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# Orientalional order in two-component plastic crystals 2,2-dichloropropane-carbon tetrachloride

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<sup>1</sup>H nuclear magnetic resonance (NMR) spectra and birefringence of noncubic plastic single crystals (CH<sub>3</sub>)<sub>2</sub>CCl<sub>2</sub>-CCl<sub>4</sub> have been measured. The investigation has demonstrated that in these crystals weak preferred orientations of molecules were observed. Concentration dependence of orientational ordering matrix of (CH<sub>3</sub>)<sub>2</sub>CCl<sub>2</sub> molecules has been obtained from computer simulations of NMR line shape and birefringence data. It has been found that all ordering matrix elements become zero at mole fraction of 2,2-dichloropropane 0.5.

## I. INTRODUCTION

Plastic crystals are molecular crystals with low entropy of fusion. They are characterized by high rotational mobility of molecules which changes a little on melting, and relatively high translational diffusion.<sup>1,2</sup> For deeper understanding of the nature of the plastically crystalline state it is important to know the degree of orientational ordering in these crystals. The information on the orientational order in one-component cubic plastic crystals may be obtained for example from optical Kerr effect<sup>3</sup> and depolarized Rayleigh scattering.<sup>4</sup> The degree of orientational order in some noncubic plastic crystals was determined from the value of birefringence,<sup>5,6</sup> from quadrupolar splitting in <sup>2</sup>H NMR spectra,<sup>7,8</sup> from dipolar splittings in <sup>1</sup>H NMR spectra.<sup>9,10</sup>

It is most interesting to study two-component systems forming plastic phases that give more detailed information about the regularities of orientational ordering. Some experimental investigations of dielectric and thermodynamic properties, x-ray studies and NMR studies of molecular motion in two-component systems have been performed.<sup>2</sup> However, as we know, there is only one communication in which orientational order has been studied in mixed plastic crystals and only in mixtures of two isotope species of the same compound, namely sulfolane.<sup>10</sup>

Here we report the results of <sup>1</sup>H NMR and birefringence investigations of orientational order of 2,2-dichloropropane molecules in the two-component system 2,2-dichloropropane-carbon tetrachloride.

Phase diagram for this system does not seem to be studied. Pure components are known to have plastic crystal modifications: 2,2-dichloropropane<sup>11,12</sup> in the temperature range 188–240 K and carbon tetrachloride<sup>13</sup> in 225.1–250.4 K form rhombohedral plastic phases (Ib). Morrison with co-workers reported<sup>14</sup> another temperature interval for noncubic plastic phase of 2,2-dichloropropane 201–253 K. Besides, both compounds in solidifying can transform into cubic modifications (phase Ia).<sup>13,14</sup>

The question about the relative stabilities of phases Ia and Ib has not been finally solved. So in the birefringence

study<sup>15</sup> of carbon tetrachloride it has been established that Ib could transform into Ia. However the thermodynamic properties show unambiguously that phase Ib should be more stable for CCl<sub>4</sub>.<sup>11,16</sup>

The situation with respect to 2,2-dichloropropane is more vague. The birefringence measurements<sup>14</sup> suggest that phase Ia is more stable for this substance, although the melting point of the phase Ib is higher than Ia and on heating the phase II always transforms into Ib.

Described in this paper NMR and optical data indicated that (1) mixtures of CCl<sub>4</sub> and 2,2-dichloropropane form solid solutions in plastic state in the whole range of mutual concentrations, (2) these mixtures have cubic and noncubic plastic modifications, which correspond to phases Ia and Ib defined by Silver and Rudman,<sup>11</sup> (3) noncubic plastic phases are uniaxial crystals, and (4) the angle  $\alpha$  of rhombohedral unit cell seems to depart from the magnitude 90° to opposite sides at mole fractions of 2,2-dichloropropane larger and smaller 0.5.

We studied orientational order of molecules in noncubic plastic phases. The polymorphism of mixed methylchloromethanes will be discussed in the particular paper.

