Dielectric Cell for Deformable Solids

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    A dielectric cell for deformable solids was constructed for simultaneous measurements of permittivity and thermal expansion. The cell equipped with two concentric guarded electrodes is able to eliminate the error due to dimensional change of specimen in the permittivity measurement and to measure the specimen thickness simultaneously. The accuracy of permittivity depends mainly on the flatness of the four concentric electrodes, which are consisted of those two guarded electrodes and their guard electrodes. The temperature range, in which the flatness of surface of the four concentric electrodes was ensured, was widely extended by an improved design of the cell. The cell is usable to measure a very low dielectric loss owing to the three-terminal configuration for each guarded electrode. The performance of the cell was tested by measuring the dielectric and dilatometric properties of undecanoic, tridecanoic, and pentadecanoic acids. These acids show a cosiderable change of their lattice spacings at the transition temperature and show an extremely low dielectric loss near 200 K. Permittivity and thermal expansion were successfully measured over the frequency range of 17 Hz to 300 kHz and the temperature range of 20 K to near the melting point of these acids.

INTRODUCTION

    The dielectric cell is an important part in the measurement of permittivity and conductivity for solid specimen. Considerable errors are caused in the dielectric measurement for deformable solids such as plastic crystal, amorphous material, and polymers. An error of permittivity is caused by the change in specimen thickness or separation between guarded and unguarded electrodes. Dielectric cells in which the electrode separation is fixed cause some troubles that the specimen is sometimes apart from the electrode and frequently includes some voids due to the thermal change of specimen. The construction of dielectric cell for deformable solids is needed for the intrinsic permittivity of specimen without voids. One of the authors[1] already designed the three-terminal cell with a simple structure and found it useful for accurate measurements on the extremely low dielectric loss of poly(tetrafluoroethylene). But the cell was not applicable to deformable solids. The error of permittivity caused by thermal expansion of specimen was not sufficiently considered. Work and colleagues[2,3,4] constructed several elaborate dielectric cells for simultaneous measurement of permittivity and thermal expansion. The test results of the cell constructed in this work show a satisfactory operation on measurement of the dielectric properties and the thermal expansion of fatty acids from the change of lattice spacings[5]. An improved design of the cell is described in this paper.

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CONSTRUCTION OF THE CELL

The design of the cell is illustrated in Fig. 1. The unguarded electrode H was lapped to optical flat plane and mouted on the Mycalex plate M which was loaded with guard G_1 and spring B. Two guarded electrodes C and T and two guard electrodes G_3 and G_4 were constructed in concentric form. The outer guarded electrode C of ring form serves to measure the permittivity of specimen. The inner guarded electrode T of disk form serves to estimate the specimen thickness by measuring the empty capacitance between electrodes T and H. The separation between the electrodes T and H should be equal to the thickness of specimen between electrodes C and H for the simultaneous measurement of permittivity and specimen thickness. There should be three conditions for these two electrode separations to be the same. Firstly both upper and under planes of specimen should be parallel to each other, secondly the plane of unguarded electrode should be flat, and thirdly the upper plane of the four concentric
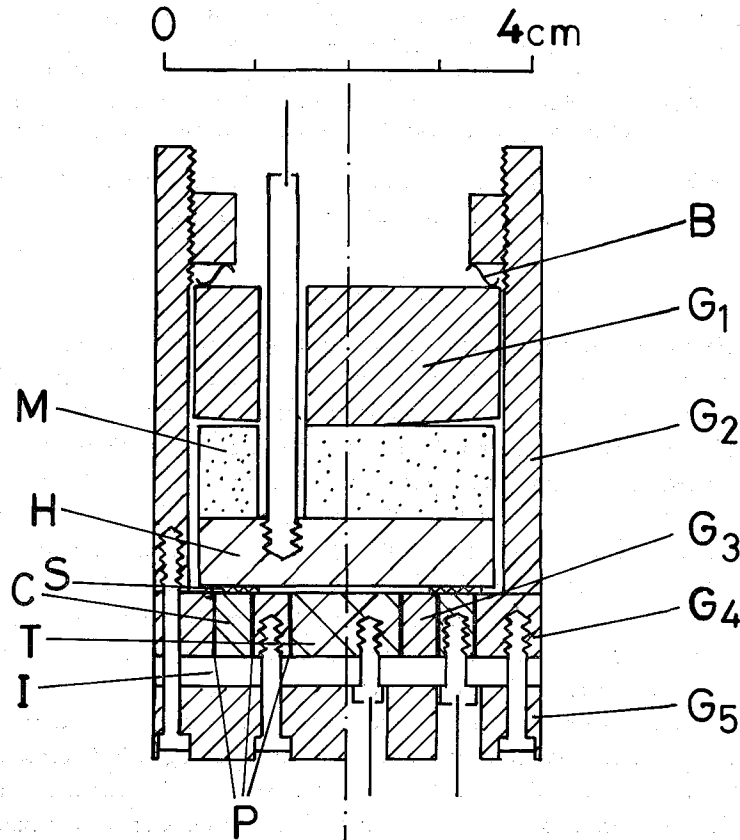

