

## Reorientations and phase transitions in $(\text{Kr})_{1-x}(\text{CH}_4\text{-nDn})_x$

R. Böhmer, Alois Loidl

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# Reorientations and phase transitions in $(\text{Kr})_{1-x}(\text{CH}_4-n\text{D}_n)_x$

R. Böhmer\* and A. Loidl

Institut für Physik der Johannes Gutenberg-Universität and Materialwissenschaftliches Forschungszentrum Mainz,  
Federal Republic of Germany

The condensed isotopic modifications of methane,  $\text{CH}_4$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CD}_4$  and their solutions with Kr were investigated using dielectric techniques. The polarizabilities were computed from the permittivities of the pure liquids. Phase diagrams of methane-krypton alloys were deduced in the liquid-solid coexistence region and for the low temperature phases ( $T < 30$  K). From the Curie-laws, which described the permittivities of the  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  mixed crystals, the permanent dipole moment of  $\text{CH}_2\text{D}_2$  is calculated to be 4 mD. In the octopolar ordered phases of the solid solutions the effective dipole moments are enhanced significantly.

## I. Introduction

The quantum solid methane and its deuterated derivatives have attracted a considerable attention during the past decades. On cooling from the orientationally disordered high temperature phases (phase I), these compounds order in rather complicated fashions. The transition temperatures strongly depend on the degree of deuteration of these compounds [1]. Below 20.4 K, the fully protonated species,  $\text{CH}_4$ , exhibits a structure which comprises eight sublattices (phase II) [2]. Six out of these exhibit orientational order due to electrostatic interaction forces. On sites belonging to the remaining two sublattices, the octopolar fields of the ordered arrangement cancel. Molecules on these sites rotate freely in a quantum mechanical sense. Under pressure, order is induced at all sites [3]. However, the detailed structure of this phase (phase III) has not been resolved unambiguously so far. In  $\text{CD}_4$  the transition from phase I to phase II occurs at 27 K. Phase III of fully deuterated methane is stable at ambient pressures for temperatures below 22.3 K [1].

On doping with krypton, which is known to be miscible with methane in any concentration [4, 5], the phase

transition temperatures decrease [6] and finally, for dopant levels larger than 20%, glassy low temperature states show up [7]. This octopolar glass has been studied more systematically only very recently [8–10], though it promises to be a model case for a multipolar orientational glass. The interpretation of results from nuclear magnetic resonance experiments which usually are employed to investigate the dynamics of such compounds, is no easy task, even for the pure methanes [11]: spin conversion effects [12] as well as the rather complicated level scheme of methane [13] have to be taken into account. These difficulties may substantiate some of the reasons, why information from this technique about the reorientational behaviour in the mixtures is rather scarce.

The dielectric method, another powerful method to explore molecular dynamics of dipoles, either permanent or induced, has rarely been used to study solid methanes. As far as we know, solid methane has been studied at ambient pressures only for temperatures close to the melting point [14]. In dielectric investigations on compressed solid methane, Costantino and Daniels found the polarizability of  $\text{CH}_4$  to be independent of density [15]. At very high pressures ( $p > 0.5$  GPa) and temperatures below 20 K Curie-Weiss behaviour showed up which was tentatively ascribed to electric order [16]. However, later attempts to confirm this rather unexpected phenomenon, which would require the distortion of the tetrahedral molecules, were not successful [15]. Another remarkable observation from these studies on pressurized methane was that small dielectric anomalies showed up near the orientational order-disorder transition. This feature was interpreted as arising from dipole moments, which were thought to be induced at the sites of the ordered molecules by the surrounding octopoles. Following this reasoning, the dielectric constant is related directly to the order parameter of the low temperature phase of  $\text{CH}_4$  [15].

One motivation for the present dielectric study was to find out, whether the concept of induced dipole moments is applicable to other isotopic species than  $\text{CH}_4$

\* Present address: Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA

and to see, whether slow molecular reorientations possibly dominating the low temperature dynamics can be detected directly. The use of partly deuterated methanes as dipolar probes seemed to be a promising approach to the latter question, not only in the case of the pure solids but also in the octopolar glass states.

