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R. J. Meakins and Joan W. Mulley

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The Thermal and Dielectric Properties of Crystalline Long-Chain Acetates

R. J. MEAKINS AND JOAN W. MULLEY
Division of Electrotechnology, Commonwealth Scientific and Industrial Research Organization, Sydney, Australia

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This investigation deals with the normal long-chain acetates with 18, 20, 24, and 28 carbon atoms. When crystallized from the melt, these compounds first give the transparent α-phase which gradually changes to the white, opaque β-phase on standing or on cooling below a certain temperature. It is found that the acetates in the α-phase all give large dielectric absorption, whereas, in the β-phase the absorption is small, or, in some cases, negligible.

Of the long-chain compounds so far investigated, the acetates in the α-phase are unique in giving two absorption regions which appear to be the result of the rotational transitions of complete molecules. The maxima for the two regions are separated by about 7 decades in frequency. Measurements of the lower frequency absorption at various temperatures show that the associated energy barrier is very large compared with previous values for compounds of similar chain-length To explain these results it is suggested that a molecule rotating in the crystal lattice of a long-chain compound possesses four positions of equilibrium instead of two, as previously proposed

In addition to the two absorption regions mentioned above, the long-chain acetates in the α-phase give further absorption at still higher frequencies, which is probably caused by independent orientation of the polar groups near the ends of the molecular chains.

I. INTRODUCTION

IT has been previously reported[1-3] that many long-chain esters in the solid state give dielectric absorption maxima at radio frequencies. The variation of the frequency of the maximum loss factor with molecular weight indicates that the absorption is associated with the orientation of complete molecules.

The previous investigations in these Laboratories included the compound n-hexacosyl acetate, which was found to be somewhat different from the other esters in its dielectric and thermal properties.[4] It therefore seemed likely that a combined investigation of the cooling curves and dielectric properties of this compound and other long-chain acetates might prove interesting.

Another feature of the long-chain acetates to be considered is the possibility of independent orientation of the polar group due to its position near the end of the molecular chain. A similar structure is present in long-chain methyl esters, and in these has been found to result in dielectric absorption in the microwave region.[2]

II. MATERIALS

The acetates of the C_{16}, C_{18}, and C_{22} n-primary alcohols were prepared by heating the appropriate alcohol under reflux with acetic anhydride for 6 hours and then distilling off the excess reagent and the acetic acid formed in the reaction. The last traces of these impurities were eliminated by the addition of light petroleum and further distillation. The product was then vacuum fractionated, using a 90 cm column packed with Monel metal gauze saddles for the two lower homologs, and a spinning band column for the C_{24} compound.

The sample of n-hexacosyl acetate was obtained from the acetates of ceryl alcohol by vacuum fractionation through a spinning band column.

After distillation the acetates were further purified by recrystallization from methanol or ethanol. This reduced the conductivity, presumably due to the elimination of oxidative degradation products formed during the distillation.[5]

III. APPARATUS AND PROCEDURE

The method of preparation of samples and methods of electrical measurement have been previously described.[6,2]

The apparatus used for determining the melting and cooling curves was similar to that designed by Skau.[7]

The relative densities, where given, were determined from the mass and dimensions of one inch diameter disks pressed at about 12 tons per sq in. With waxy long-chain compounds this method gives results almost identical with those from x-ray crystal measurements.

IV. RESULTS AND DISCUSSION

(a) Cooling Curves

Previous workers[8,9] have found that long-chain acetates exist in at least two forms. The material first obtained on crystallization from the melt is the transparent α phase which, on further cooling, changes to the opaque β phase.

These changes can be conveniently observed with a sample of n-hexadecyl acetate in a glass vessel. In this

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[1] R. J. Meakins, Australian J. Sci. Research **A2**, 405 (1949)

[2] J. S. Dryden and H. K. Welsh, Australian J. Sci. Research **A4**, 616 (1951).

[3] R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. **73**, 5401 (1950).

[4] R. J. Meakins, Unpublished results.

[5] B. V. Hamon and R. J. Meakins, Nature **166**, 29 (1950).

