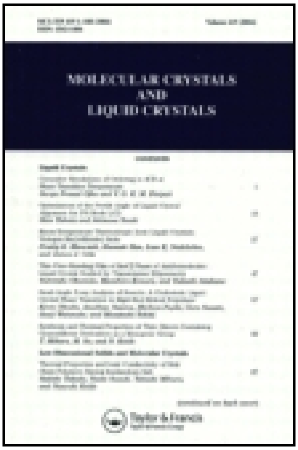

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Molecular Motion and Plastic-phase Transition of Crystalline C_2F_6 as Studied by ^{19}FNMR

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Molecular Motion and Plastic-phase Transition of Crystalline C_2F_6 as Studied by ^{19}F NMR

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Temperature dependence of ^{19}F spin-lattice and spin-spin relaxation times in hexafluoroethane, C_2F_6, was measured between 77 and 185 K. An abrupt change in T_1 was observed at the transition temperature (103.98 K). Reorientation of CF_3 groups takes place with the activation energy (E_a) of 21.6 kJ mol^{-1} in the low temperature phase. In the high-temperature plastic phase the overall rotation of the whole molecule occurs with E_a = 2.0 kJ mol^{-1}, being followed by the self-diffusion of the molecule (E_a = 30.0 kJ mol^{-1}). It is noted that the low-temperature phase transforms to the plastic phase before the averaging out of the anisotropic intermolecular interactions occurs in the C_2F_6 crystals.

Keywords: ^{19}FNMR; C_2F_6; Phase transition; Molecular motion; Plastic phase

INTRODUCTION

Hexafluoroethane, C_2F_6, has two solid phases. The low-temperature phase (Phase II) transforms to a plastic phase (Phase I) at 103.98 K, and the Phase I melts at 173.1 K. The entropy of transition is 35.95 J K^{-1} mol^{-1} and that of fusion is 15.52 J K^{-1} mol^{-1}, the latter being less than a half of the former [1]. The heat capacity measurements ascribed this transition to the hindered

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rotation of the CF_3 group about the C–C bond with the potential barrier of $V_0 = 18.2\,\mathrm{kJ\,mol^{-1}}$ [1]. The existence of the transition from the Phase II to the Phase I has been confirmed by NMR linewidth [2] and IR[3] measurements. According to a powder X-ray diffraction study, the Phase II has monoclinic symmetry with the statistical disorder of fluorine atoms [3]. Later a powder neutron diffraction experiment showed that the orientational disorder of C_2F_6 molecule exists in the Phase I which assumes the body centered cubic structure [4]. However, the neutron diffraction experiment also observed a solid–solid phase transition between 40 and 70 K instead of 103.98 K. So even the existence of the transition at 103.98 K is controversy. The microscopic nature of both solid phases as well as the phase transition between them has not yet been clarified. In order to make the phase sequence certain and to investigate the dynamic aspect of C_2F_6 molecules in both phases the ^{19}F spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_2) were measured between 77 and 185 K.

EXPERIMENTAL

Hexafluoroethane was purchased from Kanto Denka Kogyo Co., Ltd. (stated purity being 99.99%, impurities: air < 100 ppm, H_2O < 100 ppm). It was purified by repeating the vacuum distillation, and degassed by the freeze-pump-thaw cycle before use. Gaseous sample was introduced into an *in situ* NMR probe, in which a sample cell is connected to the vacuum line [5], and was condensed slowly by holding the cell at slightly higher temperature than the melting point and by monitoring the intensity of ^{19}F NMR signal. A JEOL pulsed NMR spectrometer (JNM-FSE-60SS) was used to measure ^{19}F relaxation times at 20.4 and 40.4 MHz. The spin-lattice relaxation time, T_1, was measured by the saturation $-\tau-\pi/2$ pulse sequence. The uncertainty in T_1 was estimated to be within ± 5% in the Phase I, whereas that in the Phase II increased up to ± 10% due to very long T_1. The measurements of spin-spin relaxation time, T_2, were carried out by the solid-echo sequence below 140 K and by the Carr-Purcell pulse sequence above 140 K. Uncertainty in the T_2 measurements was estimated to be about ± 5%. Magnetization recoveries were exponential within the experimental error over the whole temperature range of the measurements except in the temperature region near the melting point. The sample temperature was determined with the accuracy of ± 0.1 K using the Cu-Constantan thermocouples.

