DEFECT STUDIES OF MOLECULAR AND RARE-GAS CRYSTALS DOWN TO 50 mK AND UP TO 150 MPa

R. O. Simmons

Department of Physics and Materials Research Laboratory
University of Illinois at Urbana-Champaign
1110 West Green
Urbana, Illinois 61801

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ABSTRACT

Special challenges face the scientist interested in structural transformations in molecular crystals under unusual conditions of temperature and specimen volatility especially when the materials have either very small or very large scattering amplitudes. Techniques have been developed to prepare single crystals of condensed gases of mm or larger size, to ascertain their degree of crystalline perfection and fix their orientation, to measure Bragg spacings, changes in Bragg spacings and intensities. For precise work at higher temperatures and pressures a Be specimen cell attached to a heat exchanger is used at the focus of a large orientable back-reflection camera. Phase transitions arising from changes in molecular rotational ordering in solid CH_4 and CD_4 and lattice parameters during sublimation and melting of solid Ar, Kr, and Xe have thus been studied. For lower temperatures, the x-ray scattering specimen cell is fixed to a helium dilution refrigerator; it can be taken down to 50 mK and internally pressurized to 20 MPa. The sealed-off x-ray source is orientable about three orthogonal axes. Scattered x-rays are collected in an orientable position-sensitive detector. Two examples of investigations desirable by coherent scattering include 1) determination of the symmetries of the different phases below 1 K of the system solid ortho- and para- H_2, and 2) microscopic study of isotopic phase separation in solid ^3He-^4He mixtures below 0.4 K. In case 1), the known fcc form of solid hydrogen, stable below about 2 K for ortho-rich material, was determined by J. V. Gates and coworkers to transform to hcp form at lower concentrations and temperatures. The transformation temperatures and compositions could be followed, despite internal specimen heating due to spontaneous ortho- to para-conversion, below 200 mK. In case 2), x-ray studies of isotopic phase separation in ^3He-^4He bcc solids were carried out by H. A. Fraass. Direct determination of Bragg spacings of the daughter phases and their perfection and orientation with respect to the matrix could be made for the first time, and new characteristics of the phase separation phenomena discovered

as specimens were cooled and reheated in a range below 400 mK.

INTRODUCTION

X-ray diffraction techniques offer special advantages to the scientist interested in molecular crystals, especially those formed by condensation of gases. Such crystals are frequently easily deformed, with a typical shear strength of only 0.1 MPa near the melting temperature. Equilibrium vapor pressures and coefficients of thermal expansion are frequently high; specimen surfaces are subject to rapid change which vitiates application of many conventional techniques, such as pulse-echo ultrasonics. The temperatures of solidification and of solid-solid phase transformation are low and only small amounts of material may be available, or be suitable, for example, when low thermal conductivity dictates minimal specimen dimensions to insure temperature homogeneity.

Many interesting molecular crystals however have low absorption and small x-ray scattering amplitudes. While one gains the capacity to probe the bulk not just the surface, one must maximize the efficiency of the scattering geometry. At the same time, need to study the specimen at elevated pressures and to provide suitable thermal and vacuum shields presents unusual challenges.

During the last decade, techniques have been developed at Illinois to prepare and to study a variety of molecular crystals, including the prototype crystals formed from the condensed noble gases He, Ne, Ar, Kr, and Xe. This paper describes these techniques and indicates examples of results in each of the areas of scientific interest which motivated the technology. At higher temperatures and pressures the examples cited are solid CH_4, CD_4, and Xe. At lower temperatures the examples are solid H_2 and He. Rotational molecular disorder in the methanes and in ortho-para hydrogen solid mixtures are of special relevance to this Symposium. Studies of isotopic solid mixtures of ^3He and ^4He are a final example of the power of x-ray techniques to add new knowledge about phase separation phenomena in these so-called quantum crystals.

ROTATIONAL DISORDER IN SOLID METHANES

The methane molecule has tetrahedral symmetry but its shape departs little from spherical. Condensation into an fcc lattice provides interesting examples for the systematic study of rotational ordering phenomena as influenced by differences in isotopic mass, in molecular rotational moments of inertia, and in nuclear spin isomerism.[1] The system is somewhat simpler than that discussed in

this Symposium by Professor Raich.

By the end of the 1960's calorimetric and similar studies had established phase transition temperatures in the methanes. One particular interest was whether the lamda-type phase transitions in the region 20-30 K have any discontinuous character in carefully treated crystalline specimens. X-ray, neutron, and electron scattering data of the time had insufficient resolution to distinguish sharp changes in lattice parameter. A related challenge was precise temperature control of pure methane specimens which show rather sluggish response in the immediate neighborhood of transitions: change by 10 mdeg may require a settling time of up to hours.