[6] B. V. Hamon and R. J. Meakins, Australian J. Sci. Research **A5**, 671 (1952).

[7] E. L. Skau, Proc. Am. Acad. Arts. Sci. **67**, 551 (1932).

[8] J. W. C. Phillips and S. A. Mumford, J. Chem. Soc. **1934**, 1657 (1934).

[9] J. D. Meyer and E. E. Reid, J. Am. Chem. Soc. **55**, 1574 (1933).

compound the transition occurs much more quickly than in the higher homologues. On cooling the liquid, the transparent crystals of the α phase begin to form at 18.5°C. This crystallization then proceeds until the commencement of the transition to the β phase which sometimes occurs before the mass has completely solidified. It is indicated by the formation of a white opaque spot in the crystalline mass. In the transition region sufficient heat is liberated to cause a local liquefaction of the low-melting α phase. This liquid then resolidifies into the more stable β phase, being seeded by the crystals already present.

These changes are shown in the cooling curve given in Fig. 1. In this particular experiment the transition commenced at 7.6°C, but different experiments gave different transition temperatures, even with the same sample. A comparison of the areas under the different portions of the cooling curve shows that the heat of transition is about half the heat of crystallization of the α phase. It is thus evident that the α phase of *n*-hexadecyl acetate possesses considerably higher energy than the β phase. Similar differences have been found in other work on α and β phases of long-chain compounds.[10]

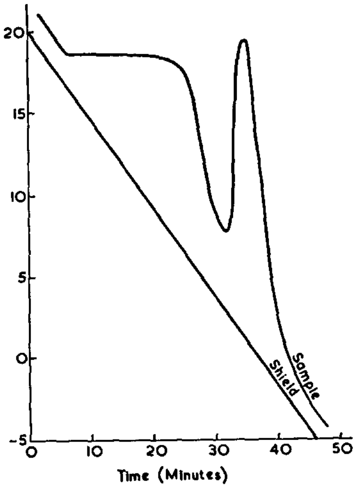

FIG. 1. Solidification and transition *n*-Hexadecyl acetate. (Readings at one minute intervals.)

The transition from α to β phase in *n*-hexadecyl acetate is not reversible. The heating curve shows that the β phase persists up to 24.0°C and then melts.

The cooling curve for *n*-octadecyl acetate is shown in Fig. 2. A superficial inspection suggests that the transition from α to β phase for this compound occurs at about 1°C. However, it is observed that the sample and shield curves are more widely separated than usual for a considerable period after solidification and it therefore seemed possible that the transition had commenced at a much higher temperature. This was confirmed by cooling a sample of *n*-octadecyl acetate from the liquid to 20°C and holding it at this temperature overnight. The cooling curve was then continued and it was found that the inflexion at 1°C was absent (see Fig. 2 sample 2). In further experiments, it was observed that samples of the transparent α-phase kept in a glass vessel at 20°C always changed to the white opaque β phase within 24 hours.

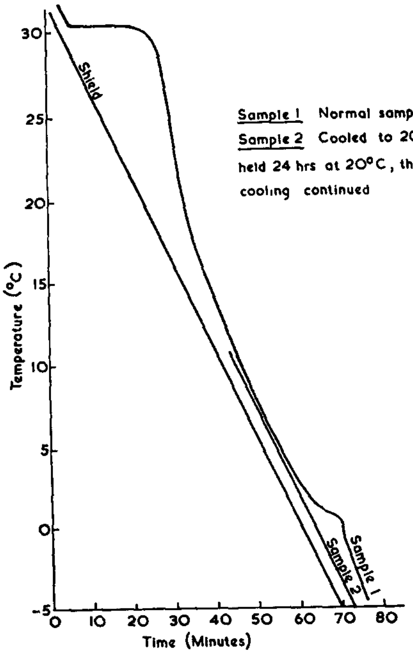

FIG. 2. Solidification and transition of *n*-Octadecyl acetate. (Readings at one minute intervals.)

