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Dielectric investigations of pure and mixed fluorocarbons in their condensed phases

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Dedicated to Professor Dr. G. Klages on the occasion of his 75th birthday.

We review recent work and present new results on the liquid and solid fluorocarbons CMF_3 with M = H, F, Cl, Br, CH_3, and CF_3. The pure compounds as well as several series of binary mixtures were investigated using dielectric measurements. The permittivities of the non-hydrogenated non-polar and polar liquids could be described using the Clausius-Mosotti and the Onsager equation, respectively. In CHF_3 and $C_2H_3F_3$ hydrogen bridging leads to deviations from this simple behavior. The trends in the miscibility of four series of fluorocarbon mixtures are in qualitative accord with regular solution theory.

The geometrical shapes of the compounds dominate the degrees of order below their melting point. Orientational liquid states (or plastic crystalline phases) are exhibited by the quasi-globular halomethanes CF_4 and C_2F_6, whereas complete dipolar order is found for the aspherical compounds CHF_3 and $CBrF_3$. The dielectric results for solid $C_2H_3F_3$ indicate a phase transition several degrees below the fusion temperature probably being due to the onset of intramolecular rotation. $CClF_3$ exhibits thermally activated dipole dynamics in the solid state. In alloys of $CClF_3$ with CF_4 and C_2F_6 the dielectric loss spectra have signaled single particle reorientations and glassy excitations.

I. INTRODUCTION

The investigation of orientationally disordered crystals has attracted considerable attention [1]. Part of the interest in this subject stems from the fact that some families of these crystals, like the spin glasses or orientational glasses, in many respects behave like ordinary glass. In these crystalline systems magnetic, electric, and other spins are diluted to a sufficient extent on a background lattice which is built up by non orientable species. In the past much of the experimental work in this field has focused on ionic crystals [2] and metals [3]. Van der Waals solids on the other hand have been studied much less intensively. Only recently low temperature disordered [4, 5] or orientational glass [6] states in inorganic binary systems have been investigated in detail. Structurally simple organic mixed crystals have remained almost unexplored [7] with the exception of the much studied methane-rare gas solid solutions. The dynamic behavior of the proto- and deuteromethanes is however largely obscured by quantum effects [8, 9]. Consequently their classical analogs the halomethanes may appear more suitable to study possible low temperature glass states in simple organic solids.

An effort was undertaken to study particularly the fluoromethanes in more detail [10 - 14]. Although this class of chemicals is technically still rather important, little is known about their physical properties below the critical point. This is not only true for mixtures of these chemicals but also for the pure compounds (with CF_4 as an exception [15]). Therefore their liquid and solid phases had to be studied first. To characterize a large number of pure and mixed fluoromethane derivatives we mainly used dielectric spectroscopy. This experimental technique has proven to be a powerful tool for the study of dynamical phenomena in molecular solids. As was shown in previous papers this method can elucidate overlapping [13] and non overlapping [11] single particle dipole reorientations as well as their glassy excitations on center of mass ordered lattices [14] and in amorphous solids [12].

In the following, we first review some details of the experimental set up. Then, we illustrate the dielectric properties of some liquid and solid fluorocarbons and discuss several molecular alloys which exhibit interesting low temperature phenomena. We conclude by briefly summarizing the various forms of disorder found in the solid fluorocarbons and alloys investigated so far.

II. EXPERIMENTAL

Various aspects associated with the preparation and measurements of condensed gases have been discussed before [5, 9 - 14]. It is suitable to make some additional comments here.

