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Dielectric Relaxations in Various Crystal Modifications of Cyclohexanol and 2,3-Dimethylbutane

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Dielectric Relaxations in Various Crystal Modifications of Cyclohexanol and 2,3-Dimethylbutane

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Abstract—The dielectric constant and loss of crystalline cyclohexanol (CHOL) and 2,3-dimethylbutane (DMB) were measured from 4 °K to the melting point, 299 °K for CHOL and 145 °K for DMB. The supercooled plastic crystal of CHOL above the glass temperature T_g exhibits a prominent relaxation (α) due to molecular rotation. The temperature dependence of the relaxation time was found to obey the Fogel–Tamman equation. A secondary relaxation (β) was observed below T_g, 149 °K for CHOL and 76 °K for DMB. The mechanism proposed for β is internal rotation; rotation of OH bond for CHOL and trans-gauche transformation for DMB. The β relaxation of DMB is well correlated with acoustic relaxation in the liquid state in the relaxation time versus temperature plot. Relaxations in the intermediate state, crystal III, of these two substances and the most stable state, crystal II of DMB were studied.

1. Intoduction

Some molecular substances form a plastic crystal below their melting point. In the plastic crystal, the centers of mass of each molecule take ordered arrangement but orientation of the molecule as a whole is random among the molecules.(1) Cyclohexanol and 2,3-dimethylbutane, which will be respectively abbreviated as CHOL and DMB in the following, are typical in forming plastic crystals below their melting point, 299 and 145 °K, respectively. The plastic crystalline phases of both substances are called crystal I (see Figs. 1 and 2). With further lowering in temperature, crystal I is transformed into another modification, crystal II, at the transition

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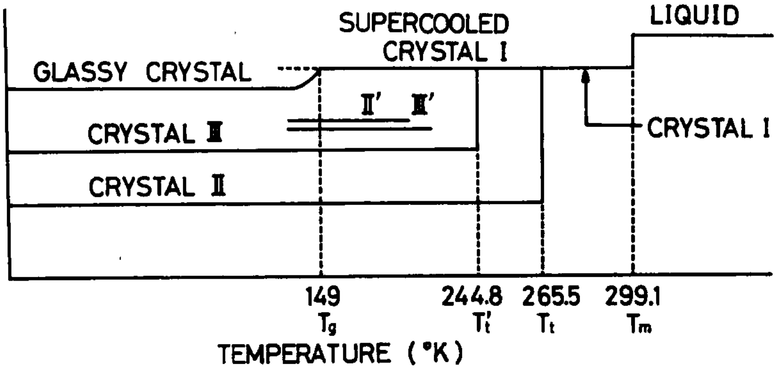

Figure 1. Polymorphism of cyclohexanol.

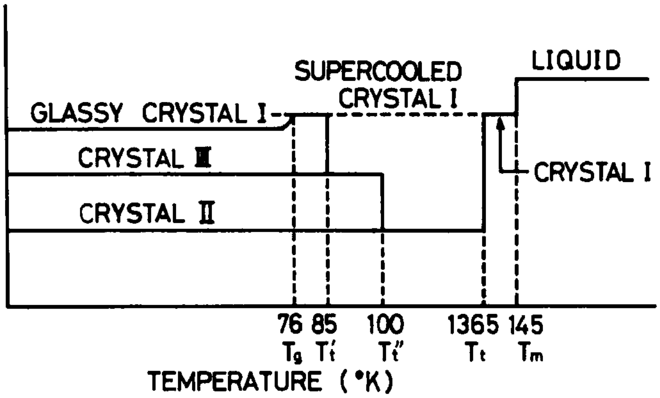

Figure 2. Polymorphism of 2,3-dimethylbutane.

point of 265.5 °K for CHOL and 136.5 °K for DMB. In crystal II, the molecules are regularly oriented and therefore have no degree of freedom of rotation in contrast to crystal I. It was confirmed that crystal II is the most stable form below the transition point to 0 °K.(2,3)

Crystal I of CHOL and DMB is, however, easily supercooled by rapid cooling and maintains the degree of freedom of molecular rotation typical of the plastic crystal even below the transition temperature.(2,3) With further cooling of supercooled crystal I, the rotation is frozen in with random orientation of each molecule. This state was called glassy crystal by Seki and his coworkers(2–4) and the transition from supercooled plastic crystal to glassy crystal is called the glass transition following the usual definition of the glass

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transition which is the change between supercooled liquid and glass, the latter being a non-equilibrium frozen-in state of the liquid. The glass transition temperature T_g is located around 149 °K for CHOL and 76 °K for DMB, and depends slightly on the cooling rate.

With slowly increasing temperature, the glassy crystal goes back to supercooled crystal I through T_g but at temperatures not so much higher than T_g, the crystal is transformed irreversibly into the stable state, crystal II. In the course of this transformation, the system passes an intermediate metastable state, called crystal III. In the case of CHOL, the intermediate state is multiple and, besides crystal III, crystals II′ and III′ are observed.(5)

The polymorphism of CHOL and DMB above described is schematically sketched in Figs. 1 and 2, respectively.

The crystal structure of crystal II of CHOL was analysed by Otsubo *et al.* and Nitta *et al.* by X-ray diffraction(5,6) and was found to be face-centered cubic with a lattice constant of 8.64 Å at 100 °K. The calorimetric study of the polymorphism of CHOL and DMB was carried out in detail by Seki *et al.*(2,3) and residual entropies at 0 °K of each state obtained.

Molecular motion of CHOL in crystal I was investigated through dielectric measurements by Smyth, Meakins, Fujimura, Davis and others.(7–11) However, the range of temperature and frequency covered was rather limited and the overall behavior of the relaxation associated with the glass transition is not yet clear. Molecular motion of DMB was investigated through NMR absorption spectra by Eades, Jones and Segall *et al.*(12–14) Dielectric relaxation of DMB has not yet been done, as far as the authors know, probably because of the very weak polarity of DMB.

The purpose of the present study is to measure dielectric properties of CHOL and DMB over a wide range of temperature and frequency and to obtain information about the molecular motion in each state of the crystal.

2. Experimental

Dielectric constant ϵ' and loss ϵ'' were measured with transformer bridges, Ando-Denki TR-1B and TR-10, over frequencies from 110 Hz to 300 kHz. A frequency higher than 300 kHz could not be

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covered because of the inductance effect of lead cables connecting the bridge and the sample cell. The measurement at 0.01, 0.1 and 1 Hz was performed with an ultra-low-frequency bridge, Ando-Denki TR-4.

