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Calorimetric and neutron scattering studies of plastically crystalline cyclooctanol*

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Abstract

The heat capacity of cyclooctanol was measured with an adiabatic calorimeter in the temperature range 5–340 K. Liquid cyclooctanol crystallized into crystal I, a plastic (orientationally disordered) phase. Crystal I was supercooled readily and underwent a glass transition at 160 K. Crystal II, obtained by annealing crystal I at about 200 K, also underwent a glass transition at 160 K, indicating that crystal II is also an orientationally disordered phase. On heating, crystal II transformed to crystal I at 261.7 K with a transition entropy of $8.06 \text{ J K}^{-1} \text{ mol}^{-1}$ and crystal I fused at 295.3 K with a fusion entropy of $7.00 \text{ J K}^{-1} \text{ mol}^{-1}$. Neutron scattering of cyclooctanol was measured in the temperature range 20–335 K, energy range 0.1–20 meV and momentum transfer range $0.23\text{--}2.7 \text{ \AA}^{-1}$. A clear boson peak was found around 2.5 meV in both orientational glasses of crystal I and II. Quasielastic scattering appeared at temperatures as low as the glass transition temperature. This may be due to a fast β process which has been observed in most glass-forming liquids. The present results indicate that glass-forming plastic crystals are similar to glass-forming liquids in their dynamical properties in terahertz region.

1. Introduction

Globular molecules often crystallize into an intermediate phase in which the molecular centre of mass is ordered as in the normal crystal while the molecular orientation is disordered as in the liquid [1]. This phase is called an ‘orientationally disordered crystal (ODIC)’ or ‘plastic crystal (PC)’ based on its plasticity under mechanical stress. ODIC is a better term than PC because it represents the structural characteristic directly related to their interesting physical properties

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such as phase transitions. However, it implies too wide a group of crystals including those in which molecules are disordered among only a small number of orientations as in the low-temperature phases of RbCN ($W = 2$) [2], C_{60} ($W = 2$) [3] and ice ($W = 1.507$) [4]; W is the number of orientations. These are ODICs but are not plastic and do not satisfy Timmermans' criterion ($\Delta S_{\text{fus}} < 20 \text{ J K}^{-1} \text{ mol}^{-1}$) [5] for PCs. These weakly disordered ODICs are not in the scope of the present research. In this paper, therefore, we use 'PCs' to describe a subgroup of ODICs in which the molecules are orientationally disordered as extensively as in liquids.

Some of the PCs can be quenched by rapid cooling into a 'orientational glasses' where the disordered molecular orientations are frozen in. So far, the following eight molecules are known to form orientational glasses: ethanol (C_2H_5OH , $T_g = 97 \text{ K}$) [6], cyclohexanol ($C_6H_{11}OH$, $T_g = 150 \text{ K}$) [7–9], cyanocyclohexane ($C_6H_{11}CN$, $T_g = 135 \text{ K}$) [10], isocyanocyclohexane ($C_6H_{11}NC$, $T_g = 129 \text{ K}$) [11], 1,2-difluorotetrachloroethane ($CFCl_2CFCl_2$, $T_g = 90 \text{ K}$) [12], 2,3-dimethylbutane ($CH_3CH(CH_3)CH(CH_3)CH_3$, $T_g = 76 \text{ K}$) [13], cyanoadamantane ($C_{10}H_{15}CN$, $T_g = 170 \text{ K}$) [14, 15] and cyclooctanol ($C_8H_{15}OH$, $T_g = 168 \text{ K}$) [16, 17]. We have excluded from this list glassy crystals with a small number of frozen disordered molecular orientations such as C_{60} [3]. Orientational glasses are often considered as simplified models of ordinary structural glasses since they have structural disorder only in molecular orientations. Thermodynamic, structural and dynamical studies have been performed to investigate the glass transitions and related orientational relaxations of orientational glasses [18, 19].

The present study deals with the fast dynamics (in the terahertz range) of orientational glasses and PCs which have not been studied much so far. For the structural glasses, there are two main research subjects in this frequency range; one is the boson peak and the other the fast β process [20]. The boson peak appears at 2–4 meV (0.5–1 THz) as a broad excitation peak. The name 'boson peak' originates from the temperature dependence of the peak intensity which is scaled by the Bose factors of a harmonic oscillator. It is of interest that the boson peak appears in a similar energy range for any amorphous solid with different local structure and bonding energy. The fast β process, also known as 'the fast process' or ' β relaxation', appears around the glass transition and its intensity increases with increasing temperature. The relaxation time of the fast β process is around 1 THz and it does not depend on temperature much. It should be noted that this is not related to 'slow β relaxation' which is sometimes called the 'Johari–Goldstein process'. The most interesting point about the fast β process is that this terahertz phenomenon appears around the glass transition, a millihertz phenomenon (the relaxation time is 100–1000 s at T_g). Recent studies have shown that both the boson peak and fast β process are localized motions in disordered but locally ordered structures of amorphous solids. However, the microscopic mechanisms of the boson peak and fast β process have not been explained with sufficient generality.