The x-ray technique applied to successful solution of this problem was use of a rigid-tail fluid-flow heat exchanger cryostat[2] combined with a large orientable back-reflection x-ray camera.[3] The cryostat-camera combination is shown in Figure 1. The cryostat provides excellent temperature control over the interval 2.5-300 K; short-term fluctuations are held below 5 mdeg and drift is less than 25 mdeg per day. Crystalline specimens of several mm diameter can be prepared by directional solidification of liquid in a cylindrical

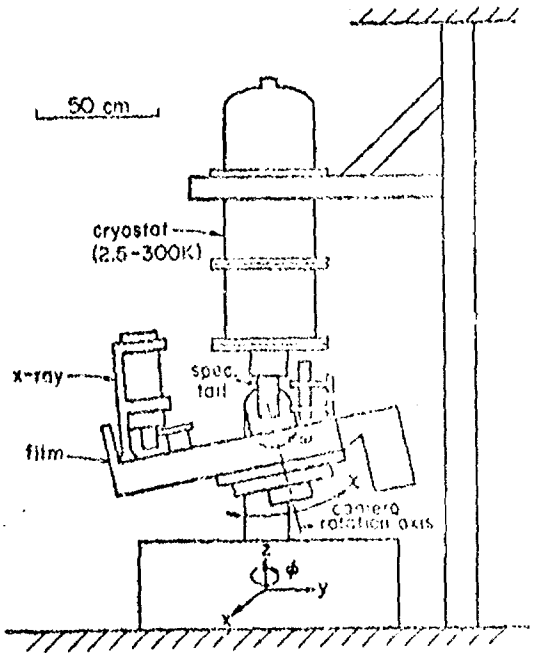

Figure 1. Cryostat-camera system for precise lattice parameter measurements on molecular crystals having freezing points below 300 K. After specimen crystal growth the camera is oriented by means of Laue diagrams and the specimen is centered by microscope.

Mylar tube.[4] Temperatures above and below 20 K are measured with Pt and Ge resistance thermometers, respectively.

Because specimen orientation cannot ordinarily be controlled, the camera is set in a large cradle so that after crystal growth the camera equator can be set in the appropriate crystalline directions. Lattice parameter films are taken with camera oscillation about two successive orientations which provide exposures on the left and right sides of the camera, shown in plan view in Figure 2. The principal error in a camera of this type is specimen centering error, which arises in part from specimen

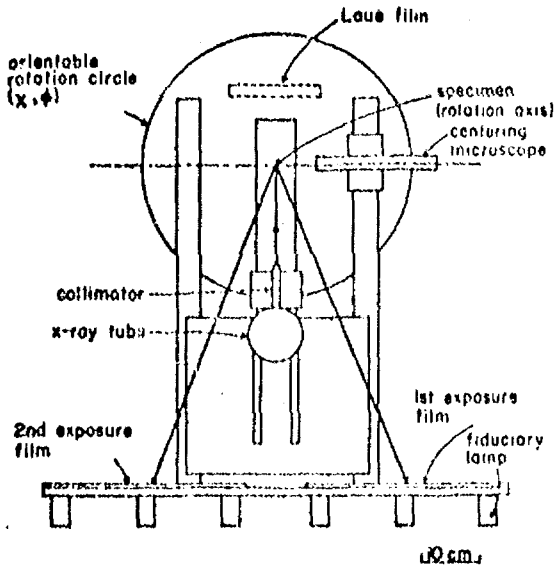

Figure 2. Plan view of rotating camera used to provide precise lattice parameters of molecular crystals and to measure lattice parameter changes due to phase changes and to thermal expansion. Camera exposure times with a gaseous He path range typically from 1-100 min.

surface roughness (in these soft volatile crystals), absorption, and deviation of the diffraction vector from the normal to the specimen surface. A centering microscope and giant dimensions for the camera control this error. Error in lattice parameter measurements, even for rather poorly crystallized specimens, is about 0.00007 A^3; this is near the intrinsic variation shown from specimen to specimen by many simple crystals. Sensitivity for lattice parameter changes in a given specimen can be as small as 3 ppm.[5]

Results obtained by Duane Aadsen[6] for the lattice parameter of Cl_4 are shown in Figure 3, together with previous work in the literature obtained by x-ray diffractometry of polycrystalline specimens. The results of Aadsen are

