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Dielectric properties of condensed fluoromethanes and fluoromethane mixtures

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Dielectric measurements were performed on liquid and solid $(CF_4)_{1-x}$ $(CMF_3)_x$ with M = H, Cl, and Br. The dielectric behavior of the polar molecules in the liquid state is well described by an Onsager equation. At the melting point, pure hydrogenated and brominated fluoromethanes condense into dipolar rigid phases, while pure tetrafluoromethane forms a plastic crystal. $CClF_3$ exhibits dipolar relaxational phenomena in the solid state. The data indicate that near the melting point this compound is close to a transition into a plastic phase. Mixtures of CF_4 with CHF_3 and $CBrF_3$ exhibit monotectic phase diagrams with a limited solubility in the liquid state and complete immiscibility in the solid state. However, formation of mixed crystals is found in $(CF_4)_{1-x}$ $(CClF_3)_x$ which exhibits a eutectic phase diagram.

I. INTRODUCTION

Mixed molecular crystals have recently attracted much interest because of the rich variety of physical phenomena that can be studied. Pure molecular compounds often exhibit elastically and electrically ordered phases. Dilution of anisotropic molecules with isotropic atoms or ions can yield crystals that transform into orientational glass states.[1] The complete miscibility of $(KBr)_{1-x}$ $(KCN)_x$[2], $(Ar)_{1-x}$ $(N_2)_x$,[3] and $(Kr)_{1-x}$ $(CH_4)_x$[4] in the solid phases allows the study of how glassy behavior develops out of the orientationally ordered phases by diluting the anisotropic molecules with isotropic defects. On the other hand, by increasing the concentration of molecular defects in the pure compounds (e.g., KBr, Ar, and Kr) the influence of molecular interactions on the single particle relaxation processes can be examined. The present study of the dielectric properties of mixtures of fluoromethanes is part of a large program to study dipolar relaxation in plastic phases, at electric phase transitions and in orientational glass states.

The dielectric properties of the fluoromethanes under consideration have already been studied in their liquid states.[5–7] Dielectric measurements on solid $CBrF_3$ and $CClF_3$ have been reported for temperatures above 77 K.[7] The solid phases of CF_4, i.e., the plastic phase above $T_{\alpha\beta} = 76.2$ K and the rigid phase below this temperature have been investigated theoretically using molecular dynamics calculations[8] and experimentally with x-ray,[9,10] NMR,[11,12] calorimetric,[13–15] Raman,[16] and infrared[17,18] techniques. At low temperatures tetrafluoromethane α-CF_4 (sometimes called CF_4II) exhibits complete ordering in a monoclinic cell (most probable space group $C2/c$).[9,10,18] Above 40 K a fraction of the molecules starts to reorient.[12,15] In constrast to α–CH_4, where the molecules on two of eight sublattices are orientationally disordered,[19] a two phase model has been proposed for α–CF_4[12]: paraelastic clusters characterized by reorienting molecules coexist with rigid lattice domains. Finally above $T_{\alpha\beta}$, CF_4 is orientationally disordered. The structure of this plastic phase, which melts at 89.5 K is not known.[8]

NMR[20] and spectroscopic[16,21] investigations on solid CHF_3 indicate that within the orientationally ordered structure the molecules reorient between symmetry-equivalent positions around their threefold axis. These reorientations were found to obey an Arrhenius law.[20] No phase transitions were detected in the solid state.[22] A Raman and infrared investigation of $CBrF_3$ carried out at 77 K indicated ordering in a monoclinic cell.[23]

The vapor pressures of a number of binary liquid mixtures containing CF_4,[24,25] CHF_3,[26] and $CClF_3$[27] have been studied. A specific heat singularity was reported for liquid $(CF_4)_{1-x}$ $(CHF_3)_x$ near the critical solution temperature,[28] where the liquids decompose. The phase diagram of CF_4 and Ar was found to be eutectic.[9]

One aim of the present study was to investigate whether simple tetrahedrally coordinated dipolar molecules can be introduced into nonpolar CF_4 in the solid state. Our experimental results indicate that $CBrF_3$ and CHF_3 are totally immiscible in solid CF_4. However, a finite miscibility exists in the case of $CClF_3$. This miscibility behavior is in accord with regular solution theory using molecular properties of the pure compounds. Therefore, in the following, the results on several pure trifluoromethanes are described together with their phase diagrams with tetrafluoromethane. Any quantitative discussion of the complex dielectric relaxation which is found in solid $(CF_4)_{1-x}$ $(CClF_3)_x$ is avoided. A full account of the results on $(CF_4)_{1-x}$ $(CClF_3)_{1-x}$ will be given, after completion of the work, in a forthcoming paper.