The purpose of this study was to investigate the boson peak and fast β process of glass-forming PCs and to compare their results with those obtained in structural glass formers. We used cyclooctanol since its plastic phase is stable over a wide temperature range [17]. The dynamical properties of cyclooctanol have also been studied by dielectric [21–23] and NMR [24] experiments. First, we measured the heat capacity of cyclooctanol to investigate its phase behaviour and glass transitions. Then we performed inelastic and quasielastic neutron scattering experiments on liquid, plastic crystalline and glassy phases of cyclooctanol to investigate the boson peak and the fast β process.

2. Experimental details

Cyclooctanol (purity 98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. The sample was dried with molecular sieves (Wako Pure Chemical Ind., Ltd) for a few days and then fractionally distilled under reduced pressure (about 19–20 mm Hg) with a concentric-type

rectifier (HC-5500-F, Shibata Kagakukikai Kogyo Co., Ltd). The final purity was determined by gas chromatography (F21, Perkin-Elmer) as higher than 99%.

The mass of the sample loaded in the calorimeter cell was 4.7740 g (0.037 235 mol). Helium gas was charged into the dead space of the sample cell (about 0.8 cm³) to enhance the thermal equilibration at low temperatures. The heat capacity of cyclooctanol was measured by an adiabatic calorimeter [25] in the temperature range 5–340 K. The measurement was carried out using a standard intermittent heating method, i.e. repetition of equilibration and energizing intervals. The temperature increment for each measurement was 0.3 K around 5 K and increased with increasing temperature to reach 3.0 K at 340 K. The accuracy of the heat capacity measurement was better than 1% at $T < 10$ K, 0.5% at $10 < T < 30$ K, and 0.1% at $T > 30$ K.

The neutron scattering experiments for cyclooctanol were performed using AGNES [26] at the Institute for Solid State Physics, University of Tokyo. This is a direct-geometry time-of-flight spectrometer installed at the cold neutron guide (C3-1) of JRR-3M (Tokai, Japan). The wavelength of the incident neutron selected by PG (002) monochromators was 4.22 Å corresponding to 4.59 meV. The energy resolution was 0.12 meV and the energy window was $-3 < \Delta E < 20$ meV where ΔE is energy transfer from a sample to neutrons. In the present experiments, 122 ³He tube counters were installed at $2\theta = 9^\circ$ – 130° with a step of 1° , covering the scattering vector Q region of 0.23–2.70 Å⁻¹ for elastic scattering. The liquid cyclooctanol was confined in a concentric double-cylinder aluminium can (35 mm height, 14.0 mm inner diameter of the outer cylinder, 13.0 mm outer diameter of the inner cylinder) using an indium gasket. The thickness of the sample was 0.5 mm, corresponding to transmission of the neutron beam of about 80%. The observed neutron cross-section was dominated by incoherent scattering from hydrogen atoms. The data were collected at several temperatures in the temperature range 20–335 K. The duration of the measurements was 8–20 h (long runs) at 100, 140, 160, 180 and 261 K and 2–3.5 h (short runs) at other temperatures.

3. Results and discussion

3.1. Heat capacity

On cooling liquid cyclooctanol, it crystallized into crystal I which was known to be a plastic phase. As reported before [16, 17], crystal I was supercooled readily down to the lowest temperature of this experiment (5 K). In the heat capacity measurement from 5 K, a glass transition with an abrupt increase of the heat capacity by 60 J K⁻¹ mol⁻¹ appeared at around 160 K and then the supercooled crystal I transformed irreversibly to crystal II with a large exothermic effect at around 200 K. The glass transition temperature (160 K) of crystal I agrees with the temperature where the dielectric relaxation time becomes about 1000 s [22, 23] which is the time scale of adiabatic calorimetry. Conversion to crystal II was attained fully by annealing the sample for more than a half day at about 200 K. In the heat capacity measurement of crystal II, a glass transition accompanied by a heat capacity increment of 46 J K⁻¹ mol⁻¹ appeared at around 160 K. The structure of crystal II is not known. But we may assume that the molecular centre of mass is ordered in crystal II because it is ordered in the higher-temperature phase crystal I. Therefore crystal II is regarded as another orientationally disordered phase (we do not know whether crystal II should be called a ‘plastic phase’). The orientational disorder in crystal II is consistent with the indications obtained in the previous thermal conductivity and dielectric studies [16, 27]. On further heating, crystal II transformed to crystal I at 261.7 K and then crystal I fused at 295.3 K. The II-to-I transition temperature (261.7 K) is close to the 265 K determined in the previous dielectric study [17]. In the present experiment, we did not detect any transition to orientationally ordered crystal III found previously in the experiment under high pressure [16, 27].