The cooling curves for *n*-docosyl and *n*-hexacosyl acetates are similar to that for *n*-octadecyl acetate. The heating curves are different, however, and show the reverse transition from the β to the α phase.

The melting and setting points of the above-mentioned long-chain acetates, determined from the cooling curves, are given in Table I.

(b) Dielectric Properties

With samples of the acetates cooled from the liquid state to room temperature in glass tubes it was found that the α phase usually persisted for at least a few hours after solidification. Attempts were therefore made to prepare disks for dielectric measurement but it was found that with the two lower homologues, the working

TABLE I. Melting and setting points of long-chain acetates.

Acetate	Formula	α Phase M pt (°C)	 S pt (°C)	β Phase M pt. (°C)	 S pt (°C)
n-Hexadecyl	$C_{16}H_{33}O\cdot COCH_3$	18.5	18.5	24.0	23.7 (seeded)
n-Octadecyl	$C_{18}H_{37}O\cdot COCH_3$	30.3	30.3	32.4	...
n-Docosyl	$C_{22}H_{45}O\cdot COCH_3$	47.6	47 5		
n-Hexacosyl	$C_{26}H_{53}O\cdot COCH_3$	59.5	59.6	Material changes to α phase before melting, and crystallizes in α phase from melt.	

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[10] Garner, van Bibber, and King, J. Chem. Soc. **1931**, 1533 (1931).

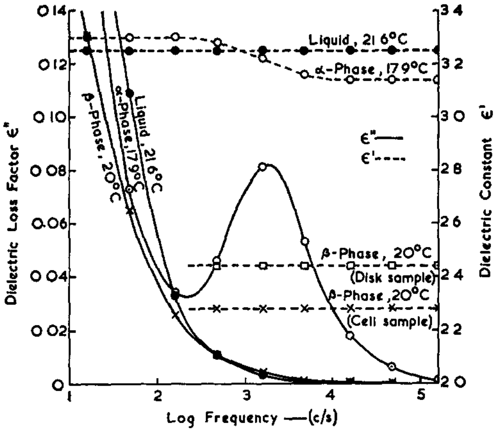

FIG. 3. Low frequency dielectric properties of *n*-Hexadecyl acetate ($C_{18}H_{36}O_2$).

of the material caused a rapid transition to the β phase. Samples of the α phases of these two compounds could be measured at frequencies up to about 10 Mc/sec, however, by allowing them to crystallize in a dielectric test cell.[6] Actually, this part of the program was limited mainly to bridge measurements up to 1.6×10^5 cps, since this frequency range was sufficient to include the whole of the low frequency absorption regions at the temperatures involved. *n*-Docosyl acetate was also included in the dielectric test cell measurements, for purposes of comparison, but there was insufficient *n*-hexacosyl acetate available to fill the cell.

In addition to the cell measurements, disks and coaxial samples were prepared from the two higher homologs in the α phase, and measured over the complete frequency range from 10^{-4} to 2.4×10^{10} cps. Similar measurements were made with all four of the acetates in the β phase.

In discussing the results it is convenient to deal first with the properties of the C_{18}, C_{20} and C_{24} compounds in the frequency range up to 160 kc/sec. This includes one important region of dielectric absorption in the α phase acetates. Further absorption regions at higher frequencies are then discussed, with reference chiefly to the C_{24} and C_{28} compounds. It is not possible to show all of the absorption regions on one diagram since some of the high frequency apparatus used in this programme was suitable for measurements only at room temperature (20°C). At 20°C, the low frequency absorption of the two higher acetates is masked by the loss due to dc conductivity.

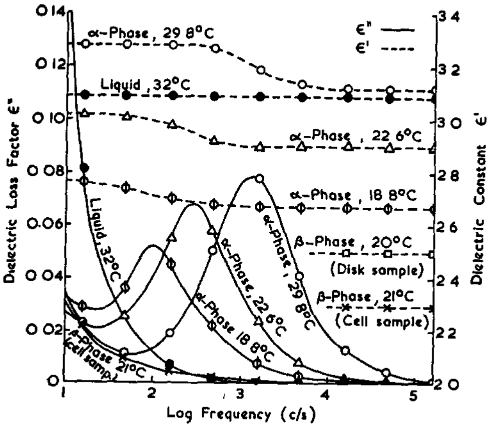

FIG. 4. Low frequency dielectric properties of *n*-Octadecyl acetate ($C_{20}H_{40}O_2$).