The nominal purity of $C_2H_3F_3$ (obtained from Messer-Griesheim) was about 99%. The purities of the other chemicals were stated by the supplier (Linde Co.) to be either 99.8% (CHF_3, $CBrF_3$) or 99.999% (CF_4, C_2F_6, $CClF_3$). All gases were used without further purification. They were mixed (in the case of the alloys) and condensed through a heated capillary into a dielectric cell. The cell, shown in Fig. 1, is of cylindric design which combines good mechanical stability with a high but slightly temperature dependent empty cell capacitance C_0 of about 51 pF. The long term stability of $C_0(T)$ over a period of 3 years was excellent. The major disadvantage of the cell is that below 4 K spurious dielectric losses show up for frequencies larger than 20 kHz. These were ascribed to the Stycast epoxy which was used as a spacer material (see Fig. 1). This effect is of little concern here since only measurements for temperatures $T > 10$ K are reported. The cell was manufactured mainly from brass to ensure rapid thermalization. The cell temperature was measured with a silicon diode. Usually the dielectric data were sampled while the temperature of the capacitor was ramped with a rate of 0.3 K/min. It is noted that a complete frequency scan typically took half a minute. Thermal gradients within the cell were not a problem. This was confirmed by the excellent reproduction of phase transition temperatures as reported in the literature.

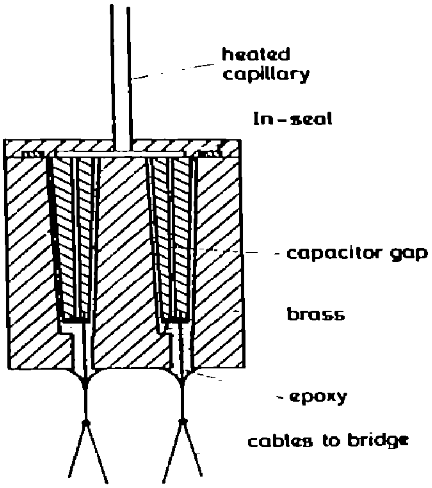

FIG. 1. Schematic cross sectional drawing of the cylindric capacitor used for the dielectric studies.

The complex dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ was recorded using the LCR-meter 4274A from Hewlett-Packard. This instrument operates at eleven frequencies between 100 Hz and 100 kHz and is able to resolve the dissipation $\varepsilon''/\varepsilon'$ down to 10^{-4}. The main error in the determination of the dielectric constants of the solidified gases arises from the incomplete filling of the sample holder. These effects are due to the different thermal expansivities of brass and the solidified gases and have been discussed earlier [9 - 11].

III. RESULTS AND DISCUSSION

A. Liquids

The temperature dependence of the dielectric constant of nonpolar liquids is dominated by density variations according to the Clausius-Mosotti equation. In most cases this leads to a permittivity which is linearly increasing with decreasing temperature. Such a behavior is well known for rare gas liquids and other inorganic fluids [16, 5] but has also been documented for simple organic compounds like the methanes CX_4 with X = H, D [16, 9] and the fluoroalkanes CF_4 [17, 10] and C_2F_6 [13].

A stronger temperature dependence is usually found for the dielectric constant of polar liquids. The major problem in computing the permittivity ε' of polar liquids is the calculation of the local electric fields from macroscopic quantities such as external electric field, the high frequency dielectric constant n^2, the temperature T, and density ρ. By properly solving the major part of the problem, Onsager derived an equation which was modified by Kirkwood to have the following form [18],

$$(\varepsilon' - n^2)(2\varepsilon' + n^2) \,/\, [\varepsilon'(n^2+2)] = 4\pi g \rho \mu^2 / (9 k_B T). \qquad (1)$$

The Kirkwood factor g can account for strong correlations among the polar molecules which may be produced by a large dipole moment μ or by other forms of association like e. g. hydrogen bridging. The Onsager-Kirkwood equation has been applied successfully to a great number of liquids [19] including the fluoromethanes $CClF_3$ and $CBrF_3$ [10]. However, deviations from this simple behavior showed up for the partly hydrogenated compounds CHF_3 [10] and $C_2H_3F_3$. Figure 2 depicts the permittivity of the latter compound as a function of temperature. The solid line is a fit using a modification of equation (1), where the Curie term on the right hand side has been replaced by a Curie-Weiss term $1/(T - \Theta)$. This is a particular way to introduce a temperature dependent factor $g(T)$ and has worked quite well for CHF_3 [10]. It is however not completely satisfying for $C_2H_3F_3$ (see Fig. 2). The parameters used to calculate the solid line shown in Fig. 2 are given in the figure caption.

