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Transition data and kinetics of the hcp-fcc ^{4}He transition between 4 and 9 kbar

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The transition hcp-fcc ^{4}He was studied from 4 to 9 kbar using an optical method. It was found that the estimated transition line is essentially linear in this range with a slope of 622 bar/K. This line deviates increasingly from theoretical predictions at higher pressures. The temperature hysteresis of the transition increases from 1 to 2.8 K, and the athermal width from 0.1 to 2 K. Detailed study of the kinetics near 9 kbar showed that both athermal and isothermal transformations are possible. The isothermal transformation goes to completion in heating, but not in cooling. Reproducibility of the c-axis orientation was also established for the athermal transition if prolonged annealing is avoided.

I. INTRODUCTION

In previous work[1-3] on the first-order transition between the two close-packed phases of ^{4}He (hcp and fcc) the method of thermal analysis was used. That work covered the range from the triple point at $T = 14.99$ K and $P = 1.127$ kbar to a pressure of nearly 4 kbar. It was discovered that the transition shows temperature hysteresis, which increases with increasing pressure. It was also found that the transition has an inherent temperature width if it is traversed at not too low heating or cooling rates, the so-called athermal width. This athermal width also increases considerably with rising pressure. Self-cooling during the heating transition, and self-heating during the cooling transition were also occasionally observed, particularly close to the triple point. The observations showed that parts of the transition could proceed at high speed. The kinetic aspects of the transition were similar to those commonly observed for martensitic transformations,[4] and it was therefore proposed that the transformation is of this type.

Apart from the kinetics of the transition, there is also considerable interest in the establishment of the equilibrium phase diagram. Theoretical calculations of the phase diagram by Holian *et al.*[5] predict a gradually steepening phase line in the PT plane, leading eventually to negative slope and a maximum transition pressure at 0 K estimated in the range 15 to 80 kbar. The thermal investigations[1-3] did not show this steepening, but gave a linear PT relationship, with the exception of the vicinity of the triple point. It appeared, therefore, that the experimental phase line deviated from theoretical predictions, although this deviation was not yet very pronounced at 4 kbar.

From the foregoing discussion it becomes clear that it would be of interest to extend the phase diagram beyond 4 kbar, as well as to make a more detailed study of the kinetics of the transition. For both purposes the thermal method is not well suited. Work above 4 kbar using this method becomes very difficult because of the increasing athermal width, which has the practical effect of making the thermal signal fainter. At a pressure of 4 kbar one has, probably, reached the practical limit for studying the transition by the thermal method. Other drawbacks of the method are that it is not suited to the study of either very fast or very slow transition phenomena. For fast processes one has to contend with the inevitable thermal smearing because of the finite heat conductivity and the heat-capacity background of container and helium sample. Very slow transition rates, on the other hand, cannot be distinguished from the background heat capacity. It was therefore decided to use an optical method to distinguish between the two phases, making use of the optical birefringence of the hcp phase as opposed to the optical isotropy of the fcc phase.[6,7] This method is essentially instantaneous; it has the further advantage of discriminating against effects not directly connected with the transition (with the possible exception of stress birefringence).

We were able by using this method to extend the experimental range of the phase diagram to near 9 kbar. The phase line continues with linear slope to this pressure, disagreeing increasingly with the theoretical prediction. The temperature hysteresis near 9 kbar reaches a value of about 3 K and the athermal width of about 2 K.

The optical signal of the transition was very well resolved in favorable cases, making a more detailed study of the kinetics in some crystals possible. Burst-like phenomena of very short duration ($\lesssim 0.01$ sec) were observed frequently. The progress of the transition during isothermal holding was also studied; the heating transition was found to go to completion with a time constant of many hours; the cooling transition, on the other hand, did not go to completion. The cooling transition also showed stabilization. Reproducibility of the *c*-axis orientation of the hcp crystal was observed for repeated passes through the transition. These observations give further evidence for the proposed martensitic character of the transition.[8,9]

II. EXPERIMENTAL DETAIL

The pressure cell is shown in Fig. 1. The cell containing the crystal was machined from Berylco 25; this piece was pressed into an outer support cylinder made from type 416 stainless steel. The helium space is a cylinder 4.76 mm in diameter and 13-mm long. Two optical windows were provided, using sapphire windows of 2.4-mm thickness and 6.35-mm diameter. The windows were sealed using suitable rings and pushpieces, well polished and indium coated. A spacer and several springs inside the cell provided an initial window seal. The clear optical aperture of the cell is 1.59 mm. The helium space was connected at the midpoint to a high-pressure capillary of 0.15-mm inside diameter. The capillary leads to a room-temperature pressurization system, using a Harwood[10] intensifier for its last stage. The filling capillary could be kept unblocked using a heater wound onto its outside between the low-temperature and liquid-nitrogen stage.

The composite pressure cell, in turn was press fitted into a massive aluminum alloy block providing 127 cm^2 of contact area. The alloy block carries a calibrated germanium thermometer[11] and a heater (Fig. 2); it was mounted onto the regulated temperature stage of an optical cryostat. The optical cell is surrounded by heat shields at the cell temperature and at liquid-nitrogen temperature. Heat contact between the helium sample and the thermometer was excellent, the thermal relaxation time of the assembly at the working temperature being of the order of 1 min.

Helium of research grade (Linde ultrahigh purity, 99.999% ^{4}He) was used. The crystals were frozen usually at constant pressure, and occasionally at constant volume, by lowering the cell temperature. Growth at constant pressure usually produces crystals with larger grain sizes. The growth of the crystals was observed using the elliptometric system to be

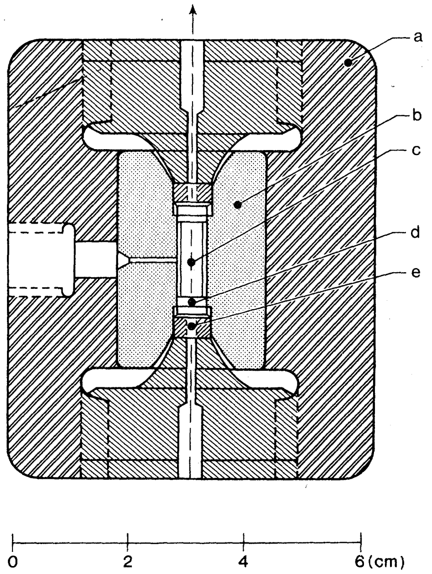

FIG. 1. Pressure cell. (a) Outer cell body, (b) inner cell, (c) helium space, (d) sapphire window, (e) push piece.

