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Interpretation of Initiation Pressure Hysteresis Phenomena for Fixed-Point Pressure Calibration

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An interpretation of initiation pressure hysteresis phenomena for fixed-point pressure calibration is presented according to the theory of nucleation in condensed systems and is substantiated for the bismuth I–II point by hydrostatic pressure experiments with a manganin pressure gauge. Kinetic initiation and completion of the bismuth I–II transformation were observed at constant pressure and temperature, and several different isobaric initiation pressures were measured at the same temperature. An asymmetrical relationship of the equilibrium pressure between the initiation pressures of the forward and reverse transformations was measured, and it was demonstrated that the high-pressure side of the strain hysteresis of initiation is within 0.17 kbar of the equilibrium pressure. The microstructure and thickness of the sample influenced the initiation pressures and the region of indifference, but the center of the region appeared reproducible. A region of indifference of 0.03 kbar was measured. The origin of the real strain hysteresis of initiation is identified for polymorphic transformations and initiation pressures are discussed in terms of the strain energy and chemical kinetics of nucleation. It is shown that other interpretations of hysteresis phenomena are not satisfactory. It is reasoned that the equilibrium pressure rather than a higher pressure value is a more accurate calibration pressure for the initiation of the bismuth I–II transformation in solid-media apparatus.

I. INTRODUCTION

Although the high-pressure scale is based on fixed-point pressures assigned to various polymorphic phase transformations, the calibrant transformations have not yet been characterized for standard pressure calibration. The lack of information regarding the thermodynamic and kinetic aspects of the solid-state phase changes can be related to much of the inconsistency that presently exists in calibration techniques, particularly for solid pressure systems. There is a fundamental discrepancy regarding the use of the equilibrium pressure or a higher pressure value to calibrate the initiation of the forward transformation, and sometimes the equilibrium pressure is assigned to the center of the initiation pressure hysteresis. In addition to the relationship between the equilibrium and initiation pressures, other factors pertaining to calibration such as the width and nature of the initiation pressure hysteresis, the sharpness of the transformations, the magnitude of the pressurization rate, the width and reproducibility of the center of the region of indifference, and the nature of the calibrant sample, are all related to the basic mechanism and characteristics of the transformations. The extent to which these factors differ from one calibration to another with different investigators and types of apparatus affects the accuracy and precision of high-pressure measurement. The present investigation was undertaken to test current interpretations of hysteresis phenomena, and is an attempt to standardize fixed-point pressure calibration and measurement from a study of the basic thermodynamic and kinetic behavior of a calibrant transformation.

The phenomenological transformation features pertinent to the present investigation are schematically represented in Fig. 1. The pressure P_{I-II} represents the initiation of the I–II transformation with increasing pressure on a sample composed completely of bismuth I. Subsequent to initiation the appearance of the transformation depends on the nature of the pressure medium and on the pressurization rate. After sufficient overpressurization to completely convert all of phase I to phase II, the initiation of the reverse II–I transformation on decreasing pressure is represented by P_{II-I}. The interval between the initiation pressures is conventionally denoted as an initiation pressure hysteresis, and it is reported to have an average value of about 0.72 kbar in hydrostatic pressure.[1] The initiation pressure interval is at least several kbar wide in solid-media systems due to the apparatus hysteresis resulting from gasket friction and hysteresis of the pressure medium. When both phases are present in the sample the transformations can be reversed over a much smaller range. Bridgman denoted this pressure range as the region of indifference[2] and he reported a value of about 0.06 kbar for bismuth I⇌II.[3] The center of the region of indifference is considered the equilibrium pressure. The region of indifference is conventionally assumed to be centered within the initiation pressure hysteresis but this relationship has not been measured previously.

In almost all solid-media systems the existence of apparatus hysteresis prevents measurement of the equilibrium pressure, and in these cases the initiation of the forward transformation is generally calibrated. Originally the equilibrium pressure was used for the calibration, but on the basis of an interpretation of hysteresis phenomena Jeffery, Barnett, Vanfleet, and Hall[4] concluded that bismuth I–II initiated at a fixed pressure significantly higher than the equilibrium pressure in solid-media systems. Apparatus hysteresis was
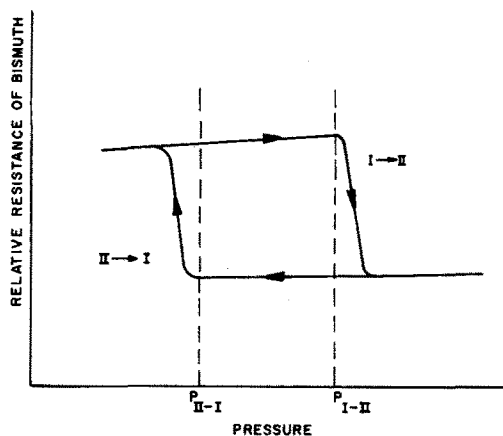
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FIG. 1. Schematic representation of the relative resistance of bismuth for increasing and decreasing pressure in the vicinity of the I–II calibration point. The initiation pressure of the I–II and II–I transformations are denoted by P_{I-II} and P_{II-I}.