To explain a temperature dependent Kirkwood factor or a variation of mutual dipolar correlations one has to bear in mind that the strength of the hydrogen bond is determined by its effective length which in turn depends on the density. The fact that the non-hydrogenated fluoromethanes could be described by a constant value of g, but not the CHF_3 and $C_2H_3F_3$ hydrocarbons, suggests that the thermal energies in the liquid state of the latter compounds and the energy of the H- - -F bridges are of the same order of magnitude. Then the increase of g upon cooling reflects the increasing number of unbroken hydrogen bonds which tend to align the molecules in parallel and are responsible for correlated or super-paraelectric reorientations. Super-paraelectric effects have also been observed in the electrically disordered phases of some ferroelectrics. [20]. The fluoro-hydrocarbons crystallize at temperatures far above their Curie-Weiss temperatures. Hence ferroelectricity here seems unlikely to occur and has not been reported so far.

From the large correlation factor g we can expect clustering to be effective in several of the polar fluorocarbon liquids. This expectation is confirmed by the limited solubility of the polar CHF_3 molecule in the nonpolar CF_4 solvent liquid [21]. For solid CF_4-CHF_3 complete immiscibility was found and together with the data of the liquid state provides evidence for a monotectic phase diagram [10]. A diagram with the same topology was found for CF_4-$CBrF_3$ where dipolar attraction forces are less important as indicated by the relatively small Kirkwood factor $g = 1.2$ and a vanishing Curie-Weiss temperature [10].

Here apparently the size mismatch of the CF_4 and the $CBrF_3$ molecules makes solubility unfavorable.

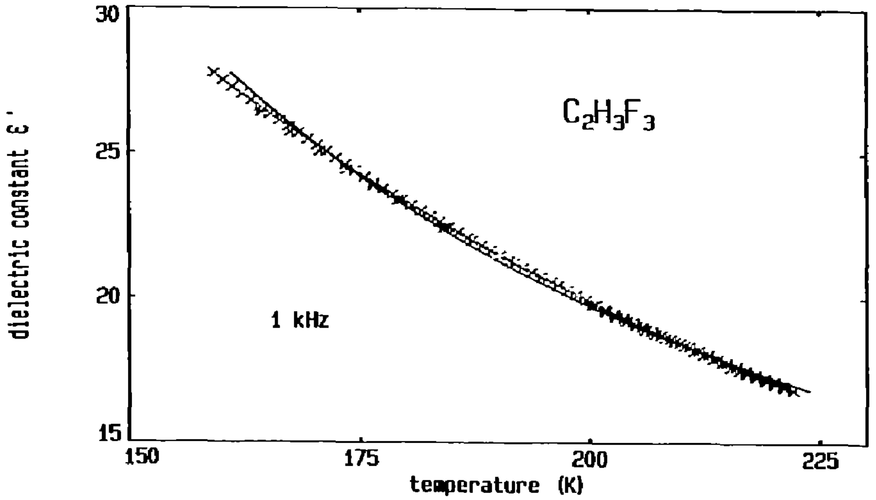

FIG. 2. Dielectric constant of liquid $C_2H_3F_3$ measured at 1 kHz. The solid line is calculated using equation (1) extended by a Curie-Weiss temperature Θ as described in the text. For the dipole moment $\mu = 2.32$ D [36] and the number density $\rho = 8.34 \times 10^{21}$ cm^{-3} [30] literature values were used. A least square fit to the experimental data yielded $n^2 = 1.63$, $g = 1.9$, and $\Theta = 70$ K.

To put these observations on a semi-empirical basis simple arguments from regular solution [22] theory can be used. This thermodynamic model predicts phase separations whenever the difference in the cohesive energy densities of solute and solvent exceed a certain threshold. Due to the approximations made in the theory [22], it is not expected to yield quantitatively accurate results. Surprisingly and possibly fortuitously so [23], it is able to predict the phase separation temperature of CHF_3 and CF_4 correctly [24]. Applying this theory to other fluorocarbon mixtures indicated [25] that the solubility of CF_4-$CClF_3$ and C_2F_6-$CClF_3$ may be better than that of the binary systems CF_4-CHF_3 and CF_4-$CBrF_3$ as is indeed the case (see Sec. III.C).