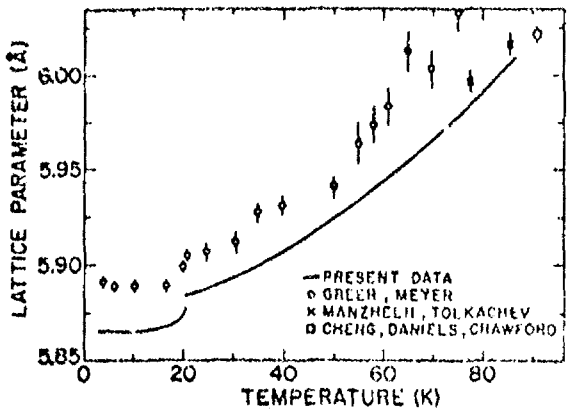

Fig. 3. Lattice parameter of pure Cl_4 in the temperature range 2.5-86 K, according to D. R. Aadsen (Ref. 6). The mixed continuous-discontinuous character of the transition due to molecular rotational ordering near 20.4 K is clearly shown, whereas previous diffraction work was of insufficient resolution. Agreement of the lattice parameter value at high temperature with bulk equation of state research by Cheng and coworkers is shown.

represented by a solid line in Figure 3; to show scatter in his data it is necessary to make a greatly enlarged diagram.

This is Figure 4, which shows clearly the discontinuous part of the transition and also exhibits the hysteresis present, of about 90 mdeg. Such hysteresis, incidentally, is characteristic of martensitic-type transition behavior. No long-range diffusion of the molecular centers is involved in the transition, yet the free energy differences between the phases are modest at the transition temperature. X-ray work does provide a

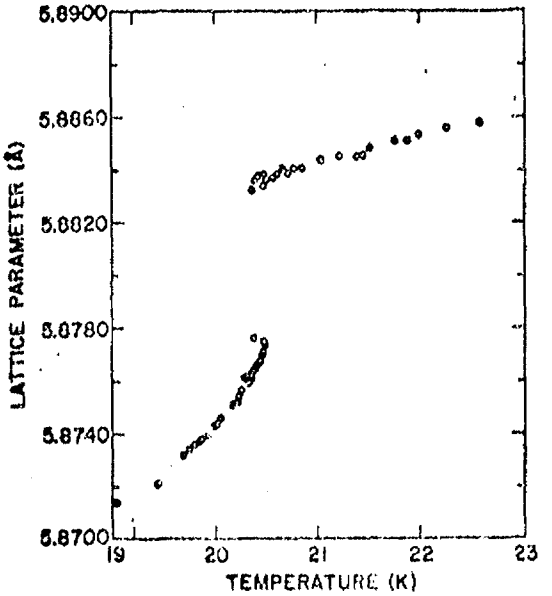

Fig. 4. D. R. Aadsen's high resolution lattice parameter study of the I-II phase transition in crystalline CH_4 (Ref 5). Both phases I and II are fcc, but the lower temperature phase is characterized by orientational order of 3/4 of the molecules. Hysteresis of about 90 mdeg is present upon heating and cooling.

good value of the volume change, and hence via Clausius-Clapeyron of the entropy difference, at the transition. It is 0.65 cal/mol/deg, which compares closely with theoretical estimates.

One other interesting feature of this transition is the steep rise in thermal expansion coefficient on the low-temperature side. This parallels heat capacity results. Unfortunately, calorimetry is of less use for pursuit of detailed comparisons in the region of hysteresis and above. The accepted model for this transition represents the upper fcc phase (I) as molecules with essentially unhindered rotation and the lower fcc phase (II) as one with 3/4 of the molecules oriented in an 8-sublattice "antiferrorotational" arrangement and with 1/4 still unhindered (i.e. in an octahedral crystal field). Investigation of the dynamics of the rotating molecules is best done by neutron scattering.[1]

Another methane example, CD_4, is worth presenting to show the capacity of suitable x-ray methods to clarify some static features of similar rotational phase transitions. Compared to the light methane, CH_4 at saturated vapor pressure shows an additional phase at low temperatures (called III). This phase is of tetragonal symmetry and it is supposed that it is fully ordered although the structure has so far resisted complete analysis. Figure 5 shows the considerable scatter in various experimental data by

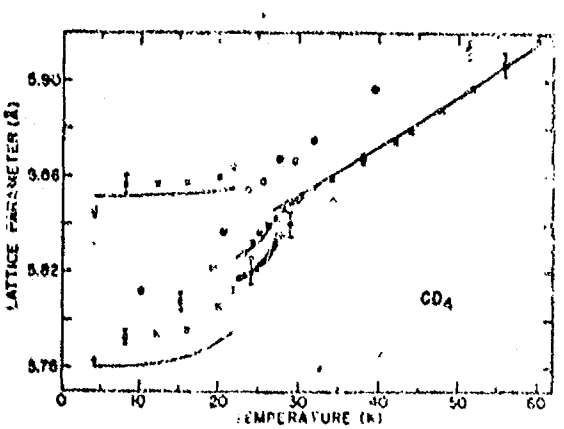

Fig. 5. Lattice parameters of solid CD_4 as measured with the cryostat-camera system by D. R. Baer and coworkers (solid lines, Ref. 7). Scatter in their data is too small to be shown. On the other hand, previous x-ray and neutron data from the literature are shown as individual points with stated errors indicated.

