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Dielectric Anomalies in Solid Methane at Low Temperatures and High Pressures*

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Measurement of the static dielectric constant of solid methane crystals grown at high pressures show several anomalous regions. One set is associated with the well-known solid-solid phase transitions, while another is suggestive of ferroelectric behavior.

Both normal methane and the deuterated species exhibit a series of solid-solid phase transitions below about 30 K.[1] The various phases have been the subject of extensive investigations, both in theory and experiment, and the transitions are generally described in terms of orientational ordering of the methane tetrahedra on the crystalline fcc lattice.[2,3] Both the higher (α-β) and lower (β-γ) temperature transitions are recognizable in the deuterated methanes for crystal densities along the vapor-pressure curve. However, for light methane, the β-γ transition appears only at pressures above 0.15 kbar,[4,5] indicating that the existence of the phase is density dependent. Furthermore, the data of Stevenson[6] suggest the possibility of a fourth phase, δ, which exists only at very high densities.

We wish to report a portion of the results obtained while studying the static dielectric constant (ϵ_0) and the solid-solid phase diagram of dense solid methane. Three sets of anomalies in the dielectric constant were observed. The first two were associated with the two well-known low-temperature phase changes, while the third occured at densities comparable to those of Stevenson's δ phase. A discussion of this latter anomaly follows a brief description of the experiment.

Determination of ϵ_0 for solid methane at high pressures and low temperatures was accomplished using sample-preparation and capacitance-measuring techniques developed in this laboratory.[7] In this method, the crystalline sample is grown from the melt at high pressures, filling a guarded, coaxial capacitor in which the pressure cell serves as the outer electrode and a cylindrical conductor within the cell forms the inner electrode. This technique provides dense polycrystalline samples that are relatively strain free and chemically pure. Measurements are made along pseudoisochores, with corrections necessary only for thermal expansion and elastic deformation of the cell. Eight crystals were grown at points along the melting curve ranging from 3.4 kbar and 159 K to 9.8 kbar and 252 K, corresponding to densities between 0.537 g/cm^3 and 0.590 g/cm^3.[8] All of the crystals showed anomalies in ϵ_0 upon crossing the α-β, β-γ, and α-γ phase lines. Such irregularities make a good probe for determining the P-T phase diagram, and the results will be published later. Here, attention is centered on the two highest-density crystals ($P_m = 8.89$ kbar, $T_m = 240.8$ K, $\rho_m = 0.584$ g/cm^3; and $P_m = 9.81$ kbar, $T_m = 252.5$ K, $\rho_m = 0.590$ g/cm^3), which exhibited a further and more interesting anomaly at low temperature.

Figure 1 shows representative data for the

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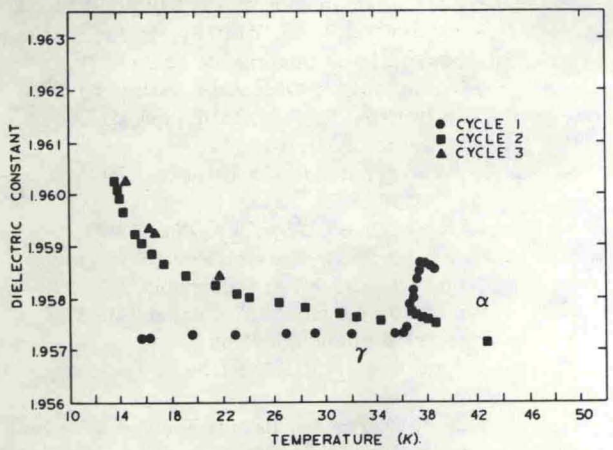


FIG. 1. Static dielectric constant versus temperature for a methane crystal with melting density 0.584 g/cm^3. Each symbol represents data taken with both increasing and decreasing temperature. Data near the α-γ transition were not taken during cycle 3. See text for discussion of cycles.