In this paper we summarize the results from our dielectric investigations [17] of three isotopic modifications and their solutions with Kr. Firstly, some details on the experimental technique are given. In Sect. II.A the permittivities and polarizabilities of the pure liquid methanes are presented, and the melting diagrams for the Kr-solutions are derived from the dielectric measurements in the coexistence region. The remainder of the article is devoted to the quantum systems in their solid states. Dielectric constants of pure methanes and of mixed crystals with krypton, from which low temperature phase diagrams were deduced, are presented in Sect. II.B. From the results on the partly deuterated species, the low temperature reorientational processes of the solid methanes are discussed briefly (Sect. III.A). Finally, in Sect. III.B, the dipole moments of  $\text{CH}_2\text{D}_2$  are determined in the orientationally ordered as well as in the disordered phases.

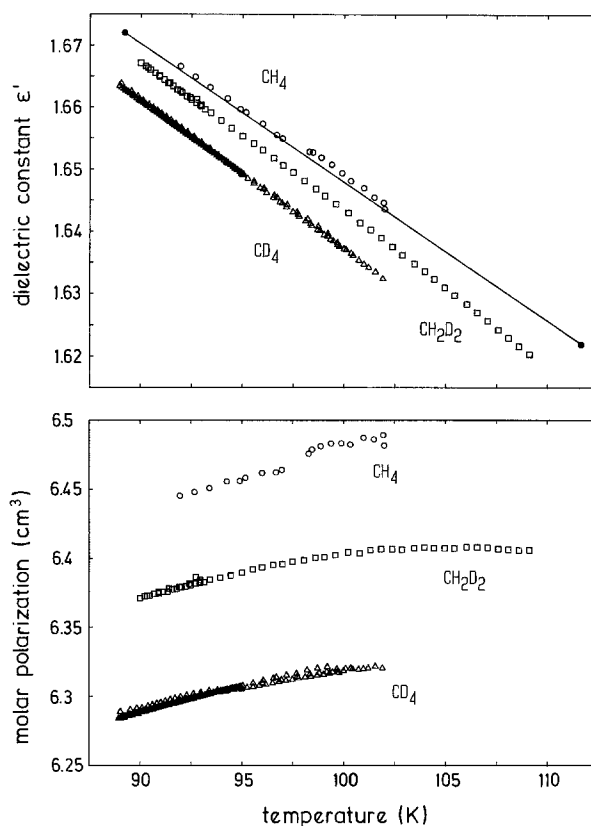
## II. Experiments and results

Gases in bottles from various sources were used. The (partly) deuterated methanes  $\text{CH}_2\text{D}_2$  and  $\text{CD}_4$  had a nominal purity of 99%, with approximately 1% of  $\text{CH}_4$  impurities. The purity level of the other gases was 99.95% ( $\text{CH}_4$ ) and 99.99% (Kr). The chemicals were mixed (in the case of the alloys) and condensed as liquids into a cell of cylindrical design. To homogenize the solid solutions, they were kept at temperatures several degrees below the melting point for at least one hour. The dielectric constants of the samples were measured in the frequency range from 100 Hz to 100 kHz as described previously [18]. The lowest temperature accessible with our home manufactured variable flow He-cryostat was 2 K. Within the experimental resolution, the permittivities were independent of the measuring frequencies for all temperatures. Thus, only data taken at a single frequency, usually 10 kHz, are reported.

It has been found that the properties of methane depend on the thermal history of the crystals [19]. It is therefore noted that our experiments were usually done with samples which, in the solid state, were cooled or heated with rates of typically 0.1–0.3 K/min. However, except for pure  $\text{CD}_4$  crystals, good reproducibility of the results was achieved. In addition,  $\text{CH}_4$  and  $\text{CH}_2\text{D}_2$  were cooled with larger rates from their plastic states and kept at constant temperatures in the ordered phases. This was done in order to detect time dependent effects, e.g. spin conversion processes. However, the dielectric response was time independent at all temperatures.

### A. Liquids

1. *Dielectric constants and polarizabilities.* The permittivities of the methanes  $\text{CH}_4$ ,  $\text{CH}_2\text{D}_2$  and  $\text{CD}_4$  in their