RESULTS AND DISCUSSION

Temperature dependence of the ^{19}F spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 is shown in Figure 1 and the detailed behavior of T_1 in the Phases I and II is shown in Figure 2. Distinct jumps of the T_1 value at 104 and 173 K indicate a phase transition and the melting, respectively. In order to investigate the molecular motional process precisely in both phases, T_1 data in Figures 1 and 2 are compared with the temperature dependence of ^{19}F NMR linewidth reported by Gutowsky and Pake: [2] According to them, the second moment of ^{19}F resonance line assumes 15.1 G^2 (linewidth = 11 G) below 90 K, corresponding to the rigid lattice value. On heating the linewidth decreases down to 2.5 G between 95 and 110 K. This linewidth remains constant up to 130 K. Above 130 K it decreases to 0.5 G corresponding to the width by the magnet inhomogeneity, and shows no further change at the melting point.

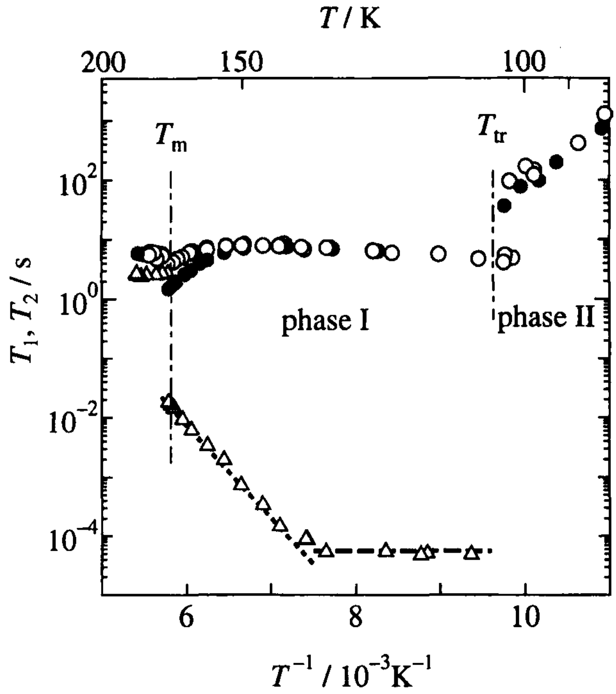

FIGURE 1 Temperature dependence of the ^{19}F spin-lattice relaxation time, T_1, at 20.4 MHz (●) and at 40.4 MHz (○) and the spin-spin relaxation time, T_2, (Δ) in C_2F_6. The broken and the dotted lines are the theoretical T_2 (see in the text).