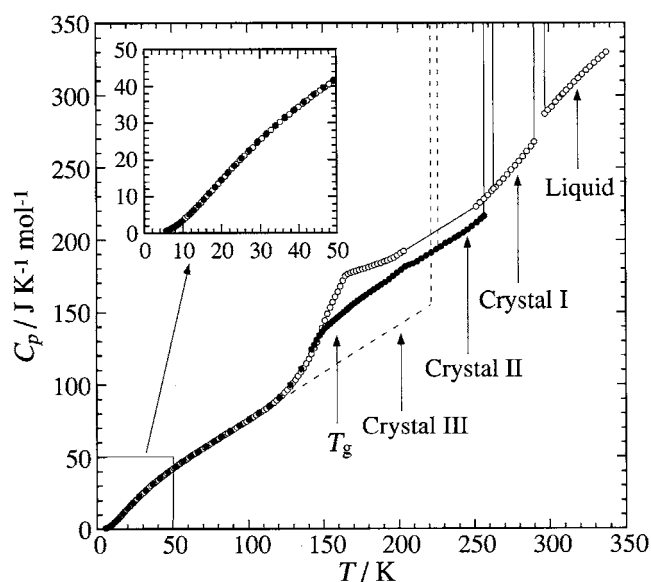


Figure 1. Molar heat capacities of cyclooctanol in the temperature range 5–340 K: ○, liquid, crystal I (plastic phase) and its orientational glass; ●, crystal II and its orientational glass.

The molar heat capacities of cyclooctanol in the temperature range 5–340 K are collected in table 1 and also plotted in figure 1. The inset shows the molar heat capacities in the low-temperature range (5–50 K). The open circles denote the data on liquid, crystal I and its orientational glass. The closed circles denote the data on crystal II and its orientational glass. In order to show the relation of all phases, the hypothetical heat capacity of crystal III (orientationally ordered phase) is added with a dashed line by extrapolation of the heat capacities of glassy crystal II. The transition temperature from crystal III to crystal II is 221 K [27] as shown by dashed lines. It is of interest that the glass transition temperature (T_g) of crystal I is the same as that of crystal II though they are different phases. The heat capacity of crystal I is also close to that of crystal II below T_g . The enthalpy and entropy of the II to I transition were $2.103 \pm 0.003 \text{ kJ mol}^{-1}$ and $8.06 \pm 0.01 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The fusion enthalpy and entropy of crystal I were $2.062 \pm 0.003 \text{ kJ mol}^{-1}$ and $7.00 \pm 0.01 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. It is thermodynamic evidence for the plastic-crystallinity of crystal I that the fusion entropy is smaller than $20 \text{ J K}^{-1} \text{ mol}^{-1}$, a criterion given by Timmermans [5].

To compare the orientational disorder of the phases, the temperature dependence of the configurational entropy was calculated from the heat capacity and transition and fusion entropy data. The vibrational heat capacity of each phase was assumed to be the same as that of crystal II below T_g and its extrapolation to higher temperatures. The extrapolation up to 310 K was made by fitting the C_p data for crystal II (60–105 K) to a straight line. Figure 2 gives the configurational entropy relative to that of crystal II at 0 K. It should be noted that this entropy is not the ‘absolute’ configurational entropy because crystal II is still disordered even at 0 K; the complete ordered crystal is crystal III which could not be formed in this study. Figure 2 demonstrates that large fraction of configurational entropy changes in the normal region of crystal I and II (more than at the II to I transition and fusion). The configurational entropy of crystal I ($37 \text{ J K}^{-1} \text{ mol}^{-1}$) is more than 80% of that of the liquid ($45 \text{ J K}^{-1} \text{ mol}^{-1}$) at the fusion temperature 295 K, indicating that crystal I is orientationally disordered as much as the liquid. It is noteworthy that the configurational entropy of crystal I is considerably larger than

Table 1. Molar heat capacities of cyclooctanol.