1. *Dielectric Properties at Frequencies below 1.6×10^5 cps*

The results of electrical measurements of the C_{18}, C_{20} and C_{24} compounds in the dielectric test cell are shown in Figs. 3—5. With each compound there is a striking difference between the loss factor curves for the α and β phases. Apart from the dc conductivity effects at the lowest frequencies, the β phases show no dielectric loss. The α phases, on the other hand, give well-defined absorption maxima at frequencies which vary between about 150 and 1000 cps according to the molecular chain-length and the temperature of measurement.

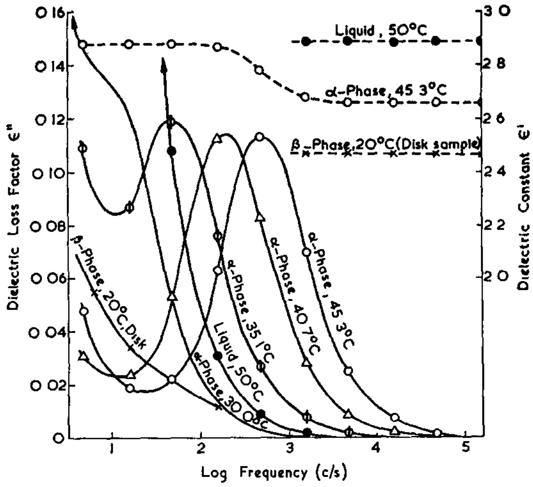

FIG. 5. Low frequency dielectric properties of *n*-Docosyl acetate ($C_{24}H_{48}O_2$).

The dielectric absorption in the α-phase acetates is accompanied by an increase in the dielectric constant with decreasing frequency. In each case, the difference between the high and low frequency values of the dielectric constant ϵ' is found to be twice the value of the maximum loss factor $\epsilon''_{\max}$, indicating that the absorption is due to a relaxation mechanism possessing a single relaxation time.[11] This is unusual in crystalline long-chain compounds, which generally give wide absorption curves indicating the presence of a range of relaxation times. It should be pointed out, however, that most previous measurements of this type have probably been made with β-phase material.[2]

As indicated in the diagrams, the C_{20} and C_{24} compounds were sufficiently stable in the α phase to enable

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[11] P. Debye, *Polar Molecules* (The Chemical Catalog Co. Inc., New York, 1929).

measurements to be made at several different temperatures. From these results it is possible to determine the energy barrier H for the process causing the absorption, by applying the relationship

$$f_{\max}=C\exp\left(\frac{-H}{kT}\right), \qquad (1)^{12}$$

where $f_{\max}$ is the frequency of the maximum loss factor, C is a constant, k is Boltzmann's constant, and T is the absolute temperature.

This gives the values shown in Table II.

The values of H are very much larger than those observed for methyl esters of similar molecular weight.[2] This is not unexpected, since the absorption regions indicated above in the acetates are at least 5 decades lower in frequency than those for the corresponding methyl esters.

In *n*-hexadecyl and *n*-octadecyl acetate, dielectric measurements of the α phase were made at temperatures close to 18°C. A comparison of the loss factor curves for the two compounds indicates that the maximum is considerably displaced to lower frequencies with increasing molecular weight. No direct comparison can be made with *n*-docosyl acetate, due to the higher temperature of the measurements, but an indication of the probable frequency of the maximum at 18.8°C can be obtained by extrapolation. The resulting value is included in Fig. 6, which shows the variation of $\log f_{\max}$ with molecular chain-length for the three acetates. The approximately linear relationship is similar to that previously obtained for other long-chain compounds. It suggests that the absorption is due to the rotational transitions of complete molecular chains.[1,13] This conclusion is supported by the observation that the energy barrier for *n*-docosyl acetate (see Table II) is slightly larger than that for *n*-octadecyl acetate.