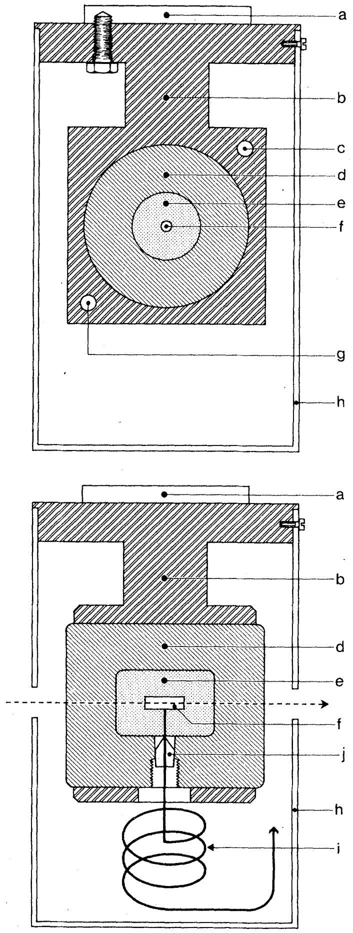

FIG. 2. Cell mounting. (a) Controlled temperature state, (b) aluminum alloy holder, (c) thermometer, (d) outer cell, (e) inner cell, (f) helium space, (g) heater, (h) radiation shield, (i) pressure capillary, (j) cone seal.

described, and in a few cases also visually.

The optical detection system utilizes linearly polarized helium-neon laser radiation from a Spectra Physics 145P laser, which traverses the cell, Fig. 3. The optical path consists of two room-temperature windows in the cryostat (glass), the two sapphire cell windows, and the helium crystal. The two sapphire windows showed quite severe stress birefringence, so that they are optically equivalent to retardation plates with a certain optical retardation and axis orientation. Inserted between these two retardation plates is the helium sample, which in the hcp phase is equivalent to a third retardation plate with retardation ϕ_{He} and a given axis orientation. A combination of several retardation plates can always optically be represented by one retardation plate with effective retardation ϕ_{eff}, and axis orientation, preceded (or followed) by an optical rotator.[12,13] If linearly polarized light enters such a combination, it will therefore emerge elliptically polarized. The best signal-to-noise ratio was obtained in the following way: With the helium crystal in the hcp phase, the ingoing rotator (Fig. 3) was used to obtain elliptical light of maximum ellipticity b/a, where b and a are the minor and major half-axis. Once this setting was obtained, the outgoing light was passed through a $(\lambda/4)$ plate, analyzer combination, which was adjusted for extinction. In this setting the axis of the $(\lambda/4)$ plate are parallel to the axis of the ellipse, and the analyzer is perpendicular to the resultant linearly polarized light. As the helium crystal transforms from hcp to fcc, the retardation due to the helium varies. The effective rotator-retardation plate representing this system (i.e., only the two sapphire windows for a fully transformed crystal), will in general be different. The transmitted elliptic light will therefore have different ellipticity and axis orientation resulting in partial transmission through the $(\lambda/4)$ plate, analyzer combination. This radiation is detected by a Spectra Physics model 404 power meter, and monitored on a strip-chart recorder, together with the temperature of the cell. Very clear signatures of the transition could be obtained in this way.

The optical properties of hcp ^{4}He crystals for the density range of this work can be estimated from the work of Vos *et al.*[6,7] The hexagonal helium phase is positively birefringent, i.e., the index of refraction of the extraordinary ray, n_e, is larger than that of the ordinary ray, n_o. If γ is the angle between the hexagonal c axis and the light direction, then the phase retardation is given by

$$\phi_{\mathrm{He}} = 2\pi \frac{d}{\lambda} (n_e - n_o)_{\max} \sin^2\gamma \quad , \tag{1}$$

where d is the thickness of the crystal, λ the wavelength, and $(n_e - n_o)_{\max}$ the maximum difference in index of refraction (corresponding to propagation in the basal plane). The slow axis is the projection of the c axis on a plane perpendicular to the light direction; the fast axis is perpendicular to this. Both the phase retardation and the axis orientation of the phase plate representing the helium crystal depend on the orientation of the c axis; one can therefore use the optical system to test for reproducibility of the c-axis orientation for repeated traverses of the transition. Since the optical system is initially adjusted for extinction with the helium crystal in the hcp phase, one will in a sequence hcp → fcc → hcp only again get extinction in the hcp phase if the c axis is reproduced in its original orientation. This appears to be the case under certain conditions, as will be shown later on.

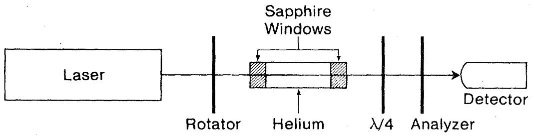

FIG. 3. Optical system, schematic.

The difference $(n_e - n_o)_{\max}$ in refractive index was measured by Vos *et al.*[7] For small pressures between 30 and 1064 bars it was found to vary between 2.8×10^{-6} and 6.3×10^{-6}. In order to obtain estimates at higher pressures we used the calculations of Kronig and Sonnen,[14] which were shown to be in good agreement with the measurements of Vos *et al.* Kronig and Sonnen give the following expressions for n_o and n_e.

$$\begin{aligned} n_o^2 - 1 &= \left(\frac{\epsilon_0}{N\alpha} - 1 - \tfrac{1}{2}\psi_y \right)^{-1} \quad , \\ n_e^2 - 1 &= \left(\frac{\epsilon_0}{N\alpha} - 1 - \tfrac{1}{2}\psi_z \right)^{-1} \quad , \end{aligned} \tag{2}$$

where ϵ_0 is the dielectric constant of vacuum, α the polarizability of ^{4}He, and $N = N_A/V$ the number of atoms per volume. ψ_y and ψ_z are constants which depend on the axis ratio c/a. With $\alpha = 2.29 \times 10^{-41}$ C m^2/V as quoted by Kronig and Sonnen, one finds that $\psi_y = 1.333\,862$ and $\psi_z = 1.332\,276$ reproduces the experimental data of Vos *et al.* These ψ_y, ψ_z values correspond to an axis ratio c/a of 1.63 235, which is within 0.04% of the ideal axis ratio for a hexagonal crystal. Using these expressions one calculates the predicted birefringence $n_e - n_o$ given in Table I, and shown in Fig. 4.

One finds, incidentally, that the estimated birefringence $n_e - n_o$ depends only very little on the value of the polarizability α, as long as the constants ψ_y and ψ_z are adjusted to reproduce the experimental data of Vos *et al.* A 5% increase in α leads in this way to a change of less than 0.2% in $n_e - n_o$ at $V = 7$ cm^3/mole.

TABLE I. Estimated birefringence of hcp ^{4}He.