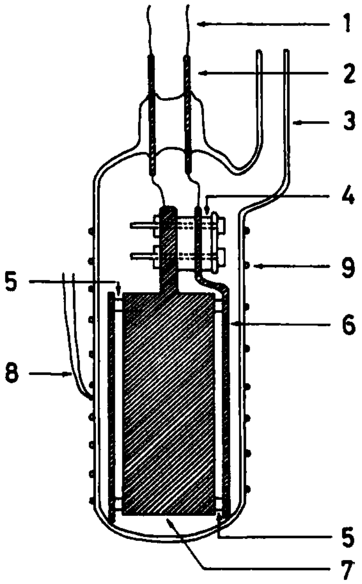

Figure 3. Cross-section of sample cell: 1—copper lead wires, 2—molybdenum wires, 3—inlet of sample, 4—Teflon insulator, 5—Teflon spacers, 6—outer brass cylinder, 7—inner brass cylinder, 8—Cu-constantan thermocouple, 9—heater winding.

The cross section of the sample cell is illustrated in Fig. 3. The inner bulk cylinder (7) and the outer hollow cylinder (6), both made of brass, compose a capacitor and are set in a glass tube. The spacing of the electrodes was kept constant by Teflon spacers (5). The capacitance of the empty cell, C_0, was 38 pF. The temperature dependence of C_0 due to thermal expansion of the brass was found negligibly small. The large heat capacity of the capacitor was effective in keeping the temperature constant through measurements over a wide frequency range.

Figure 4 shows the inner part of the cryostat. The cell was suspended by threads in the inner metal can. The outer can was immersed in a Dewar vessel containing liquid He or N_2 according to

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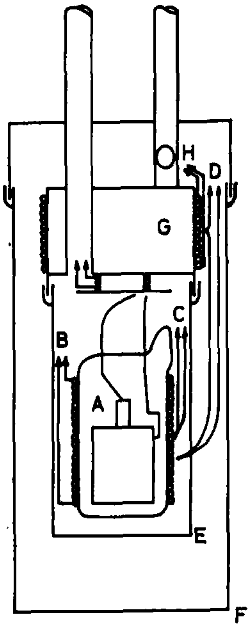

Figure 4. Inner part of cryostat: A—sample cell, B—heater winding, C—thermocouple, D—thermocouple for detecting temperature difference between A and G, E—inner can, F—outer can, G—copper block, H—heater winding.

the temperature range of measurement. The Dewar vessel was further surrounded by another Dewar containing liquid N_2. When the sample was required to be cooled, the cans were filled with He gas to obtain good thermal contact. In the course of the measurement, however, the cans were evacuated to make the temperature drift small.

The temperature of the sample cell was raised by electric current through a constantan wire winding outside the glass tube, and measured by a copper–constantan thermocouple attached to the wall of the sample cell.

The commercial sample of CHOL was purified by fractional distillations and the purity was determined to be 99.97% from measurement of the melting point.⁽²⁾ Starting material of DMB was supplied by Tokyo Kagakuseiki Co., the purity being higher than 99%, and it was further purified by vacuum distillation. The purified samples were dried with CaO and then transferred into the cell by vacuum distillation in order to avoid contamination with water. By employing this procedure, the air bubbles in the sample between the electrodes were completely removed. The cell was sealed after the He gas had been introduced. The surface level of the sample in the cell was so high that the effect of level change by thermal expansion on the measurement of dielectric properties was negligible.

A. CYCLOHEXANOL

Overall Behavior of Cyclohexanol

The dielectric constant and loss at 30 kHz are shown in Figs. 5 and 6, respectively, as a function of temperature for various states of CHOL. The most stable state, crystal II, has the smallest loss and has an upswing in ε″ near the transition temperature. The supercooled crystal I exhibits a most prominent peak around 210 °K which is designated α relaxation. A minor but distinct peak, called β, is observed in the glassy crystal I around 120 °K.

After the supercooled crystal I had been left at 200 °K for 30 min,

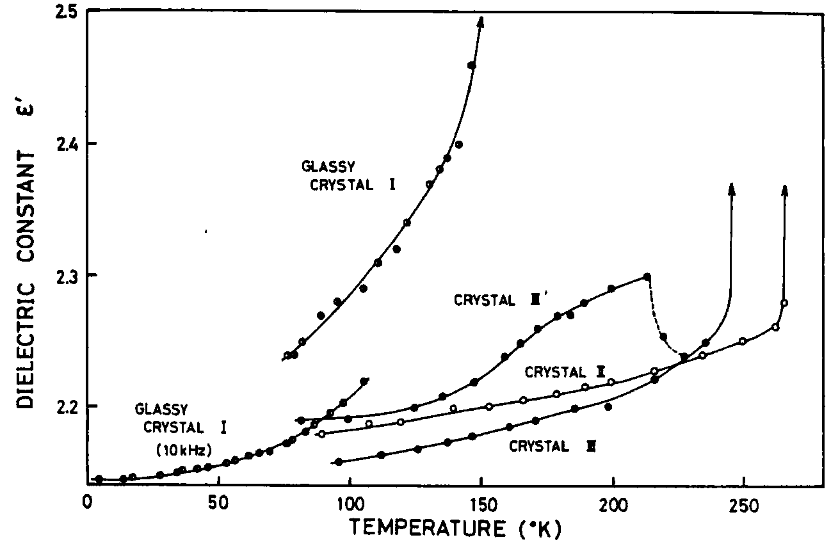

Figure 5. Dielectric constant at 30 kHz for various crystal modifications of cyclohexanol.

