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POLYMORPHISM OF THE CRYSTALLINE 1,1,1-TRICHLORO-2,2,2-TRIFLUOROETHANE. A NEW PLASTIC CRYSTAL

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DTA and Raman spectra showed that slowly cooled CF_3CCl_3 has two transitions from a metastable to the intermediate phase (112 K) and then to the plastic phase (145 K) on heating. The stable low temperature phase obtained by quenching the plastic phase has the transition at 140 K instead of 112 K.

The methyl chloromethane compounds, $(CH_3)_nCCl_{4-n}$ (n=0 to 4), undergo one or more solid-solid phase transitions and their highest temperature phases have been recognized to be plastic crystalline phases. The structure and the molecular dynamic properties of these plastic crystalline phases as well as other brittle phases of these substances have been studied extensively.[1)] We can anticipate that 1,1,1-trichloro-2,2,2-trifluoroethane, which assumes the same molecular symmetry as 1,1,1-trichloroethane (n=1), would show a phase relation similar to that of the methyl chloromethanes. This letter describes the results of differential thermal analysis (DTA) and Raman spectra which were obtained to establish the phase relation of this compound prior to more detailed investigation by magnetic resonance methods. Possible existence of a plastic phase in this material will be proposed.

CF_3CCl_3 was purchased from Aldrich Chemical Company Inc. (stated purity was 99%), dried by Molecular Sieves 4A, and purified by repeating vacuum distillation three times. The final purity was estimated to be better than 99.9% by means of gas chromatography with a Polapack-Q column. The specimens for DTA and the Raman measurements were placed in glass ampules with appropriate diameters, which were sealed under a pressure of helium gas. DTA experiments were carried out on the specimen cooled down to 77 K in two different manners, 1) slow cooling at a rate of 1-2 K/min. and 2) a rapid cooling for which the specimen was quenched by use of liquid nitrogen after slow freezing. Raman spectra were recorded both for the slowly cooled specimen and for the rapidly cooled specimen as in the case of DTA. Temperatures were measured by a Chromel-P-Constantan thermocouple with an accuracy of ±1 K .

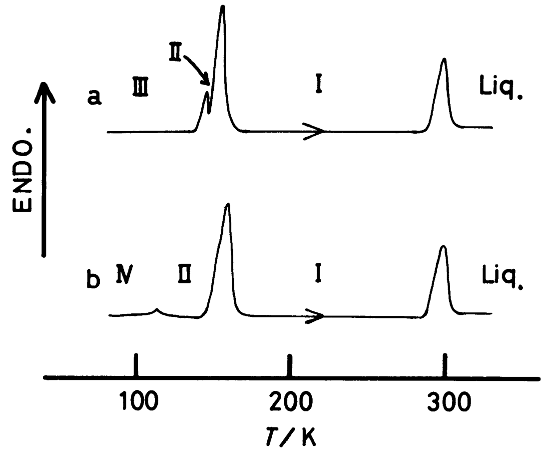
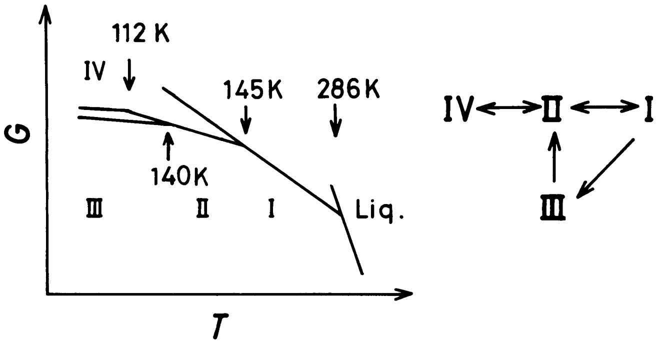


Fig. 1. DTA curves for CF_3CCl_3.
a) Heating run after rapid cooling.
b) Heating run after slow cooling.



a) b)

Fig. 2. a) Schematic Gibbs energy diagram and b) allowed phase transitions in CF_3CCl_3.

The DTA results of heating runs are shown in Fig. 1. In this figure it is found that two solid-solid phase transitions occur in both the slowly cooled and rapidly cooled samples. The phase transitions in the slowly cooled sample occured at 112 K and at 145 K . The anomalous heat effect at 112 K was very small , being suggestive of a higher-order phase transition. The anomaly at 145 K was twice as large as that of melting (at 286 K) and super-cooled by about 6 K . Therefore, the entropy of transition at 145 K is at least four times as large as that of melting; this is a result typical for a plastic crystal. In the case of rapidly cooled specimen, two anomalies appeared at 140 and 145 K on heating, the latter corresponding to the upper phase transition of the slowly cooled sample. Thus we concluded that at least four solid phases can be realized in this material. The phase relation between these four phases (Phase Ⅰ through Ⅳ) is schematically illustrated in Fig. 2a. It should be noted that Phase Ⅲ can appear only when Phase Ⅰ is quenched down to the liquid nitrogen temperature and it can not be obtained by slow cooling or even by annealing Phase Ⅱ as indicated in Fig. 2b. In other words, the