the literature on CD_4 (taken using x-ray and neutron scattering) as respective individual points (circles, triangles, etc.) prior to the work of Baer and coworkers.[7] Individual references to the earlier work are cited in Reference 7. No consistent pattern is available from the previous work. There are lattice parameter differences outside stated errors, there is insufficient resolution to obtain a lattice parameter discontinuity at the upper (I-II) transition, the c/a ratio of the tetragonal phase (III) is poorly defined and its temperature dependence (an order parameter for the phase) is unknown.

The work of Baer and coworkers[7] is of a quality comparable to that of Aadsen and is shown as solid lines on Figure 5. For reasons of space a diagram analagous to to Aadsen's area of Figure 4 is omitted, but the data are similar, except that CD_4 shows a larger region of hysteretic behavior.

The methane II-III transition between fcc and tetragonal phases shows some macroscopic similarity to transitions in minerals. The tetragonal phase in methane presumably reflects full ordering of the molecules, with complete hindrance to their rotation. Unfortunately, there is no space here to discuss other interesting effects, such as lattice thermal contraction in CH_4 phase II, which arise from nuclear spin isomer effects at lower temperatures.[6]

EQUATION OF STATE OF NOBLE GAS SOLIDS

The capacity of x-rays and of neutrons to penetrate suitable pressure vessels is well-known, and has been exploited in our laboratory using the same cryostat-camera system. The physical systems of interest were the noble gas solids initially, because of their simplicity compared to molecular crystals and the suspicion (shown to have a basis!) that conditions inside pressure vessels are not uniform.

A Be cell for the 200 MPa (2 kilobar) range was designed by Dr. R. K. Crawford and applied by him and A. T. Macrander.[8] This reliable pressure cell is shown in Figure 6. A cone-type seal is made

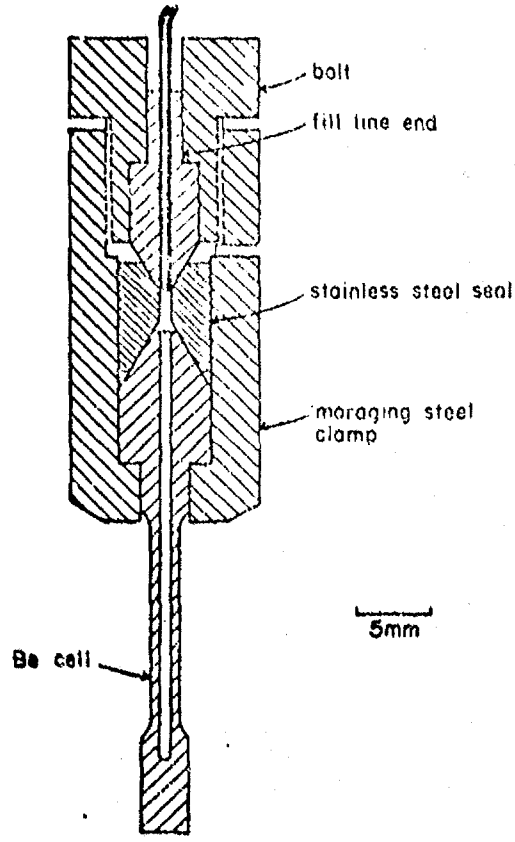

Fig. 6. Be sample cell of 0.79 mm diameter bore and its high-pressure seal to a specimen fill line of 0.15 mm inside diameter. In use, temperature differences between top and bottom of the cell are typically less than 30 mdeg, except when the cell temperature is being changed, when internal pressure gradients also arise in the self-pressurized specimen.

between the machined Be cell and a fill-line leading outside the cryostat to a high-pressure source of specimen material. Crystalline specimens are prepared by directional solidification of liquid in a temperature gradient. Transmission Laue diagrams verify crystal orientation.

In this arrangement the specimens are self-pressurized. When the cell is filled entirely with solid or with both solid and liquid, temperature changes are accompanied by changes in pressure. At large pressures, elasticity of the cell permits some changes in cell shape and consequent plastic flow of the solid contained therein. Precise x-ray lattice parameter measurement permits sensing of pressure gradients in the specimen about down to the 0.1 MPa level. The x-ray method therefore has a built-in check for equilibration of the system.