## II. EXPERIMENT

The sample preparation was the following. 2,2-dichloropropane was fractionally distilled. The melting point of noncubic phase, 239.7 K, agreed with the literature value.<sup>11,12</sup> Chromatographically pure carbon tetrachloride with the melting point 250.4 K (phase Ib) was used without further purification. As soon as the dissolved gases prevented the growth of single crystals the samples were degassed by freezing-pumping-thawing procedure. The mixtures prepared were sealed into NMR glass tubes.

For the registration of <sup>1</sup>H NMR spectra we used a high resolution "Tesla" spectrometer BS 487.

From polycrystal spectra (representing broad structureless lines) it is difficult to obtain information about orientational order. Therefore it was necessary to study the single crystal samples. The melting points of investigated compounds and their mixtures are essentially lower than room temperature. Consequently it is preferable to grow the crystals directly in NMR spectrometer.

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For visual optical control of the single crystal quality two holes were made in the NMR probehead, Fig. 1. A light guide was inserted into one hole to illuminate the sample. The light passed through a polarizer installed in the probehead, the thermostating system Dewar, the sample and got out through the second hole. The polarizer was mounted so that polarization plane was parallel to the tube axis. The analyzer was placed beyond the probehead. Measurements were performed with crossed polarizer and analyzer. The walls of Dewar and tube did not show appreciable birefringence and did not complicate the observation.

On slow cooling of liquid solutions cubic phases were formed as a rule. Such behavior was observed in the studies of polymorphism in pure carbon tetrachloride and 2,2-dichloropropane.<sup>13,14</sup>

Single crystals of the phase Ib were grown in the following way. A sample was cooled by liquid nitrogen and after solidifying its large part was heated above the melting temperature. When almost all the sample was melted and only a little crystal left, the temperature was lowered to necessary level and the crystal growth was observed.

In case of noncubic single crystal the fringe pattern was uniform along the whole sample. In case of several single crystals the grain boundaries could be clearly seen. We investigated only the single crystals which had no defects visible in the polarized light.

The probehead construction allows the sample to rotate around only one axis. To measure the tube rotation angle  $\alpha$

limb was mounted on the tube. The orientation of single crystal was determined with the help of crystal optical observations and angular dependence of NMR spectra as described beneath.

Maximum resolution of the spectra is reached at the angle  $\theta_{zH}$  between crystal optical axis and magnetic field equal zero. Therefore it is desirable to grow the single crystals with the orientation of optical axis perpendicular to the tube axis. After a number of attempts the single crystals were obtained with more or less suitable orientations. Minimum values of the angles  $\theta_{zH}$  were close to zero and differed a little for different crystals (Fig. 2).

The method of measuring optical birefringence has been fully described elsewhere.<sup>6</sup>

### III. RESULTS AND DISCUSSION

We have found that 2,2-dichloropropane in noncubic plastic phase exhibit angular dependence of  $^1\text{H}$  NMR spectra being similar to that obtained earlier in another uniaxial plastic crystal—sulfolane.<sup>9,10</sup> The analogous angular dependence has proved to be observed also in noncubic plastic phases of mixtures  $(\text{CH}_3)_2\text{CCl}_2\text{--CCl}_4$ .

$^1\text{H}$  NMR spectra of mixed plastic single crystals were measured at various concentrations and temperatures. Typical spectra are shown in Fig. 2.

Angular dependence of NMR spectra may be due to various factors: heterogeneity of a sample, anisotropy of chemical shift, anisotropy of quadrupolar interactions, and intra- and intermolecular dipolar interactions. The first factor may not be taken into account because the uniform cylindrical samples were used. Neither the second nor the third factors can explain the orientational dependence of NMR