T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)
	Crystal I and its orientational glass	42.321	36.160	105.11	78.882	194.67	186.68
		43.474	37.095	106.77	80.029	196.84	187.67
5.6068	0.69881	44.623	37.991	108.44	81.177	199.03	189.03
5.9590	0.84205	45.767	38.884	110.13	82.366	201.24	190.79
6.3028	0.99679	46.908	39.730	111.83	83.609	203.49	192.03
6.6393	1.1627	48.045	40.599	113.55	84.871	251.42	222.84
6.9701	1.3398	49.180	41.486	115.27	86.211	253.98	225.51
7.2963	1.5260	50.312	42.361	117.01	87.638	256.55	228.13
7.6365	1.7350	51.441	43.189	118.77	89.161	259.13	230.79
8.0014	1.9714	52.569	44.031	120.53	90.796	261.72	233.45
8.3881	2.2384	53.695	44.885	122.30	92.527	264.32	236.16
8.8051	2.5440	54.820	45.732	124.07	94.400	266.93	239.09
9.2527	2.8921	55.944	46.519	125.85	96.443	269.54	241.98
9.7195	3.2738	57.068	47.151	127.64	98.572	272.16	245.03
10.197	3.6983	58.194	47.906	129.43	100.86	274.79	248.17
10.688	4.1416	59.320	48.663	131.22	103.24	277.42	251.21
11.199	4.6276	60.447	49.448	133.02	105.75	280.06	254.40
11.727	5.1443	61.576	50.205	134.82	108.43	282.70	257.67
12.270	5.6948	62.705	50.984	136.62	111.25	285.35	260.96
12.841	6.2941	63.856	51.749	138.43	114.30	288.00	264.43
13.449	6.9474	65.031	52.489	140.23	117.54	290.15	267.63
14.084	7.6436	66.212	53.293	142.03	121.10		Crystal II and its orientational glass
14.736	8.3717	67.424	54.119	143.82	125.03	5.5862	0.69423
15.411	9.1335	68.670	54.913	145.61	129.31	5.9408	0.84342
16.113	9.9436	69.927	55.748	147.38	134.01	6.2851	0.99787
16.840	10.785	71.237	56.671	149.14	139.06	6.6217	1.1636
17.590	11.659	72.603	57.545	150.89	144.18	6.9520	1.3471
18.328	12.519	73.982	58.455	152.63	148.92	7.2774	1.5305
19.141	13.477	75.386	59.378	154.37	153.14	7.5991	1.7310
19.998	14.482	76.819	60.318	156.12	156.89	7.9179	1.9416
20.908	15.547	78.270	61.276	157.86	160.44	8.2338	2.1530
21.855	16.634	79.132	61.781	159.59	164.00	8.5617	2.3937
22.831	17.736	79.738	62.247	161.32	167.76	8.9231	2.6673
23.832	18.855	80.427	62.636	163.03	171.66	9.3192	2.9856
24.858	19.966	81.839	63.588	164.74	174.83	9.7382	3.3357
25.905	21.086	83.325	64.559	166.46	176.33	10.172	3.7115
26.988	22.212	84.787	65.500	168.19	177.12	10.643	4.1445
28.114	23.406	86.264	66.458	170.04	177.72	11.154	4.6321
29.267	24.712	87.757	67.440	171.98	178.31	11.683	5.1517
30.442	25.741	89.264	68.427	173.95	178.91	12.234	5.7195
31.638	26.904	90.785	69.417	175.94	179.57	12.812	6.3256
32.853	28.080	92.320	70.426	177.95	180.24	13.418	6.9791
34.069	29.238	93.870	71.428	179.97	180.91	14.051	7.6735
35.272	30.359	95.434	72.451	182.02	181.61	14.702	8.4029
36.466	31.392	97.011	73.504	184.08	182.36	15.375	9.1731
37.651	32.420	98.602	74.549	186.16	183.20	16.076	9.9862
38.828	33.397	100.21	75.619	188.26	183.99	16.802	10.832
39.999	34.346	101.83	76.677	190.38	184.87	17.550	11.707
41.163	35.290	103.46	77.748	192.52	185.75		

Table 1. (Continued.)

T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)	T (K)	C_p (J K ⁻¹ mol ⁻¹)
18.317	12.609	64.221	52.179	124.27	95.458	204.05	181.14
19.102	13.538	65.487	53.023	126.04	97.615	206.69	182.33
19.902	14.498	66.755	53.870	127.82	99.945	209.36	183.42
20.724	15.460	68.027	54.736	129.60	102.45	212.06	185.02
21.559	16.414	69.302	55.582	131.38	105.09	215.06	186.88
22.419	17.393	70.580	56.428	133.15	107.87	218.35	188.98
23.316	18.404	71.861	57.294	134.93	110.82	221.67	191.14
24.246	19.430	73.146	58.131	136.71	113.95	224.86	193.24
25.206	20.476	74.434	58.956	138.48	117.25	227.90	195.31
26.195	21.520	75.726	59.791	140.24	120.68	230.92	197.37
27.223	22.596	77.023	60.678	142.01	124.15	233.92	199.28
28.296	23.754	78.312	61.547	143.76	127.55	236.90	201.05
29.400	25.024	79.594	62.403	145.52	130.81	239.86	203.01
30.531	25.949	80.893	63.253	147.27	133.87	242.81	204.91
31.687	27.108	82.243	64.138	149.03	136.43	245.74	207.05
32.865	28.242	83.663	65.077	150.79	138.54	248.65	209.29
34.062	29.379	85.117	66.031	152.56	140.35	251.55	211.66
35.273	30.511	86.587	66.985	154.35	142.03	254.42	214.39
36.491	31.552	88.072	67.966	156.14	143.64	256.56	216.47
37.715	32.616	89.571	68.942	157.94	145.23		Liquid
38.956	33.643	91.086	69.943	159.76	146.80	297.23	287.14
40.224	34.651	92.614	70.959	161.58	148.37	299.27	289.57
41.518	35.734	94.157	71.993	163.41	149.90	301.79	291.78
42.809	36.785	95.714	73.028	165.25	151.45	304.32	295.26
44.083	37.753	97.285	74.074	167.10	153.01	306.85	298.22
45.354	38.729	98.870	75.154	168.96	154.55	308.85	300.45
46.619	39.691	100.47	76.218	170.83	156.03	309.39	300.92
47.881	40.663	102.08	77.324	172.71	157.48	311.45	303.36
49.140	41.639	103.71	78.421	174.60	158.94	314.06	306.18
50.398	42.583	105.35	79.527	176.50	160.36	316.67	309.01
51.653	43.536	107.00	80.687	178.66	161.90	319.29	311.72
52.908	44.488	108.67	81.849	181.10	163.61	321.92	314.44
54.161	45.414	110.35	83.050	183.56	165.37	324.55	317.16
55.413	46.355	112.05	84.297	186.04	167.09	327.20	319.83
56.666	47.152	113.76	85.587	188.55	168.90	329.85	322.43
57.921	47.906	115.49	86.950	191.09	170.72	332.51	324.97
59.178	48.789	117.23	88.362	193.64	172.64	335.17	327.46
60.436	49.654	118.97	89.922	196.22	174.77	337.85	329.91
61.695	50.491	120.73	91.598	198.82	176.99		
62.957	51.341	122.50	93.429	201.43	179.10		