When the cell is sealed off with an amount of material such that both liquid and solid are present, precise study of the solid at melting over a range of temperatures is possible. An example of data taken on two specimens of Xe is shown in Figure 7.[9] Along the line from the triple point to point C, lattice parameters are seen to decrease corresponding to the increase in pressure of the melting transition. From separate determinations of the equilibrium P-T relation, this precise V-T relation can be used to obtain an improved equation of state.

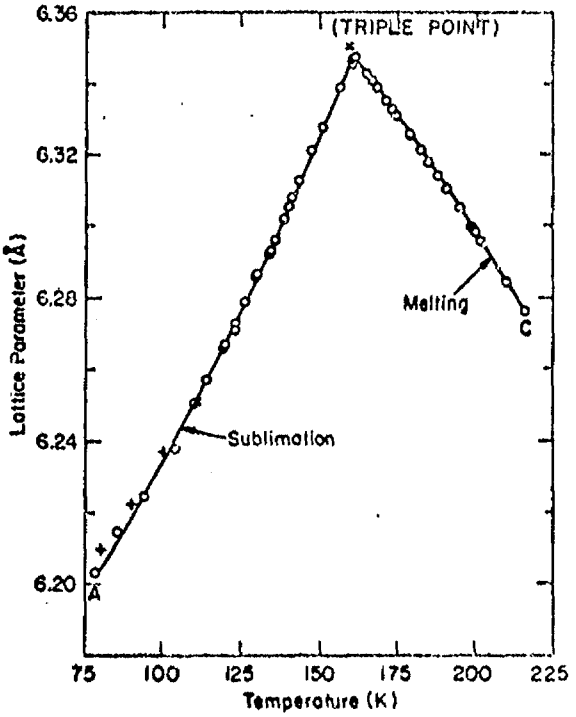

Fig. 7. Precise lattice parameters of crystalline Xe (Ref. 9) for specimens confined in the Be cell of Fig. 6 at pressures from the triple point up to about 140 MPa (point C) and at saturated vapor pressure from the triple point down to point A. Data like these yield information about the equation of state.

Indeed, further refinements are possible. Consider the data in Figure 7 obtained by cooling the specimen below the triple point temperature (toward point A). The specimen in this case is at its

saturated vapor pressure and the Be cell serves only for mechanical support of the specimen and confinement of the vapor phase. Conventional thermal expansion measurements are then possible and for Xe these have been analyzed to deduce some properties of the thermal vacancy in Xe. In addition, because all the temperatures are above the Xe Debye temperature, isochores in the P-T plane of the phase diagram are expected to be essentially straight lines. One can then combine these x-ray data with existing values of melting and of sublimation pressures, to obtain values for $(\partial P/\partial T)_V$ and its volume dependence. Finally, from this volume dependence one can obtain the isochoric temperature derivative of the bulk modulus, B_T. For Xe the result is $(\partial B_T/\partial T)_V = (1.08 \pm 0.60)$ MPa/K at a molar volume of 37.6 cm^3/mole.[9] Such high-order derivatives of the crystal free energy are difficult to obtain for (soft) molecular crystals. Their sign and magnitude are sensitive tests for intermolecular potentials which are generally difficult to investigate quantitatively in the condensed state.

When information about molecular crystal compressibility at low pressures is sufficient, one can apply the same cryostat-camera system, with a thin-walled specimen cell and He fluid as a pressure medium. In this case, hydrostatic conditions obtain, and the only concern is for possible small interactions between the He fluid and the specimen surface.[10]

SOLID HYDROGEN - MOLECULAR ORDERING AT LOW TEMPERATURES

Solid hydrogen (H_2) provides a fascinating system for the investigation of molecular ordering phenomena. The solid is usually a mixture of the nuclear spin species called ortho- and para-H_2, respectively. For hydrogen the spacing between molecular rotational levels is large compared to the solidification temperature and very large compared to the temperatures marking the boundary between different crystallographic phases. At these temperatures, therefore, molecules are predominantly in their rotational ground states, which have different symmetries. The intermolecular interactions consequently depend upon the concentration, x, of ortho-H_2 in the solid. Pure para-H_2 has central interactions between the molecular centers whereas in ortho-H_2 to this central interaction is added a quadrupolar term.