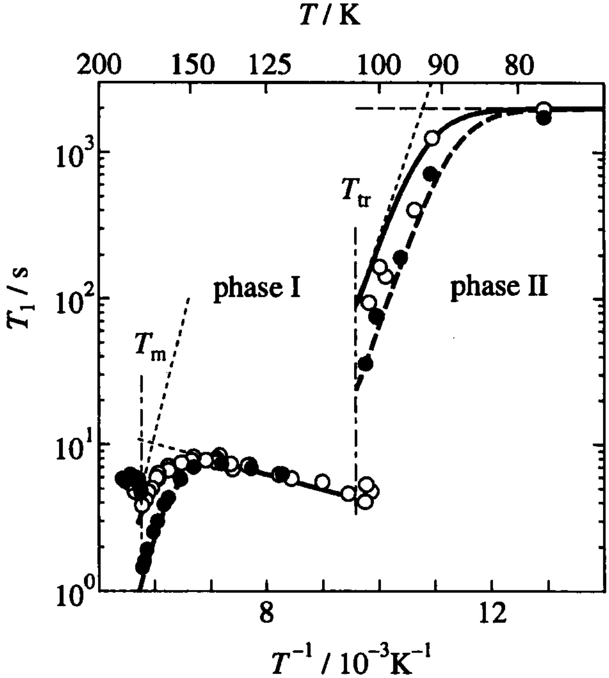

FIGURE 2 Temperature dependence of the ^{19}F spin-lattice relaxation times in C_2F_6 at 20.4 MHz (•) and at 40.4 MHz (o). The solid and the broken curves are the theoretical T_1 (see in the next).

Low-temperature Phase (Phase II)

The decrease in the T_1 observed in the Phase II above 90 K on heating (Fig. 2) is attributed to a slow motion ($\omega_0 \tau_c > 1$, where ω_0 is the angular Larmor frequency and τ_c the correlation time for the motion), being consistent with the reduction of the linewidth observed in Ref. [2]. The dipolar T_1 for a thermally activated classical motion is given by the BPP theory [6] as

$$T_1^{-1} = C\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right), \tag{1}$$

where the dipolar coupling constant C depends on the mode of the motion. τ_c is assumed to obey the Arrhenius relation,

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right), \tag{2}$$

where E_a is the activation energy for the specified motion and τ_0 a pre-exponential parameter. By subtracting the temperature independent contribution of a trace of possible impurities to the T_1 from the observed T_1 we carried out the data fitting and obtained the theoretical T_1 as shown by the solid and the broken lines in Figure 2. From the slope of the T_1 *vs.* 1/T curves the activation energy, E_a, was determined to be 21.6 kJ mol^{-1}. A theoretical analysis of T_1 data by Das [7] showed that it is almost impossible to distinguish between correlated or uncorrelated motion of the CF_3 group about the C – C axis and the rolling of the molecule as a whole. The value of E_a is consistent with the value of the barrier height for the "internal" rotation in the crystal determined by a calorimetry (18.2 kJ mol^{-1}) [8] and with that deduced for the isolated molecule by a Molecular Mechanics calculation (23.7 kJ mol^{-1}) [9]. In addition, this value may also be compared with the height of the potential barrier for the reorientation of CF_3 group in CF_3CCl_3 (16 kJ mol^{-1}) [10], and with the averaged height for the combined $C_2 + C_3$ reorientation of CF_4 (18.6 kJ mol^{-1}) [11 – 14] as recorded in Table I. Therefore the reorientation of the CF_3 group may be responsible for the T_1 in the Phase II of C_2F_6. The possibility that uniaxial molecular rotating about its figure axis takes place can not however be ruled out.

Assuming that the dipole interaction in the CF_3 group dominates the relaxation, and using a second moment data [2] we can estimate the lower limit of the correlation time at transition temperature (103.98 K) to be 1.4×10^{-5} s. This value is much longer than the correlation times for the molecular rotation in many plastic crystals (10^{-9} – 10^{-11} s). The relationship between the correlation time and the transition temperature will later be discussed.

High-temperature Phase (Phase I)

According to Timmerman's criterion for "the plastic crystal", a crystal for which the entropy of fusion, $\Delta S_f/R$, is less than 2.5, (*i.e.*, $\Delta S_f < 20.8$ J K^{-1} mol^{-1}) is regarded as a plastic crystal [15]. For C_2F_6 the entropy of fusion is 15.5 J K^{-1} mol^{-1} [1], suggesting that the Phase I of this compound is a typical "plastic phase" from the thermodynamic point of view.