separated from sample hysteresis and they recommended that calibration of this transformation should not utilize the standard 25.4-kbar calibration point but rather a value higher by half the width of the initiation hysteresis of the sample. The validity of this calibration procedure appears questionable, however, since (1) thermally activated nucleation is a kinetic process that can be accomplished isobarically at more than one pressure rather than at a single fixed pressure, and (2) the criterion for nuclei growth that was utilized for the hysteresis interpretation is completely kinetic dependent and does not define a real sample hysteresis of the initiation pressures. Also, as noted by Jeffery et al.[4] and others, there is no reason to expect the equilibrium pressure to be centered between the forward and reverse initiation pressures. In addition to the nature of the initiation pressure hysteresis, the influence of sample characteristics on the transformation behavior is not clear. Davidson and Lee[1] state that the transformation pressure and transformation rate are independent of the grain boundaries and associated anisotropy-induced deformation, but they report different kinetic behavior of their samples. Jeffery et al.[4] show that flat strip samples yield smaller hysteresis and sharper transitions than cylindrical wire samples when embedded in NaCl.

In view of the importance of understanding the nature of the transformations on which the calibration point is based, hydrostatic pressure experiments were specifically focused on the following aspects of the bismuth I–II and II–I transformations: (1) the kinetic dependence of the initiation pressures, (2) the location of the equilibrium pressure relative to the initiation pressures of the forward and reverse transformations, and (3) the dependence of the initiation and completion of the transformations on the microstructure of the sample. Information was obtained on

other facets of the transformations relating to sharpness, pressurization rate, and region of indifference. The results differ in important respects from those of previous investigators. An alternative interpretation of initiation pressure hysteresis phenomena is presented to explain the data and to indicate the calibration procedure for solid pressure systems in which the equilibrium pressure cannot be measured directly.

II. EXPERIMENTAL

The basic apparatus was a hexahedral press with 2000-ton capacity rams and a cubic pressure chamber 5.7 cm on an edge. The hydrostatic pressure cell[5] was vertically centered within a pyrophyllite cube of this size, and the simultaneous convergence of the rams generated hydrostatic pressure within the cell by means of an equivolume liquid mixture of normal and isopentane. This pressure-transmitting medium is hydrostatic at pressures of 50–60 kbars.[6,7] In addition to the experimental samples, the hydrostatic pressure cell contained a well-seasoned manganin coil for the measurement of pressure. The resistance of the coil was measured with a Leeds and Northrup G-2 Mueller Bridge having a sensitivity of 0.1 mΩ, which for our coils is equivalent to about 0.6 bar. The sample pressures obtained in this manner do not depend on the usual "load" or on apparatus hysteresis and are therefore independent of pressure cycling. The particular experiment reported lasted about one month during which time the pressure was maintained and cycled about 20 times for the repeated observation of the characteristics of the I–II and II–I transformations. Ten electrical leads from the hydrostatic pressure chamber were employed and four-lead measurements were made on the samples and on the manganin gauge.

Two samples of bismuth (American Smelting and Refining Company, 99.999% purity) which differed in both microstructure and thickness were examined. Different grain sizes were conveniently prepared by alternately annealing and rolling bismuth shot to a thickness of 0.028 cm and 0.001 cm. Each sample was about 1.8-cm long and 0.3-cm wide. Constant current was passed through the samples and the bismuth relative resistance was monitored on a Varian Model G-11A recorder driven by a Keithley Model 150A microvoltammeter. Variations of 0.02% of the relative resistance of bismuth were detectable.

The conventional initiation hysteresis was determined with very slow and constant pressurization rates. The relative resistance of a sample was recorded as the pressure was changed at rates less than 10 bars/min in either pressure direction. In pressure cycling the sample was taken about 1–2 kbars beyond the equilibrium pressure for at least several hours and sometimes overnight so that only a single phase component was present in the sample at the initiation

of the I–II and II–I transformations. The region of indifference was reached from either pressure direction on any particular pressure cycle. From the high-pressure side, pressure release was started after the I–II transformation initiated and proceeded to about 40% completion. As pressure was released, the recorded relative resistance decreased at a slower rate and eventually reversed and began to increase after the equilibrium pressure was passed. The pressure was then increased in increments of about 10–15 bars and the relative resistance was recorded for a period of 20–30 min at each pressure until reversal was again detected, the sensitivity of the rate being about 0.001%/min. The pressure range over which this rate was invariant and essentially zero is noted as the region of indifference.