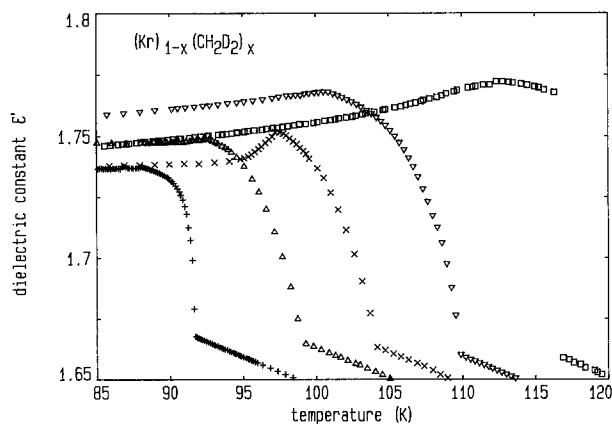


**Fig. 1.** Upper frame: The dielectric constant of  $\text{CH}_{4-n}\text{D}_n$  for  $n=0, 2$ , and  $4$  from this work. The permittivity of  $\text{CH}_4$  was also measured by Amey and Cole [14] (●, the straight line interpolates between reported values). Lower frame: The temperature dependent molar polarization of several isotopic modifications of liquid methane

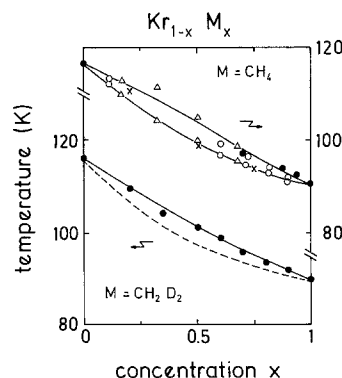
liquid states are presented in Fig. 1. They increase approximately linearly with decreasing temperatures. Only the data for  $\text{CH}_4$  can be compared with values as cited in the literature. As can be seen in Fig. 1, the agreement with the results obtained by Amey and Cole [14] is excellent. Dielectric constants measured by McLennan et al. [20] are roughly 3% larger and are not included in Fig. 1. The absence of any Curie-type of behaviour in the permittivity of  $\text{CH}_2\text{D}_2$  indicates that, in the liquid state, the contribution of the permanent dipole moment to the total polarization is negligible. Hence, the Clausius-Mosotti equation may be used to calculate the molar polarizability

$$P = (\varepsilon - 1)/(\varepsilon + 2) \times V_m. \quad (1)$$

The molar volumes  $V_m$  of liquid  $\text{CH}_4$  and  $\text{CD}_4$  have been determined experimentally by several authors [21, 22]. From a comparison of various results [22], the temperature dependence of the molar volume for  $90 \text{ K} < T < 100 \text{ K}$  was estimated to be  $V_m/\text{cm}^3 = A + BT$ , with  $B = 0.1235 \text{ K}^{-1}$ . For  $\text{CD}_4$  the constant  $A_{\text{CD}_4} = 23.715$  turned out to be somewhat smaller than the value  $A_{\text{CH}_4} = 24.095$  for  $\text{CH}_4$ , i.e. the fully protonated methane is more dense as compared to its deuterated counterpart. This was explained to arise essentially from differences in the intermolecular potentials of these com-



**Fig. 2.** The dielectric constants of  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  for various concentrations  $x$  ( $\square$ , 0;  $\nabla$ , 0.2;  $\times$ , 0.35;  $\triangle$ , 0.6;  $+$ , 0.9) in the liquid solid coexistence region. The spectrum of dielectric constants measured for different compositions at  $T=85$  K, say, gives an estimate for the absolute reproducibility of the solid state data, which is better than 1%



**Fig. 3.** Melting diagram of  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  from this work ( $\bullet$ ) and from calorimetric ( $\circ$  [4],  $\triangle$  [5]) and NMR experiments ( $\times$  [44]). The solid lines are drawn to guide the eye. For  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  the filled circles represent the results from this work. The supposed solidus is indicated as dashed line

pounds [23]. The polarizations of the liquid methanes resulting from the calculations using Eq. (1) are also shown in Fig. 1. For the molar volume of  $\text{CH}_2\text{D}_2$ , we have used the mean of the numbers  $A$  given above. The polarization shows a clear isotope effect, with an almost temperature independent ratio of  $P_{\text{CH}_4}$  and  $P_{\text{CD}_4}$  in the order of 1.024. This figure has to be compared with the somewhat smaller ratio ( $\lesssim 1.02$ ) determined from measurements of the refractive index [24]. The polarization is slightly decreasing with  $T$  in all three liquids (Fig. 1). Similar results have previously been documented for gaseous and liquid  $\text{CH}_4$  [25, 14].