As can be seen in Figure 2 there are two molecular motional contributions to the spin-lattice relaxation in the Phase I of C_2F_6: One is a fast motion ($\omega_0\tau_c \ll 1$) with a very low activation energy in the low temperature region and the other a slow motion ($\omega_0\tau_c \gg 1$) against a high potential barrier in the high temperature region of the Phase I. There are three possible molecular motional modes that contribute to the nuclear spin relaxation in

TABLE I The activation parameters for molecular motions in crystalline CF_3CF_3, CF_3CCl_3 and CF_4

Compound	*Phase*	*CF_3 reorientation*		*Overall rotation*		*Self-diffusion*	
		(E_a/kJ mol^{-1})	(τ_0/s)	(E_a/kJ mol^{-1})	(τ_0/s)	(E_a/kJ mol^{-1})	(τ_0/s)
CF_3CF_3	I	–	–	2.0 ± 0.3	$(3.6 \pm 0.3) \times 10^{-12}$	30.0 ± 2	$(3.5 \pm 0.5) \times 10^{-15}$
	II	21.6 ± 1.5	$(2.0 \pm 0.5) \times 10^{-16}$[*1]	–	–	–	–
CF_3CCl_3 [10]	I	–	–	5.9	–	35	–
	II and IV	16.1	1.8×10^{-13}[*1]	–	–	–	–
CF_4 [11]	Plastic	–	–	–	–	11.1 ± 0.21	$(7.2 \pm 2.1) \times 10^{-14}$
	Low temp.	18.6	6.6×10^{-23}	–	–	–	–

[*1] The values of τ_0 for the CF_3 reorientation are estimated by using a second moment data [2].

[*2] Averaged value for $C_2 + C_3$ reorientation.

the Phase I, that is, the molecular axial rotation or reorientation about the molecular figure axis, the molecular overall reorientation, and the translational self-diffusion of the molecule. The linewidth of ^{19}F drops from 11 G at 95 K to 2.5 G at 110 K by passing over the transition point, T_{tr} [2], implying that some additional molecular motion to the C_3-rotation is excited above 95 K, though this new motion as well as the C_3-rotation is still too slow to cause an efficient relaxation in the Phase II. This motion which causes to reduce the linewidth down to 2.5 G is certainly assigned to the molecular overall tumbling which may triggers the plastic phase transition.

The ^{19}F T_2 was measured as a function of temperature above ≈ 100 K (see in Fig. 1). At temperatures below about 130 K, we found that $T_2 \approx 5 \times 10^{-5}$ s. If a Gaussian line shape is assumed for the FID,

$$M_2(\text{obs}) = \frac{2}{\gamma^2 T_2^2}. \tag{3}$$

Using $T_2 = 5 \times 10^{-5}$ s, we obtain M_2 (obs) $= 1.3\,G^2$. In the plastic phase, the molecules reorient very rapidly; hence the nuclear dipolar spin-spin interaction is averaged over the motion, and if the reorientation is assumed to be isotropic, the intramolecular interaction is averaged to zero. The intermolecular interaction, on the other hand, is averaged to a value which can be calculated exactly by placing all nuclear spins at the centers of the respective molecules as

$$M_2(\text{theo}) = 6 \times 3I(I+1)\gamma^2 \hbar^2 a_0^{-6} S_1, \tag{4}$$

where a_0 is the cell constant (0.614 nm at 110 K) [4] and S_1 a lattice sum over bcc lattice sites (assuming 5.809 for a powdered sample) [16]. Using Eq. (4), a total second moment M_2(theo) is evaluated to be $1.0\,G^2$, being compared with the value of the M_2(obs). In Figure 1 one can see that the T_2(obs) data are well reproduced by the broken line of T_2(theo) calculated using Eq. (3). We therefore conclude that the motion responsible for a fast motion ($\omega_0\tau_c \ll 1$) in the low temperature region of Phase I is isotropic molecular reorientation.

