

## Preliminary solid–solid phase diagram for nitrogen–methane mixtures by x-ray diffraction

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limit,<sup>10</sup> as is expected from results in simpler organic aromatic dimer systems.<sup>8</sup> Properties of the triplet state may therefore be utilized within the strong spin coupling limit to calculate geometrical features of the chlorophyll dimer both in model systems and, potentially, for the chlorophyll dimer *in vivo*.<sup>3</sup>

We are grateful to Professor G. L. Closs who originally supplied by pyrochlorophyllide samples used in these experiments and to Pradip Mitra for technical help with the EPR experiments.

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## Preliminary solid-solid phase diagram for nitrogen-methane mixtures by x-ray diffraction

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Molecular crystals made of rare gas atoms and nearly spherical molecules are the simplest known solids, so they are of fundamental importance to the theoretical understanding of the solid state. The structures of all pure solidified rare gases heavier than helium are well studied and without exception, these solids take on the closest packed face-centered-cubic structure. In theory, one would expect very nearly the same free energy for a hexagonal-closest-packed lattice as for the cubic-closest-packed if only two body, radial forces between molecular centers are considered.<sup>1</sup> The weak orientational forces present with slightly nonspherical molecules may favor one closest-packed lattice over another and with sufficiently clever theoretical analysis serve as a probe of the subtle free energy differences between the fcc and hcp structures.<sup>2,3</sup>

Methane seems to have a face-centered-cubic lattice of molecular centers in each of its solid phases, according to the most recent structure determinations.<sup>4,5</sup> However, in one of the first structure determinations for presumably pure methane, Schallamach<sup>6</sup> found "parasitic" x-ray diffraction lines at the lowest temperatures, which were later shown to be consistent with the presence of hexagonal closest packed crystallites in his powderlike samples.<sup>7</sup> On the other hand, pure nitrogen has a face-centered-cubic structure (fcc) below 36 K and a hexagonal-closest-packed (hcp) structure between 36 K and its melting point at 77.3 K.

The phase diagram for nitrogen-argon mixtures by Barrett and Meyer<sup>8</sup> shows that small amounts of nitrogen mixed with argon gas can lead to an hcp molecular lattice and that equal mixtures of the two molecules lead to an hcp lattice at all solid temperatures. This suggests that packing or similar orientational effects in a mixture of nearly spherical molecules with more oblate molecules, such as nitrogen would favor hexagonal closest packing. One then suspects nitrogen impurities as a cause of the Schallamach "parasitic" lines.

The argon and methane molecules are nearly the same size; methane, although nearly spherical, has an electrostatic octupole moment and interacts with other molecules through weak orientational forces. Because of these similarities and differences between argon and methane, a comparison of the argon-nitrogen phase diagram with the nitrogen-methane phase diagram should be useful. Therefore, we have made a preliminary investigation of the solid phase diagram of nitrogen-methane mixtures. We have used an x-ray diffraction method that is suitable primarily for distinguishing between fcc and hcp lattices of molecular centers.

Test samples were collected in a 1/8 in diam, cylindrical sample holder constructed of thin Mylar, mounted at the end of a long 1/8 in diam stainless steel tube and terminated at a copper block. The copper block contained a heater and two germanium thermometers; one was used for temperature monitoring and the other as a

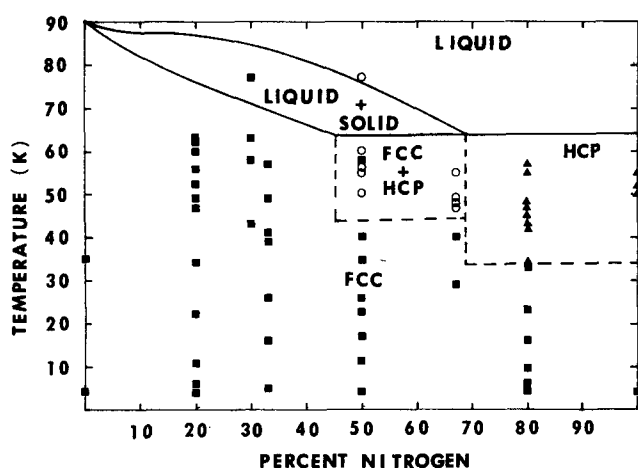


FIG. 1. Solid phase diagram for nitrogen-methane mixtures. Plotted points represent x-ray determinations of the lattice of molecular centers and dashed lines are the preliminary solid phase boundaries. Solid squares: fcc; Solid triangles: hcp; Open circles: fcc and hcp mixture; Solid lines: Solid-liquid phase boundaries from Federova<sup>11</sup>; Dashed lines: Preliminary solid-solid phase boundaries.

