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

Received November 27, 1989

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 \((T<30\,\text{K})\). 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 \((p>0.5\,\text{GPa})\) 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 \(\text{CH}_4\).
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 CH$_2$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 CH$_2$D$_2$ and CD$_4$ had a nominal purity of 99%, with approximately 1% of CH$_4$ impurities. The purity level of the other gases was 99.95% (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 CD$_4$ crystals, good reproductibility of the results was achieved. In addition, CH$_4$ and CH$_3$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 CH$_4$, CH$_2$D$_2$ and CD$_4$ in their liquid states are presented in Fig. 1. They increase approximately linearly with decreasing temperatures. Only the data for 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 CH$_2$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

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

The molar volumes $V_m$ of liquid CH$_4$ and 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 K $< T < 100$ K was estimated to be $V_m$/cm$^3 = A + BT$, with $B=0.1235$ K$^{-1}$. For CD$_4$ the constant $A_{CD_4} = 23.715$ turned out to be somewhat smaller than the value $A_{CH_4} = 24.095$ for 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-