The transition between different solid phases of H_2 depends upon pressure, temperature, and ortho-concentration x present. The high-temperature solid phase is hcp for all concentrations with apparently a uniform angular distribution

for the rotation axes of the molecules. Slightly above 2 K, however, pure ortho-H_2 at low pressure exhibits a crystallographic transformation to an ordered fcc phase of symmetry Pa3. The transformation temperature is lower for smaller concentration, reaching, for example upon cooling, 0.6 K (600 mK) at about a χ of 60%. Hysteresis is exhibited in the transformation, which is supposed to be martensitic (i.e. diffusionless) in nature. Above 600 mK the transformation has been investigated by many different techniques, among them heat capacity, cw NMR line shape, changes in $(dP/dT)_V$, Raman effect, and neutron and x-ray scattering.

Below 600 mK experimental evidence about the transformation was sparse prior to 1979. Studies by NMR (cw, pulsed, and T_1) however suggested further broad temperature dependence of a transformation upon χ, for concentrations below 60%, although the NMR criteria for the transformation varied and the various deduced temperatures differed by a factor of two. Citations of extensive work in the literature are given in Reference 11.

Clearly, direct structural information was to be a useful element in understanding the low-χ low-temperature behavior. Just as clearly, however, fairly sophisticated scattering techniques would be required. The specimens had to be taken controllably to temperatures well below 600 mK and structural data collected reasonably quickly. Because the ground-state energy of ortho-H_2 is higher than that of para-H_2, conversion of the ortho-species into para- occurs at a rate of about 2% per hour, accompanied by considerable release of energy. This appears as volume evolution of heat in a specimen of relatively poor thermal conductivity, which aggravates problems of refrigeration and of thermometry. Small specimens were therefore indicated, but this makes rapid x-ray diffraction studies difficult in the case of a solid such as H_2 which contains only two electrons per molecule.

For his x-ray study John Gates[11] chose to use a modification of the cryogenic arrangement of Steve Heald. Heald's cryostat has been described in the literature.[12] More detail appears in his thesis.[13] The general arrangement of the specimen region of Heald's tail-type cryostat is shown in Figure 8. A ^{3}He-^{4}He dilution refrigerator is mounted below a ^{4}He chamber ("cold plate") pumped to about 1 K. The Lucite specimen chamber is fixed to the refrigerator mixing chamber, whose cooling is balanced against electrical heating to achieve temperatures in the region 50-1000 mK. The entire assembly is

enclosed within successive thin-walled

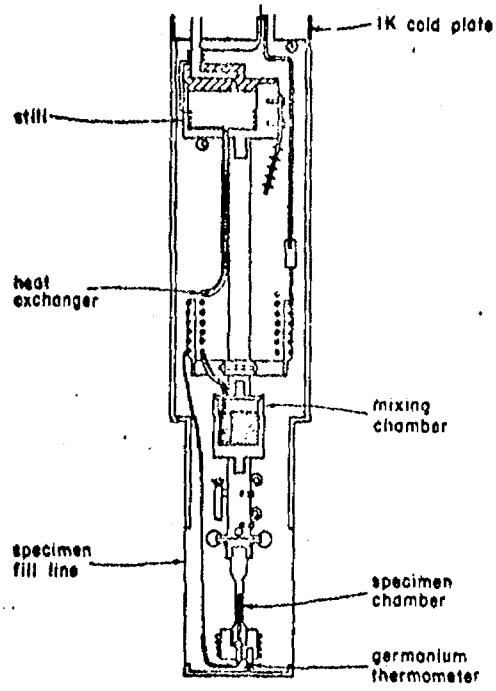

Fig. 8. S. M. Heald's ^{3}He-^{4}He dilution-refrigerator cryostat tail for x-ray diffraction studies down to 50 mK and up to 25 MPa (Ref. 12). The still, which separates ^{3}He from the mixture for flow through an external circuit (not shown), is mechanical support for the colder mixing chamber through a vertical graphite post. The molecular crystal specimen is prepared in the chamber at the bottom.

thermal radiation shields at about 1 K, 4 K, and 80 K, respectively, and finally within a cylindrical Be cryostat vacuum jacket.

Hydrogen crystal growth was a challenge, because the solidification temperature near 14 K was far higher than those available previously in this cryostat. The problem was solved by the addition of an additional volume in the specimen gas fill line, which itself had additional heaters, so that sufficient H_2 would be available for crystallization. These modifications are shown schematically in Figure 9, which also illustrates the external system used to convert the starting material to a concentration of 75% ortho-H_2.