B. Pure solids

The pure and mixed fluorocarbons show a fascinating variety of order and disorder phenomena at low temperatures. In the crystalline phases, the rotational degree of freedom is governed by the shape of the constituent molecules. The quasi-globular shapes of CF_4 and C_2F_6 favor plastically crystalline states below their melting points [1]. This phase is characterized by almost free molecular reorientation. On the other end of the spectrum we find oblate and prolate molecules like CHF_3 and $CBrF_3$ [10]. Here only jumps around the threefold molecular C_3 axes are detectable [26, 27]. Apparently the strain energy necessary to reorient the dipolar C_3 axis is larger than the thermal energy available in the solid state. Consequently the dielectric audio-frequency response of these compounds is devoid of orientational polarization effects and dominated by the lattice vibrations [10].

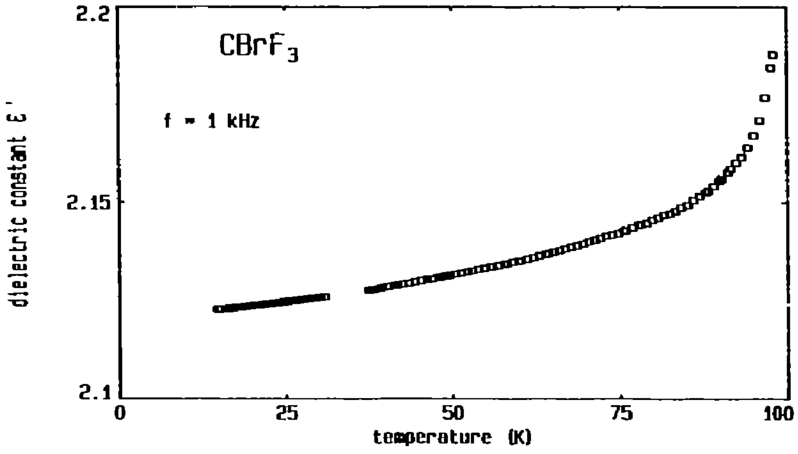

FIG. 3. Real part of the dielectric constant of solid $CBrF_3$ as a function of temperature.

As an example, Fig. 3 depicts the dielectric constant of solid $CBrF_3$. The magnitude of the permittivity of this compound is typical for van der Waals solids. ε' shows no dependence on the measuring frequencies employed in the present study. The overall increase of ε' from lowest temperatures to roughly 90 K amounts to only a few percent. Close to the melting point the dielectric constant rises more rapidly. This steep increase in ε' is only partly caused by the thermal expansion of the solid within the cell. A considerable part of the increase is probably due to large angle molecular librations [28]. A quantitative assessment of these effects awaits density measurements on solid $CBrF_3$. On melting, the dielectric constant of $CBrF_3$ more than doubles indicating the release of all orientational degrees of freedom [10]. Similar behavior was found for other dipolar fluoromethanes [10, 29].

For molecules with internal degrees of rotational freedom, like e. g. $C_2H_3F_3$, the dielectric behavior is more complicated. In solid $C_2H_3F_3$ a discontinuity in the permittivity could be detected several degrees below the melting point T_m = (161.5 ± 2) K [25] and confirmed earlier calorimetric investigations by Russell et al. [30]. These solid state anomalies are possibly due to an intramolecular rotational transition. Although the strongly hindered internal torsion of the $C_2H_3F_3$ molecule has been studied extensively [31] more work is needed to understand the nature of the phase transition. Finally we note that at low temperature (T = 10 K) the dielectric constant of $C_2H_3F_3$ is $\varepsilon' =$ 2.45.