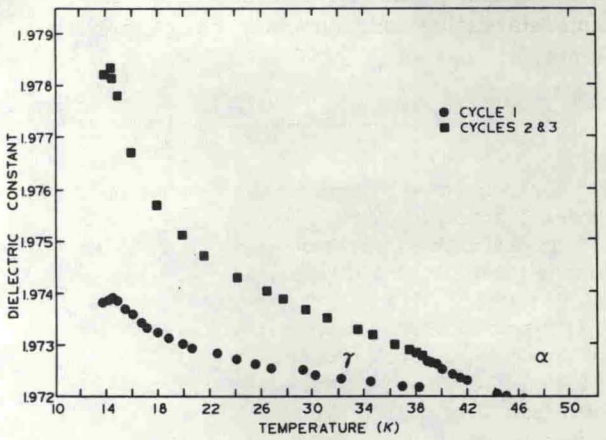


FIG. 2. Static dielectric constant versus temperature for a methane crystal with melting density 0.590 g/cm^3. Each symbol represents data taken with both increasing and decreasing temperature.

0.584-g/cm^3 crystal. The three symbols represent cycles in temperature from 50 to 14 to 50 K, each cycle lasting about 48 h and with data taken on both warming and cooling. The temperature of 14 K was the minimum attainable with the present cryogenics. The circles in Fig. 1 show behavior in the γ phase typical of all of the other (low-density) crystals; ϵ_0 versus T is flat and reproducible upon warming or cooling in that phase. However, upon cooling to the α-γ transition from 50 K during the second cycle (squares in Fig. 1), only a small decrease in ϵ_0 is seen at the transition and the expected γ phase dependence of ϵ_0 on T is not present. Instead, ϵ_0 increases with decreasing temperature, first linearly and then, for $T < \sim 22$ K, follows a curve fitted closely by a $C(T - T_c)^{-1}$ form. The third cycle (triangles in Fig. 1) shows no decrease upon cooling through the α-γ transition and again follows a $C(T - T_c)^{-1}$ form, although displaced from that of the second cycle. In the 0.590-g/cm^3 crystal (Fig. 2), no typical γ-phase behavior appeared, and cycling through the α-γ transition produced results similar to those above. An additional feature can be seen in Fig. 2 near 14 K. The $C(T - T_c)^{-1}$ behavior was interrupted and ϵ_0 began to decrease. This change was reproducible as temperature was cycled several times between 14 and 16 K.

For $T < 22$ K the data for each run may be fitted to a few parts in 10^4 by a Curie-Weiss form $\epsilon_0 = \epsilon_1 + C(T - T_c)^{-1}$. Such a temperature dependence is highly suggestive of the electric ordering in a ferroelectric or antiferroelectric (FE or AFE) transition. In the more usual FE behavior, the constant ϵ_1 is not required since the anomalous permittivity is several orders of magnitude larger than the permittivity in the paraelectric phase. In this case, however, the permittivity changes by less than 1% throughout the anomalous region. Efforts to observe hysteresis in the switching of the polarization vector were not successful as a result of electric breakdown of the stressed leads into the pressure vessel. No attempt was made to detect a permanent polarization.

Although the crystal structure in the γ phase is not certain, all suggested structures are noncentrosymmetric and thus, according to Aizu,[9] the crystal may form an FE phase. In this case, the most likely mechanism for a transition to an electrically polarized state is the softening of a lattice vibrational mode, probably the one associated with the ν_4 mode of the methane molecule.[10] This mode has the lowest frequency among the vibrational modes, is infrared active, and, if a $D_{2d}{}^2$ crystal symmetry is assumed,[11] allows an antiparallel alignment of the permanent dipoles resulting from the condensation of ν_4 mode phonons at $q = 0$. Such a structure could be associated with an AFE phase which interrupts the Curie-Weiss region in the 0.590-g/cm^3 crystal, discussed above.

These results are being supplemented by further experiments on the methane system and suggest the possible generality of such behavior in other systems having similar molecular structures, e.g., CD_4, CF_4, and CCl_4. If this is in

fact the case, this class of materials forms a new and interesting addition to the list of ferroelectrics.

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