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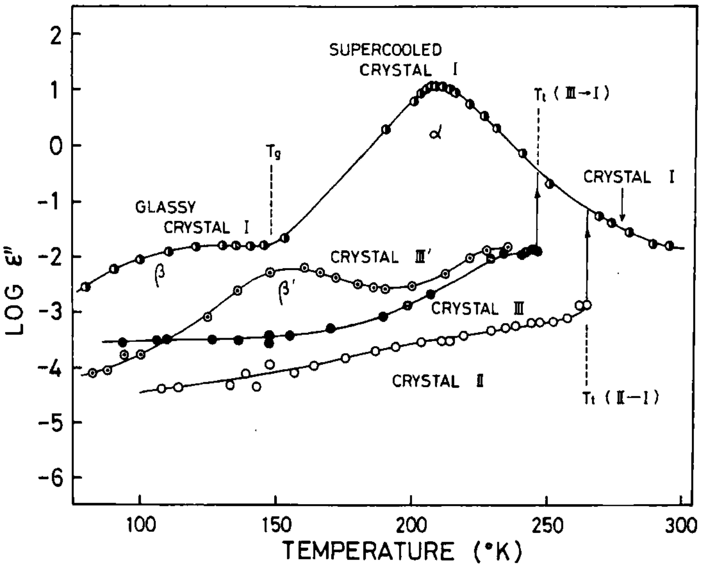

Figure 6. Dielectric loss at 30 kHz for various crystal modifications of cyclohexanol.

the sample was rapidly cooled to 70 °K. The curve designated crystal III′ was obtained in the course of heating this sample and exhibits a peak (β') at 155 °K. According to the calorimetric study,⁽²⁾ this state seems to be crystal III′ including crystal III as a fraction. After the temperature reached 240 °K, the sample was again cooled to 70 °K. The repeat run in the course of heating shows a peak β'' around 230 °K, designated as crystal III in Fig. 6, because the sample is almost transformed into crystal III.⁽²⁾

Supercooled Crystal I

A prominent dielectric relaxation (α relaxation) was observed in supercooled crystal I as illustrated in Figs. 7 and 8.

It was observed that crystal I is transformed gradually into more stable phases when it was allowed to stand around 200 °K. Therefore, the measurements around 200 °K were carried out carefully as follows. The sample cell was cooled rapidly with a rate of about 20 °K/min from room temperature to a definite temperature around 200 °K and then was allowed to stand at that temperature for five

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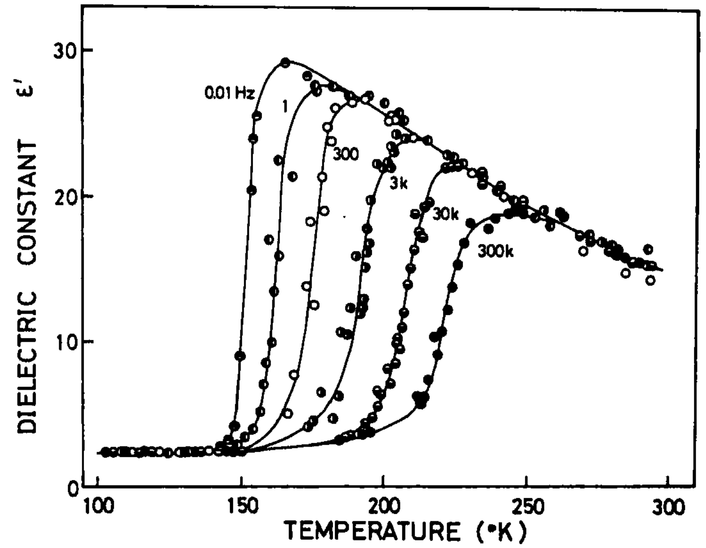

Figure 7. Dielectric constant of supercooled crystal I of cyclohexanol at various frequencies.

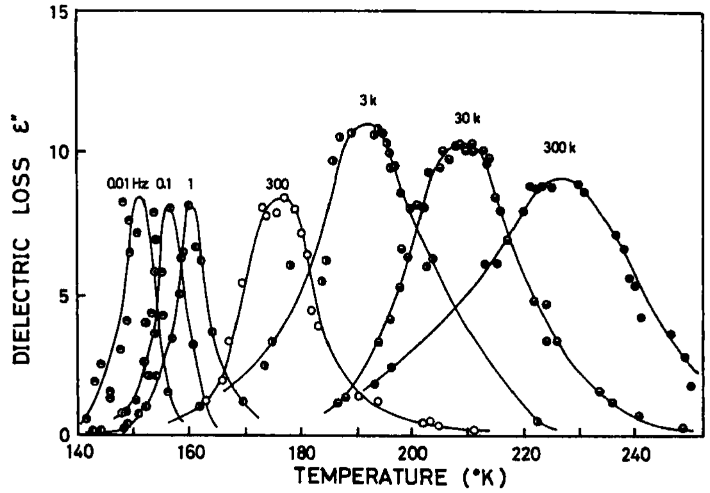

Figure 8. Dielectric loss of supercooled crystal I of cyclohexanol at various frequencies.

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minutes to remove any temperature gradient in the cell. After these operations the dielectric constant and loss were measured. Then the temperature was increased to room temperature and again the procedures described above repeated. Accordingly, the values of dielectric constant and loss are scattered to a considerable extent as is seen in Figs. 7 and 8. This is presumably due to the error in temperature measurements.

At higher temperatures, loss due to d.c. conduction was observed which was inversely proportional to frequency. The conductivity is 6×10^{-12} ℧/cm at 260 °K and increases with increasing temperature with an activation energy of 6.9 kcal/mol.

The previous data(7–11) of the dielectric constant agree well with the present data between 250 and 300 °K. Below 250 °K, our data agree with those of Smyth *et al.*(7) However, the values of the maximum of the loss in the present study are about 25% higher than the previously reported values in the region above 200 °K.

Since rotation of the molecules is allowed in crystal I above T_g and the molecule of CHOL has a large dipole moment, it is reasonable that the α relaxation is attributable to rotation of the molecules. With decreasing temperature through T_g, the relaxation time for the rotation of the molecules becomes very long and the α relaxation becomes undetectable.