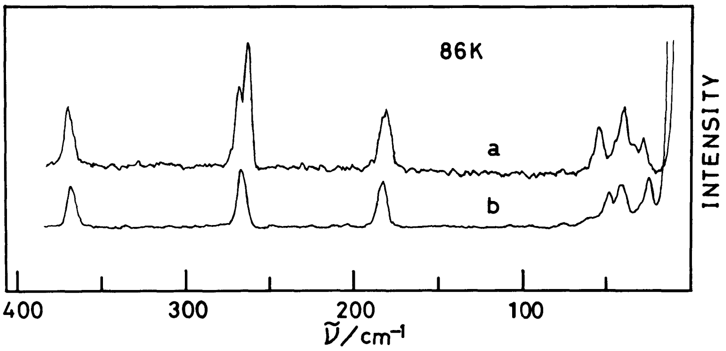


Fig. 3. Raman spectra of polycrystalline CF_3CCl_3 measured at 86 K after a) rapid cooling and b) slow cooling.

transitions I-III and III-II are monotropic.

Phase III and Phase IV gave different Raman spectra from each other as shown in Figs. 3a and 3b, respectively; the CF_3 degenerate rocking mode$^{2)}$ in Phase IV gave only a single peak at 267 cm^{-1} while that in Phase III split into two peaks. In addition, the bands in the lattice vibrational region in Phase III are more complicated than those in Phase IV. These facts suggest that Phase IV has a higher symmetry than Phase III. The Raman spectra of Phase IV showed only a small shift and a slight broadening of each band with an increase in temperature up to 145 K where the lattice vibrational modes coalesced, forming a broad envelope near the Rayleigh line as shown in Fig. 4. No significant changes in the spectra in the low-frequency region were observed at the higher-order phase transition point (112 K), which fact implies that the change in the crystal structure from Phase IV to Phase II, if any, must be very small. The drastic broadening above the phase transition point from Phase II to Phase I strongly suggests that a rapid overall reorientation of molecule as a whole is taking place in Phase I ; this fact also supports the idea that Phase I is a plastic crystal.

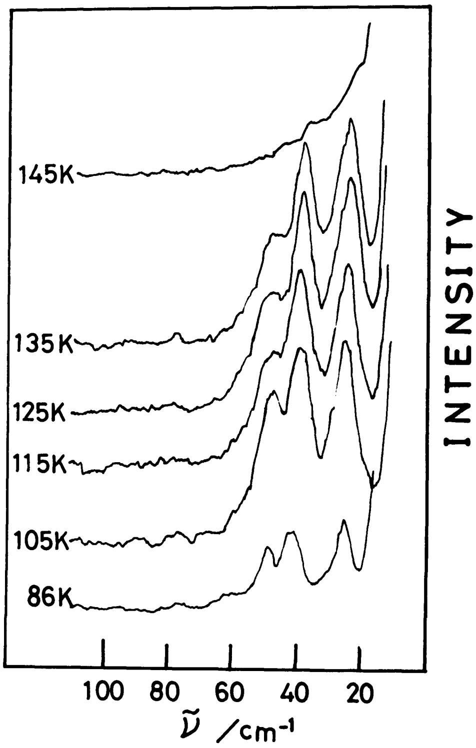


Fig. 4. Temperature dependence of Raman spectrum of slowly cooled polycrystalline CF_3CCl_3.

Our preliminary ^{35}Cl nuclear quadrupole resonance(NQR) and ^{19}F nuclear magnetic resonance(NMR) experiments gave results consistent with those from Raman measurements: we observed only one NQR line in Phase IV at 40.707 MHz at 77 K indicating that crystal symmetry in Phase IV is higher than C_3, whereas Phase III gave three lines at the same frequencies as those reported by Barton.3) We also have evidence based on the relaxation time measurements of ^{19}F NMR in Phase I which shows that the molecules are rapidly reorientated randomly and that molecular self-diffusion is also excited near the melting point; this is what is usually expected for a plastic crystal or an orientationally disordered crystal.

In conclusion, the sequence of the most stable phases of 1,1,1-trichloro-2,2,2-trifluoroethane below its melting point is Phase III below 140 K, Phase II between 140 and 145 K, Phase I between 145 and 286 K (a plastic phase), and Liquid above 286 K. There is another metastable Phase IV which exists only below 112 K. It is interesting to note that the ultimate phase at the lowest temperature studied (Phase III) is not accessible from Phase II but can only be realized through rapid cooling of Phase I.

References

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