A new motion which brings about a sharp increase of T_2 (Fig. 1) above *ca.* 130 K and a sharp decrease of T_1 above the same temperature is assigned to the molecular self-diffusion. This assignment is consistent with the fact that the line width is only 0.5 G above 130 K as a result of complete averaging of both the intra- and intermolecular dipolar interactions [2]. We can therefore write the observed spin-lattice relaxation rate $T_{1,\mathrm{obs}}^{-1}$ as

$$T_{1,\mathrm{obs}}^{-1} = T_{1,r}^{-1} + T_{1,d}^{-1}, \tag{5}$$

where $T_{1,r}^{-1}$ is the spin-lattice relaxation rate due to the molecular overall reorientation which is dominant in the low temperature region of Phase I and $T_{1,d}^{-1}$ to the molecular self-diffusion which is dominant in the high temperature region. Since the overall reorientation is so fast that the relation that $\omega_0\tau_r \ll 1$ holds above T_{tr}, where τ_r is the rotational correlation time, we can put that

$$T_{1,r}^{-1} \propto \tau_r \tag{6}$$

between the transition temperature and 130 K. The slope of T_1 in Figure 2 below 130 K gives the activation energy of 2.0 kJ mol^{-1}. This value may be compared with 5.9 kJ mol^{-1} for the molecular overall reorientation of CF_3CCl_3 in its plastic phase [10]. Provided that only the intramolecular dipole–dipole interaction dominates the relaxation in the low temperature region of Phase I, we can estimate the "lower" limit of the correlation time of the overall rotation just above the II–I Phase-transition point (103.98 K) to be 3.6×10^{-11} s, being the similar order of magnitude to the rotational correlation times in many plastic crystals.

The decrease of the linewidth and T_1 above 130 K is due to the onset of the self-diffusion of the C_2F_6 molecule. According to the random walk theory of Wolf, which is based on the vacancy diffusion model in a monatomic bcc lattice of a polycrystalline material [17], T_1 and T_2 are given by

$$\begin{aligned} T_1^{-1} &= 6 \times \frac{3}{8}\gamma^4\hbar^2 I(I+1)\omega_0^{-2}\tau_d^{-1}a_0^{-6} \\ \text{and} \quad T_2^{-1} &= 6 \times \frac{3}{8}\gamma^4\hbar^2 I(I+1)\tau_d a_0^{-6} \end{aligned} \tag{7}$$

under the condition that $\omega_0\tau_c \gg 1$. Here, τ_d is the correlation time of the self-diffusion, a_0 the average jump distance ($\approx$0.614 nm) [4], and γ the gyromagnetic ratio. Equation (7) was used to calculate τ_d from the T_2 data and the dotted line in Figure 1 shows the result. τ_d at the melting temperature is 4.0×10^{-6} s, which may be compared with the mean value of τ_d($1.2 \pm 0.6 \times 10^{-7}$ s) [18] observed at the melting temperature of various bcc solids. The activation energy, 30.0 kJ mol^{-1}, for self-diffusion is comparable with 35 kJ mol^{-1} for CF_3CCl_3 [10].

Since our τ_d data obey closely the Arrhenius activation process, it is reasonable to consider that only a single diffusion mechanism works over the temperature range studied. A quantity which has frequently been used to infer the diffusion mechanism is the ratio of the activation enthalpy ΔH^* to the heat of sublimation L_s. ΔH^* is the sum of the enthalpy of vacancy formation and the enthalpy of molecular migration, each of which equal approximately to L_s when the self-diffusion takes place *via* the single vacancy mechanism [19, 20]. To discuss this point for C_2F_6, we assume that E_a is used for ΔH^*, because the contribution of the $P\Delta V^*$ term to the activation enthalpy, $\Delta H^*(= E_a + P\Delta V^*)$, is usually small (less than 1%). In the case of C_2F_6, the ratio of E_a to L_s [1] is

$$\begin{aligned} E_a/L_s &= 30.0\,\mathrm{kJ\,mol^{-1}}/18.8\,\mathrm{kJ\,mol^{-1}} \\ &= 1.60, \end{aligned}$$

suggesting that the self-diffusion in the plastic phase of C_2F_6 is controlled by the single vacancy mechanism.

