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Dielectric Absorption in Polycrystalline 2-Fluoronaphthalene in Relation to the Dynamic Nature of Disorder in the Crystal

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A conspicuous dielectric absorption in the low-frequency region (from 0.1 to 10^4 Hz) has been observed in the crystal of 2-fluoronaphthalene at temperatures between 8.5 and 55.1 °C, which could be fitted to a Debye type with a slight distribution of relaxation time. The result seems to confirm that the disorder observed by the X-ray crystal structure analysis of Chanh and Haget-Bouillaud is dynamic in nature. Further, a phase change at about 40 °C is suggested from the sudden decrease in the magnitude of dielectric permittivity.

Chanh and Haget-Bouillaud1) have shown by the X-ray crystal structure analysis at 25 °C that the crystal of 2-fluoronaphthalene is in a state of disorder as to the orientation of molecular dipole: the molecule possesses an apparent center of symmetry with the fluorine atom at 2-position being distributed statistically among the four 2-positions of the naphthalene ring with equal probability of 0.25. The crystal is monoclinic, $P2_1/a$ with Z=2, and the lattice constants are very close to those of naphthalene. In order to explain that the molecule has the symmetry C_i in the crystal, we should assume the molecule at the lattice makes reorientation about at least two of the axes, X- and Z-axes, as shown in Fig. 1. As the potential barrier against rotation of the molecule is expected to be large, it is not certain whether we could observe such a reorientational motion experimentally or not.

With an aim of disclosing the nature of this disorder, a study of dielectric absorption of this material has been performed, specifically concentrating on the dielectric behaviors in ultra-low and low-frequency region (0.1 to 10^4 Hz).

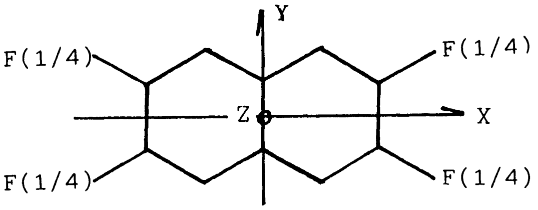

Fig. 1. Apparent molecular structure of 2-fluoronaphthalene in the crystal and assumed axes of rotation.

The sample of 2-fluoronaphthalene, which was kindly provided by Prof. Mamoru Ohashi, was purified through a zone-refining procedure(40 passes), and then ground into fine powders in an agate mortar. A disc for the dielectric measurement(40 mm in diameter, 0.72 mm thick) was prepared in a steel dice under the pressure of 10 t/cm^2, and put into a cell after being annealed for several hours at about 50 °C. The measuring apparatuses are a transformer bridge(ANDO TR1-C) and an ultra-low frequency bridge(ANDO TR-4) with a conductance shifter as reported before.2) A three-terminal cell capacitor was kept in an air thermostat regulated electrically within ± 0.2 °C.

Observed dielectric absorption ε'' at various temperatures is plotted as a function of frequency in Fig. 2. It is clear that the molecule of 2-fluoronaphthalene in the crystal behaves like a rotator subject to a potential field, giving rise to fluid-like dielectric absorption. It seems that a certain change of state occurs around 40 °C, which contradicts the result by Chanh and Haget-Bouillaud who found there is no phase change in the crystal between -140 °C and the melting point(60.1 °C).1) The Cole-Cole plots are shown for the data at 11.5 and 43.9 °C in Fig. 3, which suggest the Debye type relaxation process with a slight distribution of relaxation time.