This article is organized as follows: First, we describe the experimental setup that was used for the dielectric measurements and for the supplementary optical investigations. Then the results on the pure fluoromethanes are presented in the liquid and in the solid state. Finally, the mixed fluoromethanes are discussed and the experimentally determined phase diagrams are shown.

II. EXPERIMENTAL

Fluoromethanes with a nominal purity of 99.8% and 99.999% ($CClF_3$ and CF_4) were purchased from LINDE. The single compound systems were condensed as liquids into a dielectric cell of coaxial design[29] and a volume of about 0.7 cm^3. Mixtures were prepared in a vessel assuming ideal gas behavior and additivity of partial pressures and allowed to

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condense into the capacitor. To homogenize the solid samples, they were liquified again under their vapor pressure and cooled into the solid phase. Cooling rates between 10^{-1} and 10^{-4} K/s were used in order to test for the formation of voids during solidification. However, it was found that the measured dielectric constants did not depend on the cooling rate, except for $CClF_3$. Since the mixtures were prepared under their vapor pressure, the concentrations in the samples containing CHF_3 differ considerably from the nominal ones. Under the assumption of a linear interpolation of the polarizabilities between the pure compounds, the sample with a nominal composition of $(CF_4)_{0.5}$ $(CHF_3)_{0.5}$ had a concentration of 62% of trifluoromethane. The concentration of mixtures with $CBrF_3$ and $CClF_3$ is believed to be accurate to within 3%.

Dielectric constants were measured in the frequency range from 10^2 to 10^5 Hz using a HP4274A LCR meter and for temperatures between 2 and 300 K. Since no frequency dependence was observed in the liquid state, only the 10 kHz data are shown, since at that frequency the LCR meter exhibits the highest accuracy. The error in the dielectric constant is estimated to be less than 0.1% for the liquids and to be at least one order of magnitude larger for the solid phases due to defects and due to the thermal expansion of the samples. These effects lead to an incomplete filling of the measuring cell at temperatures far below the melting point of the sample.

An optical cryostat was used to observe the liquid–liquid decomposition directly. Approximately 1 cm^3 of mixtures of fluoromethanes was introduced into the measuring cell at a temperature well above where decomposition was expected. A divergent beam of light transmitted through the sample was observed on a screen. The formation of an interface between the two liquids was taken as evidence for the decomposition. The temperature was slowly cycled around the critical solution temperature to maintain thermal equilibrium.

III. RESULTS AND DISCUSSION

A. Liquid fluoromethanes

In Fig. 1 the real part of the dielectric constant $\varepsilon'(T)$ of the fluoromethanes CF_4 and CHF_3 is compared with measurements by Tremaine and Robinson.[5] Results on CHF_3 by Gerschel *et al.*[6] are not included in the figure. They show slight deviations at low temperatures which may be due to the presence of approximately 2% of impurities in their samples. Our results on $CClF_3$ and $CBrF_3$, shown in Fig. 2, are in excellent agreement with measurements by Miller and Smyth.[7]

The nonpolar liquid CF_4 exhibits a linear increase of the dielectric constant with decreasing temperature. This was attributed to a corresponding effect in the mass density by applying the Clausius Mosotti equation.[5] The Curie-like $1/T$ behavior in the dielectric constant of the polar fluoromethanes is well described by the Onsager equation[30]

$$\frac{(\varepsilon'-\varepsilon\infty)(2\varepsilon'+\varepsilon\infty)}{\varepsilon'(\varepsilon\infty+2)^2}=\frac{4\pi}{9}\cdot g\cdot\frac{n\mu^2}{k_B(T-\Theta)}, \qquad (1)$$