V (cm^3/mole)	$(n_e - n_o)$ (10^{-6})
12.5	6.31
12.0	6.83
11.0	8.17
10.0	9.92
9.0	12.30
8.0	15.64
7.0	20.57

Using the extrapolated values of $(n_e - n_o)$, one finds a maximum retardation of 83° at $V = 9.37$ cm^3/mole, rising to 121° at $V = 7.83$ cm^3/mole, which covers the range of the present work.

No attempt was made in the present work to experimentally obtain the actual phase retardation of the crystals used. Such a determination is made difficult because of the large stress birefringence in the sapphire windows as well as uncertainty about the crystallinity of the samples. It probably cannot be assumed that the crystals used were single crystals. This means that the total phase retardation was probably considerably less than the maximum values possible.

The schematics of a run are shown in Fig. 5. We define the temperature at which the transition in heating starts as T_h, the "transition temperature in heating." The "transition temperature in cooling," T_c, is similarly defined as the temperature at the start of a cooling transition. This terminology is identical to that used in previous publications on this subject.[1-3,9] In the literature of martensitic transformations, the term A_s is used for T_h, and M_s for T_c. Both heating and cooling transitions have a finite width, the athermal width, which we denote by $\delta T_{\mathrm{tr},h}$ and $\delta T_{\mathrm{tr},c}$.

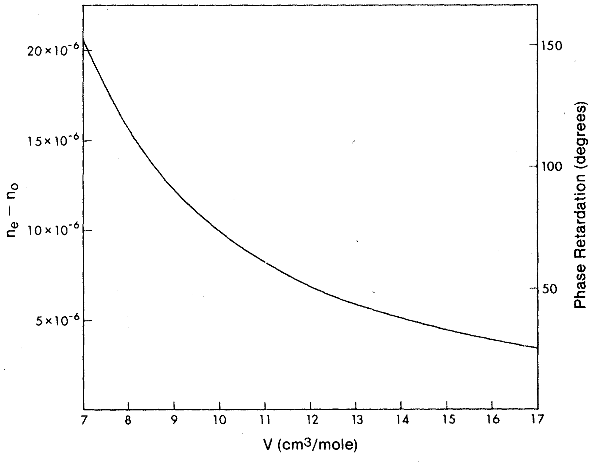

FIG. 4. Estimated birefringence of hcp ^{4}He (left-hand scale), and corresponding optical retardation of the pressure cell (right-hand scale), as a function of molar volume. The estimate is based on Refs. 7 and 14.

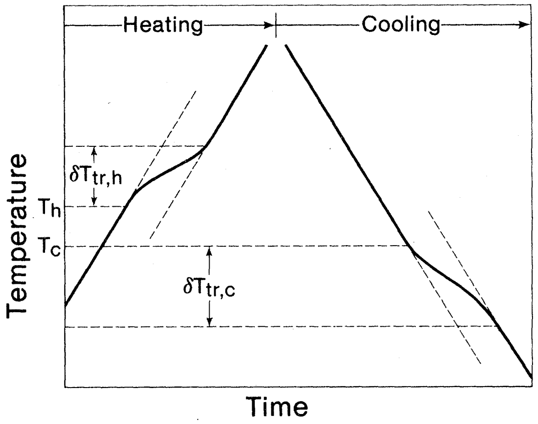

FIG. 5. Schematic of an experimental run. T_h transition temperature in heating, T_c transition temperature in cooling, $\delta T_{\mathrm{tr},h}$ transition width in heating, $\delta T_{\mathrm{tr},c}$ transition width in cooling.

In order to obtain the density of the crystal and the transition pressure, we observed the start of the melting transition, T_m. From visual observations of the melting process in some of these crystals we know that melting always starts at some heavily faulted regions of the crystal; these regions grow in volume and complexity dramatically during the melting interval. The beginning of the melting interval was therefore always noticed through a drop in transmitted intensity. From the observed melting point, T_m, the melting pressure, P_m, was calculated using the melting curve of Crawford and Daniels[15]:

$$P_m = 17.835\,18\,T_m^{1.541\,71} - 31.86 \text{ (bars)} \ . \qquad (3)$$

This melting curve was experimentally established for pressures up to 10 kbar, and therefore covers the range of the present experiments; it also reproduces within experimental uncertainty the recently established melting point of ^{4}He at room temperature.[16] The pressure drop along an isochore between T_m and the transition was calculated using the equation of state calculations of Spain and Segall.[17] This isochoric pressure drop varies between 250 and 720 bars for the range of pressures of this work (3.9 to 8.7 kbar), corresponding to between 6.1 and 7.6% of the melting pressure.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Phase diagram

The phase transition was observed in a total of nine different crystals. Each crystal, after it had been grown, was taken a number of times through the heating and cooling transition at large rates of heating or cooling. After this the transition temperatures were taken at heating or cooling rates between 10 and 50 mK/min. Each transition temperature was determined two or three times. Differences in the observed heating transition temperature, T_h, between different passes were not more than 50 mK; for the cooling transition temperature the differences were slightly larger (ca. 80 mK). These differences refer to observations on the same crystal. Differences for different crystals appear to be somewhat larger, but even then the T_c temperatures show no more than 300-mK deviation from a common line, with the scatter of T_h being somewhat less. No definite difference, within the limits mentioned, was observed between crystals grown at constant volume and at constant pressures, as long as the growth was relatively slow (total time for forming the crystal at least 10 min). In one case, at a molar volume of $V=8.26$ cm^3/mole, a crystal was grown accidentally at constant volume and a very large cooling rate (less than 1 min for total growth). This crystal showed very poor light transmission. The heating transition temperature was found in agreement with other crystals; its cooling transition temperature, on the other hand, was about 700-mK lower than for other crystals. This shows that crystal perfection does influence the transition, in particular the cooling transition. It is also evident from the observations on this crystal that large-scale imperfections do not anneal out over periods of the order of a day.

Average values for transition temperatures of these crystals are given in Table II. Included in Table II are also the observed temperatures at the start of melting, T_m. The pressure at the transition, P_{tr}, and the molar volume, V, were obtained from T_m in the manner described in Sec. II. The transition pressures given refer strictly to the average transition temperature, $(T_c+T_h)/2$. The isochoric pressure change between T_c and T_h is quite small (10 bars at 9.44 m^3/mole, and 30 bars at 7.83 cm^3/mole), well within the experimental uncertainty. Uncertainties in the transition pressure arise predominantly from uncertainties in the determination of T_m; they are estimated at about ±150 bars.

In Fig. 6 we show the phase diagram in the PT plane. For continuity we have included points taken below 4 kbar by the thermal analysis method,[1,3] excluding only the region near the triple point where anomalous behavior is observed.[2,3] As can be seen, excellent agreement exists between the two methods.