The relaxation strength $\Delta\epsilon$ is defined by the difference between the static dielectric constant $\epsilon(0)$ for $\omega\tau \ll 1$ and that at a sufficiently high frequency, $\epsilon(\infty)$ for $\omega\tau \gg 1$, where ω is the angular frequency and τ is the relaxation time. At sufficiently high temperature, where $\omega\tau \ll 1$, ϵ' becomes frequency-independent and, below T_g where the rotation of the molecules is frozen, ϵ' is also frequency-independent as is observed in Fig. 7. The relaxation strength at each temperature is therefore approximated by the difference between the highest value of ϵ' at the specified temperature and ϵ' at the glassy state. The value of $\Delta\epsilon$ thus obtained is plotted in Fig. 9 as a function of the reciprocal of the absolute temperature. It is clearly seen that $\Delta\epsilon$ is inversely proportional to the absolute temperature. In Fig. 9, twice of the maximum of ϵ'' in Fig. 8 is also plotted. The value of ϵ''max is equal to $\Delta\epsilon/2$ if a single relaxation process is assumed. The result in Fig. 9 indicates that the relation $\epsilon''\text{max} = \Delta\epsilon/2$ almost holds above 3 kHz but fails below, probably because (1) the relaxa-

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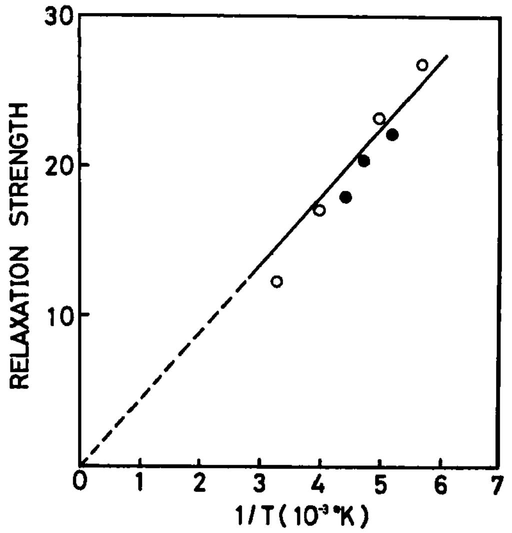

Figure 9. Relaxation strength of α relaxation of supercooled crystal I of cyclohexanol plotted against reciprocal absolute temperature. Open circles are obtained from dielectric constant and closed circles from loss.

tion process becomes multiple at low temperatures or more likely (2) the true peak of ϵ''max is missed at ultra-low frequencies on account of the sharp peak of ϵ''.

The fact that $\Delta\epsilon$ is inversely proportional to the absolute temperature indicates that the rotation of the dipoles is almost free and the hindering potential is negligibly low. In this case, $\Delta\epsilon$ is expressed, following Onsager's theory,(15) in the form,

$$\Delta\epsilon = \frac{4\pi N\mu^2}{3kT}\left(\frac{\epsilon(\infty)+2}{3}\right)^2\left(\frac{3\epsilon(0)}{2\epsilon(0)+\epsilon(\infty)}\right) \qquad (1)$$

where N is the number of molecules per unit volume (5.9×10^{21} cm^{-3}(16)) and μ is the moment in vacuo of the molecule. From Eq. (1), μ is calculated from the data of $\Delta\epsilon$ as 2.8D, which is considerably larger than the moment of the CHOL molecule, 1.69D.

In crystal I of CHOL, orientation of the molecules has a short-range correlation because of intermolecular hydrogen bonding and in this case, according to Kirkwood and Fröhlich,(17) μ^2 in Eq. (1) should be replaced by $\mu^2\,(1+z\langle\cos\theta\rangle)$ where z is the number of nearest neighbors and $\langle\cos\theta\rangle$ is the average of the cosine of the

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angle θ between dipoles of the central molecule and the neighboring one. To get the best fit with experiment, the factor $(1+z\langle\cos\theta\rangle)$ should be taken as 3. In other words, approximately three molecules are rotating cooperatively in crystal I.

The temperature dependence of the relaxation time is discussed on the basis of the loss peak temperature. In Fig. 10, the reciprocal of the loss peak temperature of α relaxation as a function of frequency is indicated by open circles. The data are well correlated with the relaxation time of enthalpy change in the calorimetric study,(2) in which the corresponding frequency f_M is determined from the relation $f_M = (2\pi\tau)^{-1}$. The relation of log f_M vs. $1/T$ in Fig. 10 is convex upwards above T_g, following the Fogel–Tamman equation(18) or the Williams–Landel–Ferry equation,(19).

$$\tau = \tau_0 \exp\left(\frac{C}{T-T_0}\right) \tag{2}$$

where τ_0, C and T_0 are constants.

Below T_g, however, the relation becomes concave upwards,

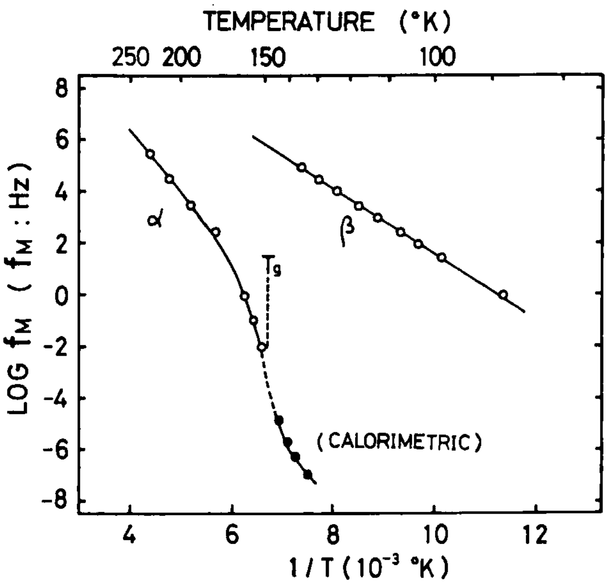

Figure 10. Relaxation map of cyclohexanol. Open circles represent loss maximum and closed circles are obtained from relaxation time of enthalpy.(2)

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indicating the freezing process. The value of T_0, which is the limiting value of T_g at infinitely low cooling rate, is determined as 120 °K which is lower than T_g by 29 °K, and roughly agrees with $T_0 = 128$ °K where the configurational entropy vanishes.(2,20)

Glassy Crystal I

A dielectric relaxation (β relaxation) is found in glassy crystal I of CHOL as shown in Fig. 11, where the loss is plotted against temperature at various frequencies. At each frequency the loss exhibits an upswing at high temperatures due to α relaxation. Figure 12 indicates the loss plotted against frequency after elimination of the contribution of α relaxation. In order to know the relaxation strength of the β relaxation, it is necessary to integrate the