The polarizability of liquid  $\text{CH}_4$  may be compared to the results on the compressed solid by Costantino and Daniels [15, 16] who find  $P=6.54 \text{ cm}^3$ , almost independent of pressure ( $0.1 \text{ GPa} < p < 0.7 \text{ GPa}$ ) and temperature ( $60 \text{ K} < T < 260 \text{ K}$ ). From this polarizability which is slightly larger as the values given above, we conclude that the molecular vibrations giving rise to the observed values of  $P$  are only weakly affected by melting. This behaviour which seems plausible for compounds with plastically crystalline phases was also found in fluoromethane [18] and other compounds [27].

**2. The melting of alloys with krypton.** As an example for measurements from which melting diagrams were deduced, Fig. 2 shows the permittivities of several  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  solutions. The dielectric constants obtained in the liquid state shift upon variation of composition. The increase of  $\epsilon$  can be explained by the higher density [28] of the solid phase. The  $\epsilon(T)$ -data abruptly change slope when the samples start to solidify, i.e. when the binary mixtures cross the temperatures which define the liquidus line. The slopes for the  $\epsilon(T)$  curves in the two phase region are smallest for medium concentrations where the liquid-solid coexistence region has its widest extension. However, from the dielectric constants it is not clear where to locate the temperature at which the alloys have transformed completely into a solid. Results

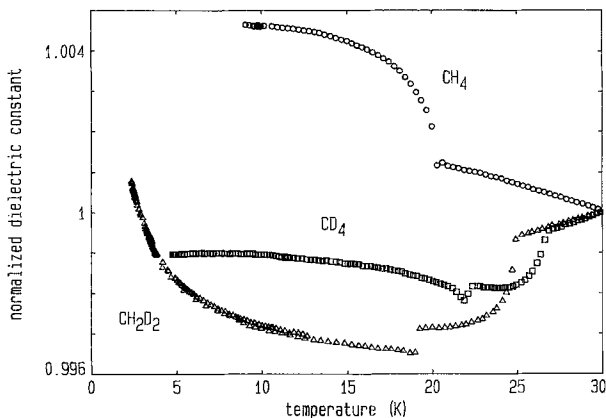
similar to the ones presented in Fig. 2 were obtained also for the  $(\text{Kr})_{1-x}(\text{CD}_4)_x$  and the  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  solutions.

Comparison with published melting diagrams can be made for the latter system only (Fig. 3). Figure 3 also includes the liquidus line of  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  deduced from experiments of the present work. Our results for  $(\text{Kr})_{1-x}(\text{CD}_4)_x$  are in good agreement [27] with those from unpublished calorimetric work [8]. All melting diagrams are indicative of complete solid state miscibility.

## B. Solids

**1. Pure methanes.** Typical results of the temperature dependent permittivities of three isotopic modifications of methane are shown in Fig. 4. At the phase transition temperatures, marked discontinuities show up in the dielectric constants. On cooling  $\text{CH}_4$ ,  $\epsilon$  varies like the order parameter [29] and finally saturates at low temperatures. A significant variation of  $\epsilon(T)$  also appears just below the order-disorder transitions in  $\text{CH}_2\text{D}_2$  and  $\text{CD}_4$ . But while the slope is reproducibly positive for the partly deuterated compound and always negative for  $\text{CH}_4$ , the variation of  $d\epsilon/dT$  is not reproducible for  $\text{CD}_4$  (see also the data on  $\text{CD}_4$  presented in Fig. 6). It should also be noted that  $\epsilon(T)$  behaves different already in the disordered phases. Finally, at the lowest temperatures the dielectric constant of the partly deuterated compound,  $\text{CH}_2\text{D}_2$ , exhibits an increase which is completely absent in  $\text{CH}_4$  and  $\text{CD}_4$ : The observed  $1/T$ -dependence in  $\text{CH}_2\text{D}_2$  is due to the existence of a permanent (but small) dipole moment that will be calculated below (Sect. III.B).

The mechanisms leading to the variations of  $\epsilon$  near the phase transitions is unclear at present. Three possibilities to explain the origin of these phenomena have to be considered: *i*) the thermal expansion of the samples, *ii*) octopole induced dipole moments, and *iii*) soft optical phonons.