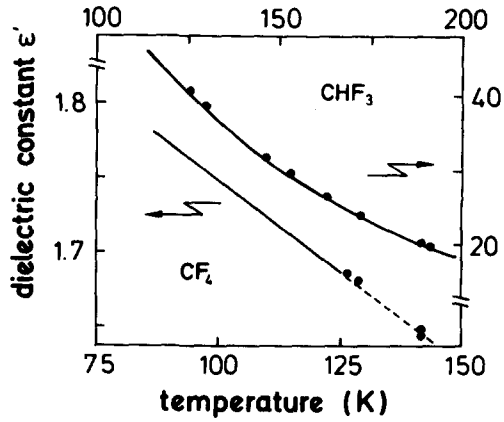

FIG. 1. Dielectric constants of liquid CF_4 (lower and left scales) and CHF_3 (upper and right scales) vs temperature. The data of this work are represented as solid lines. They were taken at 10 kHz. The results of Tremaine and Robinson (Ref. 5) (full circles) were taken at 50 kHz. The fit to the dielectric constant of CHF_3 using Eq. (1) and the parameters given in Table I coincides with the solid line. The broken line is an extrapolation of our results towards higher temperatures.

where $\varepsilon\infty$ denotes the dielectric constant in the high frequency limit, n the particle density, μ the dipole moment, and g the Kirkwood correlation factor. The factor g is a measure of the short range order in the liquid state. For CHF_3 a Curie–Weiss constant Θ has to be included. Although these quantities may not be constant in the considered temperature range, good fits were achieved with the parameters given in Table I. The choice of n (the boiling point values were taken) may lead to an overestimation of g by some 10%–20%. Moreover, $\varepsilon\infty$ and g are correlated. By fitting the liquid state data of CHF_3, $\varepsilon\infty$ turned out to be the mean value of that determined by microwave absorption.[6]

For CHF_3 the positive value of Θ and the relatively large correlation factor g might be experimental evidence that *at least in part the molecular dipoles tend to align parallel, perhaps due to hydrogen bonding.*[5] This was also concluded by Tremaine and Robinson on the basis of a modified Onsager equation.

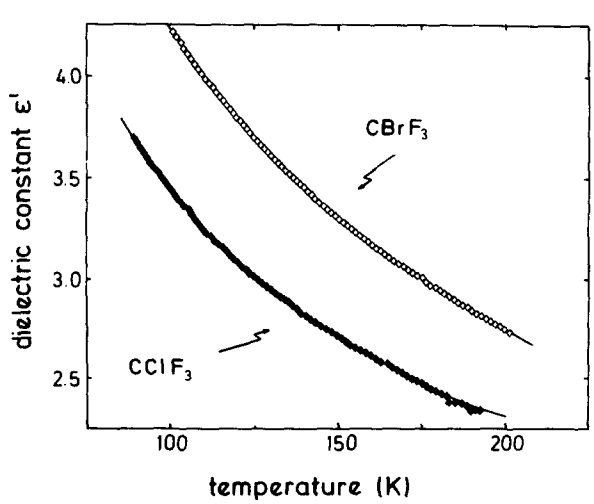

FIG. 2. Dielectric constants of liquid $CClF_3$ and $CBrF_3$. Excellent agreement with measurements by Miller and Smyth (Ref. 7) is achieved. The results of fits using Eq. (1) are shown as solid lines.

TABLE I. Dipole moment in the gas phase μ, particle density n, as calculated from the mass density (Refs. 36 and 37) and heat of vaporization ΔH(Ref. 36) at the boiling point were taken from the literature. From ΔH the solubility parameters δ are obtained (Ref. 34). These values are compared to $\delta_0 = 14.7(\mathrm{J/cm^3})^{1/2}$ for CF_4 at the boiling point of this substance (Ref. 36). Fitting the liquid state data of the fluoromethanes to Eq. (1) yields the dielectric constant in the high frequency limit $\varepsilon\infty$, the correlation factor g and the Curie–Weiss temperature Θ.

CMF_3 M =	H	Cl	Br
μ/D	1.65[a]	0.5[a]	0.65[b]
$n/(10^{21}\,\mathrm{cm^{-3}})$	12.4	8.80	8.06
$\Delta H/\mathrm{J/cm^3}$	371.7	228.7	241.8
$\lvert\delta-\delta_0\rvert/(\mathrm{J/cm^3})^{1/2}$	6.6	2.5	3.9
$\varepsilon\infty$	2.7	1.3	1.45
g	1.6	1.5	1.2
Θ/K	60	0	0

[a] Reference 33.
[b] Reference 35.