that of crystal II at the transition temperature (262 K) but close to that of crystal II below T_g . This indicates that the extent of orientational disorder is comparable in both crystals I and II below T_g . This is consistent with the fact that T_g of crystal II and C_p below T_g of crystal II are nearly the same as those of crystal I.

3.2. Neutron scattering

Figure 3 shows the $S(Q, E)$ spectra of crystal I measured by AGNES at 100, 140, 160, 180 and 261 K. These spectra were obtained by summing up the data from 32 counters placed at

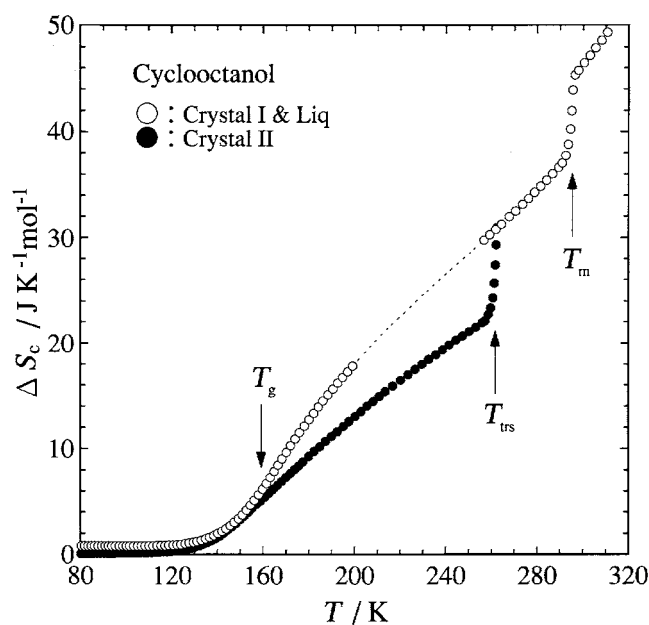


Figure 2. Temperature dependence of configurational entropy of liquid (○), crystal I (○) and crystal II (●) cyclooctanol. See text for the details of the calculation.

scattering angles of 89° – 120° ; the average Q value for elastic scattering was 2.36 \AA^{-1} . A clear boson peak was observed at around 2.5 meV for the data at 100 and 140 K. Broadening of the elastic peak due to quasielastic scattering appeared for the data above 160 K. The intensity of the quasielastic scattering drastically increased with increasing temperature.

Figure 4 shows the $S(Q, E)$ spectra multiplied by a ratio $n(100 \text{ K})/n(T)$ where $n(T)$ is the Bose factor at temperature T . The open circles (○) and triangles (△) denote the data for crystal I at 100 and 140 K respectively. The data for crystal II (●) at 100 K are also plotted for comparison. The intensity of the broad peak was scaled well by the Bose factor, as has been confirmed in various structural glasses. The boson peak of cyclooctanol found in this study is the second example of the boson peak of the orientational glass following the boson peak of the ethanol orientational glass found by Ramos *et al* [28]. This result suggests that the positional disorder is not essential for the mechanism of the boson peak in agreement with the conclusion by Ramos *et al* [28]. Another important finding is that the boson peak of crystal II is quite similar to that of crystal I. This is consistent with the fact that the low-temperature heat capacity of crystal II is close to that of crystal I as described in the preceding section.

