression

$$\epsilon_{\mathrm{II}'} \simeq \bar{\epsilon} = \frac{\sqrt{\epsilon_a(\epsilon_c - \epsilon_a)}}{\tan^{-1}\sqrt{(\epsilon_c/\epsilon_a) - 1}}. \tag{6}$$

We can now calculate from (6) values for ϵ_a in form II. These values for selected temperatures are contained in Table 1. It will be noticed that the calculated values for ϵ_a are somewhat lower than the observed values for II obtained with the glass plate capacitor. This

TABLE I. Cyclopentanol form II: values of ϵ_c assumed from the highest dielectric constants observed for II in the cylindrical capacitor; values of ϵ_a calculated from Eq. (6) and the observed values for II′ in the cylindrical capacitor; values of n, the chain length, and g, the fraction of chains lined in the c-direction calculated from the modified Onsager Eqs. (11) and (12).

T °K	ϵ_c	ϵ_a	n	g
235.5	46.0	21.1	2.86	0.2991
232.7	50.4	20.1	2.90	0.3524
228.9	55.9	19.3	2.98	0.4086
222.9	63.4	18.2	3.08	0.4764
214.5	73.2	16.8	3.18	0.5534
210.0	77.8	16.2	3.21	0.5853
204.2	83.9	15.4	3.26	0.6228

results from a small amount of misalignment of the crystal axes because of the large value of ϵ_c relative to ϵ_a.

To interpret these results, we consider a model in which chains are formed of n molecules each. A fraction g of the chains is oriented so that the resultant dipole moment $\mu = n\mu_0$ is along the c-axis, while the remaining fraction $(1-g)$ of the chains is oriented isotropically. If an assemblage of items with dipole moment μ can line up only parallel or antiparallel to a fixed direction, the effective polarizability per item in that direction is given by

$$\alpha_f = \mu^2/kT, \tag{7}$$

whereas, if the items can orient isotropically, the effective polarizability per item in any direction is

$$\alpha_i = \mu^2/3kT. \tag{8}$$

The total effective polarizability in the c-direction would then be given by

$$\alpha_c = g\alpha_f + (1-g)\alpha_i = (1+2g)\mu^2/3kT \tag{9}$$

whereas, that in the a- and b-directions is given by

$$\alpha_a = (1-g)\alpha_i = (1-g)\mu^2/3kT. \tag{10}$$

We can now use the Onsager equation to compare the dielectric constants in the c- and a-directions:

$$\frac{\epsilon_c - 1}{\epsilon_c + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{3\epsilon_c(\epsilon_\infty + 2)}{(2\epsilon_c + \epsilon_\infty)(\epsilon_c + 2)} \frac{4\pi N_a \rho}{3MkT} \frac{(1+2g)n}{3} \mu_0^2 \tag{11}$$

and

$$\frac{\epsilon_a - 1}{\epsilon_a + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{3\epsilon_a(\epsilon_\infty + 2)}{(2\epsilon_a + \epsilon_\infty)(\epsilon_a + 2)} \frac{4\pi N_a \rho}{3MkT} \frac{(1-g)n}{3} \mu_0^2. \qquad (12)$$

Using the values we have assigned ϵ_a and ϵ_c, we can solve for g and n as functions of temperature. The values so calculated are also included in Table 1.

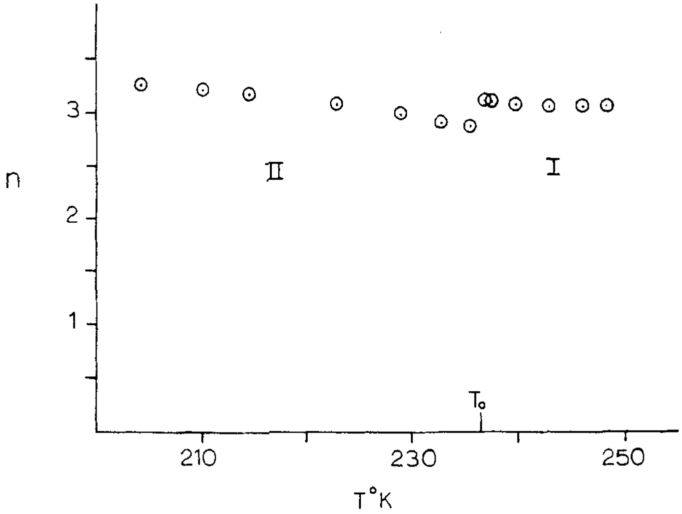

Figure 7. Chain lengths for cyclopentanol in forms I and II as a function of temperature obtained from the Onsager equation modified to take orientational effects into account.

The effective chain length n does not change appreciably over this temperature range. Indeed, if the values just obtained for n are plotted together with the earlier values n_e obtained for form I,† as shown in Fig. 7, we find that the chain length n is the same in both of the rotational forms and is essentially independent of temperature.