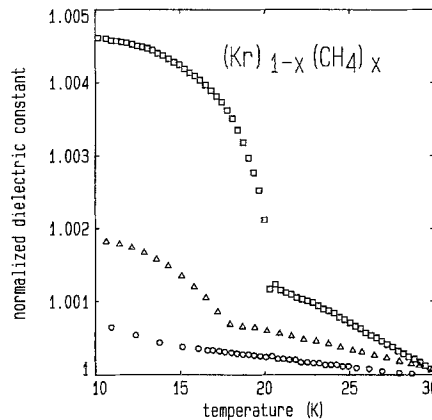


**Fig. 4.** The dielectric constants of  $\text{CH}_{4-n}\text{D}_n$  with  $n=0, 2,$  and  $4,$  normalized to their values at  $T=30$  K. Except for  $\text{CD}_4,$  the results showed good reproducibility. In some runs the permittivity of  $\text{CD}_4$  resembled that of  $\text{CH}_4$  (cf. Fig. 6)

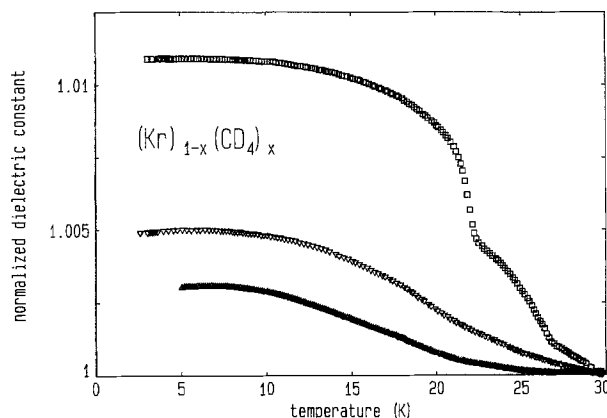
*i)* The total volume expansion  $\Delta V/V$  of  $\text{CH}_4$  up to the order-disorder transition at 20.4 K amounts to roughly 1% [30] and is therefore in the same order of magnitude as the effect seen in the variation  $\Delta \epsilon/\epsilon$  of the dielectric constant. However, there are several arguments which suggest that the thermal expansion is not responsible for all of this variation: The contraction of the sample inside the measuring cell leads to an incomplete filling of the capacitor and hence reduces the measurable capacitance (or the apparent dielectric constant). Given that the polarization remains unaffected by the shrinking of the sample, i.e.,  $P$  is independent of the density  $d$ , then the increase in  $d$  effectively compensates the decrease of the capacitance according to Eq. (1). Furthermore, if we only would measure thermal expansion effects, then similar behaviour in all isotopic modifications of methane were expected, at least in the vicinity of the upper (order-disorder) transitions.

*ii)* The concept of octopole induced dipolar moments was applied by Costantino and Daniels to explain their dielectric measurements on pressurized solid methane [15]. According to these authors, the polarization due to induced moments  $\mu_\omega$  is proportional to  $\mu_\omega^2 \Phi/T$ , with  $\Phi$  being the order parameter of the low temperature phase. In order to explain the decrease of the polarizability at the rotational transition of pressurized  $\text{CH}_4,$  they arrive at an induced moment of  $\approx 0.4$  mD. It is questionable whether this number has any significance, since the Curie term they introduce heuristically into their Eq. (5) gives an appropriate description only for permanent moments. Here, we are concerned with electronic contributions to the polarization, which, in analogy to magnetic problems, would require a treatment in terms of a Van Vleck model. While a thorough theoretical treatment of these problems seems to be unavailable at present for the methane crystals, the question of soft optic phonons has to be answered experimentally.

*iii)* The temperature dependence of the low lying absorption bands of methane crystals has not been investigated systematically at ambient pressures and low tem-



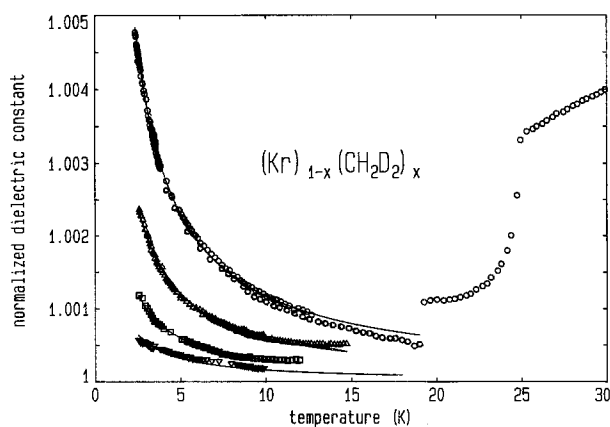
**Fig. 5.** The permittivities of  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  mixed crystals for  $x=1$  ( $\square$ ),  $0.94$  ( $\triangle$ ), and  $0.8$  ( $\circ$ ), normalized to their values at  $T=30$  K