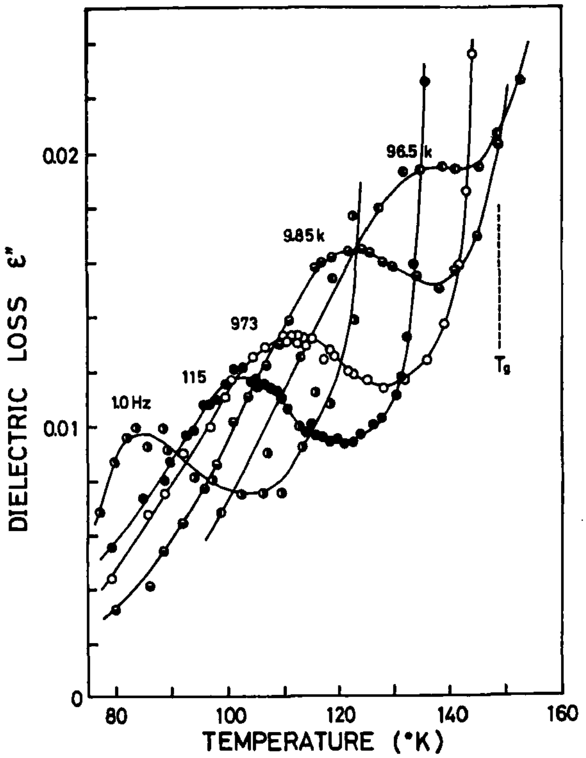

Figure 11. Dielectric loss of glassy crystal I of cyclohexanol plotted against temperature at various frequencies.

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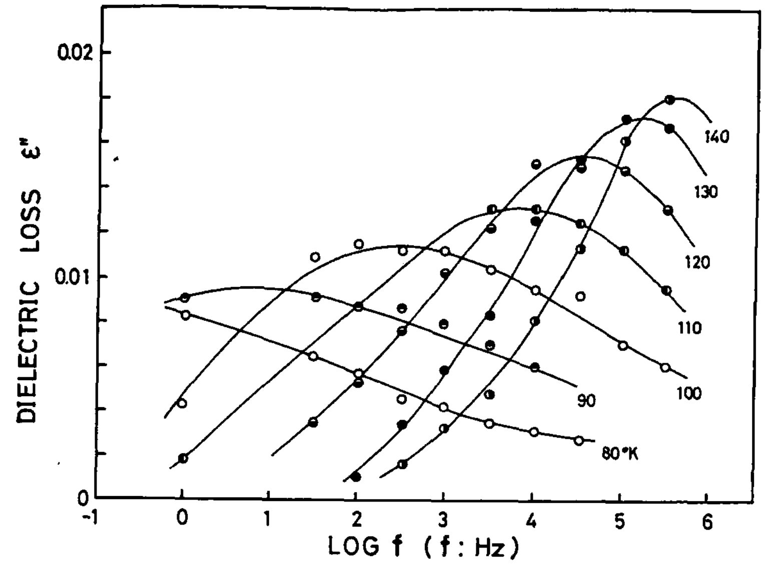

Figure 12. Dielectric loss of glassy crystal I of cyclohexanol plotted against logarithmic frequency. Contribution of α relaxation is eliminated.

loss peak with respect to logarithmic frequency. Taking into account the scatter of the data, we employed the approximation that the area of ε'' versus log f is equal to the ε'' maximum times the half width of the peak.

Based on this assumption, it was found that the relaxation strength $\Delta\epsilon$ of the β relaxation increases with increasing temperature, in contrast to α relaxation, indicating the involved molecular motion occurring under hindering potential. According to the two-state model theory,$^{(21)}$ $\Delta\epsilon$ is expressed by

$$\Delta\epsilon = \frac{4\pi N\mu^2}{3kT'}\left(\frac{\epsilon(\infty)+2}{3}\right)^2\left(\frac{3\epsilon(0)}{2\epsilon(0)+\epsilon(\infty)}\right)\frac{K}{(1+K)^2}, \qquad (3)$$

where μ is the difference of dipole moment between the two states, K is the equilibrium constant between the two states and is expressed in terms of the free energy difference, $\Delta G°$, as

$$K = \exp\left(\frac{-\Delta G°}{kT}\right). \qquad (4)$$

Assuming that the entropy difference is zero between the two states, i.e. $\Delta G^\circ = \Delta H^\circ$ (enthalpy difference) and K is much smaller than unity, Eq. (3) leads to the relation,

$$\ln T\Delta\epsilon = \text{const.} - \frac{\Delta H^\circ}{kT}. \tag{5}$$

The slope of the linear relation between $\ln T\Delta\epsilon$ and $1/T$ gives ΔH°. In the present case we obtain $\Delta H^\circ = 0.5$ kcal/mol.

The activation energy, ΔH^*, of the β relaxation is obtained as 5.7 kcal/mol from the logarithmic frequency for maximum loss plotted against $1/T$ as shown in Fig. 10.

Impurity effect as an origin of β relaxation is concluded to be eliminated on account of the high purity of the sample. Since free rotation of the molecule is frozen-in in the glassy crystal, the origin of the β relaxation may be an intramolecular freedom of CHOL molecules. Possible origins are; (1) puckering motion between axial and equatorial form, or (2) rotation of the OH bond.

According to Hendrickson,(22) the activation energy of puckering motion is estimated as 12.7 k cal/mol for CHOL, which is twice as large as that of β relaxation. Karpovich(23) found an acoustic relaxation due to the puckering motion in liquid CHOL at 32 °C with the relaxational frequency of 120 kHz, which is not correlated with the temperature dependence of relaxation time of β in Fig. 10. These facts indicate that the puckering motion as an origin of β relaxation is to be discarded.

By use of Eq. (3), the dipole moment difference between the two state, μ, is obtained as 0.25D from the observed value $\Delta\epsilon = 0.036$ at 140 °K, assuming that N is the number density of whole CHOL molecules. This value is considerably smaller than the bond dipole moment of OH, 1.68D. Interpretation of the β process in terms of OH rotation is possible as follows. Most OH groups in glassy crystals are in equilibrium between hydrogen-bonded and non-bonded states. In this case the energy difference ΔG° is very large and, at low temperatures, the equilibrium constant K in Eq. (3) is almost zero and the rotation results in no observable relaxation. A minor fraction of OH groups, however, is moving between two hydrogen-bonded states with a small energy difference through an unbonded state. The β relaxation may be attributed to this reaction because the observed energy difference ΔH° is small but the activation energy ΔH^* is similar to the energy of a hydrogen bond. The value

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of N in Eq. (3) is a fraction of the whole number of molecules and the reduction of N results in an increase in μ. If μ is assumed to be equal to the bond moment of OH, N is approximately 3% of all the CHOL molecules. In any case, the mechanism of β relaxation is still obscure and must await further work.