Fig. 1. Design of the dielectric cell for deformable solids.
S, specimen; C, guarded electrode lapped *optical parallel* of ring form; T, guarded electrode lapped *optical parallel* of disk form; C, unguarded electrode lapped *optical flat*; G_1, G_2, G_3, G_4, and G_5 are guard electrodes; I, sapphire plate lapped *optical flat*; M, Mycalex plate; P, polyimido film; B, spring.

electrodes should be flat at any temperature. The first condition can be satisfied by the careful preparation of specimen and is not discussed here. The second condition was easily attained. The third condition should be carefully examined. The third condition is not satisfied by lapping *only* the upper plane of these electrodes to optical flat. The following designs were adopted to satisfy the third condition. The upper plane of the four concentric electrodes was designed to be parallel to the under plane. The four concentric electrodes were fixed on the optically flat sapphire plane. These electrodes were made of the same kind of metal to obtain the same thermal expansion. The upper plane of these electrodes can be made parallel to the under plane and to the plane of sapphire plate, even though the electrodes expand as temperature changes. The four concentric electrodes in the cell designed in this work can show an optical flat plane over wide range of temperature. The cell designed here enables the simultaneous measurement of permittivity and thermal expansion and eliminates the error of permittivity due to dimensional change of specimen. The four concentric electrodes actually lapped to parallel within an error of 1.5 μm. These electrodes were made of sus-304 stainless steel to avoid any chemical reaction with specimen. The guards G_1 and G_5 were copper and the guard G_2 was aluminium.

A heating wire was wound around G_2 and a copper *vs* constantan thermocople was set at the top of G_2 to contol the temperature. Another copper *vs* constantan thermocouple and Au-0.07 at% Fe *vs* KP (90 % Ni+10 % Cr alloy) couple were imbedded in the guard ring G_4 to measure the temperature of specimen. The thermocouples were occasionaly calibrated with a germanium thermometer.

According to Work's work[3] the permittivity ε of specimen can be given as $\varepsilon = A(C_c/C_T)$, where C_c is the capacitance between electrodes C and H, C_T the capacitance between T and H, and the coefficient A a constant over wide temperature range. The coefficient A was determined as 0.3750 by Work's method[3]. The thickness of specimen, equal to the separation between T and H, was obtained[3] by dividing the area of electrode T by the capacity C_T. The area was corrected for the thermal expansion[6] of sus-304 stainless steel.

The arrangement of the cell and a cryostat is shown in Fig. 2. The cell was set in a vacuum tight vessel sealed with an indium ring A. The cell and the vessel was flashed with dry nitrogen after mounting the sample. A little helium gas was introduced in the vessel for heat exchange. Liquid helium or liquid nitrogen was poured in the outer space I of vessel, inside the Dewar vessel. Four co-axial cables led from four vacuum tight BNC receptacles on flange to the cell. Two cables served the unguarded electrode and other two cables served the guarded electrodes for permittivity measurement and specimen thickness measurement. Leads for the heater and themocouples were introduced into the vessel through the hermetic seals. Silica gel particles as drying agent were placed on the bottom of the vessel.