TABLE II. Transition data, hcp ^{4}He → fcc ^{4}He.

T_m (K)	V (cm^3/mole)	T_c (K)	T_h (K)	$\bar{P}_{tr}$[a] (bar)
34.37[b]	9.44	18.98	20.09	3882
35.16	9.37	19.26	20.35	4017
40.08	8.92	20.36	21.78	4898
45.26	8.58	22.20	23.99	5893
49.12	8.34	22.94	25.02	6665
50.42	8.26	22.81	25.85	6943
50.56	8.25	23.82	25.78	6960
55.07	8.00	24.87	27.45	7943
56.43	7.93	25.68	28.19	8243
58.43	7.83	26.23	29.01	8687

[a] Pressure corresponds to $(T_c+T_h)/2$.

[b] Thermal analysis.

Although the T_c and T_h temperatures depend somewhat on crystal quality, their scatter is sufficiently small to define curves of T_c and T_h as functions of pressure; our estimates of these are shown in Fig. 6. It is remarkable that the line for the transition in heating is linear from about 1.7 kbar to about 9 kbar,

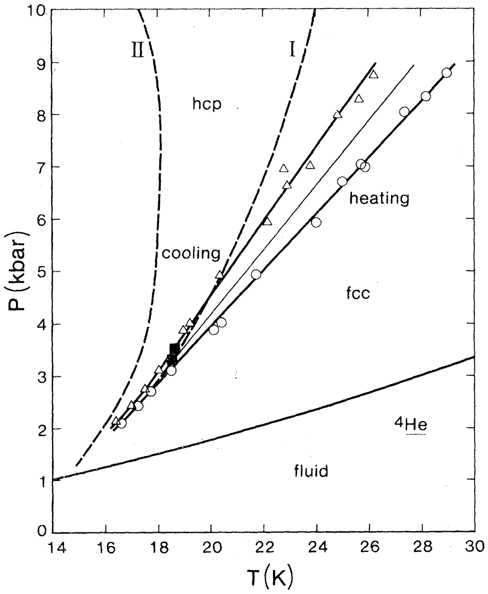

FIG. 6. Phase diagram of ^{4}He, PT plane. Open circles, heating transition temperature T_h; open triangles, cooling transition temperature T_c; solid squares, hcp and fcc mixed phase, Ref. 18; light line, possible equilibrium transition line, given by $\frac{1}{2}(T_h+T_c)$, slope 622 bar/K; dashed lines I and II, theoretical estimates from Ref. 5.

and the slope of this line is 537 bars/K. The cooling transition line shows gradually increasing slope between 1.7 and 2.5 kbar. Above 2.5 kbar, however, the cooling transition again follows a straight line, and its slope is 707 bars/K. The equilibrium transition line, which is defined by the equality of the Gibbs free energy of the two bulk phases, will lie somewhere in between the cooling and heating transition lines, but its exact position becomes increasingly uncertain at higher densities because of the large temperature hysteresis. If one assumes, as is common practice in the field of martensitic transitions, that the equilibrium transition temperature is given by $\frac{1}{2}(T_c + T_h)$, then the equilibrium line has a constant slope of 622 bars/K from 2.5 to about 9 kbar. Between 2.5 and 1.7 kbar the slope decreases somewhat, due to the decreasing slope of the cooling transition line, to about 550 bars/K. Below 1.7 kbar the slope increases again as the anomalous region near the triple point is entered.[2] It is, however, somewhat dubious whether the decrease in slope between 1.7 and 2.5 kbar and the following increase to 622 bars/K is in fact a property of the true equilibrium line. As can be seen, such a change in slope is not present in the heating transition line; it is solely brought about by the behavior of the cooling transition line. Since the heating transition is noticeably less sensitive to crystal quality one might be inclined to place the equilibrium line closer to the heating transition. In fact, a straight line can be drawn which at 1.7 kbar is halfway between T_c and T_h, but at higher pressures lies closer to T_h. Such a line has constant slope of 585 bars/K, at 8.5 kbar it is 0.7 K below T_h and 1.4 K above T_c. It is unfortunate that the hysteretic character of the transition prevents any more accurate placing of the bulk equilibrium line. It can be seen, however, that the experimental data up to about 9 kbar do not support curving over of the transition line and are in best accord with a linear phase-transition line, from at least 2.5 kbar upwards.

Included in Fig. 6 are also two points near 3.5 kbar reported by Mills and Schuch.[18] These points represent crystals which showed both hcp and fcc reflections in x-ray Laue diagrams. They were assumed to lie on the phase-equilibrium line. From the description of the experiments of Mills and Schuch it is likely that these points represent the cooling transition; good agreement indeed exists with the cooling transition line of the present work. Since the x-ray exposure time of Mills and Schuch was about 12 h, during which their crystals were held at constant temperature, one has to consider the isothermal transformation rate. As we will show later, the isothermal transformation for the cooling transition does not go to completion; the transformation in fact stops after about 40 min at about 50% completion. One can therefore expect a mixed hcp-fcc crystal anywhere within the athermal temperature width, which at 3.5 kbar is about 80 mK, even for prolonged holding of the crystal. This might explain the data of Mills and Schuch.

In Fig. 6 we also show the two theoretical estimates for the transition line by Holian *et al.*[5] Here line II was calculated with lattice-dynamics corrections to the cell model internal energy, line I does not include these corrections. As can be seen, the experimental phase line deviates with rising pressure increasingly from the theoretical predictions. In particular, no evidence for an increasing slope can be detected for pressures up to 9 kbar.

As was stated by us before,[9] it is not clear at present which element in the calculation is responsible for the deviation between experiment and theory. The phase line calculations depend on the accurate calculation of a number of small terms which contribute to the latent heat $(\Delta H)_{\rm tr}$ and the transition entropy $(\Delta S)_{\rm tr}$, and which therefore influence the transition temperature given by

$$T_{\rm tr} = (\Delta H)_{\rm tr}/(\Delta S)_{\rm tr} \ . \tag{4}$$

Only a systematic investigation of all these terms can lead to a possible improvement in the theoretical predictions.