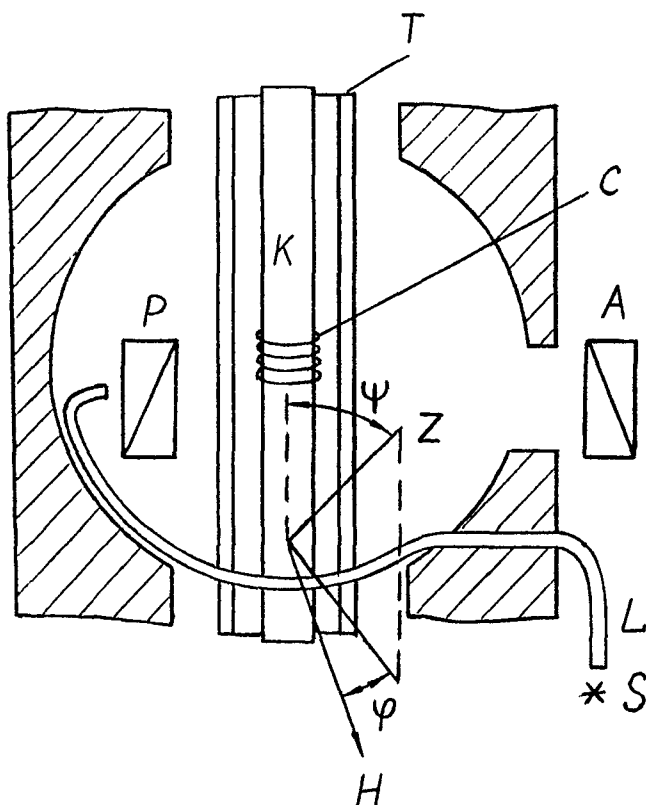


FIG. 1. Probhead of NMR spectrometer. A—analyzer, P—polarizer, L—light guide, S—light source, K—tube with the single crystal, z—crystal optical axis, T—Dewar, C—rf coil, H—magnetic field.

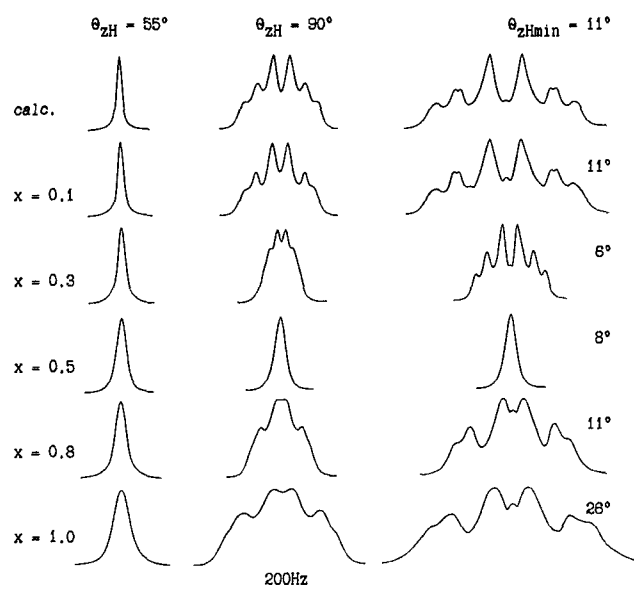


FIG. 2. 80 MHz  $^1\text{H}$  NMR calculated and observed spectra of two-component plastic single crystals  $(\text{CH}_3)_2\text{CCl}_2\text{--CCl}_4$  at various mole fractions  $x$  of  $(\text{CH}_3)_2\text{CCl}_2$  and angles  $\theta_{zH}$ .  $T = 228$  K. Calculated spectra were obtained for  $S_{aa} = 0.040$ ,  $S_{bb} - S_{cc} = 0.022$ ,  $\Delta\nu = 30$  Hz.

spectra in investigated system, since the value of anisotropy of proton chemical shifts is small and proton spin is equal to  $1/2$ .

In such systems as liquids in external fields, liquid and plastic crystals having one symmetry axis not lower than the third order, in case of rapid molecular motion (reorientation, diffusion) the secular part of intramolecular dipolar Hamiltonian has the form:<sup>17</sup>

$$\hat{H}/h = \sum_{i>j} \frac{3}{2} b_{ij} \left( \hat{I}_{Hi} \hat{I}_{Hj} - \frac{1}{3} \hat{I}_i \hat{I}_j \right), \quad (1)$$

where  $b_{ij}$  are dipolar couplings constants:

$$b_{ij} = \frac{\gamma^2 \hbar}{2\pi r_{ij}^3} \sum_{\alpha, \beta} S_{\alpha\beta} (3 \cos \theta_{ij\alpha} \cos \theta_{ij\beta} - \delta_{\alpha\beta}) \times \frac{1}{2} (3 \cos \theta_{zH} - 1), \quad (2)$$