sensor in a temperature control circuit. This sample assembly was mounted vertically in the tail section of a Janis Model 8-DT Vari-Temp Helium Dewar. Beryllium windows mounted in the Dewar to accommodate the primary and reflected x-ray beams limited the diffraction angles ( $2\theta$ ) to less than 35 degrees. The diffraction pattern, using molybdenum  $K\alpha$  ( $\lambda = 0.711 \text{ \AA}$ ) x-rays was recorded on flat plate type 57 film in a Polaroid XR-7 cassette camera.

Our intent was to create powderlike samples. High purity, research-grade gases were premixed at approximately 1 atm pressure in a plenum and then permitted to flow into the evacuated sample holder tube. Acceptable samples were made by one of two procedures; one was to condense and freeze the gas mixtures in the stainless steel tube above the sample chamber, followed by melting and rapid resolidification in the Mylar tube. The second method was to condense the gas in the Mylar tube, followed by rapid solidification. On occasion, a sample frozen directly from the gas phase would appear. These samples generally were not sufficiently powderlike to be usable. Samples were prepared at various methane-nitrogen concentrations from pure methane to 80% nitrogen. X-ray diffraction photographs were taken as the samples were warmed from 4.2 K to the melting point of the samples. Generally, exposure times of a few minutes were required with a few minutes between exposures. Samples were rotated through angles of approximately  $60^\circ$  during exposure.

The x-ray diffraction patterns recorded on the film, consist of concentric rings of bright "dots" corresponding to the various reflections recordable with this apparatus. In general, samples of fcc crystals gave a record of two primary rings, each with many dots, corresponding to the (1 1 1) and (2 0 0) reflections.

Some photographs of fcc crystals recorded additional rings due to (220) reflections. These, however, contained fewer and less intense reflection dots. When a hexagonal or mixed sample appeared in warming from a cubic phase, the appearance of the pattern changed from a sparse ring of bright dots to a multitude of dots that formed nearly continuous and more distinct rings. Apparently a given cubic crystallite formed several smaller hexagonal grains. The data was analyzed by comparing the measured ring diameters with those expected for fcc and hcp structures from calculations based on the known molecular sizes.

Results of the study are presented in Fig. 1 as a plot of crystal structure as a function of temperature and methane-nitrogen concentration. The structure is fcc below the nitrogen  $\alpha$ - $\beta$  transition temperature (36 K) for all mixture concentrations. Above this temperature, a hexagonal structure appears for nitrogen concentrations of 80% or higher. Finally, there is a region of apparently mixed structures at high temperatures in the region of 50%-70% nitrogen concentration. The liquid-solid limit was not uniquely defined by the experiment, nor were the boundaries between solid phases precisely located.

The lattice constants for the solid mixtures as functions of concentration and temperature were measured but with poor precision. There was a general trend of increasing lattice constant with increasing methane concentration and increasing temperature; this trend is consistent with the results of argon-methane mixture studies of Greer and Meyer.<sup>9</sup> Lattice constant determinations for pure methane were in general agreement with those tabulated by Aadsen,<sup>10</sup> although detailed comparisons were masked by the experimental uncertainties.

There are clear differences in kind between the argon-nitrogen phase diagram of Barrett and Meyer and these preliminary results for methane-nitrogen mixtures. Apparently, small percentages of nitrogen are not sufficient to cause otherwise pure solid methane to become hexagonal at any temperature, in contrast to the case of nitrogen in argon. Also, methane-nitrogen mixtures are cubic at all temperatures below the  $\alpha$ - $\beta$  transition temperature of pure nitrogen at all concentrations, while 50% nitrogen-argon is hexagonal at all temperatures below the melting point. These results indicate that cubic methane is more stable relative to hexagonal packing than is cubic argon.

