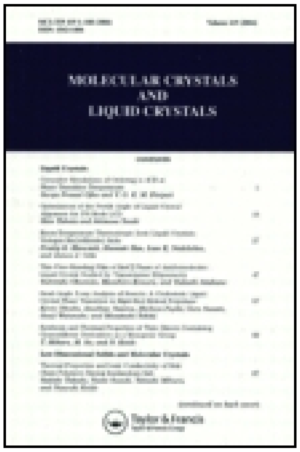

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Polymorphism of the Crystalline Methylcholoromethane Compounds, II

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Polymorphism of the Crystalline Methylchloromethane Compounds, II

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Abstract—A single-crystal X-ray diffraction study, based on results obtained from differential scanning calorimetry, showed that methylchloroform and 2,2-dichloropropane behave in a manner similar to carbon tetrachloride.

The results of a low-temperature X-ray diffraction study of the methylchloromethane compounds have been reported in a previous publication (*MCM–I*).[1] These compounds, which have the general formula, $(CH_3)_n$ C Cl_{4-n}, where n varies from 0 to 4, are composed of approximately spherical molecules. The solid phases undergo crystallographic transitions as the temperature is lowered.

In the previous paper, it was reported that carbon tetrachloride ($n = 0$) was unusual in that two different crystallographic phases (*Ia* and *Ib*) were found to exist in the high-temperature region. It was also reported that only three of the compounds ($n = 0,3,4$) formed a high-temperature, disordered crystallographic phase that was face-centered cubic with a unit cell dimension of approximately 8.5 Å.

In a recent differential scanning calorimetry (DSC) investigation,[2] the five methylchloromethane compounds were studied over a temperature range from −150° to their melting points. Analysis of these data indicated that methyl chloroform ($n = 1$) and 2,2-dichloropropane ($n = 2$) also formed face-centered cubic phases (*Ia*) in the high-temperature region, in addition to the other phases (*Ib*) already noted. A single-crystal X-ray diffraction investigation, utilizing the techniques described in *MCM–I*, verified this fact. The results of the X-ray study are given in Table 1, which follows the same format as Table 2 of *MCM–I*.

TABLE 1 Crystal Data for Face-Centered Cubic Phases of Methyl Chloroform and 2,2-Dichloropropane

Name	Methyl Chloroform	2,2-Dichloropropane
Data obtained at (°C)‡	−49	−49
Unit Cell Dimensions (Å)	8.39	8.45
Molecules/Unit Cell	4	4
Volume/molecule (Å 3)	148	151
Density, calc. (g/cc)	1.50	1.24

‡ These temperatures are for supercooled samples of the materials, while corresponding figures reported in Table 2 of *MCM–I* are for samples that have been warmed from below the transition temperature. For this reason the two sets of temperatures cannot be compared directly.

The results of the present DSC investigation[2] are in agreement with two other studies of carbon tetrachloride ($n = 0$)[3,4]. In each case it is found that Phase *Ia* is formed directly from the melt, while Phase *Ib* is formed either by warming from Phase *II* or by cooling past a critical temperature within the region in which the disordered high-temperature phases (*I*) exist.

In the study reported in *MCM–I*, the technique used to prepare crystals of methyl chloroform ($n = 1$) and 2,2-dichloropropane ($n = 2$) always bypassed the face-centered cubic phase. These two materials tended to supercool to a great extent, and crystallization was always initiated by touching the glass tube holding the samples with a cotton swab dipped in a dry-ice-acetone mixture. In this manner the formation of the face-centered cubic phase was consistently prevented.

In the present investigation the sample was cooled by the gas-stream until crystals started to form. At this point the gas-stream was quickly warmed up to a temperature well above the point where Phase *Ib* would occur. In this manner it was possible to isolate the face-centered cubic phases of methyl chloroform and 2,2-dichloropropane.

No other unreported phases were detected for the methylchloromethane compounds.

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