**Fig. 6.** The permittivities  $\epsilon(T)/\epsilon(T=30$  K) of  $(\text{Kr})_{1-x}(\text{CD}_4)_x$  mixed crystals for methane concentrations of  $1$  ( $\square$ ),  $0.85$  ( $\nabla$ ), and  $0.7$  ( $\triangle$ )

peratures, so far. However, a Raman investigation of  $\text{CH}_4$  III at pressures near 0.25 GPa has documented that absorption processes exist (near  $40$   $\text{cm}^{-1}$ ) which strongly depend on temperature [31]. An extension of spectroscopic studies to lower pressures and other isotopic modifications is highly desirable in order to clarify, whether soft optic phonons give rise to the observed temperature dependence of the dielectric constant as is the case in the rigid phase of  $\text{CF}_4$  [18].

**2. Mixed crystals.** Figures 5, 6, and 7 show the temperature dependences of the dielectric constants of  $(\text{Kr})_{1-x}(\text{CH}_{4-n}\text{D}_n)_x$  with  $n=0, 4,$  and  $2,$  respectively. It is clearly shown that with increasing krypton concentration, the phase transitions shift to lower  $T$  and rapidly smear out. (The corresponding experimental results for  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  are not explicitly shown here for reasons of clarity, see Fig. 7). In the mixed crystals, the observations resemble those made in the pure methanes: The samples containing  $\text{CH}_4$  or  $\text{CD}_4$  exhibit a dielectric constant which, at the lowest temperatures, tends to a constant value. On the other hand, in all  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  mixed crystals a behaviour shows up,



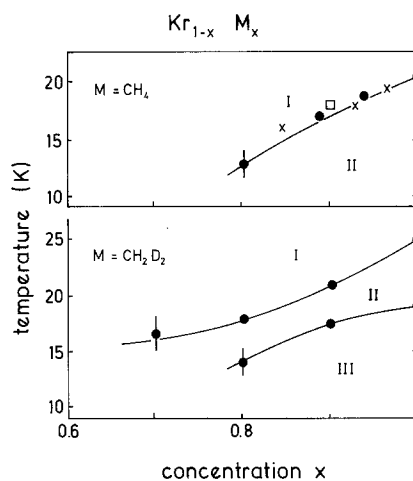
**Fig. 7.** The dielectric constants of  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  for temperatures below 30 K and for various concentrations  $x$  (1,  $\circ$ ; 0.7,  $\triangle$ ; 0.35,  $\square$ ; 0.2,  $\nabla$ ). Lines are least square fits using  $\epsilon = \epsilon_\infty + 4\pi C/T$ . The permittivities are normalized to the high-frequency dielectric constant  $\epsilon_\infty(x)$  which was found to be  $1.70 \pm 0.04$ . The dielectric constants of the mixed crystals have been omitted for clarity, at high temperatures

which can be described by Curie laws. In this paragraph we will focus on the phase transitions.

Figure 8 shows a  $x, T$ -phase diagram, where the temperatures of the dielectric anomalies are plotted versus the methane concentrations. For  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  excellent agreement with results from other experimental techniques is obtained. The detailed structure of the I  $\rightarrow$  II phase boundary near the critical concentration  $x \approx 0.8$  was not studied thoroughly in this investigation. However, it is noted that the dielectric constant of  $(\text{Kr})_{0.7}(\text{CH}_4)_{0.3}$  was featureless in the low temperature region, i.e. without any indication of a structural phase transition. This is in accord with results from magnetic resonance and neutron scattering studies from which an octopolar glass state was reported to occur at least for  $x \leq 0.75$  [9, 10].

The phase diagrams of the mixed crystals of the deuterated methanes are more complex. For methane concentrations  $x \geq 0.8$  a sequence of two phase transitions is resolved in the dielectric constants of  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$ . The lower transition line of this system is shaped similarly as the one of  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  (Fig. 8). The upper phase boundary exhibits a different curvature. However, the anomaly observed in  $(\text{Kr})_{0.7}(\text{CH}_2\text{D}_2)_{0.3}$  is very broad, making a precise determination of the transition temperature difficult. In equimolar mixtures of Kr and  $\text{CH}_2\text{D}_2$  no low temperature transition anomalies could be detected.