Figure 5 shows the temperature dependence of the elastic scattering intensity (integrated over -0.2 to 0.2 meV) divided by that at the lowest temperature (20 K). The plot is made in a logarithmic scale. The open (○, △, □) and closed (●, ▲, ■) symbols represent the data for crystal I and crystal II respectively. The symbols +, ▽ and ◇ denote the data for liquid. For each phase, the plot is made for three different mean Q values of 0.44 , 1.60 and 2.46 \AA^{-1} . The mean square displacement was also calculated by using the relation $I = I_0 \exp(-\langle u^2 \rangle Q^2/3)$ and is plotted in figure 6 for crystal I, crystal II and liquid. In figures 5 and 6, all of the data lie on a straight line below T_g as expected from the mean square displacement of a harmonic oscillator ($\langle u^2 \rangle \sim T$). This is the ordinary temperature dependence observed for most of crystalline materials in the classical high-temperature regime. For both crystals I and II and for all Q values, excess decrease of the elastic intensity occurred at $T \geq T_g$ corresponding to the

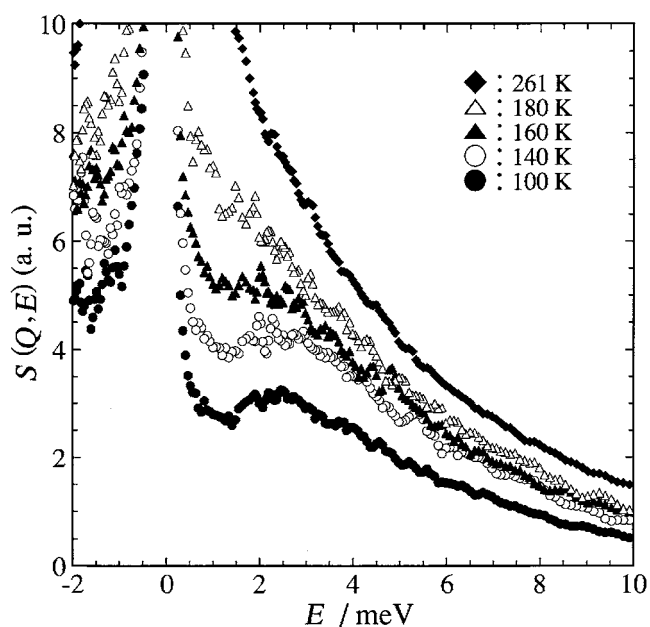


Figure 3. Dynamic structure factor $S(Q, E)$ of crystal I of cyclooctanol at several temperatures (●, 100 K; ○, 140 K; ▲, 160 K; △, 180 K; ◆, 261 K). The spectra were obtained by summing up the data for the counters at scattering angles of 89° – 120° ; the average Q value for elastic scattering was 2.36 \AA^{-1} .

quasielastic scattering observed in figure 3. The temperature and Q dependence of the elastic intensity similar to those shown in figures 5 and 6 has been observed for the fast β process in structural glasses and polymer glasses. This appears to show that there is also a fast β process in a glass-forming PC.

Figure 7 shows the elastic scattering intensity recorded by individual counters in the scattering angle range between 30° and 70° . This plot is equivalent to powder diffraction patterns measured on an angle-dispersive powder diffractometer. The open and closed symbols denote the data for crystal I (PC) and liquid respectively. There are two curves for 285 K. One was obtained on the sample heated from below to 285 K, and the other on the sample cooled from above to the same temperature. Though the background level is high due to incoherent scattering from hydrogen atoms, two Bragg peaks are evident at $2\theta = 46^\circ$ and 51° for crystal I. These scattering angles correspond to d -spacing of 5.4 and 4.9 \AA respectively, and indexed to (111) and (200) reflections of an fcc lattice ($a = 9.6 \text{ \AA}$) respectively. For the PCs, it is known that only (111) and (200) reflections have a large intensity and other reflections are very weak [1]. Figure 7 is therefore direct evidence that crystal I is a plastic phase at 285 K and the liquid supercooled down to 285 K.

For further investigation of the quasielastic scattering shown in figures 3 and 5, we have calculated the imaginary part of the density susceptibility χ'' by dividing $S(Q, E)$ data by the Bose factor. Figure 8 shows the logarithmic plot of χ'' for crystal I (160–285 K) and liquid (285–335 K). The data were obtained by summing up the data for the counters at scattering angles of 105° – 120° ; the average Q value for elastic scattering was 2.48 \AA^{-1} . There is a peak of χ'' corresponding to quasielastic scattering at all temperatures. The peak frequency is about 1 THz and it is insensitive to temperature in the same way as the fast β process of ordinary structural glasses. The χ'' becomes larger at lower frequency and higher temperature