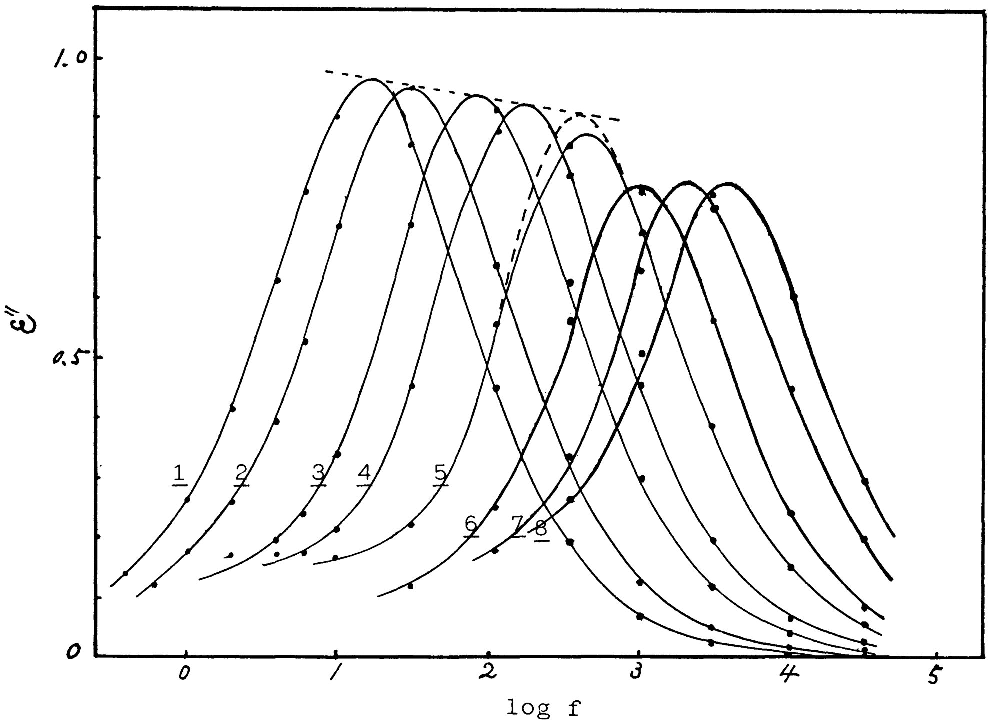

Fig. 2. Dielectric absorption in the crystal of 2-fluoronaphthalene at various temperatures as a function of frequency. 1, 8.5 °C; 2, 13.7 °C; 3, 21.3 °C; 4, 26.8 °C; 5, 34.4 °C; 6, 43.9 °C; 7, 50.8 °C; 8, 55.1 °C. Broken curve in 5 means a transition starting around here.

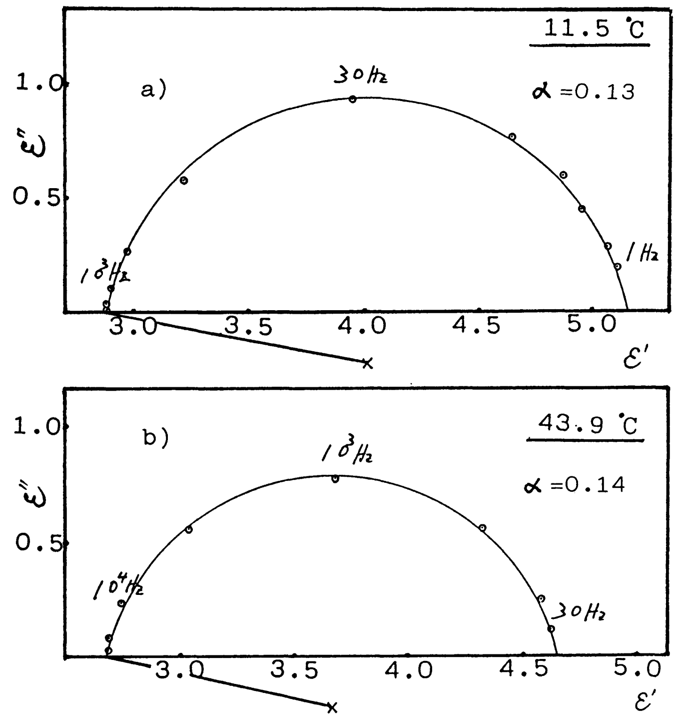

Fig. 3. Cole-Cole plot.

a)-----Phase II
b)-----Phase I

The experimental Cole-Cole arcs are well analyzed by the empirical Cole-Cole equation,[3]