The linear relation of Figure 3 implies that τ_d is given empirically by

$$\tau_d = \tau_{d,0} \exp\left(\frac{bT_m}{T}\right), \tag{8}$$

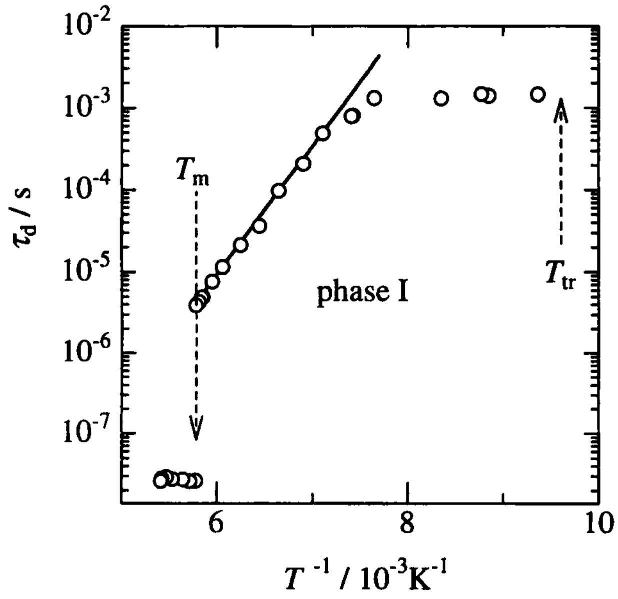

FIGURE 3 Temperature dependence of the correlation time for the self-diffusion in C_2F_6.

where pre-exponential factor $\tau_{d,0} = 3.5 \times 10^{-15}\,\mathrm{s}$, $T_m = 173.1\,\mathrm{K}$ for C_2F_6 and b a constant depending on the structure of the lattice in which diffusion takes place [19]. We estimated b to be 20.9 ± 0.2 for C_2F_6, the value being consistent with $b = 20$ observed in many plastic crystals [18].

Correlation Time and the Phase Transition

A neutron diffraction measurement of the Phase I pointed out the existence of an orientational disorder of C_2F_6 molecules in the crystal lattice [4]. Our ^{19}F relaxation time measurements also confirmed that the self-diffusion of molecules takes place in this phase. These facts as well as the small entropy of fusion indicate that Phase I is definitely a plastic phase. There has been a lot of T_1 measurements on various plastic crystals composed of globular molecules. Based on these works two empirical rules have been established [21, 22]:

(1) Correlation time of the molecular reorientation or the axial rotation in the low temperature phase reaches some value between 10^{-9} and $10^{-11}\,\mathrm{s}$ at the transition temperature to the plastic phase.
(2) Correlation time of the self-diffusion in the plastic phase reaches $\approx 10^{-7}\,\mathrm{s}$ at the melting temperature.

The criterion (1) does not hold in C_2F_6 because the correlation time of CF_3 group reorientation, τ_r, is larger than $1.4 \times 10^{-5}\,\mathrm{s}$ (at 103.98 K) and the axial rotation does not seem to occur in Phase II as mentioned previously. On the other hand the correlation time for the molecular overall rotation becomes $3.6 \times 10^{-11}\,\mathrm{s}$ in the plastic phase just above the transition temperature.

The temperature dependence of ^{19}F T_1, therefore, confirms that the low-temperature phase of C_2F_6 suddenly transforms to the plastic phase before averaging out the anisotropic intermolecular interactions in the low temperature phase. However once it transforms to the plastic phase, the overall rotation of the C_2F_6 molecule is accelerated dramatically and is governed by surprisingly low activation energy above T_{tr}.