The measurements in  $(\text{Kr})_{1-x}(\text{CD}_4)_x$  show that the dilution effect on the transition anomalies is very strong, and the transformation anomalies were determined from the discontinuities of the  $T$ -derivative of the dielectric constant [27]. Since only a few  $(\text{Kr})_{1-x}(\text{CD}_4)_x$  mixed crystals were investigated so far, we defer presenting a phase diagram until our continuing studies on this system are complete. It is noted, however, that the results from our dielectric experiments are in accord with unpublished specific heat measurements [8].



**Fig. 8.** Low temperature phase diagrams of  $(\text{Kr})_{1-x}(\text{CH}_{4-n}\text{D}_n)_x$  solid solutions with  $n=0$  and 2. For  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  results from this work ( $\bullet$ ) are compared with those from calorimetric ( $\times$  [6]) and NMR ( $\square$  [36]) investigations

### III. Analysis and discussion

#### A. Reorientational behaviour

At high temperatures the reorientational motion of the methanes is governed by rotational diffusion [2]. This dynamics slows down as the order-disorder transitions are approached [29]. However, the corresponding jump rates remain always larger as compared to the measuring frequencies of the present dielectric experiments. At low temperatures on the other hand, tunneling excitations still keep the torsional motion in the quantum solids fast. This is due to the relatively large ratio of rotational constants and orientational potentials of the methanes. The tunneling frequencies depend roughly exponentially on the potential strength and were calculated using variational methods by Hüller and co-workers [32]. They have been determined experimentally in several isotopic modifications of methane [33, 34] as well as in solid solutions with krypton [10]. Some information about tunneling excitations is also available from calorimetric [35] and magnetic resonance investigations [11, 36, 37]. As a common result, the tunneling rates are found in the radio-frequency range. For the fully deuterated compound  $\text{CD}_4$  where the rate is lowest, the lowest tunneling line is found at  $12 \mu\text{eV}$  [34] (corresponding to roughly 0.3 GHz). Within the experimental resolution of the present audio frequency experiments and down to 2 K, dielectric loss could not be detected in  $\text{CH}_2\text{D}_2$  and its alloys with Kr. This is consistent with the results given above.

The simplest way to shift the low temperature reorientational rates into the audio-frequency range is to increase the potential strength. Monte Carlo simulation studies of methane indicated that glassy low temperature states can be obtained by quenching the plastic phase [38]. Therefore, in the pure methanes, we tried to achieve higher barriers by rapid cooling of  $\text{CH}_2\text{D}_2$ , starting from temperatures between 70 and 80 K. Below 45 K the cool-

ing rates down to 4 K were larger than 1.5 K/s. On heating, the dielectric constants of these samples again followed Curie laws without any indications of dispersion.

In alloys of rare gases and methanes, the crystal fields depend on the radii of the spherical dopants. Argon atoms, which are much smaller than methane molecules, yield relatively large potential barriers. However, Ar is not fully miscible with the methanes [39].

### B. Dipolar moments

At low temperatures the dielectric constants of all  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  solid solutions followed Curie laws  $\epsilon = \epsilon_\infty + 4\pi C/T$ . Least square fits to the permittivities (Fig. 7) yielded the high-frequency permittivities  $\epsilon_\infty$  and the Curie constants  $C$ . Figure 9 shows the concentration dependence of the latter quantity from which the Lorentz-field corrected effective dipole moment

$$\mu = \sqrt{\frac{27 k_B C}{g N (\epsilon_\infty + 2)^2}}, \quad (3)$$

was calculated. Vegard's law was applied to compute the dipole number densities  $N$  of the mixed crystals from the lattice constants  $a$  of methane ( $a = 5.84 \text{ \AA}$  [40]) and krypton ( $a = 5.646 \text{ \AA}$  [41]). To obtain effective moments, the coefficient  $g$  which gives a measure of correlated dipolar alignment, was set to unity. Figure 9 shows that for  $x \leq 0.8$  the dipole moment of  $\text{CH}_2\text{D}_2$  is approximately 4 mD. This result is in accord with rough estimates from bond moments [42]. The difference of these quantities for C–D and C–H, as determined from a number of covalent bonds, and hence the moment of a hypothetical linear D–C–H molecule is 10 mD. This is only slightly larger than the moment of  $\text{CH}_2\text{D}_2$ . It is interesting to note that from dielectric measurements of partly deuterated ammonium hexachlorostanate, Gilchrist re-