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/1+(j\omega\tau)^{1-\alpha},$$

where ε^* is the complex permittivity, ε_0 and ε_∞ are those at static and extremely high frequency electric field, respectively, j the imaginary unit, ω the angular frequency and τ is the relaxation time. The calculated distribution parameters α are 0.13 at 11.5 °C and 0.14 at 43.9 °C. These values remain constant over the temperature range studied. Static permittivity ε_0, estimated from the Cole-Cole diagrams is plotted as a function of temperature in Fig. 4, which suggests a certain change of state at about 40 °C, as mentioned before. As the crystal structure of the upper temperature phase is not clarified as yet, let us tentatively designate it as phase I and the lower temperature one as phase II. The variation of static permittivity with temperature, as is shown in Fig. 4, is similar to that observed with H_2S in the solid state,[4a)] where a phase change within the disordered phase has been confirmed.[4b,c)] The gradual decrease in permittivity with temperature is a feature characteristic of the non-associative liquids. Therefore, trial calculation of the dipole moment of 2-fluoronaphthalene has been made for the phases I and II, with use of the Onsager equation[5)]

$$\mu^2 = \frac{9kT(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{4\pi N_0 \varepsilon_0(\varepsilon_\infty + 2)^2},$$

where μ is the dipole moment, T the absolute temperature, k the Boltzmann constant, and N_0 is the number of molecules per cm^3, which has been estimated from the volume of the unit cell[1)] as $5.14\times10^{21}/cm^3$ (25 °C), because of the lack of density data. The result of calculation is : μ=1.21 D(4.04×10^{-30}C m) for the phase I, and 1.17 D (3.90×10^{-30}C m) for the phase II, which can be compared with the literature value, 1.50 D(5.00×10^{-30}C m) measured in benzene solution.[6)] The value of μ for the phase I, 1.21 D, would certainly become closer to 1.50 D if the value of N_0 for the phase I is corrected.

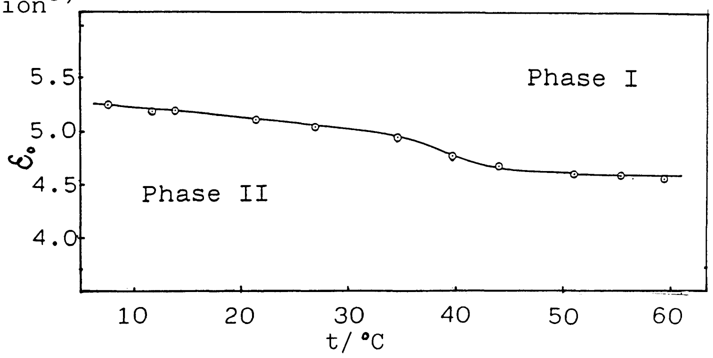

Fig. 4. Variation of permittivity ε_0 with temperature.

Activation energies of the reorientation of 2-fluoronaphthalene molecule in both the phases I and II have been obtained from the Arrhenius plot of log f_{max} vs. reciprocal temperature as 24.0±1.0 kcal/mol(100.4 kJ/mol) and 21.3±1.0 kcal/mol (89.1 kJ/mol), respectively. Here, f_{max} is the frequency at which ε'' becomes maximum at each temperature. These values are close to the activation energy of rotation of naphthalene molecule in the crystal, 25±2 kcal/mol, obtained by von Schütz and Wolf$^{7)}$ from the NMR relaxation time measurement(T_1). Andrew$^{8)}$ failed to detect the rotational motion of the naphthalene molecule in crystalline state in his pioneering work on the broad-line NMR, probably because of the time-scale of the measurement being too small.$^{7)}$ Apart from the reorientational motion of the molecules of naphthalene in certain complex compounds,$^{9)}$ we believe that the result obtained here by the measurement of dielectric absorption in the crystal of 2-fluoronaphthalene offers an evidence of very slow molecular motion in the crystal of naphthalene derivatives.

The larger value of activation energy in the phase I than that in the phase II of 2-fluoronaphthalene would suggest the occurrence of three-dimensional rotation at higher temperatures in addition to the in-plane as well as around the X-axis rotation which may be much easier than the rotation about the Y-axis; Tay and Walker$^{10)}$ have shown in their measurement of dielectric absorption of 2-fluoronaphthalene in a polymer matrix that the activation energy of rotation of the molecule is 5.50 kcal/mol(23.0 kJ/mol), with the rotational volume V_Y being the largest among the three(V_X, V_Y, V_Z).

The order-disorder transition in this crystal is expected at much lower temperatures than -140 °C, the minimum temperature mentioned in the paper of Chanh and Haget-Bouillaud.$^{1)}$

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