$\gamma$  is gyromagnetic ratio of the proton,  $r_{ij}$  is the distance between protons  $i$  and  $j$ ,  $\theta_{ij\alpha}$  is the angle between  $r_{ij}$  and the molecular axis  $\alpha$ ,  $\theta_{zH}$  is the angle between crystal optical axis  $z$  and magnetic field,  $S_{\alpha\beta}$  is the ordering matrix:

$$S_{\alpha\beta} = \frac{1}{2} \langle 3 \cos \theta_{z\alpha} \cos \theta_{z\beta} - \delta_{\alpha\beta} \rangle, \quad (3)$$

where  $\alpha, \beta = a, b, c$  are the axes of molecule-fixed Cartesian system.  $\theta_{z\alpha}$  is the angle between the axis of molecule  $\alpha$  and the optical crystal axis;  $\delta_{\alpha\beta}$  is the Kroneker symbol. Averaging in Eq. (3) is done over all the orientations of molecules.

If  $a$  axis lies along the  $C_2$  symmetry axis,  $b$  and  $c$  lie in the two mirror planes and  $b$  axis connects C atoms of methyl groups then the ordering matrix will be diagonal and only two independent parameters  $S_{aa}$  and  $S_{bb} - S_{cc}$  will be left. Since the methyl groups in a 2,2-dichloropropane molecule rotate around C–C bond, values  $b_{ij}$  should be averaged over methyl groups rotations.

Unfortunately precise geometry of 2,2-dichloropropane molecules in plastic phase is not known. Molecular structure was studied by electron diffraction.<sup>18</sup> The values of the angles C–C–C and Cl–C–Cl equal to  $110.5 \pm 5^\circ$  and  $109.5 \pm 2^\circ$ , respectively, and the length of C–C bond  $1.54 \pm 0.02$  Å have been obtained.

The information on molecular structure in noncubic plastic phase may be obtained in principal from  $^1\text{H}$  NMR spectra.<sup>10</sup> But in the case of 2,2-dichloropropane there are only two different dipolar coupling constants: between the protons belonging to the same methyl group and between the protons of different methyl molecular groups. The number of unknown order parameters is also equal to 2. Thus for 2,2-dichloropropane it is impossible simultaneously to get information on order parameters and geometry of molecules.

Factors in the formula (2) depending on the geometry of 2,2-dichloropropane molecule were calculated using a model of free rotation of methyl groups, assuming tetrahedral valence angles H–C–H and C–C–C and the bond lengths 1.1 Å for C–H and 1.54 Å for C–C.

Intramolecular dipolar interactions depend on the angle  $\theta_{zH}$  as one can see from formula (2). The orientation of crystal optical axis relatively to magnetic field was determined with the help of observations in the polarized light and from the angular dependence of intramolecular dipolar interaction by the following way. As the polarizer in the

NMR probehead has been mounted so that polarization plane was parallel to the tube axis it was easy to arrange the crystal optical axis into the polarization plane with the help of observation of fringe pattern in the white light. Such orientation corresponded to the angle  $\varphi$  between the magnetic field and the plane passed through the tube axis and optical axis being equal to  $90^\circ$ . The angle  $\psi$  between optical axis and tube axis could be measured also by optical method.<sup>6</sup> However in this experiment it appeared easier to use NMR data. NMR spectra have minimum width at the angle  $\theta_{zH}$  equaled to magic one, and measuring corresponding angle  $\varphi$  it is easy to calculate the angle  $\psi$  because three angles are connected by a relation:  $\cos \theta_{zH} = \sin \psi \cos \varphi$  (see Fig. 1).