TABLE II.

Compound	H(kcal/mole)	C
n-Octadecyl acetate	32	5×10^{26}
n-Docosyl acetate	35	5×10^{26}

At the beginning of this Section, reference was made to the presence of dc conductivity in the acetates. This is indicated by the shape of the dielectric loss factor curves at the lowest frequencies, and by the results of further measurements which showed that, in each case, ϵ'' continued to increase with decreasing frequency down to 10^{-3} cps. The actual values of the dc conductivity, measured with disk samples between mercury electrodes[6] were all in the region of 10^{-16} mho cm^{-1}. Freshly melted material gave larger values, up to 4×10^{-14} mho cm^{-1}, but these decreased to about the initial value on standing. Similar results were obtained with all samples, irrespective of the method of preparation or purification, and also with *n*-hexacosyl acetate, which was supplied from a different laboratory (see Sec. 6). It appears that the observed dc conductivity is either an inherent property of the long-chain acetates, or is due to the presence of impurities which are very difficult to remove.

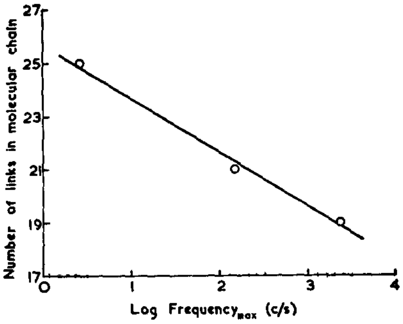

FIG. 6. Effect of molecular chain-length on frequency of maximum absorption of acetates in the α phase.

It should be mentioned that, in the loss factor curves for *n*-octadecyl acetate given in Fig. 4, $\epsilon''_{\max}$ shows a progressive decrease with decreasing temperature. This is due to a partial transition to the β-phase during the measurements, which were commenced on the liquid at 32°C and continued in order of decreasing temperature. To check this point, the sample was held at 22.6°C for $1\frac{1}{2}$ hours, during which period $\epsilon''_{\max}$ was found to decrease from 0.077 to 0.058. With *n*-docosyl acetate the α-phase is more stable and $\epsilon''_{\max}$ shows no significant decrease during the measurements.

In previous work by Crowe and Smyth[3] on the α phases of a number of long-chain esters, including *n*-octadecyl acetate, it was found that the dielectric constant varied from one experiment to another, possibly due to different rates of solidification from the melt. In the present investigation also, variations in the dielectric constant and maximum loss factor were observed in different experiments with a particular compound. Thus, with *n*-octadecyl acetate $\epsilon''_{\max}$ at 29°C varied from 0.08 to 0.17 in different experiments.

Measurements of disk samples of *n*-docosyl and *n*-hexacosyl acetates in the α phase were made only at room temperature (20°C). No absorption maxima of the type shown above were observed, apparently because, at this temperature, such absorption would be completely masked by dc effects.

In the results for the dielectric constants given in Figs. 3–5, the values for the α-phase samples are appreciably larger than those for the corresponding β phases, even at frequencies above the dispersion region. This indicates that acetates in the α phase give further dielectric absorption at higher frequencies.

The dielectric constants of the β phases (disk samples) are between 2.44 and 2.50 throughout the frequency range of measurement. This is only about 10 percent larger than the value (2.25) for paraffin wax under the same conditions. Taking into account the larger specific

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[12] H. Frohlich, *Theory of Dielectrics* (Oxford University Press, London, 1949).

[13] R. W Sillars, Proc. Roy. Soc. (London) **A169**, 66 (1939).