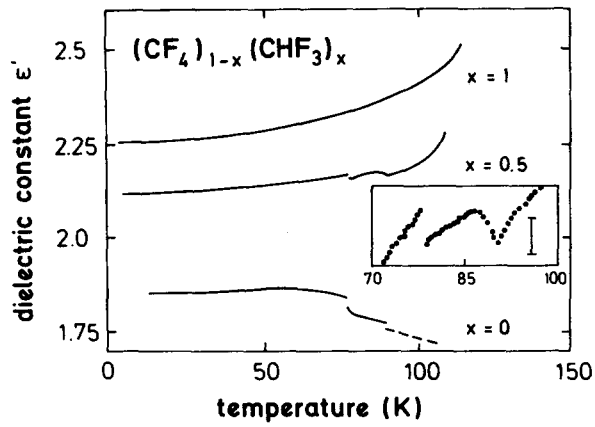

FIG. 3. Dielectric constants of solid $(CF_4)_{1-x}$ $(CHF_3)_x$ mixtures for $x = 0, 0.5$, and 1 shown as solid lines. The broken line represents liquid state data. The behavior of the solid state phase transitions in a $(CF_4)_{0.5}$ $(CHF_3)_{0.5}$ sample is shown in the inset. The discontinuities are due to the α–β transition and the melting point of the part of the sample that contains CF_4. The bar corresponds to $\Delta\varepsilon' = 0.005$.

In the halogenated trifluoromethanes where hydrogen bonding is obviously absent, strong correlation effects are not expected. The values for the correlation factor g confirm this assumption. For $CBrF_3$ g is compatible with unity while correlation effects show up in $CClF_3$.

B. Solid fluoromethanes

With rising temperature the dielectric constant of CF_4 (Fig. 3) passes through a slight maximum near 50 K, drops at the α–β transition and falls again at the melting point. In some runs however, the dielectric constant showed discontinuities at around 65 K and increased at the α–β transition. This may be due to different crystal structures of CF_4 in the α and the β phase. Depending on the orientation of the plastic crystal within the sample holder strains may occur within the sample which crack it some degree below $T_{\alpha\beta}$. This hypothesis is supported by very reproducible measurements of the dielectric constant of methane.[31] CH_4 is cubic above and below the plastic phase transition.[19]

Under the assumption that the Clausius Mosotti equation also holds for the solid state of CF_4, molar polarizabilities were calculated using the dielectric constant and mass densities from x-ray experiments.[9,10] At $T = 76.5$ K, just above the α–β transition, the molar polarizability P is (9.6 ± 0.08) cm^3 which is almost identical to the value for the liquid phase.[5] The polarizability drops by about 1% at $T_{\alpha\beta}$ and decreases upon further cooling. Since the polarizability is inversely proportional to the frequency Ω_{TO} of the corresponding transverse optical mode,[32] the increase of Ω_{TO} is estimated to be 20% between 77 and 40 K. This coincides with the temperature dependence of the lowest and strongest far infrared absorption band in CF_4.[18] While the lattice effects can easily be monitored with the dielectric technique, the reorientational behavior seen with NMR[11,12] is unobservable here. This is due to the fact that CF_4 has no permanent dipole moment.

The temperature dependence of the dielectric constant ε' of CHF_3 is shown in Fig. 3. ε' decreases continuously with decreasing temperatures indicating that no solid state phase transitions take place. Calorimetric investigations have shown that the entropy of CHF_3 is zero at $T = 0$.[22] Together with our dielectric constant data, this provides clear evidence that the dipoles freeze into an ordered phase at the melting point. The reorientations of the CHF_3 molecules around their threefold axis[20] leave the orientation of the dipole moment fixed. The complete lack of dispersion in our dielectric data demonstrates that no relaxations other than that around the C–H molecular axis take place. However, librational modes of the dipolar axis lead to an increase of the dielectric constant when the melting point is approached. To estimate the magnitude of the tilt angle of these modes, reliable values for the refractive indices and mass densities in the solid state are required.

The dielectric constant of solid $CBrF_3$ behaves like that of CHF_3. No discontinuities are observed between the melting point ($\varepsilon' = 2.20$ which compares favorably with measurements by Miller and Smyth[7]) and $T = 10$ K ($\varepsilon' = 2.12$). While the structure of films of $CBrF_3$ was reported to be monoclinic,[23] qualitative conclusions concerning the dynamics of this compound cannot be drawn from low frequency dielectric measurements alone. Possible reorientations around the threefold axis of $CBrF_3$ should be observable in NMR experiments. An analysis of the librations of the molecules is possible only on the basis of our dielectric measurements, if refractive indices and mass densities are available. Also, like CHF_3, $CBrF_3$ exhibits no dipolar relaxations in the solid state and becomes an electrically ordered solid.