ELECTRICAL MEASUREMENTS

Two methods were employed to measure the permittivity, conductivity, dimension, and temperature. The first method for the measurement employed an Ando Electric Co. TR-10 transformer bridge, a low noise null detecter, and a Kikusui Electronics
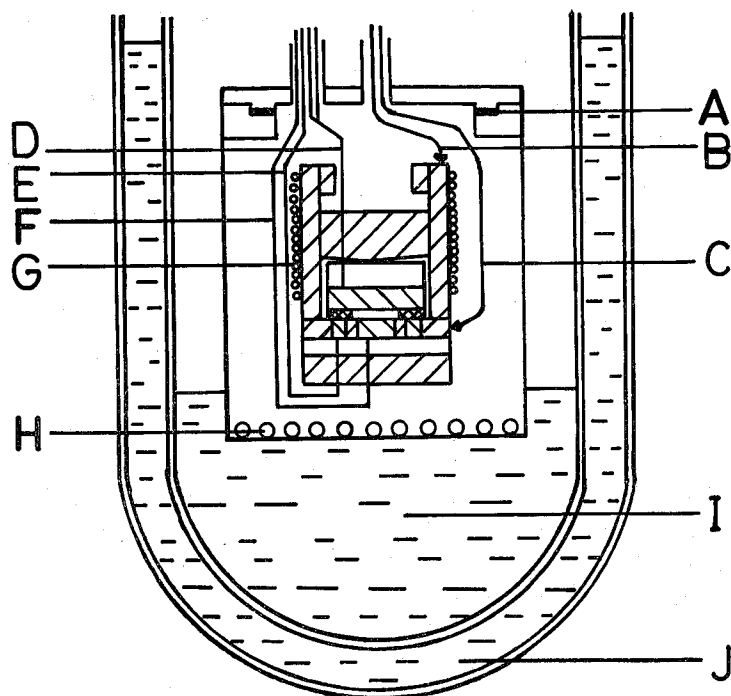
Fig. 2. The arrangement of the cell and the cryostat.
A, indium wire seal; B, thermocouple to control the temperature;
C, themocouple to measure the specimen temperature; D, lead
for the unguarded electrode; E, lead for the outer guarded ele-
ctrode; F, lead for the inner guarded electrode; G, heater; H,
silica gel; I, liquid helium (sometimes liquid nitrogen); J, liquid
nitrogen.

Corp. Model 433 RC oscillator. This method using the transformer bridge, equipped
with the Wagner arm circuit, gave a higher accuracy but consumes much time in the
measurement. The permittivity and conductivity were measured over a frequency range
of 17 Hz to 300 kHz and a temperature range of 20 K to near the melting point of
specimen. The dimension of specimen was estimated from the capacitance at 10 kHz.
The temperatures were measured with an Iwatsu Electric Co. VOAC-757 digital mul-
timeter. In the second method a data acquisition system was used for the measurement.
A micro-computer PC-9801E by Nippon Denki Co, accumulated the data of permitti-
vity, conductivity and dimension from a Yokogawa Hewlett Packard Co. Model 4274A
multi-frequency LCR meter and the data of temperatures from a Keithley Instruments
Inc. Model 177 microvolt digital multimeter, or from a Takeda Riken Industry Inc.
Model TR-6840 digital multimeter, through an IEEE-488 interface. The system measur-
ed the permittivity at the frquency range of 100 Hz to 100 kHz and the specimen
thickness from the capacitance value at 16 kHz.

EXPERIMENTAL

Materials Commercial reagents of undecanoic acid $C_{10}H_{21}COOH$, tridecanoic acid

$C_{12}H_{25}COOH$, pentadecanoic acid $C_{14}H_{29}COOH$, lauric acid $C_{11}H_{23}COOH$, myristic acid $C_{13}H_{27}COOH$, and palmitic acid $C_{15}H_{31}COOH$ were purified by the recrystalization over five times from methanol or n-hexane. Melting points of these acids were 28.3 °C (lit,[7] 28.4 °C) for undecanoic acid, 41.0 °C (lit,[5] 41.4 °C) for tridecanoic acid, 52.4 °C (lit,[5] 52.1 °C) for pentadecanoic acid, 44.3 °C (lit,[5] 44.0 °C) for lauric acid, 54.6 °C (lit,[5] 54.2 °C) for myristic acid, and 62.8 °C (lit,[5] 62.9 °C) for palmitic acid. Purities of methyl ester with these acids were checked by gas chromatography. Purities of these acids were believed over 99.9%.