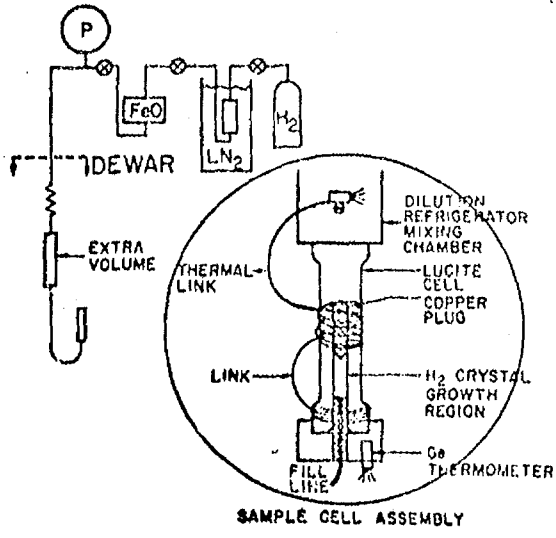

Fig. 9. Schematic diagram of the arrangement used by Gates and coworkers (Ref. 11) to prepare mm size crystals of initial 75% ortho-H_2 content. Because of self-evolution of heat by the samples, special thermal links to the thermometers were used. X-ray Bragg peaks on transforming samples were obtained at temperatures well below 200 mK.

Another concern was rapid acquisition of x-ray Bragg peak data. Successive scanning of a range of angles by a moving slit in front of a scintillation detector had proven sufficient in pioneering studies of solid He by Reinhard Balzer.[14] Because, similar to the rationale described in a previous section for the cryostat-camera system, angular orientability of the x-ray source was

needed, a sealed-off (and therefore relatively low power) x-ray tube was used. For H_2 better speed, and the capability to examine a range of angles simultaneously, was necessary. The detector of choice was a gas-flow position-sensitive counter, whose output registered on a multichannel analyzer. A subsequent version of this system is described by B. A. Fraas.[15] Figure 10 shows typical results for a Bragg peak of diminishing intensity during crystallographic transformation; data for an individual low-order peak (200) could be collected in

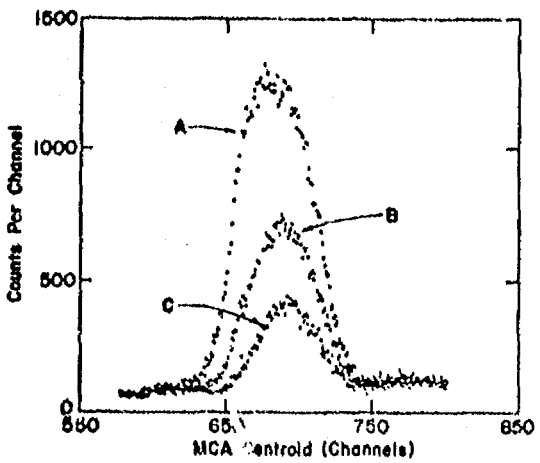

Fig. 10. Typical low-order Bragg peaks each collected in about 100 sec, as displayed on the multichannel analyzer of a position-sensitive detector. The full background is shown; it is contributed both by the specimen and by its chamber and many associated shields. One degree in Bragg angle corresponds to about 100 channels (Ref. 15).

about 100 sec. Parameterization of the integrated peak intensity versus H_2 specimen temperature permitted precise and reproducible characterization of a transition temperature T^* and its uncertainty, which could then be put on a graphical plot of T^* versus χ.

The results of this work by Gates and coworkers are summarized, together with previous work, on Figure 11. At

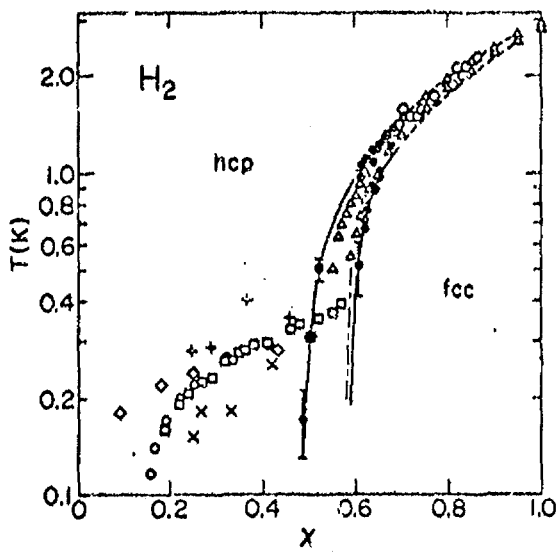

Fig. 11. Collected results for the apparent transition temperatures of solid H_2 at low pressure (Ref. 11). Abcissa χ represents concentration of ortho-H_2. X-ray data by Gates and coworkers are solid circles, connected by solid lines. Separate lines for heating and for cooling transitions are shown. The major result of Gates is that the low temperature - low χ phase has hcp not fcc structure as previously supposed on the basis of previous work based upon NMR alone.

temperatures above 600 mK the various techniques employed previously all generally agree, including agreement in the hysteresis exhibited upon cooling and heating (lower and upper curves, respectively). The Gates data (solid circles) also agree. However, at low temperatures the wide variability among

the previous NMR results is evident (crosses and various open symbols).