The time dependence of the initiation of the transformations was examined by maintaining pressure constant at a value between that of the region of indifference and the pressure previously measured as part of the initiation hysteresis. For the I–II transformation for example, the sample was generally left overnight at a pressure about 1 or 2 kbars below the region of indifference so that only bismuth I was present in the sample. Then for each examination of the transformation, pressure was raised and stabilized quite close to, but below, the equilibrium pressure in order to remove the time-dependent pressure change that results from the flow effects of pyrophyllite.[6] Subsequently the pressure was quickly raised to a selected value higher than the equilibrium pressure and was maintained constant. The bismuth samples were monitored at this constant pressure above the equilibrium pressure at room temperature. An analogous procedure was employed for investigation of the time dependence of the II–I transformation. The variation of room temperature during the course of a day was less than 1°C, but the temperature fluctuation of the sample was even less due to the large steel mass of the hexahedral press.

The bismuth transformations were examined during experiments that were primarily concerned with improving the reliability and capability of the original pressure cell.[6] Due to the contingent nature of the experiments, bismuth samples were conveniently included but time was not expended to calibrate the manganin pressure gauge or make temperature corrections for the manganin resistance. Although important for quantitative measurements, these expediencies have no bearing on the conclusions presented herein that are based on relative pressures and on a comparison of different samples simultaneously exposed to the same conditions of pressure and temperature.

III. RESULTS

The location of the region of indifference relative to the initiation pressures of the bismuth I–II and
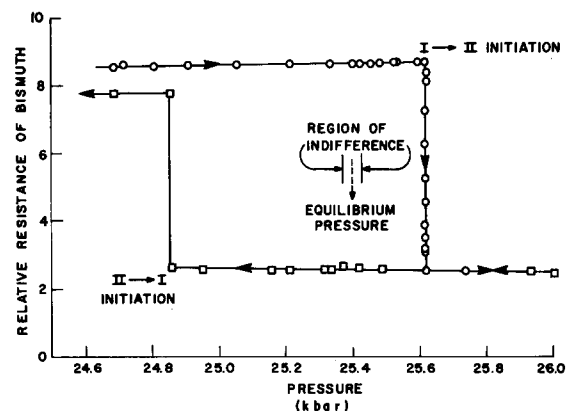

FIG. 2. The region of indifference of bismuth relative to the initiation pressures of the I–II and II–I transformations for a rolled-strip sample 0.028-cm thick, 99.999% purity. The I–II transformation (O) was detected with a pressurization rate of about 1 bar/min. The II–I transformation (□) was detected with a depressurization rate of about 6 bars/min.

II–I transformations is shown in Fig. 2. The data are for a particular pressure cycle around the I–II point with a slow and constant pressurization rate on the sample possessing larger thickness and grain size. The initiation pressures were separated by about 0.76 kbar and the width of the region of indifference was 0.05 kbar. The center of the region of indifference was about 0.22 kbar below the I–II initiation pressure, demonstrating that the equilibrium pressure is not centered between the initiation pressures but is located appreciably closer to the I–II transformation. The same general relationship was observed for each sample with different pressurization rates on different pressure cycles. The initiation pressures of the II–I transformation varied toward *lower* values within a range of about 0.2–0.3 kbar on cycling and were not as reproducible as those of the I–II transformation. With the kinetic behavior reported next for the I–II transformation, the 0.76-kbar initiation pressure interval does not represent the true strain hysteresis of initiation and is discussed later. No importance is attached to the observation that the relative resistance of the samples was not reproducible on any particular pressure cycle because of the polycrystalline nature of the samples and the volume and dimensional change associated with the transformations. The width of the region of indifference in the sample with the larger thickness and grain size ranged between 0.03 and 0.05 kbar for repeated determinations. The region of indifference in the sample with smaller thickness and grain size overlapped the region for the other sample but was about twice as wide. For the two samples, the center of the region differed by only 0.02–0.03 kbar.