Specimen mounting Specimens were setted with crystalizing on the electrode plane from the melt or with evaporating in vacuum onto the electrode chilled with liquid nitrogen. The electrodes with specimen were assembled into the cell and the cell was placed in the vessel. Unfortunately the voids were introduced in course of crystalization or evaporation into the specimen. The voids can be removed by the plastic flow of these acids stressed with electrodes at higher temperature. The temperature of the cell was kept 1 K below the melting point over three days for this purpose.

RESULTS AND DISCUSSION

A suitable specimen to test the new cell is the solid which considerably varies its dimension with temperature or time, because the error in the thickness measurement decreases the accuracy of the permittivity as well as the capacitance measurement. Odd numbered fatty acids exhibit large change in their dimension with the plastic flow of the crystal, the discontinuous change at the transition temperature, and the large thermal expansion. The measurements by using the new cell were performed on the dielectric and dilatometric properties of undecanoic acid $C_{10}H_{21}COOH$, tridecanoic acid $C_{12}H_{25}COOH$, and pentadecanoic acid $C_{14}H_{29}COOH$ (hereinafter abbreviated to A-11, A-13, and A-15) over the temperature range of 20 K to the melting point.
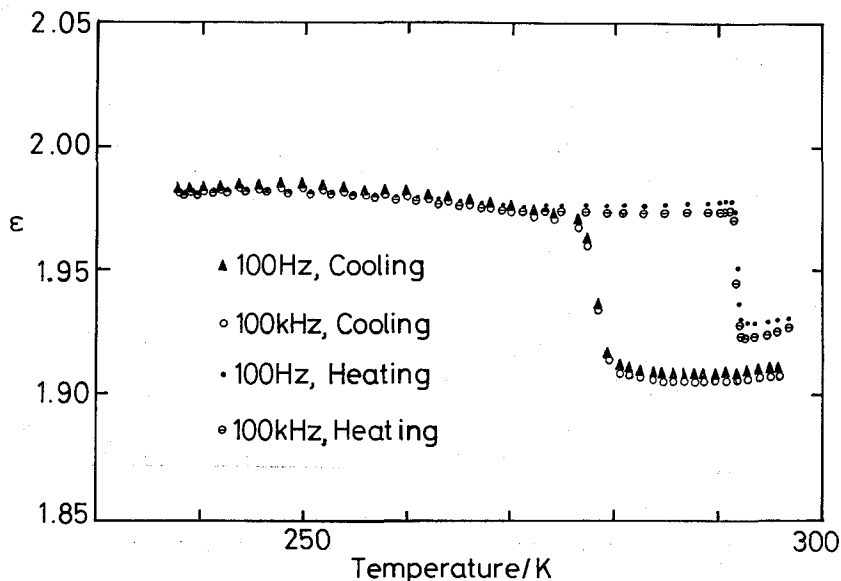

Fig. 3. Relative permittivity ε vs temperature for undecanoic acid.