To determine orientational order parameters from spectrum line shape we found the eigenvalues of Hamiltonian (1) and calculated the transition probabilities for the six-spin system. The LAOCN 3 program,<sup>19</sup> modified to include dipolar coupling was used. Indirect spin–spin coupling were not taken into account because of their small value. Intermolecular dipolar couplings were considered by convolving with the Lorentz line. Its width  $\Delta\nu$  was found from the spectra obtained at  $\theta_{zH} = 55^\circ$ , because with such crystal orientation, as it may be seen from Eq. (2), intramolecular dipolar couplings are equal to zero. By varying orientational order parameters a complete coincidence of the calculated and experimental spectra was achieved (Fig. 2).

The coincidence of the calculated and experimental spectra directly proved the fact that spectra anisotropy and shape are defined first of all by intramolecular dipolar interactions. Note, that we have not found angular dependence of the Lorentz line width used for the calculation of intermolecular interactions.

Calculating NMR spectra we assumed that phase Ib of mixtures is uniaxial crystal as well as corresponding phases of pure substances. It is obvious that in the case of biaxial crystal with rapid molecular motion (reorientation, diffusion), the NMR spectra depend on two angles characteriz-

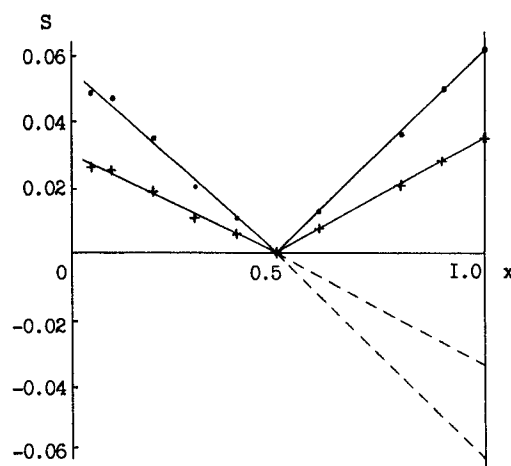


FIG. 3. Absolute values of orientational order parameters  $S_{aa}$ —• and  $S_{bb} - S_{cc}$ —+ of 2,2-dichloropropane molecules obtained from NMR data.  $T = 228$  K. Dashed line—order parameters obtained with the use of birefringence data.  $x$ —mole fraction of 2,2-dichloropropane.

ing the orientation of crystal with respect to magnetic field. Measured experimental angular dependence of NMR spectra for all investigated single crystals with various crystal orientations with respect to NMR tube is finely described by formula (2). It is the evidence of uniaxial nature of these crystals. Another proof can be obtained by optical measurements as will be shown below.

The absolute values of the order parameters  $S_{aa}$  and  $S_{bb} - S_{cc}$  of 2,2-dichloropropane molecules and the sign of their ratio were obtained from NMR line shape calculation. The results are presented on Fig. 3. The error does not exceed 10%.

Analogous calculations have been performed for angles C-C-C different from tetrahedral ones. Order parameters obtained for pure 2,2-dichloropropane at various angles C-C-C are represented in Table I.

The same character of concentration dependence as on Fig. 3 was observed at other temperatures. However on cooling the value of  $\Delta\nu$  increases, that decreases the spectra resolution and accuracy of the determination of order parameters at low temperatures, especially at large concentrations of 2,2-dichloropropane, since the value of  $\Delta\nu$  rises strongly also with the increase of proton contents in the sample. Therefore the detailed investigation of concentration dependence of orientational order was performed at one temperature 228 K.

$\text{CCl}_4$  and 2,2-dichloropropane have stable rhombohedral plastic phases with almost identical dimensions of the unit cells.<sup>20</sup> The absolute values of orientational order parameters of 2,2-dichloropropane molecules at concentrations of this substance tending to 0% and 100% are also very close, Fig. 3. In this respect it is rather unexpected that order parameters reduce to zero and both simultaneously.

NMR data do not allow one to define the signs of order parameters and to conclude whether the concentration dependence of order parameters is monotonous or its inclination changes by opposite one at mole fraction of 2,2-dichloropropane close to 0.5. To resolve ambiguities in the signs it is necessary to use the data of other methods.

Additional and independent information can be obtained from the birefringence measurements in this system.