We attempted to determine the temperature where the mode for this β relaxation is frozen-in. Since the glass transition point corresponds to the temperature where the relaxation time becomes of the order of a few minutes, the temperature at which the relaxation time for the β relaxation becomes a few minutes was determined to be about 75 °K from the extrapolation of the activation plot in Fig. 10. If the two states of the OH bond assumed above for this relaxation process are different in the energy, onset of the contribution of this mode to the heat capacity should be observed at 75 °K. In fact it was pointed out previously(2) that the onset of the anomalous increment of the heat capacity for the glassy crystal of CHOL was recognized around 70 °K by converting the value of the heat capacity into the apparent Debye temperature. Therefore this anomalous increment of the heat capacity is attributed to the onset of the motion of the β relaxation process. However, this increment of the heat capacity is not so sharp as in the case of the glass transition. This fact may be due to the wide distribution of relaxation times. From the energy difference between the two states, $\Delta H°$, and the value of N which is 3% of all the molecules, the contribution of this mode to the residual entropy of the glassy crystal is calculated to be 0.15 J/mol, °K by taking into account the fact that this mode is frozen-in at 75 °K. This value of residual entropy is much smaller than the observed residual entropy, 4.7 J/mol, °K(2) indicating that the molecular motion involved in the β relaxation is not the predominant origin of the residual entropy.

The dielectric loss of glassy crystal I above 4 °K is shown in Fig. 13, where one can find no relaxation except β.

Crystals III and III′

Dielectric relaxations in crystals III and III′ are observed at a single frequency as illustrated in Fig. 6. The molecular motion involved is not yet known but a possible explanation is that these relaxations have the same mechanism as the β relaxation in glassy

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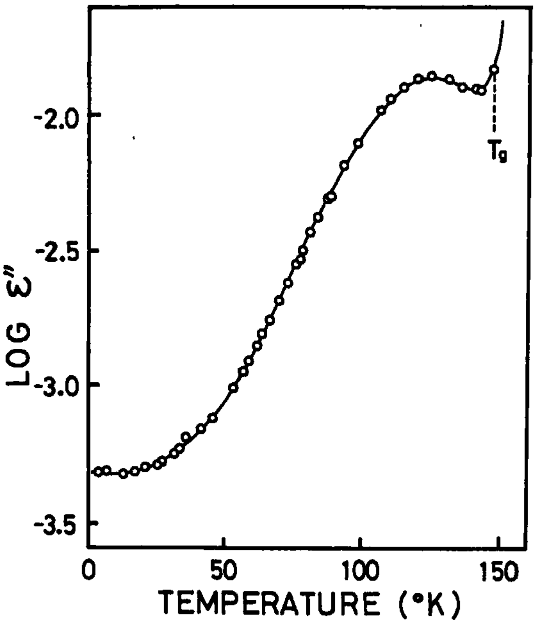

Figure 13. Dielectric loss at 10 kHz in glassy crystal I of cyclohexanol at low temperatures.

crystal I for the following reasons: (1) The peak height is of the same order of magnitude in these three relaxations and (2) in crystals III and III′, the rotation of a molecule as a whole is inhibited and the puckering motion may be also absent as in glassy crystal I.

B. 2,3-DIMETHYLBUTANE

Overall Behavior of 2,3-*Dimethylbutane*

In Figs. 14 and 15, dielectric constant and loss at 10 kHz are plotted against temperature for various states of DMB. The loss is much smaller than for CHOL, 1.4 × 10^{-3} at the highest because of the low polarity of DMB molecule.

The curve for crystal I was obtained during heating after the sample had been rapidly cooled from room temperature to helium temperature with an average rate of 5 °K/min. A dielectric relaxation (β) is observed just below T_g. When heated to 85 °K, 9 °K higher than T_g, the supercooled crystal I was transformed into

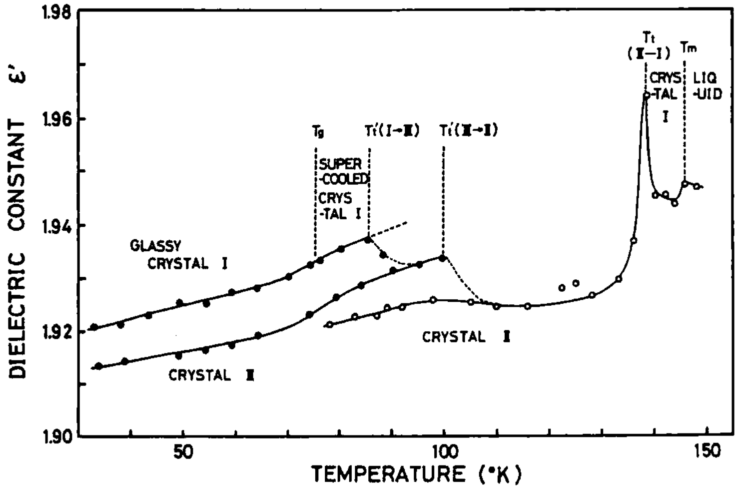

Figure 14. Dielectric constant at 10 kHz for various crystal modifications of 2,3-dimethylbutane.

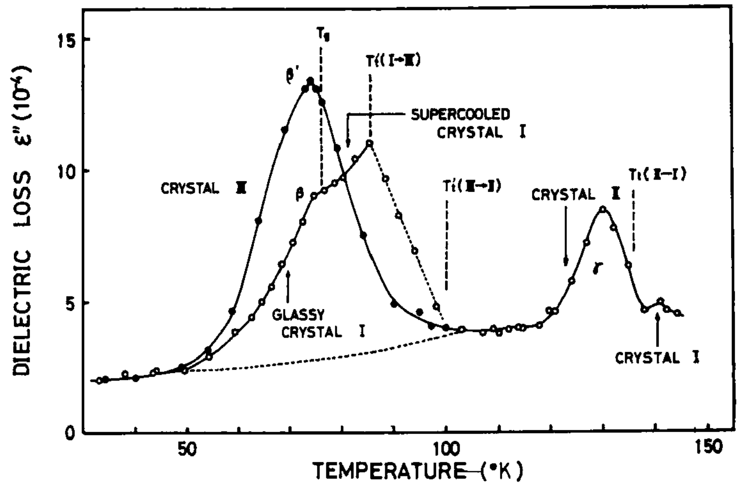

Figure 15. Dielectric loss at 10 kHz for various crystal modifications of 2,3-dimethylbutane.

crystal III with an appreciable rate so that crystal I in the temperature range from 85 to 136 °K could not be studied by dielectric measurements.