B. Transition kinetics

1. General remarks

Properties of the transition that are influenced by the kinetics include the general progress of the transition, the athermal width, the isothermal transformation rate, and the temperature hysteresis. Not all of these phenomena were studied in detail on each crystal, but the following general remarks can be made. After a crystal had been grown, either at constant volume or at constant pressure, it was usually taken quickly through the cooling transition and then cycled several times through both the heating and cooling transition. It was frequently observed that the first (virgin) cooling transition proceeded in a very sharp step, sometimes followed by more gradual transition behavior. An example of this is shown in Fig. 7. This sharp step is only seen in the virgin cooling transition. The following heating transition is much smoother, and the second cooling transition, although it shows some erratic behavior, is also much smoother than the virgin transition. In general it was found that burstlike behavior is much more common for cooling transitions although it may also occur in heating transitions. The character of each transition varies in general for different passes through the transition,. This is particularly true if the crystal has been held at temperatures significantly above T_h (in the fcc phase) or below T_c (in the hcp phase) for prolonged times (longer than about 15 min, sometimes many hours). Reproducible behavior of the transi-

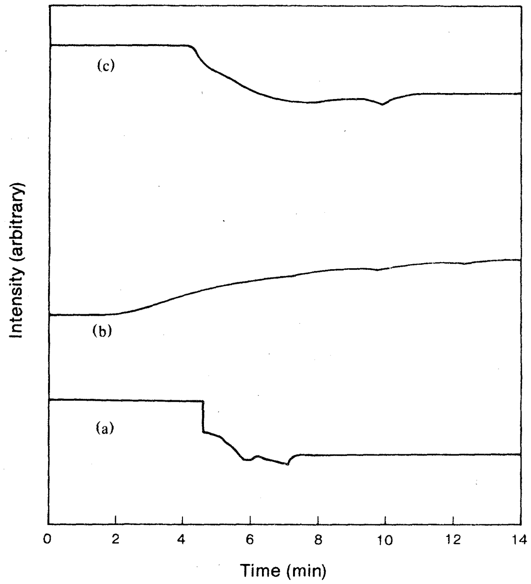

FIG. 7. Transitions in a crystal of molar volume 7.83 cm^3/mole. (a) Virgin cooling transition, (b) first heating transition, (c) second cooling transition.

tions was also observed; this was generally obtained when the crystal was cycled between T_c and T_h without prolonged holding in either phase. It was found that under no circumstances did the transition fail to start when the temperatures T_c and T_h, respectively, were reached. It appears therefore impossible to obtain the high-temperature phase at low temperatures through rapid quenching. Quench rates of up to 10 K/min were used. Under conditions of rapid quenching, or heating, the transition always takes place very fast, a fact which attests to its athermal character. An example is shown in Fig. 8. In this case the total transformation took place in a span of about 10 sec with individual steps being less than 0.01 sec in width.

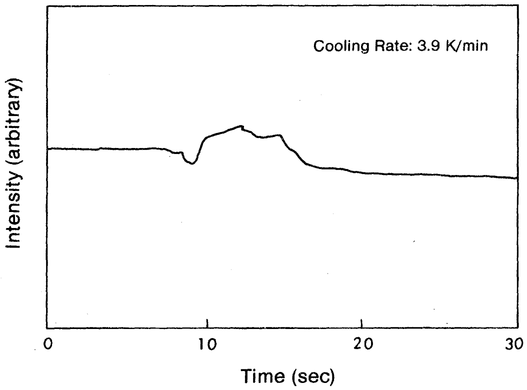

FIG. 8. Very fast cooling transition, molar volume 7.83 cm^3/mole.

2. *Temperature hysteresis*

The temperature hysteresis, defined at $(\Delta T)_{\mathrm{tr}} = T_h - T_c$, is shown in Fig. 9. The experimental points define more or less a straight line, in spite of the fact that the transition temperatures are somewhat dependent on crystal quality, in particular the cooling transition temperature T_c. The straight line which describes the average temperature hysteresis extrapolates within its uncertainty quite well into the triple point at $T_{\mathrm{tr}} = 14.992$ K for $(\Delta T)_{\mathrm{tr}} = 0$. As was shown before,[1,3] however, the temperature hysteresis does not in fact go to zero, but levels off near 30 mK close to the triple point. At the highest density of this work, the temperature hysteresis is therefore almost 100 times its minimum value near the triple point, or almost 10% of the transition temperature. The point deviating from the common curve, near $(\Delta T)_{\mathrm{tr}} = 3$ K, refers again to the crystal at $V = 8.26$ cm^3/mole, a very poor crystal of poor light transmissivity. The abnormally large $(\Delta T)_{\mathrm{tr}}$ in this case is entirely due to an abnormally small cooling transition temperature T_c.

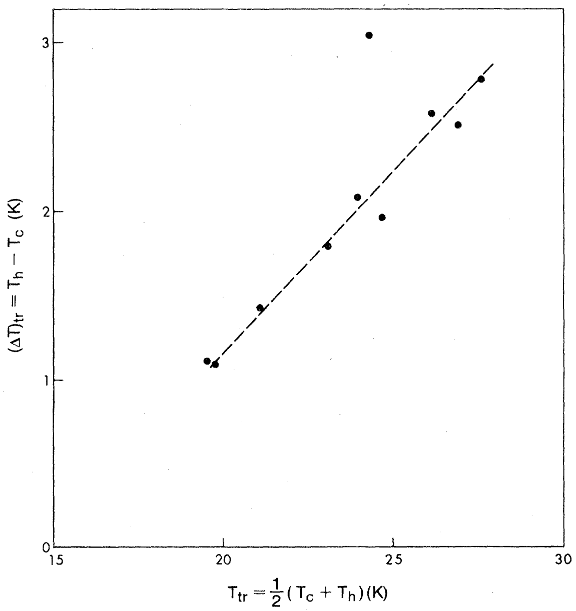

FIG. 9. Temperature hysteresis $(\Delta T)_{\mathrm{tr}}$ as function of the average transition temperature.

3. *Athermal width*

The athermal width of the transition is defined as the temperature difference between start and completion of the transition, either in heating or cooling. For the density range of this work it was found that the athermal width for the cooling and heating transitions are equal within experimental uncertainty. The existence of the athermal process of the transition was already observed in the earlier calorimetric investigations[3] below 4 kbar. In Fig. 10 we show the athermal width as a function of average transition temperature. The athermal width varies from about 100 mK near 4 kbar ($T_{tr} \approx 20$ K) to about 2 K at 9 kbar ($T_{tr} \approx 28$ K). The value near 4 kbar is in agreement with the earlier calorimetric observations.

Although the athermal progress of the transition is the one usually observed, isothermal transformation is also possible as will be shown in more detail in the next paragraph. The time constant for the isothermal transformation is of the order of many hours; athermal behavior will therefore be observed if the transition is traversed in a reasonably short time, e.g., less than 20 min.

In most crystals grown the signal-to-noise ratio of the optical signature of the transition was only sufficient to determine the transition temperatures and make the general observation mentioned so far. More detailed studies of the progress of the transition need a large signal, well removed from noise.