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## Indirect determination of concentrations in coexisting phases

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Recent theoretical studies<sup>1,2</sup> of the behavior of systems in the neighborhood of higher order critical points have stimulated interest in precise measurements of multi-component phase equilibria. When several phases are in thermodynamic equilibrium, it is frequently difficult, or at least inconvenient, to sample each phase. We report here a general method for the determination of the compositions of coexisting phases appropriate for any situation in which all the thermodynamic potentials (e.g., temperature, pressure, chemical potentials) are fixed, either by the experimenter or by rigorous thermodynamic conditions. We believe that this procedure, which is a generalization of one which has been used for determining the densities of coexisting liquid and gas phases in a one-component fluid,<sup>3</sup> is capable of wide applicability.

Our studies of tricritical phenomena in ternary mixtures of hydrocarbons<sup>4</sup> can be used to demonstrate the method of analysis. In the system methane + (2,2-dimethylbutane + 2,3-dimethylbutane) which we had already shown to be effectively "quasibinary," we needed to determine the concentrations of methane and total hexane in each of three coexisting phases. (In a truly binary mixture, setting the temperature fixes the pressure and the compositions of all three phases.) It is possible to sample each phase in turn (and we did so), but at 200 K and a pressure of 6 MPa it is inconvenient; moreover, since we could not maintain constant pressure in our constant-volume apparatus during sampling, we could not be certain that thermodynamic equilibrium was preserved.

Our current procedure is the following: the apparatus is loaded with measured amounts of methane and of a predetermined hexane mixture, amounts known or expected to yield three phases under the appropriate conditions. At a particular temperature the positions of the two interfaces are determined with a cathetometer. The cell, which is of fixed volume, has previously been calibrated, so that measurements of two meniscus positions effectively determine the volumes  $V^\alpha$ ,  $V^\beta$ , and  $V^\gamma$  of the three coexisting phases. (If the total volume  $V^t$  were variable, a third measurement would be required.) Since we are

interested in the compositions over a range of temperatures, we vary the temperature and make a series of measurements of volumes before reloading, but this is not essential for the analysis at a particular temperature.

The overall composition is now altered, either by adding additional amounts of one or both of the components or by replacing the entire contents of the cell with a new sample. (Were the measurements of unlimited precision, the number of independent loadings necessary to determine the compositions would be equal to the number of coexisting phases. In reality, however, satisfactory convergence requires that the concentrations be overdetermined.)

The analysis is straightforward. One has a series of loadings, for each of which there are determinations of the overall amounts of each component (moles  $n_1$  and  $n_2$ ) and of the volumes  $V^\alpha$ ,  $V^\beta$ , and  $V^\gamma$  of the coexisting phases. If in the  $i$ th loading we write  $c_{1i} = n_{1i}/V_i^t$  for the overall concentration of the first component and  $c_1^\alpha = n_1^\alpha/V_i^\alpha$ , etc., for its concentration in each phase, it is obvious that conservation conditions ( $n_{1i} = n_{1i}^\alpha + n_{1i}^\beta + n_{1i}^\gamma$ ,  $V_i^t = V_i^\alpha + V_i^\beta + V_i^\gamma$ ) require that

$$V_i^\alpha c_1^\alpha + V_i^\beta c_1^\beta + V_i^\gamma c_1^\gamma = V_i^t c_{1i} = n_{1i}. \quad (1)$$

There is a similar equation for each of the loadings and each of the components.

The method depends upon the thermodynamic requirement that the concentrations in each phase ( $c_1^\alpha$ ,  $c_1^\beta$ ,  $c_1^\gamma$ ) remain unchanged, independent of the relative size of the phases, so long as three phases remain in the system at the temperature in question. Equation (1) is thus one of a set of simultaneous equations that may be solved for the desired concentrations. In principle only three loadings are needed to determine three concentrations, but experimental prudence and an acquaintance with error theory suggest the wisdom of obtaining a larger number and analysing by the usual least-square methods.

It can then be shown that the concentration in one phase (say,  $c_1^\alpha$ ) is given by the equation