The experimental findings in $CClF_3$ are rather different. The dielectric constant and dielectric loss show strong frequency dependence. This demonstrates that dipolar reorientations dominate the dielectric response in the solid state. Figure 4 shows the frequency dependence of the real part of the dielectric constant vs T. However, it is important to note that the dipolar relaxation in solid $CClF_3$ depends on the cooling rate. A preliminary analysis of the dielectric measurements done so far shows the following features: the static susceptibility decreases with decreasing temperature. Between the melting point and a temperature of $T \approx 40$ K the

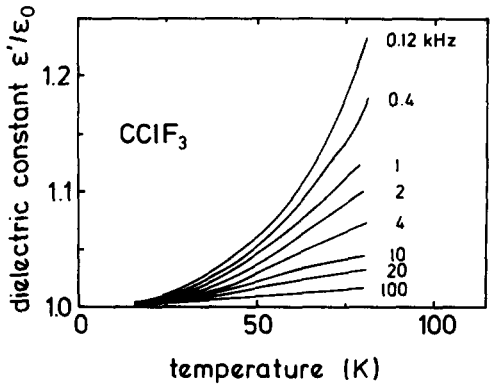

FIG. 4. Dielectric constant of solid $CClF_3$ vs temperature for different measuring frequencies. The data are normalized to the dielectric constant in the low temperature limit $\varepsilon_0 \approx 2$.

relaxation rate is almost constant and very small (roughly 10 kHz). A crossover to activated behavior is observed for $T < 40$ K with an energy of activation of the order of 100 K. The dielectric loss peaks are broader than expected for a Debye relaxator. We interpret the temperature dependence of the static susceptibility as evidence that electric order is established just below the melting point, but that $CClF_3$ is very close to a transition into a plastic phase, where the dipoles can reorient between symmetrically equivalent positions. However, in order to clarify the dynamics of $CClF_3$ further experimental work is needed.

C. Fluoromethane mixtures

1. $(CF_4)_{1-x}$ $(CHF_3)_x$ and $(CF_4)_{1-x}(CBrF_3)_x$

One aim of the present investigation was to explore the possibility of doping a simple molecular crystal like CF_4 with dipolar defects. This would have allowed the study of dipolar reorientations in the crystal field of the surrounding molecules and the influence of dipolar interactions on the dynamical responses of the polar molecules under consideration. However, our experimental results indicate a complete immiscibility of CHF_3 and $CBrF_3$ in CF_4. As can be seen from Fig. 5 for $(CF_4)_{1-x}$ $(CHF_3)_x$ mixtures, the transition temperatures remain unchanged over a wide range of concentrations. In samples with an increasing content of trifluoromethane, the step in the dielectric constant at the α–β transition decreases roughly linearly and was undetectable in $(CF_4)_{1-x}$ $(CHF_3)_x$ with $x \geqslant 0.88$. Data on a 50% sample are included in Fig. 3, clearly demonstrating the effect of decomposition. Similar results were obtained for samples with other dipole concentrations. The lowest nominal concentration of CHF_3 in CF_4 was approximately 1%. Even at this low concentration, no dipolar relaxation processes of trifluoromethane in the crystal field of tetrafluoromethane could be detected. Plotting the phase transition temperatures vs concentration, a phase diagram as shown in Fig. 5 is produced. The picture reveals all the features of a monotectic phase diagram,[38] indicating limited solubility even in the liquid state. To demonstrate the decomposition of the liquid phases, optical experiments have been performed on $(CF_4)_{1-x}$ $(CHF_3)_x$ and $(CF_4)_{1-x}$ $(CBrF_3)_x$ near $x = 0.5$. The temperatures where an interface between the two liquids became apparent are indicated in Figs. 5 and 6.

Vapor pressure measurements on liquid $(CF_4)_{1-x}$ $(CHF_3)_x$ mixtures in fact showed limited miscibility with a critical solution temperature of 130.5 K.[24] From specific heat measurements, a critical temperature of 132.1 K was concluded.[28] These results agree well with the $T_c = 131$ K found in our optical experiment. Proceeding in the same way as described above, the phase diagram for $(CF_4)_{1-x}$ $(CBrF_3)_x$ is obtained (Fig. 6). It reveals the same features as the $(CF_4)_{1-x}$ $(CHF_3)_x$ system and can also be regarded as of monotectic type.