The principal result of Gates' x-ray study was to show that the fcc to hcp transformation temperature extrapolates to zero near an ortho-H_2 concentration of 0.49. The low concentration-low temperature phase is hcp not fcc. Because NMR signatures are present between this region of the phase diagram and others it is therefore clear that at least three different phases occur in solid H_2. At this time, characterization of the third phase is a matter of dispute. It exhibits some characteristics of a frozen-in disorder of the molecular rotation axes ("quadrupolar spin glass").

ISOTOPIC HELIUM MIXTURES - POSITIONAL ORDERING

This final brief example concerns x-ray diffraction as a new tool to study isotopic phase separation in solid mixtures of the isotopes ^3He and ^4He. Much the same cryostat-detector system can be used as for the solid H_2 studies already described. Similar regimes of temperature and stringencies on x-ray scattering data collection efficiency are involved.

Helium solidifies only under applied pressure, and the resulting specimens are elusive, particularly at larger molar volumes. For example, tiny thermal or mechanical stress gradients are sufficient to produce specimen rotation, recrystallization, and other behavior difficult for x-ray diffractometry. Methodical attention will produce suitable specimens, however.[4]

The phenomenon of isotopic phase separation was discovered in solid helium mixtures by calorimetric studies of D. O. Edwards and coworkers in 1962. For nearly two decades thereafter the only data applicable to the study of the ^3He-^4He solid phase diagram were obtained by calorimetry, by measurements of total system pressure, or by studies of thermal conduction. These techniques all give information about the gross specimen, heterogeneous or not. Data on the individual separated phases was lacking.

This absence can be rectified by the application of an x-ray diffraction technique.[16] A ^3He-^4He mixture is solidified then its lattice parameter is measured upon cooling. At the higher temperatures near melting the lattice parameter of a homogeneous specimen held at constant macroscopic volume shows variations attributable to the presence of thermally-generated vacant atomic sites[14] (see Figure 12). Then upon further cooling in the range below 400 mK the Bragg peak divides into two over a narrow temperature range (a few percent of the

temperature) and one can determine the equilibrium molar volumes of the respective ^{3}He-rich and ^{4}He-rich phases in coexistence at a succession of lower

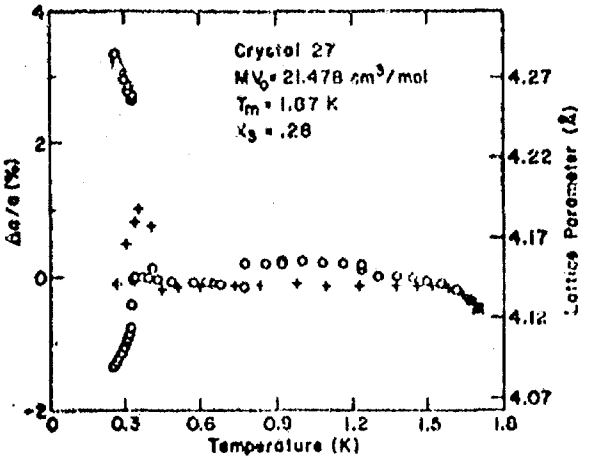

Fig. 12. Lattice parameters of an isotopic solid helium mixture of original composition 28% ^{3}He, solidified at 1.87 K and an initial molar volume shown (from Ref. 15). Data upon cooling (circles) differ from data upon heating (crosses) because of difficulties of equilibration of a bulk specimen suitable for precise x-ray diffractometry upon heating and isotope remixing. Nevertheless, near 300 mK the different lattice parameters of the coexisting daughter phases are accurately measurable.

temperatures. Because of the low absorption of solid He, the x-rays probe the bulk specimen in transmission geometry.

For the example shown in Figure 12 all the phases concerned are bcc. In other cases one or the daughter phases may show further changes upon cooling, such as melting (possible with ^{3}He-rich phases at low pressures!) or further crystallographic modification. Owing to the rapid exchange of He atoms between adjacent atomic sites these phenomena develop promptly upon gradual cooling. Regrowth of a single crystal specimen by isotope remixing in the solid phase is not easy, however, as illustrated by the scatter of data at intermediate temperatures in Figure 12.

This new technique shows promise of qualitative new contributions to the understanding of interatomic interactions is such mixtures, but much development remains to be done.

ACKNOWLEDGEMENTS

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