TABLE I. The ratio and absolute values of the order parameters of 2,2-dichloropropane molecule calculated from  $^1\text{H}$  NMR spectra for pure substance at various angles C-C-C.

Angle C-C-C	$ S_{aa} $	$ S_{bb} - S_{cc} $	$S_{aa}/(S_{bb} - S_{cc})$
104.5	0.050	0.026	1.91
105.5	0.052	0.027	1.90
106.5	0.054	0.029	1.88
107.5	0.056	0.030	1.86
108.5	0.059	0.032	1.84
109.5	0.061	0.034	1.82
110.5	0.064	0.036	1.80
111.5	0.067	0.038	1.77
112.5	0.070	0.040	1.75
113.5	0.073	0.042	1.72
114.5	0.076	0.045	1.70

The concentration dependence of  $\Delta n$  value in noncubic plastic mixed crystals  $(\text{CH}_3)_2\text{CCl}_2 - \text{CCl}_4$  is demonstrated on Fig. 4. The error of  $\Delta n$  does not exceed  $5 \times 10^{-5}$ .

Crystal optical investigation did not reveal any deflexion from uniaxiality of pure substances and their mixtures in noncubic plastic phase: rotating the tube with single crystal we observed only two minima of light intensity in crossed polaroids which corresponded to orientations of the single optical axis perpendicular and parallel to the polarization plane. Besides that we obtained the same values of  $\Delta n$  for the samples with different orientations of single crystals relatively to the tube axis, that is one more evidence of uniaxiality.

Earlier birefringence has been measured in noncubic plastic phases of pure carbon tetrachloride<sup>15</sup> and 2,2-dichloropropane.<sup>14</sup> The values of  $|\Delta n| = 1.10(\pm 0.02) \times 10^{-3}$  for  $\text{CCl}_4$  and  $1.1(\pm 0.6) \times 10^{-2}$  for  $(\text{CH}_3)_2\text{CCl}_2$  have been obtained. These results are significantly different from ours. At the same time our method has given  $\Delta n$  value for example of ice<sup>6</sup> which was in fair agreement with  $\Delta n$  obtained by other methods.<sup>21</sup> The differences in  $\Delta n$  values for  $\text{CCl}_4$  and  $(\text{CH}_3)_2\text{CCl}_2$  obtained in various studies must be referred apparently to the account of large experimental difficulties in application of method<sup>22</sup> based on measuring of components intensities of the polarized light passing through a crystal.

In order to determine the signs of order parameters from the birefringence value one of the theory is to be used which links  $\Delta n$  and the order parameters.<sup>23</sup> However we do not know precise structure of the crystal. Moreover the experimental data on tensor of polarizabilities of the 2,2-dichloropropane molecule also are not available.

Nevertheless since the sign change of the first derivative of  $\Delta n$  concentration dependence is not observed at mole fraction of 2,2-dichloropropane  $x = 0.5$  one can suppose that parameters of noncubic lattice and order parameters change monotonously in the whole range of concentrations

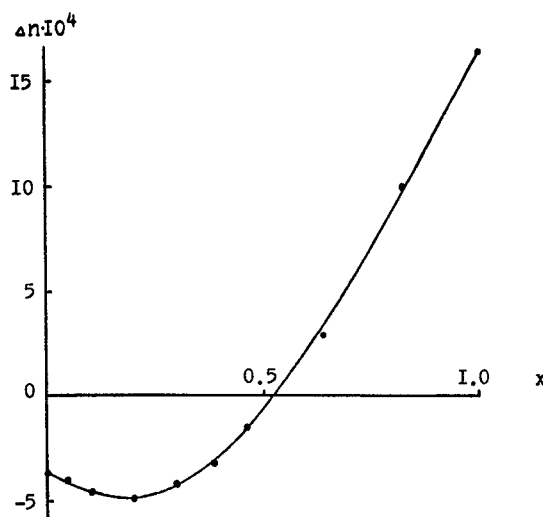


FIG. 4. Birefringence of mixed noncubic plastic crystals  $(\text{CH}_3)_2\text{CCl}_2 - \text{CCl}_4$ .  $T = 233$  K.  $x$ —mole fraction of 2,2-dichloropropane.

and at  $x = 0.5$  the signs of order parameters are replaced by opposite ones. This conclusion does not depend on the used theoretical model.