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After crystal III had formed, it was cooled to 4 °K and then the curve for crystal III was obtained in the heating run. The relaxation around 74 °K for crystal III is designated β' in the following.

The third relaxation called γ is observed in crystal II, the most stable state, just below the transition point.

Crystal I

In Fig. 16, dielectric loss in the β region is plotted against temperature for various frequencies. The relaxation strength of the β process is almost independent of temperature, as shown in Fig. 16. The activation energy, ΔH^*, of the β process determined from the activation map in Fig. 17 is 3.4 kcal/mol.

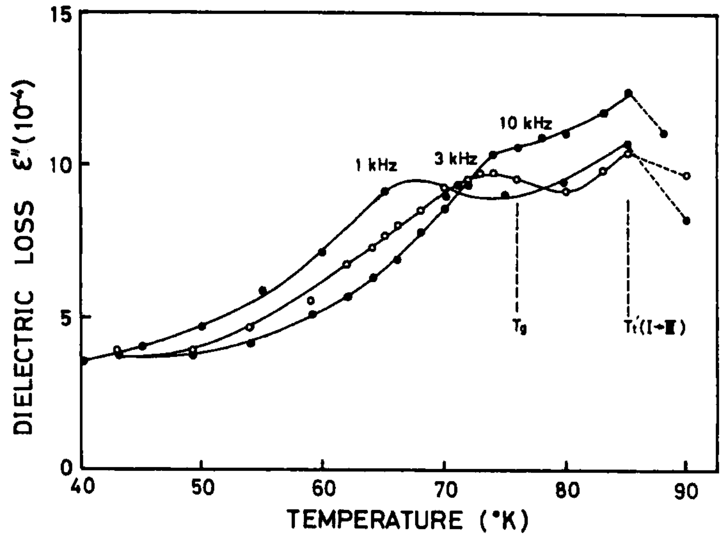

Figure 16. Dielectric loss of supercooled crystal I of 2,3-dimethylbutane at various frequencies.

The molecule of DMB has three steric isomers as illustrated in Fig. 18. The dipole moment of this molecule originates from the small difference in bond moments of C—H and C—CH_3. The vector sum of the three C—H bond moments in the methyl group is equal to a single C—H moment but the bond C—C, one being primary carbon and the other a tertiary one, may have a small dipole moment. Form (a)

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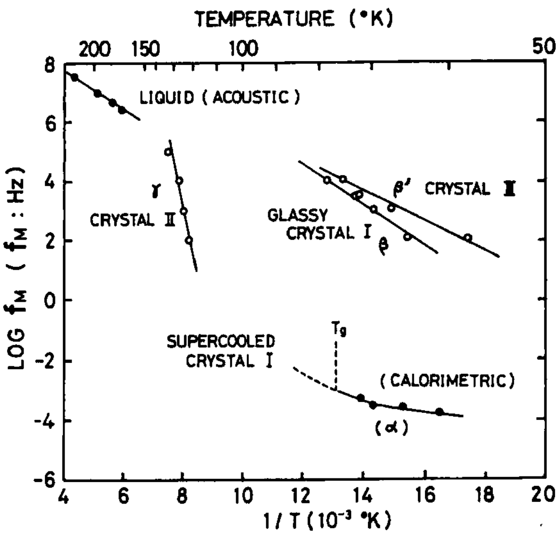

Figure 17. Relaxation map of 2,3-dimethylbutane. Acoustic relaxation in liquid(24) and relaxation in enthalpy in supercooled crystal I(9) are plotted together.

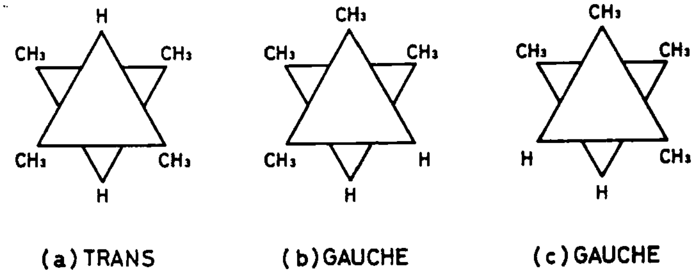

Figure 18. Rotational isomers of 2,3-dimethylbutane.

in Fig. 18 has evidently no dipole moment but forms (b) and (c) have small dipole moments, respectively, which are different in direction. The internal rotation or the transformation among (a), (b), and (c) is expected to bring about the change of moment and hence the dielectric relaxation. Since the rotation of the molecules as a whole is frozen-in in the glassy crystal, internal rotation may be assigned as an origin of β relaxation.

According to Chen and Petrauskas,(24) an acoustic relaxation due

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to internal rotation was observed in liquid DMB. The loss peak frequency is 5 MHz at 180 °K, which is located on the extrapolation of the β relaxation in Fig. 17. Furthermore, the activation energy of the acoustic relaxation is $\Delta H^* = 2.8$ kcal/mol, which roughly agrees with that of β. The activation energy of internal rotation is mostly determined by the intramolecular potential and partly by the intermolecular interaction which is different between liquid and crystal. A smaller value of activation energy in the liquid than in the crystal is therefore reasonable. The energy difference between trans and gauche form was obtained as $\Delta H^\circ = 0.1$ kcal/mol from IR data$^{(3)}$.

The value of μ for the β relaxation was calculated as $\mu = 0.02$D through Eq. (3), in which K is replaced by $2K$ on account of the two-fold degeneracy of the gauche state and the value of K obtained by use of $\Delta H^\circ = 0.1$ kcal/mol. The very small value of μ is consistent with the above interpretation of the β process.

Above the glass temperature, the loss increases with increasing temperature as shown in Fig. 16, but above 85 °K the crystal changes at an appreciable rate to crystal III, resulting in the decrease in the loss. The loss peak at 85 °K is therefore only apparent.

Since molecules are rotating as a whole above T_g, a relaxation similar to the α relaxation of CHOL might be expected if molecules have a dipole moment. Above T_g, where the internal rotation is occurring at a sufficient rate, the dipole moment averaged over all the steric isomers would be effective. Since the two gauche forms in Fig. 18 have a smaller statistical weight than the trans form, the average dipole moment does not vanish.