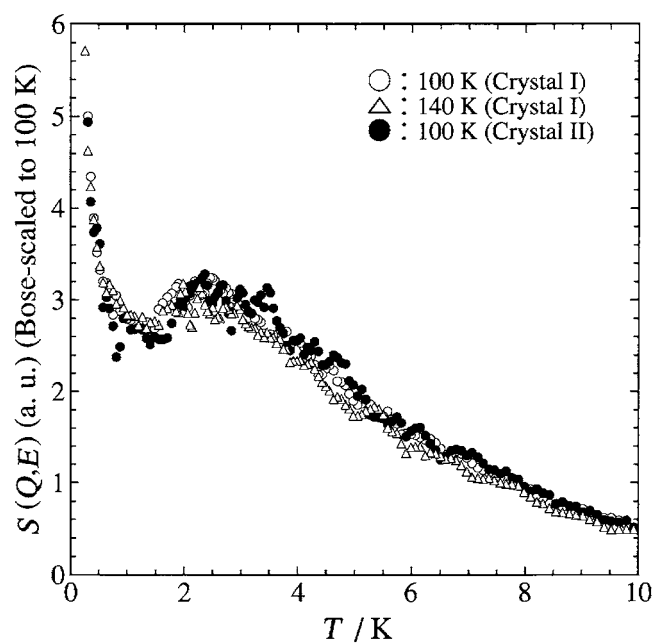


Figure 4. Dynamic structure factor $S(Q, E)$ of cyclooctanol at 100 K (○, crystal I; ●, crystal II) and 140 K (△, crystal I). The $S(Q, E)$ data at 140 K were multiplied by a ratio $n(100\text{ K})/n(140\text{ K})$ where $n(T)$ is the Bose factor at temperature T .

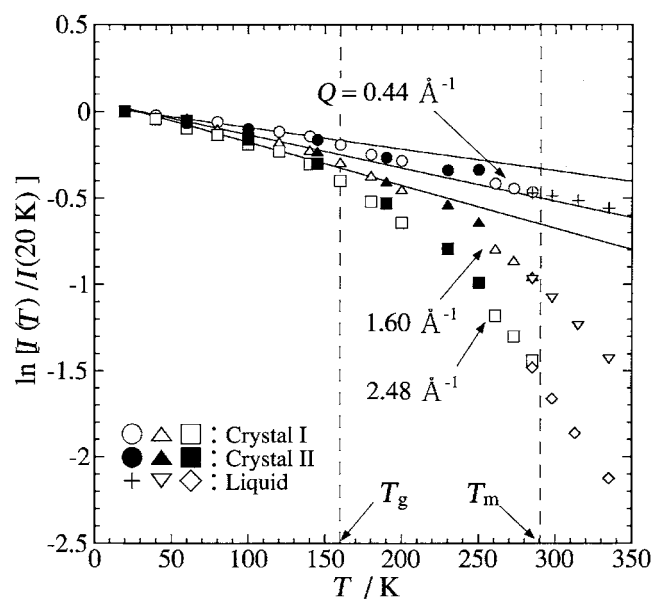


Figure 5. Temperature dependence of the elastic scattering intensities divided by those at the lowest temperature (20 K) for crystal I (○, △, □), crystal II (●, ▲, ■) and liquid (+, ▽, ◇) cyclooctanol. The symbols (○, ●, +), (△, ▲, ▽) and (□, ■, ◇) denote the data at mean Q values of 0.44, 1.60 and 2.48 \AA^{-1} , respectively.

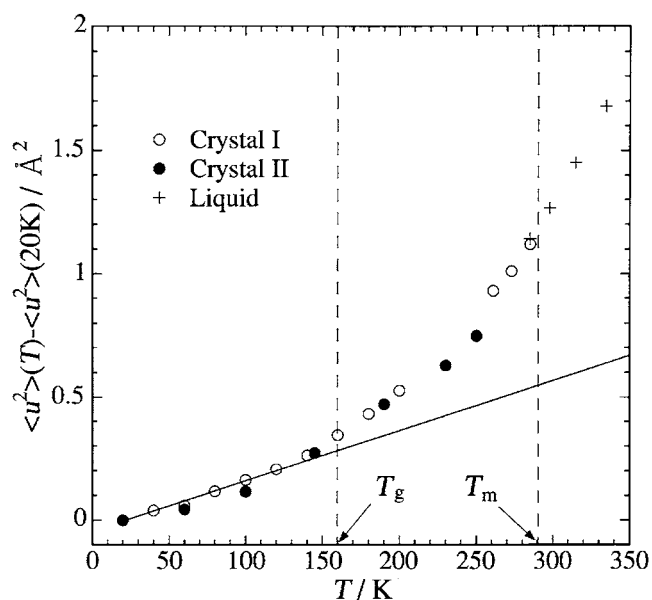


Figure 6. Temperature dependence of the mean square displacements for crystal I (O), crystal II (●) and liquid (+) cyclooctanol.