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$\varepsilon''/10^3$

221.8K

216.9K
212.4K

208.5K

202.1K

0.1   1   10   100   1000
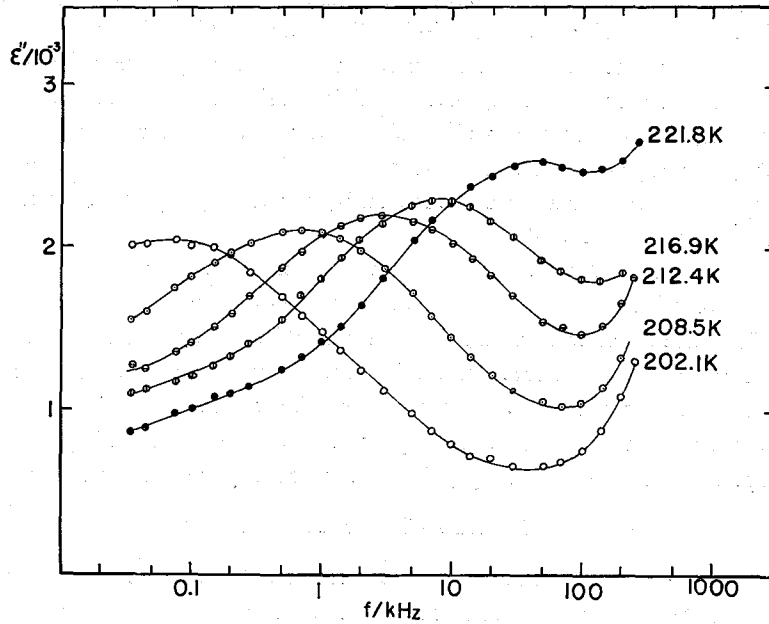
f/kHz

Fig. 4.   Imaginary part of relative permittivity ε'' against frequencies for
         undecanoic acid. Demonstration of measuring abilty for very
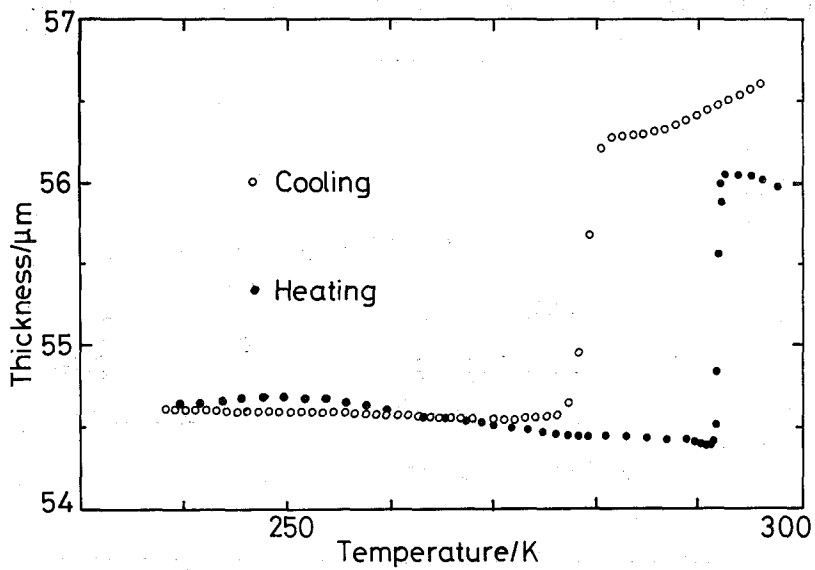   low loss. The increase of ε'' over 100 kHz is an error.

57

56

Thickness/μm

○ Cooling

• Heating

55

54

250   300

Temperature/K

Fig. 5.   Specimen thickness *vs* temperature for undecanoic acid.

The relative permittivity ε for A-11 are plotted against temperature in Fig. 3. The permittivity ε scarcely depends on the frequency and the temperature, except near the transition temperatures. The value of ε slightly smaller than 2 suggests that the voids in the specimen was not sufficiently removed. The jumps of ε about 2-3% at 281.15 K in cooling process or 290.55 K in heating process show the reversible transition[8] of odd numbered acids. The permittivity ε near the transition temperature somewhat depends on the frequency with the wedge type dielectric dispersion[9], which was more clearly observed in the measurements of the imaginary parts of permittivity but the data were not shown in this paper. The dielectric relaxation with extremely low loss was observed near 200 K as shown in Fig. 4. The similar relaxations were observed for A-13 and A-15. But the relaxation could not be detected in the even numbered acids. Gough[10] observed a dielectric loss maximum around 250 K for lauric acid and his experimental results did not agree with those by us. The dielectric loss observed by Gough, however, was dominated by impurities. The mechanism of the relaxation found only in odd numbered acids will be discussed elsewhere[11]. The system with the new cell and a TR-10 transformer bridge can measure the relaxation of such low loss dielectrics. Figure 5 shows the thickness change of A-11 against temperature. The data in Fig. 5 contains the error from the creep or the plastic flow of specimen but the error is negligeble in the temperature range below 273 K. The thickness is almost constant below the transition temperatures and discontinuously changes about 2-3 % the temperature equal to the permittivity jumping point. The thickness above the transition temperature 292 K in heating process did not coincide with that in cooling process owing to the creep of specimen. The new cell can give the correct value of permittivity by eliminating the inaccuracy from a thickness change of specimen, though the thickness of A-11 changes considerably.