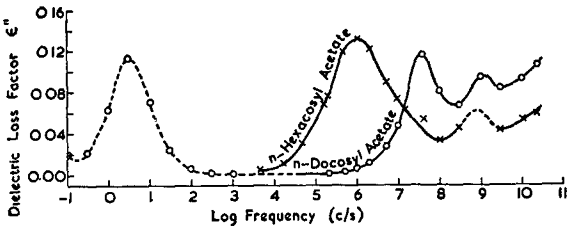

FIG. 7. Comparison of dielectric absorption in *n*-Docosyl and *n*-Hexacosyl acetates ($C_{24}H_{48}O_2$ and $C_{28}H_{56}O_2$) in the α phase at 20°C.

gravity of the acetates (0.96) compared with paraffin wax (0.87) it is evident that there can be very little dielectric absorption at higher frequencies.

The results for *n*-hexacosyl acetate are somewhat different to those for the three lower homologues. The dielectric constants of both the α and β phases (2.88 and 2.63 respectively) are larger than expected for a loss free substance, which suggests that both forms should give high frequency dielectric absorption.

2. *Dielectric Properties at Frequencies between 1.6×10^5 and 2.4×10^{10}* cps

The apparatus used for much of this frequency range was suitable only for measurements at room temperature (20°C) with disk-shaped or coaxial samples. This restricted the investigation of α-phase acetates at high frequencies mainly to the C_{24} and C_{28} compounds. The results are given in Fig. 7. Also included in the diagram is the estimated position of the low frequency absorption maximum for *n*-docosyl acetate, determined by extrapolation from the results of cell sample measurements at higher temperatures. In the actual samples measured at 20°C, the low frequency absorption maximum was masked by the loss due to dc conductivity.

The main feature of interest in the results given in Fig. 7 is the relationship between the absorption maxima for the two compounds in the frequency region between 10^5 and 10^8 cps. From previous work with long-chain compounds it seems likely that these absorption regions are due to the rotational transitions of complete molecules, the higher frequency of absorption for the lower molecular weight compound being due to the smaller energy barrier associated with the shorter molecules. Further results in support of this suggestion were obtained from some measurements, at frequencies up to 10 Mc/sec, with an α-phase sample of *n*-octadecyl acetate in the dielectric test cell. Although only a small part of the absorption region was detected, the results were sufficient to indicate that the maximum is at a higher frequency than that for *n*-docosyl acetate.

A feature of the dielectric absorption regions discussed above is the greater width of the *n*-hexacosyl acetate curve compared with that for *n*-docosyl acetate. The results for the latter are approximately in accordance with the requirements for a Debye type absorption associated with a single relaxation time, as was found also for the low frequency absorption in this compound. The wider curve for *n*-hexacosyl acetate, suggesting a range of relaxation times is more closely related to the type of absorption normally observed in β-phase long-chain compounds.

The energy barrier for the process resulting in the above absorption for the C_{24} and C_{28} acetates was not determined, owing to the instability of the α phase and the difficulty, with the present apparatus, of making measurements at a range of different temperatures in this frequency region. Some indication of the values of the energy barrier for the C_{20} and C_{24} acetates may possibly be obtained, however, from a comparison of the frequencies of the maximum loss factor of these compounds with the values previously determined for methyl esters of similar chain-length.[2] This suggests that the energy barriers for the acetates are a little less than the values of 11 and 17 kcal/mole for the corresponding methyl esters. In making the comparison it is assumed that the absorption is due to the same type of process and that the value of the constant C in Eq. (1) is approximately the same for the two series of compounds.

At frequencies above 10^8 cps, both *n*-docosyl and *n*-hexacosyl acetates give further dielectric loss. Unfortunately, with the latter compound, there was insufficient material available to prepare a sample suitable for measurement at 10^9 cps but the shape of the curve suggests that there would be a maximum in this region. *n*-Docosyl acetate is similar, and both compounds also appear to have at least one more maximum above 2.4×10^{10} cps. The similarity in the shape of the curves for the two compounds at frequencies above 10^8 cps suggests that the dielectric loss in this region is due to dipole orientation involving movement of the polar end-groups independently of the main molecular chains. The presence of more than one absorption maximum in these two acetates above 10^8 cps may be the result of different modes of orientation of the $\cdot O\cdot CO\cdot CH_3$ end-group.