Among the simple fluorocarbons studied here, the asymmetric top $CClF_3$ turned out to be the most interesting one. Earlier dielectric measurements on this rigid molecule suggested a solid-solid phase transition a few degrees below T_m [29]. Such a behavior could not be confirmed in subsequent work [32, 10, 26]. Our own dielectric experiments indicate however that a change of the dynamical behavior of solid $CClF_3$ occurs at around 60 K [11]. Above this temperature single particle excitations dominate. These can probably be characterized by jumps around the threefold C-Cl molecular axis. The reorientations are associated with the crossing of a large energy barrier [26] which reflects the sterical hindrance within the local elastic fields. On cooling the jumps slow down rapidly and below 60 K another dipolar excitation becomes predominant [11]. Among the signatures of this process are an extraordinary low apparent activation energy (135 K) and an electric susceptibility which decreases with temperature. The latter observation indicates that either an increasing number of the $CClF_3$ molecules statically freezes on cooling or that the amplitude of the collective small angle reorientations, which are thought to drive the dynamics below 60 K [11], decrease with temperature. Clearly more work is needed to unravel details of the molecular motion of $CClF_3$ at low temperatures. It is however pointed out that the investigation of this molecular solid is impeded by a partial irreproducibility of experimental results [11, 26], the microscopic basis of which is not yet understood.

C. Molecular alloys

As mentioned in Sec. III.A, two of the binary fluoromethane systems are practically immiscible in the solid state. For the other systems, $(CF_4)_{1-x}(CClF_3)_x$ and $(C_2F_6)_{1-x}(CClF_3)_x$, partial mixed crystal formation was found and enabled the study of interesting low temperature phenomena. In particular the dynamics of $CClF_3$ probe molecules in thermally equilibrated CF_4 [11] and C_2F_6 [13] host lattices was explored in detail for dipole concentrations up to about 1% and 20%, respectively. It was found that the low temperature phase separation could be suppressed by rapid cooling (30 K/min) of the high T liquid [12] and plastic [14] phases. In this article we will focus on the latter case which is particularly interesting, since supercooled $(C_2F_6)_{1-x}(CClF_3)_x$ crystals could be obtained for a large range of concentrations x.

Figure 4 depicts some representative results for quenched crystals with x = 0.32, 0.61, and 0.92. Here the dielectric loss ε'' as measured on heating is plotted as a function of log(frequency) for several temperatures. The loss curves are broadened almost symmetrically and their width increases rapidly with decreasing temperatures. Similar effects have been observed in orientational glasses [33]. The area under the loss curves is proportional to the static susceptibility. This quantity was estimated for the fluorocarbon supercooled crystals using the Cole-Cole formula [34] and was shown to scale properly with concentration and temperature [14]. This analysis also showed that cooling rates of 30 K/min are not sufficient to suppress unmixing for dipole concentrations larger than 61% [14]. This is the reason why the susceptibility of the $(C_2F_6)_{0.08}(CClF_3)_{0.92}$ sample is more than ten times smaller than that of the 61% crystal.