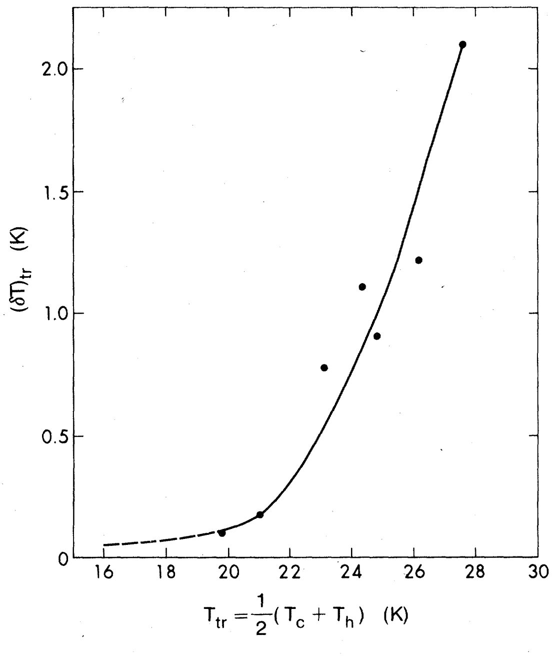

FIG. 10. Temperature width of the transition as function of average transition temperature. Dashed line from Ref. 3.

We were fortunate to grow two crystals for which such signals were observed. These are the two crystals with molar volumes of 7.83 and 8.25 cm^3/mole, with corresponding transition pressures of 8.69 and 6.96 kbar. Both crystals were carefully grown at constant pressure. It was therefore decided to perform more detailed transition studies on these crystals, in particular on the highest-density crystal ($V = 7.83$ cm^3/mole). It was first decided to study the athermal transition on this crystal in some detail. It was found that the transition proceeds between a minimum value for transmitted light in the hcp phase to a maximum value when the transition is completed in the fcc phase. For the cooling transition the process is reversed. Although some structure is present in the transition, particularly the cooling transition, it was found that the light transmission levels on both sides of the completed transition were reproducible within about 2% of the total changes: This was true, as long as no prolonged holding of the crystal in the hcp or fcc phase took place.

In Fig. 11 we show several cooling and heating transitions for the crystal at $V = 7.83$ cm^3/mole, at widely varying rates of temperature change. Although the cooling rates vary from 6.63 K/min down to 0.113 K/min, i.e., by a factor of 59, and the heating rates from 4.14 K/min to 0.099 K/min, i.e., by a factor of 42, one finds that each transition has very nearly the same temperature width. For the cooling transition of Fig. 11 one obtains a width $(\delta T)_{tr,c}$ of 2.2 ± 0.3 K and for the heating transition a width $(\delta T)_{tr,h}$ of 1.9 ± 0.4 K. It is clear therefore that the transition has an inherent width of about 2 K, independent of the heating or cooling rate.

The transitions described constituted a series, taken over about 3 h. Several such sequences were obtained, with similar results.

The second conclusion to draw from these sequences is that the *c*-axis orientation of the hcp crystal is reproducible over each observed sequence. Should the *c* axis have changed in a sequence hcp → fcc → hcp, then the retardation plate representing the new hcp crystal will be different from the original one. This change will in turn lead to a different effective retardation and axis orientation for the system window—helium-crystal window, so that extinction will not be obtained in general for the new hcp crystal. Since for these sequences we always obtained extinction again for the fully transformed hcp crystal, one has to interpret this as a reproducing *c*-axis orientation (to within about ±5% over the whole sequence observed). This explanation is made even more plausible by contrasting it with the behavior that is observed when the fcc crystal is held for prolonged times (longer than about 15 min) about 5 to 10 K above the heating transition. After such an annealing process the following cooling transition does not resemble the preceding one, and in particular

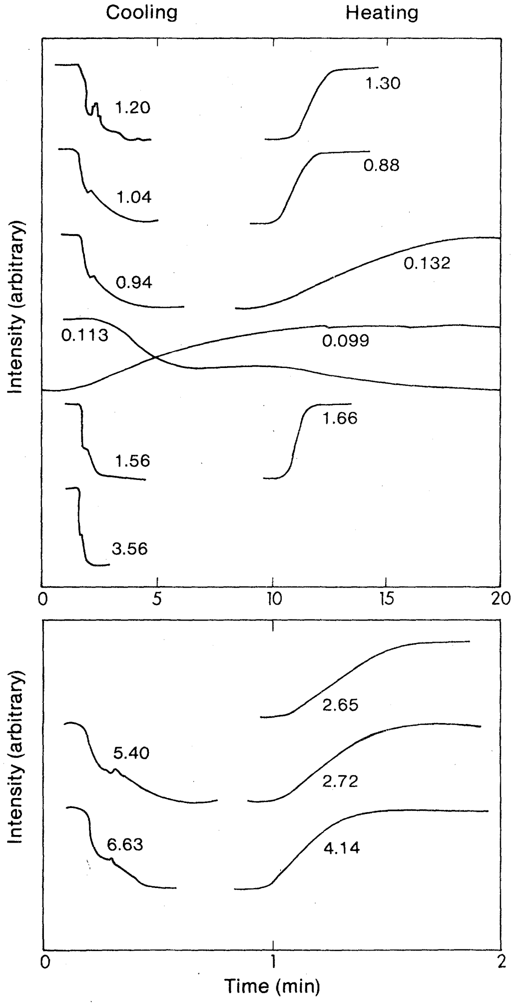

FIG. 11. Succession of heating and cooling transitions, molar volume 7.83 cm^3/mole. The transitions were taken in order from left to right and downwards. Numbers indicate the heating or cooling rate in K/min.

does not generally result in extinction for the completed hcp crystal. The annealing process in the fcc phase has therefore removed any memory of the preceding *c*-axis orientation.

While the foregoing analysis has treated the helium crystal as single, it can easily be seen that the conclusion can also be applied to the case of a polycrystal. In this case it is likely that the *c*-axis orientation is reproduced in each single-crystal grain.