2. $(CF_4)_{1-x}$ $(CClF_3)_x$

Complete liquid state miscibility is found for $(CF_4)_{1-x}$ $(CClF_3)_x$. Consequently the dielectric constants of these mixtures evolve smoothly when the concentration is varied (Fig. 7). A Curie law,

$$\varepsilon' = \varepsilon\infty + x^* 4\pi C/T, \tag{2}$$

is applicable if the dipole concentration x is not so small that the linear behavior of ε' of CF_4 dominates ($x \geqslant 0.15$). This implies a linear scaling of the Curie constant with x. The parameters are found to be $\varepsilon\infty = 1.3$ and $C = 18$ K.

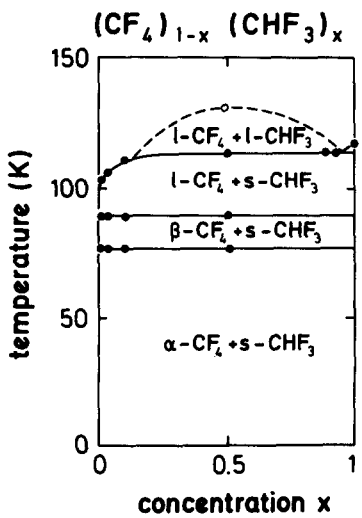

FIG. 5. Phase diagram of $(CF_4)_{1-x}$ $(CHF_3)_x$ as deduced from dielectric (full circles) and optical (open circle) measurements. Lines are drawn as required by thermodynamics. The diagram is characteristic of a monotectic phase diagram, that is, a miscibility gap appears in the liquid phase.

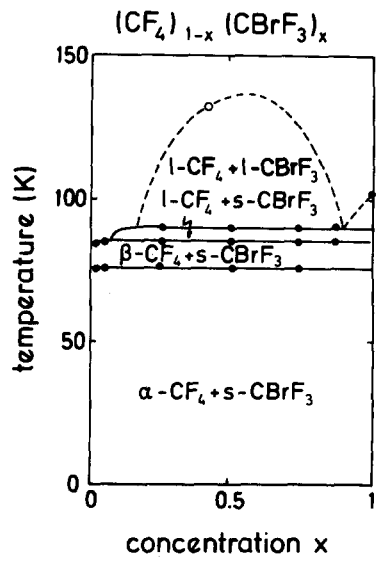

FIG. 6. Phase diagram of $(CF_4)_{1-x}$ $(CBrF_3)_x$ as deduced from dielectric (full circles) and optical (open circle) experiments. Lines are drawn to complete a monotectic phase diagram.

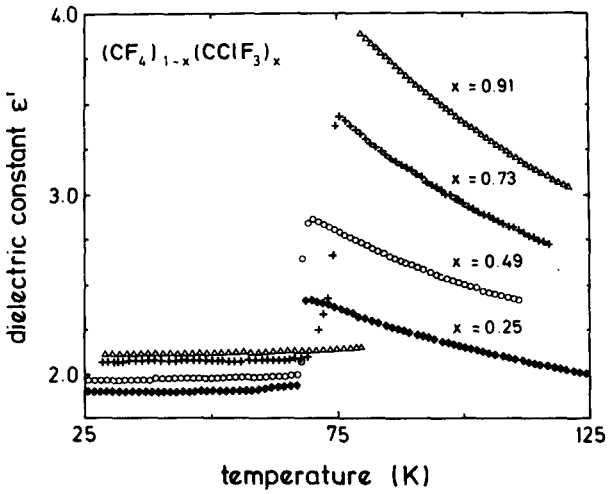

FIG. 7. Dielectric constants for condensed $(CF_4)_{1-x}$ $(CClF_3)_x$ mixtures. The data taken in the liquid state are well described by Eq. (2) with the parameters given in the text.

A preliminary phase diagram of $(CF_4)_{1-x}$ $(CClF_3)_x$ is shown in Fig. 8. Dilution of one component decreases the melting point of the other. The liquidus line starting from the melting point of CF_4 becomes smeared out if the concentration of $CClF_3$ dipoles is increased and finally lost for $x > 0.25$. With dilution the phase transition temperature $T_{\alpha\beta}$ of CF_4 also is reduced rapidly indicating the formation of mixed crystals. This temperature remains constant if x exceeds a few percent. For medium concentrations $(0.05 \leqslant x \leqslant 0.73)$ phase transitions are observed at around $T = 69$ K. Our measurements are thus compatible with a eutectic phase diagram. However, the boundaries of the eutectic line and the eutectic temperature have not been determined precisely so far.

