

Structure and compression of crystalline methane at high pressure and room temperature

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Methane, CH₄, crystallizes in the face-centered cubic metal structure (space group *Fm3m*) at 15.9 kbar and 20 °C. Cubic unit-cell edges at 16.1, 28.9, 39.5, and 52.1 kbar are 5.4434, 5.3064, 5.1963, and 5.0947 Å, respectively. The isothermal bulk modulus, calculated from a first-order Murnaghan equation of state ($K' = 4$), is 49 ± 9 kbar. Methane transforms to a second as yet unidentified high-pressure solid phase at 52.5 kbar (20 °C).

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Recent advances in the study of cryogenic fluids in the diamond-window, high-pressure cell include the ability to determine high-pressure structures and compressibilities of the solid phases of elements and simple compounds that are gaseous under ambient conditions.¹ The single-crystal, diamond cell of Merrill and Bassett² has been modified for use in the x-ray diffraction study of these crystallized gases. This letter contains data on the structure, compression, and phase transitions of solid methane at 20 °C.

A single crystal of methane was produced in a cryogenic diamond-anvil, high-pressure cell wherein the sample was contained by a T301 stainless-steel gasket. The gasket aperture (approximately 250 μm thick and 300 μm in diameter) was filled by immersion in liquid methane, and the sample was contained between the two diamonds and pressurized to about 10 kbar while at low temperature. The diamond cell was then removed from the liquid.

At room temperature a single twinned crystal of methane was formed by slowly cycling the pressure on the sample across the freezing point (15.9 kbar) until only a single crystal filled the region within the gasket. The crystal was clear and colorless, and no birefringence was observed in polarized light. The crystal therefore appeared to be under no strain.

Methane at high pressure was studied by x-ray diffraction photography and four-circle x-ray diffractometry. The crystal was first oriented from precession photographs. The cubic unit-cell dimension was then measured on an automated diffractometer³ by centering three to six reflections of classes (111), (200), and (220) in each of eight equivalent orientations.⁴ This procedure yields values of 2θ that are corrected for instrumental and crystal centering errors. Reflections measured in this way on unstrained single crystals are generally reproducible to $\pm 0.0015^\circ$ at $30^\circ 2\theta$, with Mo $K\alpha$ radiation ($\lambda = 0.7093$ Å), which corresponds to a part in 20 000 error in unit-cell axial length.

A ruby crystal 10 μm in maximum diameter was included in the sample chamber for use in pressure calibration. Pressure was determined from the wavelength shift of the R_1 fluorescence line.⁵ The ruby fluorescence lines, which become broadened if the ruby crystals are strained, remained sharp at all pressures to above 55 kbar. Crystalline methane, therefore, does not become stiff with respect to ruby at these pressures.

Methane unit-cell dimensions were measured at four pressures as recorded in Table I. The isothermal bulk modulus of methane at 20 °C, calculated with a first-order Murnaghan equation of state ($K' = 4$), is 49 ± 9 kbar.

At the lowest pressure, which was approximately 0.2 kbar above freezing, the crystal was twinned, and both parts of the twin yielded identical cubic unit-cell constants. The twin law was 60° rotation about (111). Diffraction maxima were moderately sharp at this pressure, indicating little strain in the methane crystal.

With each increment of pressure the methane was observed to recrystallize in a new orientation. As the metal gasket deformed with changes in pressure, the methane crystals maintained a state of low internal strain by recrystallizing rather than deforming with the gasket. Significant broadening of methane diffraction maxima occurred after the second and fourth pressure increments, but the peaks after the third pressure change were sharp. Differences in peak breadth are presumably related to the degree of strain in the gasketed crystal, which filled the deforming sample chamber. The crystal remained dimensionally cubic throughout the pressure range from 15.9 to 52.1 kbar.

Positions and intensities of methane diffraction maxima are consistent with the simple face-centered cubic metal structure (*Fm3m*, $Z = 4$). Quantitative intensity measurements were not attempted because of unknown x-ray shielding effects caused by deformation of the steel gasket. Relative intensities were noted, however, and are recorded in Table II. These relative intensities are close to those of other fcc structures. It was assumed, therefore, that each lattice point in the fcc unit cell is occupied by a freely rotating CH₄ molecule, as observed in the methane I structure at room pressure and below 70 K.^{6,7} Extrapolation of the pressure-

TABLE I. Methane unit-cell dimensions at several pressures and 20 °C.

Pressure (kbar)	a (Å)	V (Å ³)	V/V_0
16.1(8) ^a	5.4434(7)	161.29(8)	1.000
28.9(8)	5.3064(8)	149.42(8)	0.9264
39.5(8)	5.1963(6)	140.31(6)	0.8699
52.1(5)	5.0947(10)	132.24(11)	0.8199

^aParenthesized figures represent estimated standard deviations.

TABLE II. Relative intensities of methane diffraction maxima at 16.1 kbar and 20 °C.

<i>hkl</i>	Intensity ^a
111	vs
200	s
220	ms
311	ms
222	m
400	vw
331	w
420	vw

^avs, very strong; s, strong; ms, moderately strong; m, moderate; w, weak; vw, very weak.

temperature melting curve for CH₄ of Medina and Daniels⁷ yielded a freezing pressure of approximately 14 kbar at 20 °C. It thus appears that methane freezes directly to the fcc structure at all temperatures up to 300 K (Fig. 1).

The fcc structure persisted from the freezing point at 15.9 kbar to 52.5 kbar, at which pressure the single crystal was observed to transform into a polycrystalline aggregate. This transition was reversed several times and was observed to be rapid. The loss of the single crystal, however, indicates that the transition is reconstructive and of first order.⁸ This high-pressure transition of solid methane has also been observed by Sharma⁹ using Raman spectroscopy. Attempts to produce a single crystal of this second high-pressure form of methane have not yet been successful, and identification of the structure must await high-pressure powder diffraction measurements. It should be noted, however, that extrapolation of the methane I/methane III phase boundary¹⁰ from low temperature to room temperature (Fig. 1) yields a transition pressure of approximately 50 kbar. It is possible, therefore, that the unidentified high-pressure form of CH₄ is methane III.

It is now possible to investigate the single-crystal compressibilities and high-pressure crystal structures of materials that are gases under ambient conditions. These high-pressure phases, which are among the most compressible of any known solids, may have volume reductions ($\Delta V/V_s$, where V_s is the molar volume at the 20 °C freezing pressure) of greater than 40% at 100 kbar. Solidified gases thus undergo much larger volume reductions than other types of solids

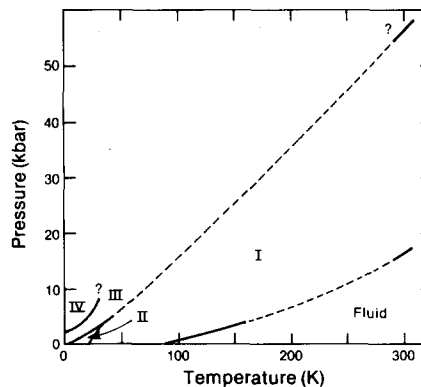


FIG. 1. Phase diagram for methane. Low-temperature data are from Ref. 7. Room-temperature data are from this study.

and consequently may be useful in determining the functional form for equations of state. Solid "gases," such as methane, are extremely soft, on the basis of birefringence, sharpness of x-ray diffraction maxima and ruby fluorescence lines, and recrystallization rather than extreme deformation. Because these gases also form single crystals, they may serve the double function of hydrostatic pressure media and internal pressure standards in future x-ray experiments.

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