4. Isothermal transition

It was found by a detailed study on the two crystals with $V=7.83$ and 8.25 cm^3/mole, that the transition can proceed not only athermally, i.e., by traversing the heating or cooling transition intervals, but also isothermally if the crystal is held at constant temperature anywhere within the heating or cooling transition interval. The time constant for isothermal transformation is many hours, and it is therefore not of importance if the transition is traversed at not-too-small rates of temperature change. In order to study the isothermal transformation reliably, we had to be satisfied that the optical signal as a function of time is a true indicator of the amount transformed. The optical arrangement was again the same as described in Sec. II. It was found during preliminary experiments on the crystal with $V=7.83$ cm^3/mole, that the optical signal always changed from near extinction (if the hcp phase is present) to a certain maximum value (for the fully transformed fcc phase). These two levels were unchanged even if the crystal was held for many hours isothermally at temperatures anywhere between those for fully transformed fcc or hcp phases. We therefore felt justified to use the transmitted intensity as an indicator for the amount tranformed. For simplicity, and because of our lack of knowledge about the phase retardation in the helium sample, we assumed that the amount transformed is a linear function of the transmitted light intensity. This is definitely true if the total retardation in the helium sample is small (i.e., small compared to $\lambda/4$). From the generally smooth and monotonous increase in transmitted intensity for heating transitions performed at constant heating rates, one can infer that the linearity assumption is not likely to be in serious error. For a more detailed study, a calibration of the optical transmission in terms of amount transformed has to be performed. We therefore use the following estimate for the molar fraction of fcc phase present

$$x_{\mathrm{fcc}}=\frac{I-I_{\mathrm{hcp}}}{I_{\mathrm{fcc}}-I_{\mathrm{hcp}}}\ , \tag{5}$$

where I is the transmitted intensity, and I_{hcp} and I_{fcc} the transmitted intensities for fully transformed hcp and fcc. A number of different experiments were performed in order to obtain a general outline of the isothermal transformation behavior.

a. Transition in heating. In this case the fully transformed hcp crystal was heated partially into the athermal heating transition interval $[T_h, T_h+\delta T_{\mathrm{tr},h}]$. The heating was interrupted when about 20 to 35% of the total fcc signal had appeared, which we interpreted as about the same amount transformed. The crystal was then held isothermally for up to 3 h. During this time the optical signal continued to increase, but at a diminishing rate indicating a transition rate which is slowing down. Although the overall transition rate slows down as a function of time, this slowing down is not always monotonous. After about 3 h we found that about 90% of the fcc signal had appeared, the transition rate at this time had fallen to quite low

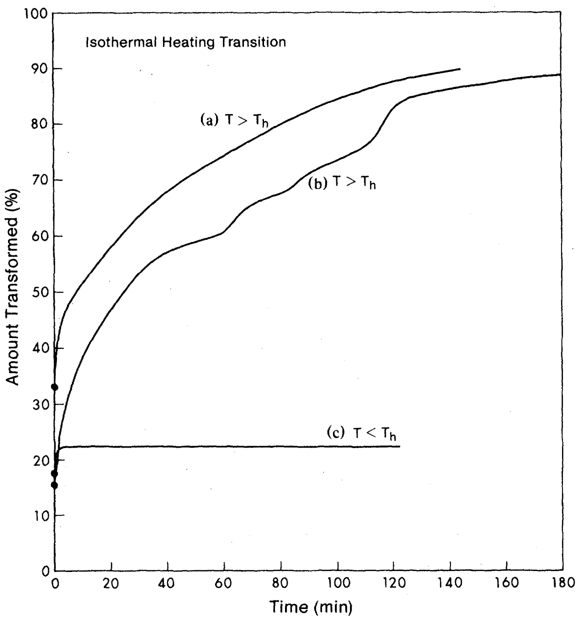

FIG. 12. Isothermal heating transition curves, molar volume 7.83 cm^3/mole. (a), (b) Temperature held above T_h, but inside the athermal transition interval. (c) Temperature held 350 mK below T_h after initial start of transformation.

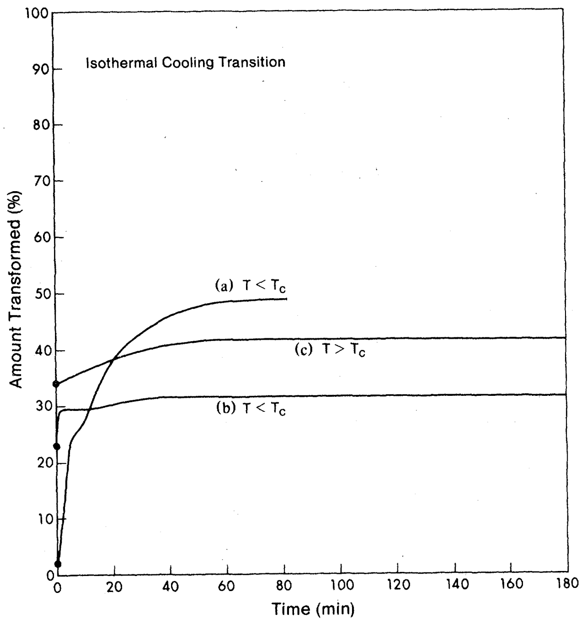

FIG. 13. Isothermal cooling transition curves, molar volume 7.83 cm^3/mole. (a), (b) Temperature held below T_c, but inside the athermal transition interval. (c) Temperature held 415 mK above T_c after initial start of transformation.

values. Upon resumption of heating the transition started again without delay and the full fcc signal was recovered. This behavior is shown in Fig. 12.

b. Transition in cooling. The fully transformed fcc crystal was cooled partially into the athermal cooling transition interval $[T_c, T_c - \delta T_{\mathrm{tr},c}]$ until about 5 to 15% of the fcc signal had disappeared, corresponding to about 5 to 15% of transformation to hcp. The crystal was then isothermally held for about 3 h. It was observed that the cooling transition proceeded for a certain time at isothermal holding (about 40 min), but after this initial interval the transformation stopped. The total amount transformed was in the range 30 to 50%. After the initial transformation period the optical signal was quite constant. This is shown in Fig. 13. At resumption of cooling, it was found that the cooling transition does not immediately start, but does so only after a certain time interval corresponding to a temperature drop of about 0.5 K, as shown in Fig. 14. The cooling transition therefore does not restart where the initial athermal transformation was terminated, but requires an additional driving force. This phenomenon is quite frequently observed in more conventional martensitic transformations, where it is called "stabilization." It is an indication that the morphology of the isothermal transformation product is different from that of the athermal transformation. The transformation does again go to 100% hcp indicated by the total loss of