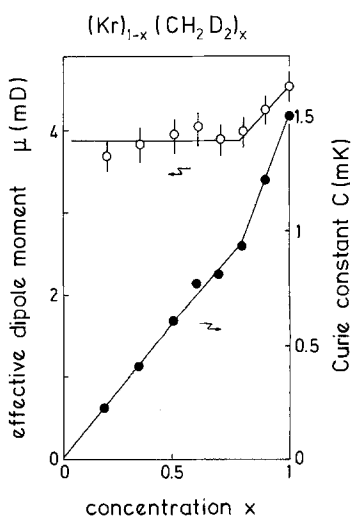


Fig. 9. The Curie constants (right hand scale) and effective dipole moments (left hand scale) from the fits to the low temperature permittivities of the  $(\text{Kr})_{1-x}(\text{CH}_2\text{D}_2)_x$  mixed crystals. Lines are drawn to guide the eye

ported a dipole moment of 7 mD for the partly deuterated ammonium group [43]. However, he discussed the possibility that this moment might be also due to impurities.

For dipole concentrations  $x \geq 0.8$ , the Curie constants are larger than extrapolated from the behaviour at lower methane concentrations (Fig. 9). It amounts to  $C = 1.5 \text{ mK}$  for pure  $\text{CH}_2\text{D}_2$ , yielding an effective moment of 4.5 mD. It seems important to note that  $x \approx 0.8$  indicates the critical concentration which marks the borderline between ordered and disordered phases. Thus, the effective dipole moment is roughly 4 mD in the octopolar disordered state of  $\text{CH}_2\text{D}_2$  and is significantly enhanced in the ordered state.

## IV. Summary and outlook

The liquid and solid phases of  $(\text{Kr})_{1-x}(\text{CH}_4-n\text{D}_n)_x$  solutions have been investigated by dielectric means. From the high temperature (liquid state) data, polarizabilities and melting diagrams have been deduced. The temperature dependence of the permittivities of the pure methanes near the low temperature phase transitions has been reported and several possibilities leading to the observed behaviour were discussed. For clarifying the role played by the thermal expansion, measurements of oxygen doped samples would be useful, since  $\text{O}_2$  is known to affect the dilatation of methane considerably [13]. However, it has become clear that the concept of octopole induced moments, as proposed by Costantino and Daniels [15], is not applicable straightforwardly to all isotopic modifications of methane.

From the low temperature dielectric constants of  $\text{CH}_4$ ,  $\text{CH}_2\text{D}_2$ , or  $\text{CD}_4$  alloyed with Kr, phase diagrams were deduced. For  $(\text{Kr})_{1-x}(\text{CH}_4)_x$  good agreement with results from other experimental techniques was achieved, while the more complex diagram of the partly deuterated system has been reported for the first time. Further investigations of  $\text{CD}_4$  and its solid solutions are needed to determine the reason for the observed lack of reproducibility of the permittivity of the pure solid and to draw definite conclusions about the low temperature phase diagram of the mixed system.

The low temperature reorientational behaviour of the samples containing the partly deuterated methane  $\text{CH}_2\text{D}_2$  was interpreted to be dominated by tunneling motions, in accord with numerous theoretical [32] and experimental [33–37] investigations. This suggests that radio-frequency dielectric measurements, the investigation of  $\text{CHD}_3$  (where the tunneling rates are lower as compared with  $\text{CH}_2\text{D}_2$ ) or studies of alloys with argon (where the crystal fields are larger) are promising candidates for future research.

The permanent dipolar moment of  $\text{CH}_2\text{D}_2$  has been calculated from the dielectric constants of five mixed crystals with Kr-concentrations  $x \leq 0.8$  to be  $\approx 4 \text{ mD}$ . The effective moments in the octopolar ordered phases ( $x > 0.8$ ) were shown to be significantly enhanced. In conclusion our results show that the use of partly deuterated

molecules or ions, such as is possible with hydrogen, methane, benzene, ammonium, etc. opens new perspectives for the investigations of dynamical properties of otherwise nonpolar compounds.

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R. Böhmer, A. Loidl  
 Fachbereich Physik der Universität  
 Staudinger Weg 7  
 D-6500 Mainz 1  
 Federal Republic of Germany