In order to clean up the cause of the very slow rotational correlation time ($\tau_r > 10^{-6}\,\mathrm{s}$) in the low temperature phase we introduce some empirical relation proposed previously by Chihara *et al.* [23, 24]. According to them the transition temperature (T_{tr}) of a plastic crystal is related to the height of the potential energy barrier (E_a) hindering the molecular rotation below or above the transition temperature. That is,

$$E_a = \alpha RT_{tr};\ \alpha = 4.1 \text{ for plastic phase,} \tag{9}$$

$$\text{and}$$

$$\alpha = 7.5 \text{ for low-temperature phase.}$$

These relationships mean that the phase transition takes place when the average thermal energy reaches a certain fraction of the potential barrier. It is noted that the factor α does not depend on a particular compound. The experimental values of the barriers in number of plastic crystals are plotted against the transition temperatures in Figure 4. If the potential barrier which hinders molecular rotation is high due to significant anisotropic molecular shape as C_2F_6, the transition must occur as a result of a concerted cooperative molecular movement. It is seen, therefore, that the potential barrier in the low temperature phase is expected to reflect the degree of the anisotropy of the molecules. CF_4 or C_2F_6 experiences a very high barrier in the low temperature phase. Hence either overall or axial molecular rotation can hardly be excited in the low temperature phase. However, suppose that some local molecular motion of the large and anisotropic molecules results

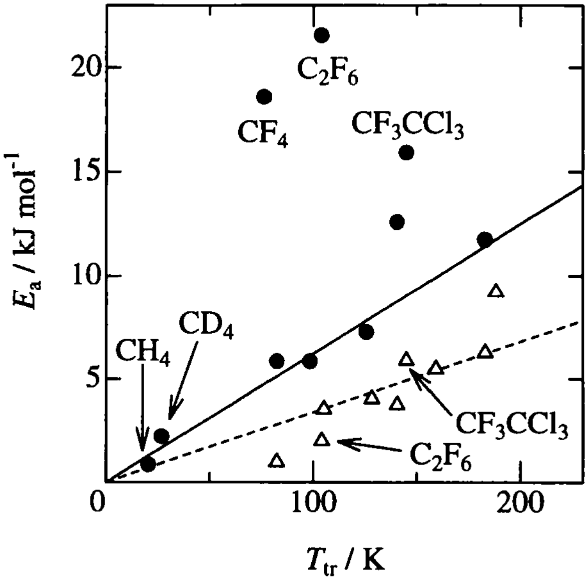

FIGURE 4 Linear relationship between the transition temperature (T_{tr}) and the potential energy barrier (E_a) hindering molecular rotation in several plastic crystals (Refs. [10, 11, 24]): ● low temperature phase, —: $E_a = 7.5\ RT_{tr}$, Δ high temperature phase, - - - : $E_a = 4.1\ RT_{tr}$.

in lowering the hindering potential for the neighboring molecules. It then trigger the cooperative or concerted lowering of the potential barrier height over the whole crystal lattice, stimulating the crystal to undergo a rotational phase transition in which the lattice parameter changes from 0.613 nm in the Phase II to 0.614 nm in the Phase I [4].

The rule (2) holds for the plastic phase of C_2F_6. The correlation time of the self-diffusion, τ_d, is 4.0×10^{-6} s at the melting point (173.1 K). Assuming the average jump distance $a_0 = 0.33$ nm in Eq. (7) corresponding to a half of the value of the lattice constant (≈ 0.614 nm at 110 K) [4], the τ_d is estimated to be 10^{-7} s, which is compared with the τ_d in many other plastic crystals.

CONCLUDING REMARKS

Present work investigated the phase sequence and the molecular dynamics in the crystalline state of C_2F_6 by measuring the nuclear magnetic relaxation times T_1 and T_2. C_2F_6 molecules are found to undergo CF_3 group reorientation with $E_a = 21.6\,\mathrm{kJ\,mol^{-1}}$ in the low temperature Phase II. The Phase II transforms to a plastic phase (Phase I) at 103.98 K. The plastic phase transition of the C_2F_6 crystal is novel in point that the low-temperature phase transforms to the plastic phase before the anisotropic intermolecular interaction is averaged out in the crystal. In the Phase I both the overall rotation of the molecule and the molecular self-diffusion are exited, the latter being understood to take place through a single vacancy mechanism. The correlation time for the self-diffusion τ_d is approximately 10^{-6} s at the melting temperature (173.1 K), as in number of plastic materials ($\approx 10^{-7}$ s).

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