If we use the assumption of Vuks,<sup>24</sup> that the local field  $F$ , effecting the molecule, coincides with the direction of external field  $E$ :

$$F = \frac{1}{3}(n^2 + 2)E, \quad (4)$$

where  $n^2 = 1/3(n_x^2 + n_y^2 + n_z^2)$ ,  $n_i$  are the principal refractive indices, then we obtain the relationships between refractive indices  $n_i$  and average values of polarizabilities of molecule  $\alpha_{ii}$ , which have the form

$$\frac{n_i^2 - 1}{n^2 + 2} = \frac{4}{3} \frac{N_A \rho}{M} \langle \alpha_{ii} \rangle, \quad (5)$$

where  $N_A$ —Avogadro number,  $M$ —molar weight,  $\rho$ —density of 2,2-dichloropropane. It is to be noted that the use of Vuks formula does not need the knowledge of crystal structure.

Since polarizability tensor is the second rank tensor, the difference of average molecular polarizabilities along and across the optical crystal axis is equal to

$$\langle \alpha_{zz} - \alpha_{xx} \rangle = \sum S_{\sigma\delta} \alpha_{\delta\sigma}, \quad (6)$$

where  $\alpha_{\delta\sigma}$  are the elements of polarizability tensor in molecule-fixed system.

Taking into account the symmetry  $C_{2v}$  of 2,2-dichloropropane molecule we obtain

$$\langle \alpha_{zz} - \alpha_{xx} \rangle = S_{aa} \left( \alpha_a - \frac{\alpha_b + \alpha_c}{2} \right) + \frac{1}{2} (S_{bb} - S_{cc}) (\alpha_b - \alpha_c). \quad (7)$$

Since the polarizability tensor was not experimentally obtained for the calculation of polarizabilities we need to use the valence-optical scheme. For polarizabilities of methyl group, bonds C–C and C–Cl the values  $\alpha_{||}^{CH_3} = 1.79$ ;  $\alpha_1^{CH_3} = 2.03$ ;  $\alpha_{||}^{C-C} = 1.56$ ;  $\alpha_1^{C-C} = 0.11$ ;  $\alpha_{||}^{C-Cl} = 3.86$ ;  $\alpha_1^{C-Cl} = 1.97 \text{ \AA}^3$  have been taken.<sup>25</sup> The bond angles have been assumed tetrahedral. As a result of the calculation we found  $\alpha_a = 10.29 \text{ \AA}^3$ ,  $\alpha_b = 9.83 \text{ \AA}^3$ ,  $\alpha_c = 10.74 \text{ \AA}^3$ . So the values of principle polarizabilities differ not more than by 10%, that is comparable with the error of such kind of calculations. Therefore unambiguous data on the anisotropy of polarizabilities may be obtained only by experimental studies.

It is obvious that from birefringence one cannot determine two independent order parameters. However we can take account of their ratio found from NMR spectra (Table I). Then the use of our crystal optical data, Fig. 4, the values of polarizabilities obtained from the valence-optical scheme and the values of  $n, \rho$  measured in liquid phase<sup>26</sup> (the difference of refractive indices and density in plastic phase from corresponding values in liquid is not important for determination of the order parameter signs), yield the following results: for pure 2,2-dichloropropane  $S_{aa} = -0.18$ ,  $S_{bb} - S_{cc} = -0.10$ . Consequently in mixed noncubic plastic crystals at large concentrations of 2,2-dichloropropane

both order parameters  $S_{aa}$  and  $S_{bb} - S_{cc}$  are negative and at low concentration—positive, Fig. 3.