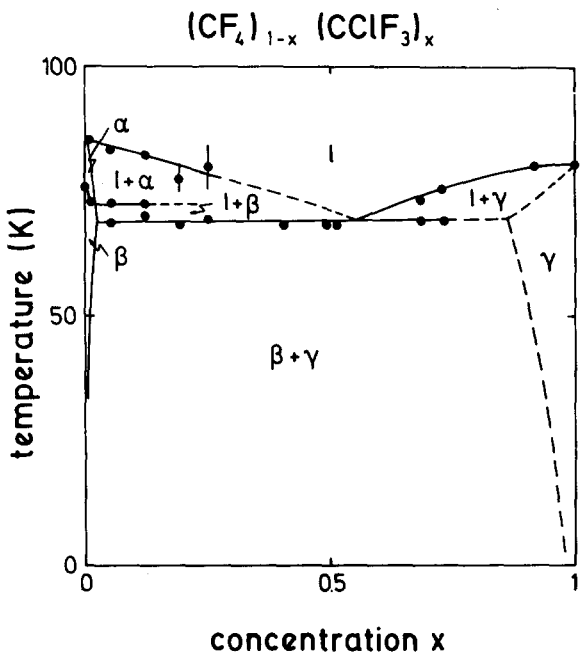

FIG. 8. Preliminary phase diagram of $(CF_4)_{1-x}$ $(CClF_3)_x$ which is characteristic of a eutectic. The dashed lines correspond to rough estimates only. The symbols denote the melt l: l–CF_4 + l–$CClF_3$ and mixed crystals α: α–CF_4 rich, β: β–CF_4 rich and γ: $CClF_3$ rich.

D. Fluorocarbon mixtures and solubility behavior

Simple arguments from solubility theory can help to explain qualitatively the observed mixing behavior. The excess free energy of mixing F is given by[34]

$$F = k(\delta_1 - \delta_2)^2, \tag{3}$$

where δ is the square root of the cohesive energy density. Depending on the theoretical *ansatz*, the coefficient k contains information on mixing ratios, volume fractions, etc. The δ^2's are in first approximation given by the heat of vaporization per molar volume. Further refinement is achieved if these estimates are evaluated at the same temperature.[34] The results of this procedure are given in Table I. The absolute difference between the solubility parameters of the polar molecules and that of CF_4 are smallest for $(CF_4)_{1-x}$ $(CClF_3)_x$. This is in accord with the experimental findings. Different mechanisms drive the decomposition in the other systems. In the mixtures containing CHF_3, interactions due to hydrogen bonding lead to an attraction between the dipoles. In the case of $CBrF_3$ where correlation effects are almost negligible, the relatively small difference in the cohesive energy densities indicates that steric effects, entering the free energy of mixing via the prefactor k in Eq. (3), are important.

IV. SUMMARY AND CONCLUSIONS

In the present investigation the dielectric constants have been measured in pure and mixed fluoromethanes in the liquid and in the solid phases:

(i) The liquid state dielectric data of the polar molecules can be described with the Onsager equation. Dipolar correlation effects are most important in CHF_3 and almost negligible in $CBrF_3$.

(ii) The dielectric data of the solid phase of CF_4 can be explained assuming a soft transverse optic mode which was observed in far infrared experiments.[18] The solid phases of CHF_3 and $CBrF_3$ exhibit dipolar order at all temperatures. Below the melting points, no further structural phase transitions became apparent. In addition, no dispersion effects could be detected demonstrating that the only possible reorientational motions of these molecules take place around their threefold axis, leaving the dipole moment unchanged.

(iii) Frequency dependence was found in the complex dielectric constant of $CClF_3$. This result demonstrates that dipolar reorientations are important in the solid phase of $CClF_3$.

(iv) The $(CF_4)_{1-x}$ $(CHF_3)_x$ and $(CF_4)_{1-x}$ $(CBrF_3)_x$ mixtures exhibit complete immiscibility in the solid state and show a monotectic phase diagram while $(CF_4)_{1-x}$ $(CClF_3)_x$ is eutectic with mixed crystal regions for low and high concentrations x. This trend is compatible with regular solution theory.

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