The behavior of ε and that of L in A-13 are shown in Fig. 6 and Fig. 7. respectively. As a whole the behavior is similar to that of A-11. The wedge type dielectric dispersion near the transition temperature and the dielectric relaxation near 200 K were slightly larger than those for A-11. The jumps of ε and L for A-13 take place in the
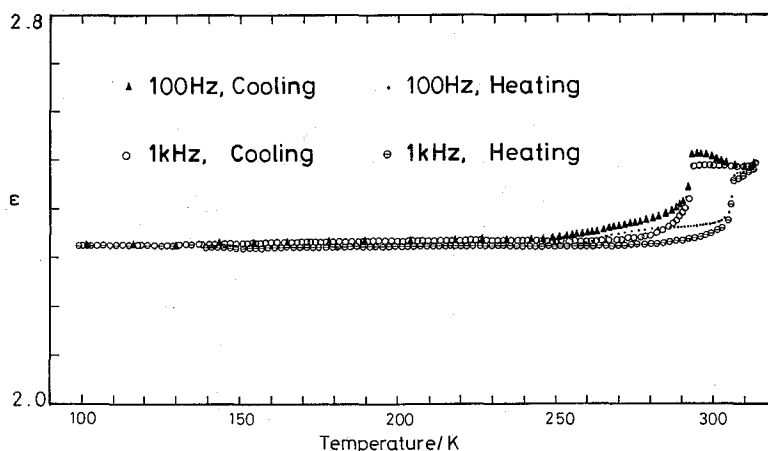

Fig. 6. Relative permittivity ε vs temperature for tridecanoic acid.
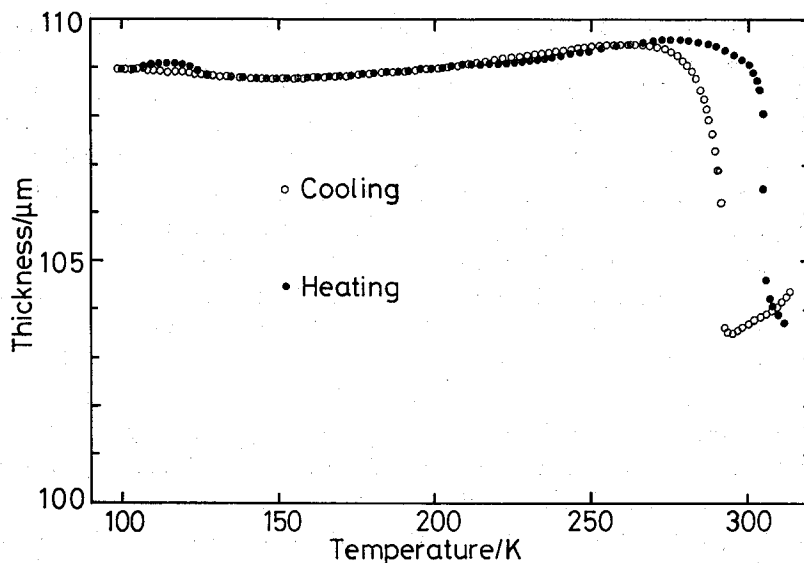
Fig. 7. Specimen thickness *vs* temperature for tridecanoic acid.

opposite directions to those for A-11 at the transition temperatures of 291.85 K in cooling and 305.75 K in heating process. On cooling A-13 expands about 5 % at the transition temperature and contracts in heating process. The thermal expansion coefficient near 200 K was estimated as 6.9×10^{-5} K^{-1} and the coefficient above the transition temperature was roughly estimated as 3×10^{-4} K^{-1} from the cooling process.