The increase in loss above T_g seems to be the evidence that DMB exhibits α relaxation above T_g in a similar way to CHOL, probably because the dipole moment does not completely vanish above T_g. In any case, it must be noted that β and α relaxations, if any, are much weaker than those in CHOL.

Crystal II

In crystal II, which is the most stable state below the transition temperature, no relaxation was observed above 4 °K except the γ relaxation just below the transition temperature. Dielectric loss is plotted for the γ relaxation in Fig. 19, in which it is evident that the relaxation strength increases with increasing temperature. Assuming

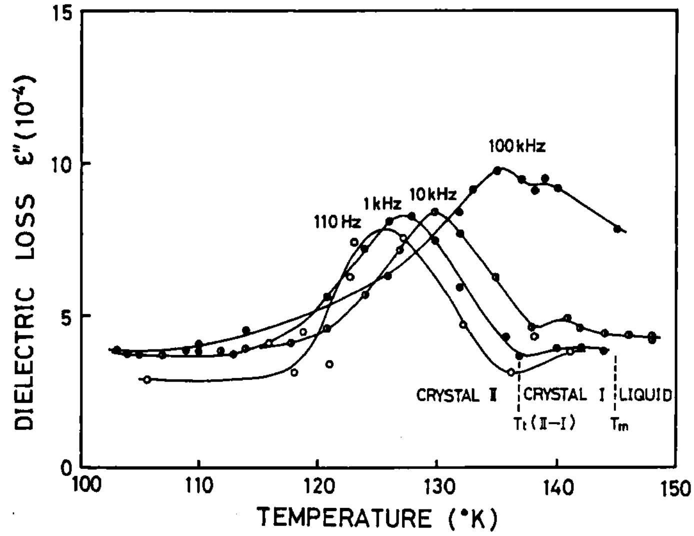

Figure 19. Dielectric loss in crystal II of 2,3-dimethylbutane.

Eq. (3) for the two-state model, the energy difference between the two states was calculated as $\Delta H^\circ = 0.4$ kcal/mol. The plot of the logarithm of loss peak frequency against reciprocal absolute temperature in Fig. 17 gives the apparent activation energy of $\Delta H^* = 25$ kcal/mol.

Since in crystal II the orientation of the molecules as a whole is fixed, the origin of this relaxation may be the internal rotation of the molecules, which is allowed only near the transition temperature. The γ relaxation is therefore assumed to come from the same type motion as the β relaxation in the glassy crystal. A magnitude of loss height of γ similar to β supports this assumption.

Infrared spectra of crystals II of DMB indicate(25) that molecules take mostly the trans form (form (a) in Fig. 18). Since the molecules are most closely packed in crystal II, it is reasonable that internal rotation between trans and gauche forms occurs only near the transition temperature and in addition, this motion is correlated among neighboring molecules. The activation energy ΔH^* and the energy difference ΔH° of γ higher than β may be caused by the cooperative motion of several molecules in the γ relaxation.

Another cause of the high activation energy may be the change in packing density near the transition temperature. When the acti-

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vation energy ΔH^*, which depends on the packing density of the molecules, is a function of temperature, the apparent activation energy ΔH_a^* obtained from the slope of $\log \tau$ vs. $1/T$ relation is given by

$$\Delta H_a^* = k\frac{\partial \ln \tau}{\partial(1/T)} = k\frac{\partial(\Delta H^*/kT)}{\partial(1/T)} = \Delta H^* - T\frac{\partial \Delta H^*}{\partial T}. \qquad (7)$$

When ΔH^* decreases with increasing temperature on account of increasing free volume in the crystal, ΔH_a^* is higher than ΔH^* itself.

Crystal III

In Fig. 20, the dielectric loss of crystal III is depicted as a function of temperature. A relaxation (β') is clearly observed, which is similar in relaxation strength and activation energy to β relaxation in glassy crystal I. The motion involved is still obscure but the above facts suggest that the mechanism may be the same as that of β, internal rotation of molecules.

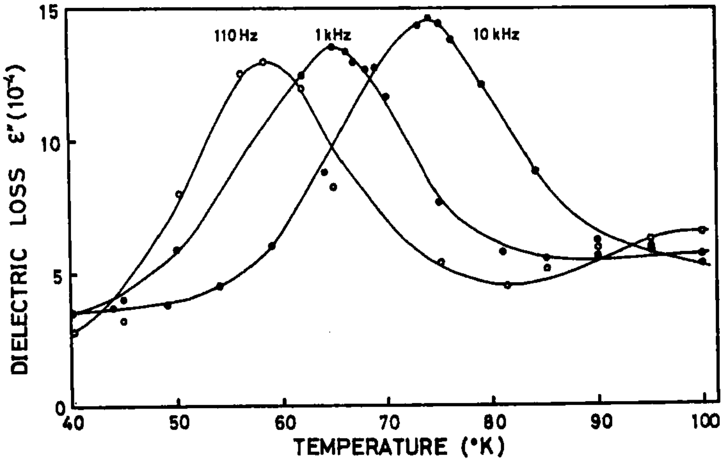

Figure 20. Dielectric loss in crystal III of 2,3-dimethylbutane.

3. Conclusions

In Table 1, relaxations occurring in cyclohexanol and 2,3-dimethylbutane are listed together with the proposed molecular mechanisms.

Rotation of methyl groups was evidenced from NMR narrowing in crystal II of DMB(12) but this would be expected in other crystal modifications of DMB.

TABLE 1. Relaxations in Cyclohexanol and 2,3-Dimethylbutane

Material	Crystal form	Symbol	Method(a)	Temperature at 10 kHz (°K)	Activation energy (kcal/mol)	Mechanism
Cyclohexanol	Liquid		A	305(120 kHz)		Puckering motion
	I	α	D, C	200	Fogel–Tamman eq.	Rotation of molecule
		β	D	120	5.7	Rotation of OH bond
	III′	β′	D	150		
	III	β″	D	230		
2,3-Dimethylbutane	Liquid		A	180(5 MHz)	2.8	Internal rotation
	I	α	D, C			Rotation of molecule
		β	D	75	3.4	Internal rotation
	III	β′	D	75	2.3	
	II	β	D	130	25	
			N	85		Methyl rotation

(a) A—acoustic, D—dielectric, C—calorimetric, and N—NMR.

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