The Cl–C–Cl and C–C–C bond angle deviations from tetrahedral by  $\pm 3^\circ$  lead to changes of the values of principal molecule polarizabilities calculated in accordance with valence-optical scheme, which, however do not influence the conclusion about the order parameter signs, the values of the order parameters changing by several times, approaching to the NMR values as the angles increase. One should not attach great importance to the difference of results obtained by two methods and make far going conclusions particularly about the geometry of molecule, since for weakly anisotropic molecules the polarizability anisotropy is highly sensitive to small changes of the valence-optical scheme parameters and as a consequence is calculated not quite exactly. Thus in our opinion the discrepancy of the optical and NMR data is due to the error in the calculation of polarizability values based on valence-optical scheme, but not due to the used Vuks model. For confirmation we can refer to the investigation of plastic tert-butyl bromide,<sup>6</sup> for which experimental values of polarizabilities are known. We have measured birefringence of noncubic plastic phase II of tert-butyl bromide. Its molecules have threefold symmetry axis, hence one parameter for the description of their orientational order is enough. Therefore it is possible to determine the degree of orientation from the birefringence. The order parameters calculated from the value of  $\Delta n$  and from experimental value of polarizability anisotropy of tert-butyl bromide molecules with the help of Vuks formula have agreed well with order parameters obtained from quadrupolar splitting of  $^2H$  NMR spectra for perdeuterated molecules.<sup>8</sup>

According to Rudman<sup>20</sup> carbon tetrachloride and 2,2-dichloropropane have rhombohedral lattice with the dimensions of the unit cells  $a = 14.42$  and  $14.68 \text{ \AA}$ , respectively. X-ray analysis does not allow us to distinguish rhombohedral lattice of plastic methylchloromethanes from primitive cubic one and detect the angle  $\alpha$  of rhombohedral unit cell equal to  $90.0^\circ$ . Birefringence and NMR spectroscopy of single crystals are more sensitive to the deflection of crystal lattice from the cubic symmetry and give additional information about the crystal structure of plastic methylchloromethanes.

Two possible explanations of concentration dependence of orientational order parameters in the investigated system may be suggested.

(1) The change of molecular interactions in mixed plastic crystals versus contents leads only to the change in orientations of molecules, the positions of molecular centers of mass being little changeable, and the difference  $\alpha-90^\circ$  keeps the sign.

(2) On changing the concentration the monotonous alteration of the angle  $\alpha$  takes place in such a way, that the difference  $\alpha-90^\circ$  changes the sign at mole fraction of 2,2-dichloropropane  $x = 0.5$ . Zero values of the order parameters and of birefringence correspond to the formation of cubic crystal lattice.

Unlike one-component crystals, in which the situation with  $\Delta n = 0$  in noncubic crystal phase is hardly imaginable, in the case of two-component crystals it is possible, e.g., un-

der the contributions of both components to the birefringence compensation.

The equality to zero of the orientational order parameters  $S_{\alpha\beta}$  is not also unambiguous evidence of the cubic symmetry. For example  $S_{aa}$  may be equal to zero if  $a$  axes of molecules are aligned at the angle  $55^\circ$  to the magnetic field.

Thus the first assumption can not be quite excluded. However it is hardly probable, while the second assumption naturally explains all experimental data, including the simultaneous reduction to zero of the intramolecular dipolar couplings and consequently both orientational order parameters and also the value of  $\Delta n$  at the same concentration of 2,2-dichloropropane.

In conclusion it should be noted that the investigation of the ordering degree in noncubic plastic crystals is to a great extent analogous to NMR investigations of the molecules dissolved in liquid crystal solvents.<sup>17</sup> This is due to the fact that in both cases the values of correlation times for molecular reorientations are sufficiently small and close to those observed in liquids. It is interesting that the degrees of molecule orientations in both systems are very close in spite of different phase states of these systems.

Because of respectively slow translational diffusion in plastic crystals as compared with the diffusion of small molecules dissolved in liquid crystal matrix, the value of intermolecular broadening of  $^1\text{H}$  NMR spectra even in mixed plastic crystals with one of the components which does not contain protons is order of  $10\text{--}10^2$  Hz. It makes impossible the determination of the order parameter signs from the angular dependence of chemical shifts or indirect spin-spin couplings, the value of which at such degree of orientation ( $S \sim 0.01\text{--}0.1$ ) is a few Hz. In this respect the combination of NMR and birefringence measurements is one of possible ways of the solution of the problem.

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