On the other hand, the fraction of chains lining up in the c-direction shows considerable variation with temperature. We can compare these results with theoretical calculations made by Fowler$^{(11)}$ for a classical rigid rotator in a field $-W \cos\theta$ where the

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† In form I $g = 0$, so that (11) and (12) reduce to (1).

potential depends on the fraction g of the rotators lined up in the preferred direction according to the relation

$$W = gW_0, \tag{13}$$

and where a rotator is defined as being non-rotational if its rotational kinetic energy is less than some fraction of the aligning energy according to the relation

$$(1/2I)(p_\theta^2 + p_\phi^2/\sin^2\theta) < \beta W(1+\cos\theta). \tag{14}$$

The result of the statistical mechanical calculation is that

$$g = 1 - \frac{e^{gW_0(1-2\beta)/kT} - e^{-gW_0/kT}}{2(1-\beta)\sinh(gW_0/kT)}. \tag{15}$$

In the special case of $\beta = 1/2$, this relation reduces to

$$g = \tanh(gW_0/2kT). \tag{16}$$

It is interesting to note that this form is identical with that arrived at in the Bragg–Williams approximation for order–disorder transformations in alloys.$^{(12)}$ This should not be surprising because the problem we are investigating also involves a statistical mechanical equilibrium between a state of cooperative order and states of disorder. The principal difference is that our problem involves rotational changes rather than translational ones. The fraction g in (16) goes to zero for the critical temperature

$$T_c = W_0/2k. \tag{17}$$

Figure 8 contains two curves based on Eq. (16). The curve marked " 1 " is calculated on the basis of the observed transition temperature of 235.7 °K and with a resultant interaction energy calculated from (17) of 936 cal/mol. We note, however, that although Eq. (16) gives a continuous change in g from unity at low temperatures to zero at the critical temperature, the dielectric constant, which changes as a result of changes in g, suddenly undergoes a discontinuous change at the transition temperature. The curve marked " 2 " in Fig. 8 is obtained from Eq. (16) when it is normalized to the deduced value of $g = .3524$ at $T = 232.7$ °K. This results in a virtual critical temperature $T_c' = 242.3$ °K and an interaction energy of 963 cal/mol. It is interesting to note that this interaction energy, which can also be interpreted as being the difference in level of the bottom of the potential valley in the c-direction compared to other possible

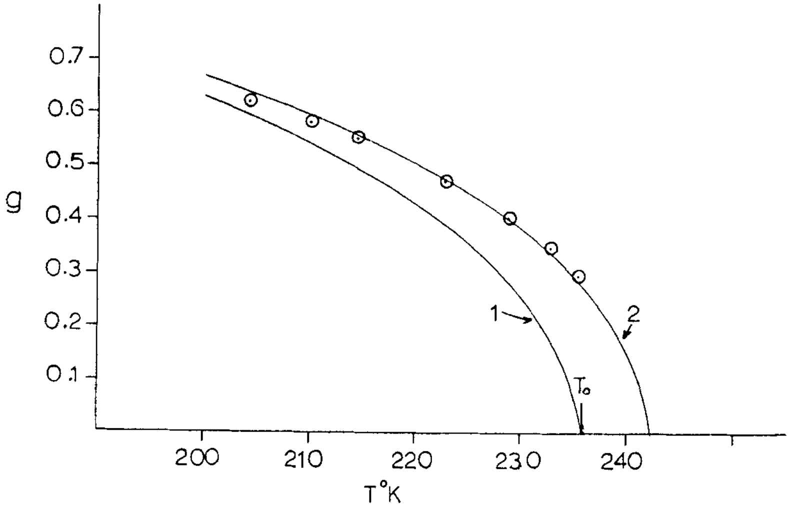

Figure 8. Fraction of chains in cyclopentanol II lining up along the *c*-axis as a function of temperature obtained from the modified Onsager equation compared with theoretical curves of Fowler(11) and of the Bragg–Williams approximation for order–disorder transformations in alloys.(12)

directions, is just equal to the difference in the heats of activation for II and II′ obtained from the measurements of dielectric dispersion.

5. Summary and Conclusions

In our view cyclopentanol I and II are solids in which there is a highly dynamic condition of statistical equilibrium. In both solids approximately three molecules associate through hydrogen bonding to produce chains that enhance the effect of the permanent electric dipole moments of the individual molecules. These chains or associations are in a state of constant change whereby individual molecules, having broken out of the association, are free to reorient in space and subsequently to participate in a new association. In form I there is essentially no restriction on the orientational freedom of the molecules nor on the direction in which the resultant dipole moment of a chain may point. In form II, to the contrary, there is a definite restriction brought about by the interaction of the chains whereby the resultant dipole moment of the chains tends to line up parallel or antiparallel to the *c*-axis of the crystals. In form II the probability that the chains form along the *c*-axis is greatest at lower temperatures, decreases at higher temperatures in accordance with the theory of order–disorder equilibrium in solid alloys, and finally falls discontinuously to zero at the transition temperature of 235.7 °K. The transition is just barely first order. The individual molecules do not change their positions in the crystal but instead change only the orientational probability distribution according to which they can form chains in the solid. We find, correspondingly, that the density and specific heats are more indicative of a second order rather than a first order transition.

In form II produced through form I directly from the melt, the growth habit between the plates of the capacitor used to measure the dielectric constant results in an extraordinarily high value for the dielectric constant because the *c*-axis, which is the axis along which the resultant dipole moment of the chains tends to line up, grows preferentially normal to the electrodes. After the highly reconstructive, nucleation-dominated transformation to form III, the form II′ that results upon transforming back consists of very small, randomly oriented crystallites. The dielectric constant resulting from these crystallites between the electrodes of the capacitor corresponds very closely to the dielectric constant of form I, which is produced by the isotropic distribution of similar chains within the entire crystal.

Beyond the results of this study in explaining the unusual dielectric behavior of two of the forms of solid cyclopentanol, we believe that this study is of even greater importance in demonstrating the existence of very complicated, coordinated activities going on among the molecules of a solid and in allowing us to deduce some of the details of these activities for one particular compound.

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