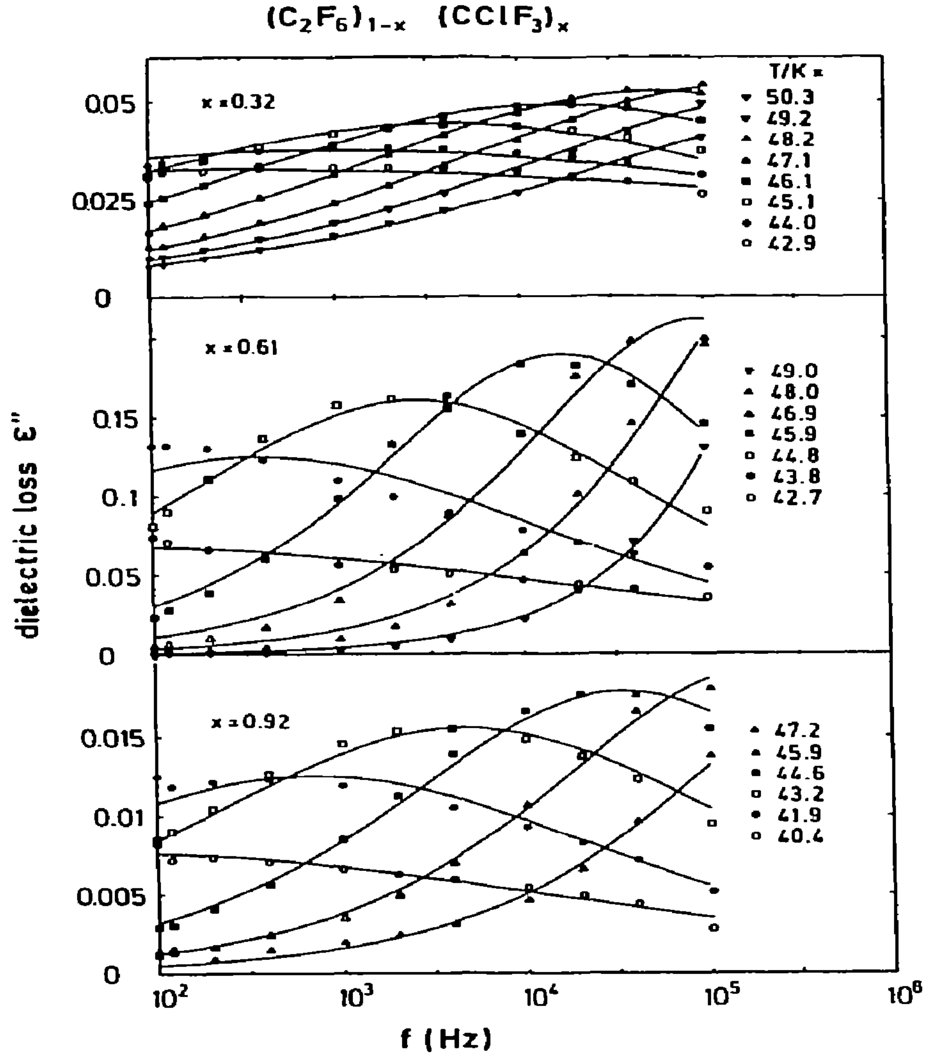

FIG. 4. Frequency dependent dielectric loss spectra of supercooled $(C_2F_6)_{1-x}(CClF_3)_x$ alloys for various temperatures T and concentrations x. The solid lines were calculated using the Cole-Cole function [34].

The temperature dependence of the average reorientation time $\tau(T)$ of the crystal with $x = 0.32$ has previously been described using a Vogel-Fulcher law [14]. Since the dielectric loss maxima are rather broad and the frequency range of the present experiments relatively limited it was also possible [25] to parametrize $\tau(T)$ for $x = 0.32$ and other concentrations in terms of an Arrhenius law $\tau = \tau_0 \exp (E / k_B T)$. The energy barriers used to calculate the solid lines in Fig. 4 turned out to be strongly concentration dependent. For the three samples with $x < 0.50$ ($x = 0.23$, 0.32, and 0.46) E increased almost linearly with x reaching a value of about 3500 K for the 46% sample; the activation energy for $(C_2F_6)_{0.38}(CClF_3)_{0.62}$ was even slightly higher [25]. The rapid increase of E with the $CClF_3$ concentration indicates that the long ranged dipolar interaction forces play an important role in the orientational freezing process.

IV. CONCLUSIONS

The investigation of some simple fluoroalkanes and their alloys have revealed a surprising variety of degrees of dynamical disorder in the solid state. Thermally activated single particle reorientations could be detected in the pure solids CHF_3 [27] and $CBrF_3$ [26] as well as in CF_4 doped with $CClF_3$ molecules [11]. The relaxation dynamics of the $(C_2F_6)_{1-x}(CClF_3)_x$ alloys were found to be more complex. Here the dielectric loss spectra could be interpreted as being due to the uncorrelated relaxation of $CClF_3$ molecules through clearly distinguishable relaxation channels [13]. In pure solid $CClF_3$ indications for both single particle and collective reorientations were found [11, 26]. The supercooled $(CF_4)_{1-x}(CClF_3)_x$ and $(C_2F_6)_{1-x}(CClF_3)_x$ alloys exhibit a sequence of two dipolar active relaxation processes [12, 14] which bear close resemblance to the α- and β-relaxations observed in canonical glasses [35]. Consequently, the main relaxation peaks found for the quenched fluorocarbons were taken as a manifestation of the glass transition.

It remains to be seen whether this analogy between the supercooled fluorocarbon alloys and the conventional glasses can be confirmed further by structural and thermodynamic investigations.

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