The properties of A-15 are given in Fig. 8 and Fig. 9. Both the thickness L and the relative permittivity ε increase with decreasing temperature. The thermal expansion
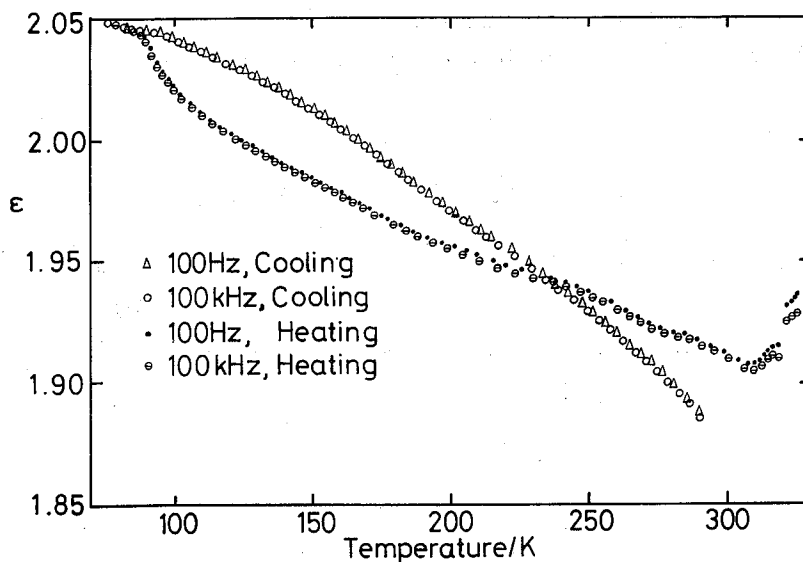

Fig. 8. Relative permittivity ε *vs* temperature for pentadecanoic acid.
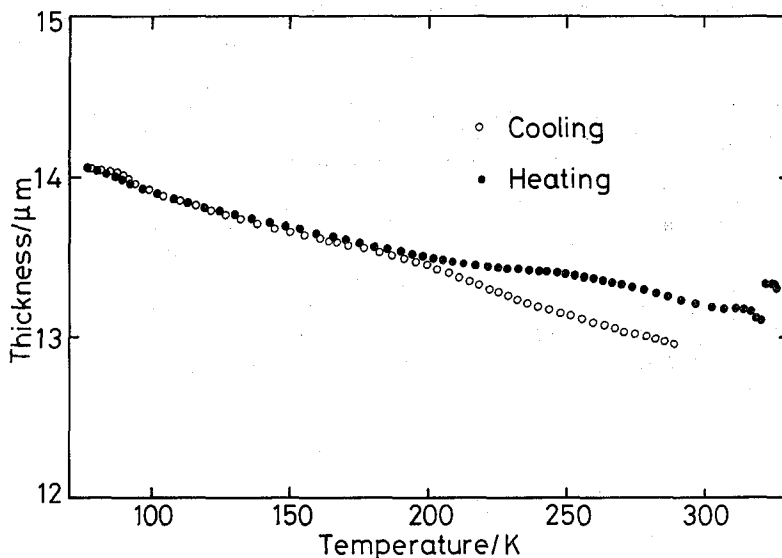
Fig. 9. Specimen thickness *vs* temperature for pentadecanoic acid.

Table I. The directions of jumping of ε and L at the transition temperature.

	ε		L	
	cooling	heating	cooling	heating
undecanoic acid	↑	↓	↓	↑
tridecanoic acid	↓	↑	↑	↓
pentadecanoic acid	↓	↑	↓	↑

↓ : discontinuous derease. ↑ : discontinuous increase.

coefficient was negative in the wide temperature range from 80 K to 300 K and was estimated as -3.2×10^{-4} K^{-1} at 150 K. The negative thermal expansion coefficient in wide temperature range suggests the large distortion of crystal lattice. In heating process both ε and L discontinuously increase at 319.15 K of the transition temperature and decrease in the cooling process at 306.15 K. The direction of discontinuous change at the transition temperature are different to that of A-11 or A-13 as shown in Table 1. The wedge type dispersion near the transition temperature and the dielectric relaxation with very low loss near 200 K were also observed in the same way as in A-11 or A-13

The new cell can give the correct value of permittivity by eliminating the inaccuracy from a dimensional change of specimen. The new cell give also the dimensional parameter measured simultaneously with permittivity. These experimental results on fatty acids indicate that the cell is stable and accurate enough to measure the permittivity of deformable solids and the relaxation of low loss dielectrics.

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