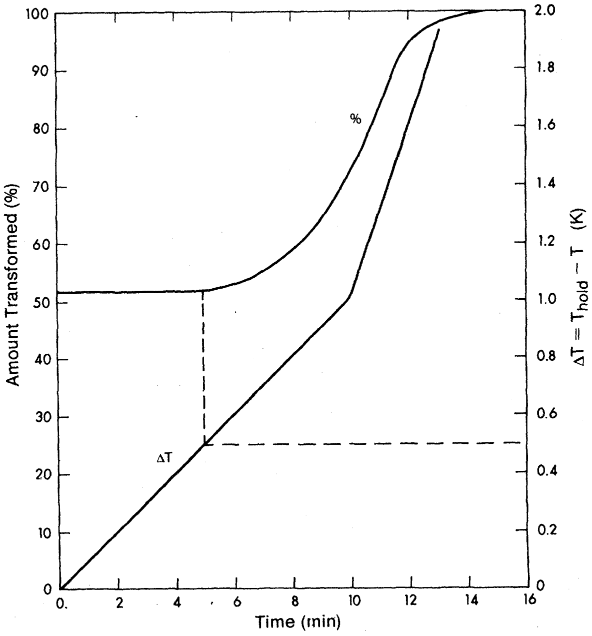

FIG. 14. Resumption of the cooling transition after isothermal holding for 65 min. The cooling transition restarts only after a reduction of 0.5 K from the holding temperature.

the fcc signal.

c. Investigation of isothermal transformation in the interval between T_c and T_h. While isothermal transformation is possible inside the athermal heating or cooling transition intervals, there is so far no indication for isothermal transformation in the temperature interval between the cooling and heating transition temperature $[T_c, T_h]$. Fully transformed hcp or fcc ^{4}He was quite frequently held in this interval for periods of many hours (up to 12 h) but no indication of transformation was ever observed, in agreement with the earlier calorimetric investigation.[1,3] It is of interest, however, to study what happens if a partially transformed crystal is taken into this interval. In this case one might expect the presence of the new phase to induce a possible isothermal transformation. In order to test this we investigated two cases. In the first we heated the fully transformed hcp crystal partially into the heating transition interval, until about 30% of the crystal was transformed to fcc. This partially transformed crystal was then cooled back into the interval $[T_c, T_h]$, about 350 mK below T_h. The crystal stopped transforming as soon as heating was interrupted. It was held then for 2 h in the interval $[T_c, T_h]$, with no apparent transformation, as shown in Fig. 12. Upon resumption of heating, the transition went to completion, starting again at T_h.

In a second experiment, the fully transformed fcc crystal was cooled below T_c, until about 30% of the crystal had transformed to hcp. It was then heated back into the interval $[T_c, T_h]$, about 415 mK above T_c. The transformation came to an almost complete stop as soon as cooling was interrupted. Slight transformation of a few percent was observed for about an hour afterwards. No further transformation was noticeable over a 3-h period, as shown in Fig. 3. Upon resumption of cooling the transition went to completion, starting at T_c.

These experiments show that not only can the fully transformed hcp and fcc crystals exist in metastable equilibrium in the interval $[T_c, T_h]$, but also partially transformed crystals. The only ranges where the transformation can take place are therefore the athermal heating and cooling ranges. In both ranges the transition can proceed purely athermally (in the limit of very fast heating or cooling rates), or isothermally. The isothermal transformation will, however, go to completion only in heating; in cooling it terminates around 50% completion. Above $T_h + \delta T_{\mathrm{tr},h}$ only the fcc phase is stable, and below $T_c - \delta T_{\mathrm{tr},c}$ only the hcp phase.

5. Discussion

The detailed kinetic behavior described gives further evidence for the proposed martensitic character of the transition. It is particularly interesting to note that no transformation takes place in the interval $[T_c, T_h]$, even with the transformation product present. This shows that the temperature hysteresis is not due to a nucleation barrier, but rather to a barrier for the continued growth of the new phase. It can probably be assumed that this barrier is due to surface and strain energies associated with the accommodation of the new phase, as is the case for conventional martensitic transformations. A second interesting observation is the reproducibility of the *c*-axis orientation for extended transformation series, as long as prolonged annealing is avoided. This phenomenon shows the essential diffusionless character of the transformation. Annealing at temperatures well above the transition does change the apparent *c*-axis orientation, whether due to actual *c*-axis reorientation in individual grains or to relative grain growth is not clear. This reorientation, however, is not a consequence of the transition itself.

A third interesting phenomenon is the asymmetry between the isothermal transformation behavior of the heating and cooling transitions. It appears that during the isothermal cooling transformation, the transformation product (the hcp phase) at about 50% completion is prevented from further growth. This might be due to various transformed regions growing into each other, and stopping growth due to strain energy. In the heating transition these regions dissolve again and are therefore growing away from each other, making a 100% transformation possible.

It should be noted that the more detailed kinetic studies were done on two crystals, both at quite high density. This work should be extended to cover the whole range of the transition, in particular the range near the triple point with the fluid.

IV. SUMMARY

The transition hcp-fcc ^{4}He was studied from about 4 kbar to near 9 kbar using an optical detection method based on the birefringence of the hcp phase. It was found that both the temperature hysteresis and the athermal width of the transition increase dramatically over this pressure interval. The temperature hysteresis increases from 1 K near 4 kbar to about 2.8 K near 9 kbar. The athermal width increases over this pressure range from 100 mK to about 2 K. Quite well-defined heating and cooling transition lines could be established; they appear to be linear with slopes of 537 bars/K (heating transition), and 707 bars/K (cooling transition). If the equilibrium transition line is chosen as $\frac{1}{2}(T_c + T_h)$, then it has a slope of 622 bars/K.

The transition line deviates with increasing pressure increasingly from the theoretical predictions of Holian *et al.*[5]; it particularly does not show the predicted increase in slope. Experiments at yet higher pressures are necessary to determine this point.

Two crystals at high densities ($V = 8.25$ and 7.83 cm^3/mole) showed sufficiently well-resolved signals of the transition to allow a more detailed study of the kinetics of the transition at these densities. The athermal transition was studied for sequences involving numerous transitions in succession. Good reproducibility was observed for the transition signal as long as prolonged annealing was avoided. This was interpreted as a reproducing c axis, giving further support for a diffusionless transition mechanism. Isothermal transformation was also observed, both in heating and in cooling. The isothermal transition in heating goes to near completion over a period of about 3 h; the isothermal cooling transition, on the other hand terminates at about 50% of completion. The cooling transition, upon resumption of cooling following isothermal holding, shows stabilization, i.e., a definite temperature drop (of about 0.5 K) is necessary to restart the transition. This phenomenon is absent in the heating transition. It was further found that in the interval $[T_c, T_h]$ no transformation takes place, even if partially transformed crystals are held for prolonged times (many hours) in this interval. On the other hand, transformation will always start at T_h or T_c, regardless of the rate of temperature change. The kinetic studies described for two high-density crystals give further support to the martensitic character of the transition. It will be interesting to extend these studies to lower densities, where the transition line approaches the melting line.

The equilibrium data show that serious discrepancies exist with present theoretical predictions[5] of the transition. This fact should not be too surprising in view of the very small energy differences involved.

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