High frequency measurements of β-phase samples were made with all four of the acetates, the results being in agreement with predictions from the low frequency dielectric constant values discussed in the previous part of this Section. The C_{18}, C_{20} and C_{24} compounds gave very little dielectric loss. The highest homologue, *n*-hexacosyl acetate, gave some loss, with a maximum near 1 Mc/sec, which is about the same frequency as the maximum for the α-phase material discussed above. The amount of the absorption was considerably less, however, $\epsilon''_{\max}$ being only 0.026, compared with a value of about 0.13 for the α phase.

3. *Mechanisms of Dielectric Loss in Long-Chain Compounds in Relation to Results for the Acetates*

The results given in the previous Section suggest that long-chain acetates in the α phase possess two regions of dielectric absorption depending on the rotational transitions of complete molecules. This has not been previously observed in long-chain compounds and it therefore seemed of interest to consider the results in relation to the proposed mechanisms of dielectric loss in crystalline solids.

A simple model explaining the presence of dielectric absorption in polar solids is that of Debye,[11] in which the dipoles are assumed to possess two positions of equilibrium, equal in energy and opposite in direction. The transitions of the dipoles from one potential minimum to another, interacting with an alternating electric field, give rise to dielectric loss and anomalous dispersion of the dielectric constant which can be described by the usual Debye equations. With this model the loss factor-frequency relationship possesses a single maximum.

If, in the above model, the potential minima differ in energy by an amount V, the dielectric absorption decreases as V increases.[12] For the systems in which V is very much larger than the thermal energy kT there is no measurable dielectric loss. This has been found to be the case in many long-chain ketones,[1] in some esters and ethers,[4] and also in the β-phase acetates described above.

Although the above model explains the electrical properties of some long-chain compounds it is not adequate to account for the two absorption peaks in the α-phase acetates which appear to be associated with the rotations of complete molecules. These can be more satisfactorily explained on the basis of a model (O'Dwyer, to be published) in which the molecules are assumed to possess four positions of equilibrium instead of two, as suggested above. This is illustrated in Fig. 8 which is a diagrammatic representation of the potential energy curve of a long-chain molecule rotating in the crystal lattice. The positions of the minima at about 0, 60, 280 and 240°, respectively, and the relatively smaller energy barriers for the rotational transitions through 60° are suggested from a study of molecular models and the available data on similar crystal structures.[14] Another point in the illustration is that the first and third positions are of equal energy differing by an amount V from the second and fourth positions which are also equal. In the results for the α-phase acetates the most important feature to be explained is the presence of two absorption regions associated with molecular rotation. On the basis of the above model, the higher frequency absorption would be due to rotational transitions between the first and second, or the third and fourth positions of equilibrium respectively, i.e., transitions involving the smaller energy barrier H. The lower frequency absorption would be associated with transitions across the larger energy barrier H' which occurs between the second and third and the fourth and first positions of equilibrium, respectively.

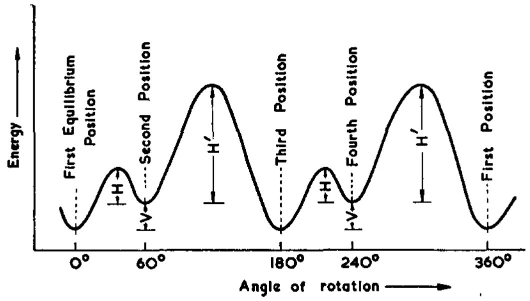

FIG. 8. Diagram illustrating potential minima and energy barriers of a long chain molecule rotating in the crystal lattice.

In the particular model described above the amounts of absorption in the two different regions would be equal, and would both depend on the value of V, the energy difference between the equilibrium positions.[12] The energy levels in the model have been arranged in this manner to account for the results for n-docosyl acetate, in which the values of $\epsilon''_{\mathrm{max}}$ for the two absorption regions were found to be approximately equal. In the most general model, however, the energy levels of the equilibrium positions could be all unequal.

ACKNOWLEDGMENTS

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[14] A. Müller, Proc. Roy Soc (London) **A127**, 417 (1930).