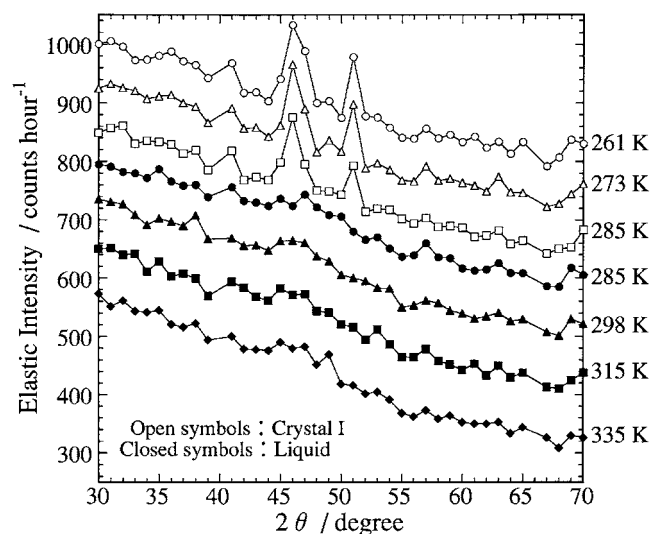


Figure 7. Powder diffraction patterns of crystal I (O, 261 K; Δ , 273 K; \square , 285 K) and liquid (●, 285 K; \blacktriangle , 298 K; \blacksquare , 315 K; \blacklozenge , 335 K) cyclooctanol.

due to the effect of α relaxation. Figure 9 shows χ'' at three different Q values (2.48, 1.60 and 0.44 \AA^{-1}) at 285 K where both plastic and liquid (supercooled) phases could be studied. The open and closed symbols denote the data for plastic and liquid phases respectively. The spectra for plastic and liquid phases are quite similar to each other for all Q values. This result shows an important physical insight that the PC is very similar to liquid in its relaxation dynamics in the terahertz region.

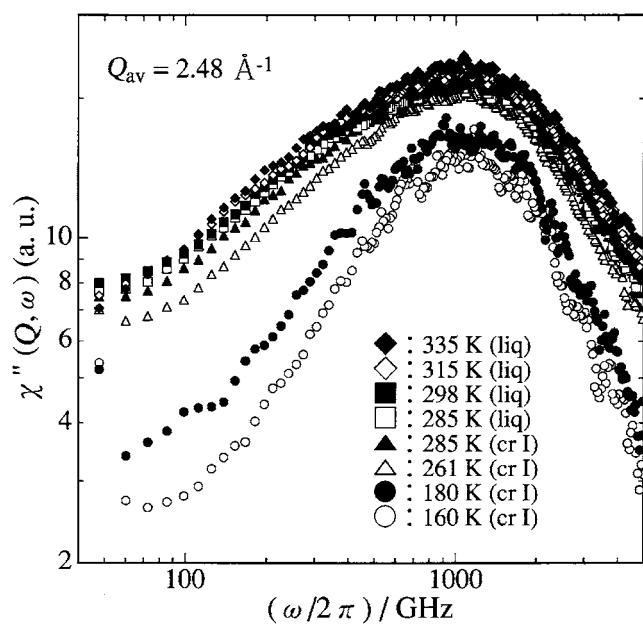


Figure 8. Imaginary part of the density susceptibility of crystal I (○, 160 K; ●, 180 K; △, 261 K; ▲, 285 K) and liquid (□, 285 K; ■, 298 K; ◇, 315 K; ◆, 335 K) cyclooctanol. The data were plotted for the mean Q value of 2.48 \AA^{-1} .

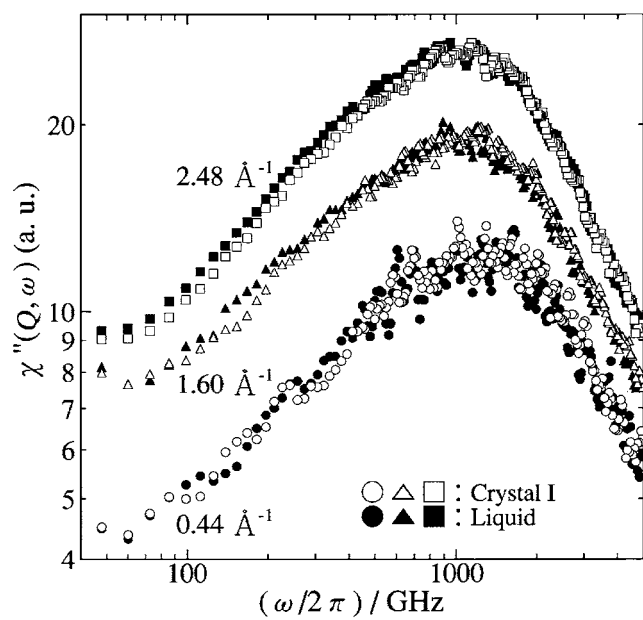


Figure 9. Imaginary part of the density susceptibility of crystal I (○, △, □) and liquid (●, ▲, ■) cyclooctanol at 285 K. The lower (○, ●), middle (△, ▲) and upper (□, ■) data have mean Q values of 0.44 , 1.60 and 2.48 \AA^{-1} respectively.

4. Conclusions

We have found a boson peak and fast β process in the orientational glasses of cyclooctanol. All of the features of these phenomena are similar to those of structural glass formers studied so far. The present results suggest that both the boson peak and fast β process of molecular glass formers are associated with the rotational motions of molecules since the plastic phase and orientational glasses have disorder only in molecular orientations.

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