The transformation behavior with respect to kinetic time at a holding pressure of 0.17 kbar above the equilibrium pressure is shown in Fig. 3 for both sam-
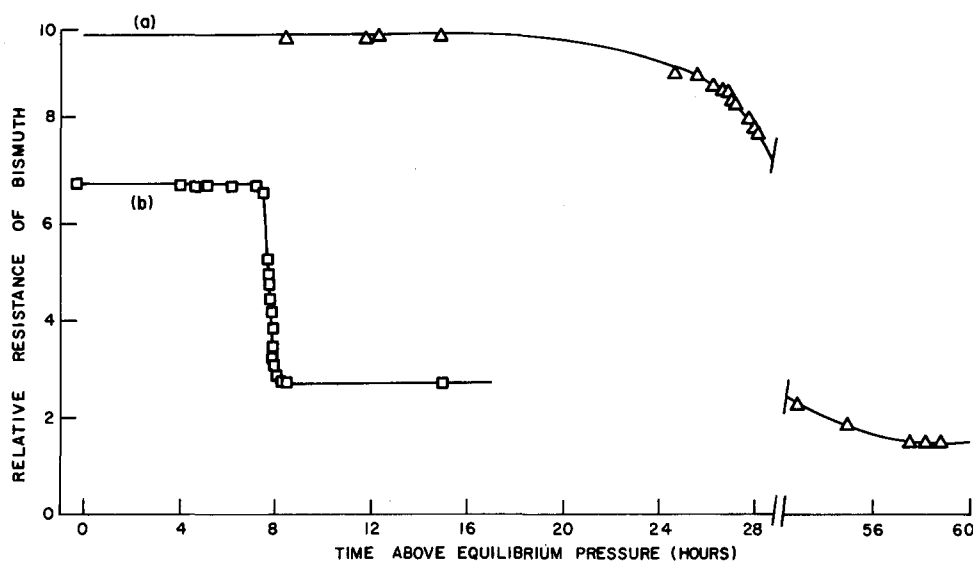
FIG. 3. Kinetic initiation and completion of the bismuth I-II transformation at constant hydrostatic pressure about 0.17 kbar above the equilibrium pressure. (a) Sample with smaller thickness and grain size ($\triangle$), and (b) sample with larger thickness and grain size ($\square$); each sample polycrystalline, strip shaped, 99.999% purity. Pressure and both samples were monitored simultaneously.

ples. The resistance of the manganin pressure gauge and the relative resistance of the samples were all measured simultaneously. Pressure was quickly raised about 0.12 kbar above the equilibrium pressure and allowed to drift an additional 0.05 kbar upward during the first 2 h. No transformation was observed in either sample through the next 5 h as the pressure was stabilized and controlled within a total variation of 0.005 kbar. The I-II transformation initiated in the sample with larger thickness and grain size at about 7 h and proceeded to completion in less than 1 h. A pressure decrease of about 0.02 kbar was concurrent with completion of the transformation and is attributed to the volume decrease associated with the transformation relative to the volume of the hydrostatic cell. Such a pressure decrease with the I-II transformation and a pressure increase of about the same magnitude with the II-I transformation were always observed with this type experiment. At 12 h, the pressure was returned to its original value but the I-II transformation did not initiate in the thinner sample for an additional 2 h while pressure was constant within 0.005 kbar. Subsequently the pressure dropped about 0.05 kbar overnight during which time the transformation behavior was recorded. The transformation rate was extremely slow even after the pressure was adjusted back to the original value at 26 h. Pressure was maintained constant during the next 10 h after which the transformation was about 50% complete. Following an overnight pressure drop of 0.06 kbar the transformation completed at ~57 h. The waiting periods prior to transformation initiation were about 7 h for the thick sample and 14 h for the thin sample, and the average transformation rates were about 2%/min and 0.04%/min, respectively. The low value of the latter rate was partially due to overnight pressure loss but nevertheless the transformation was markedly slower in the thin sample.

The data in Fig. 3 reveal that the I-II transformation initiated after a waiting period at constant pressure and temperature, and that transformation initiation and completion differed for the two different samples. Similar behavior was observed at higher holding pressures on other pressure cycles. For each sample the duration of the waiting periods and the times required for completion of the transformations were shorter for higher holding pressures above the equilibrium pressure. The transformations always proceeded to completion isobarically when sufficient time was allowed. The sample with the larger thickness and grain size always exhibited faster initiation and completion. For this sample the waiting periods for initiation decreased rapidly for small changes in the holding pressure according to an approximate average pressure coefficient of −6 min/bar between 0.17 and 0.22 kbar above the equilibrium pressure.

Although initiation times were observed for the II-I transformation, it was not certain whether initiation was due to kinetic time or to small pressure and temperature fluctuations. Experimentally it was difficult to locate pressures for measurement of kinetic initiation in a reasonable period of time because of the variation of the transformation on pressure cycling. Initiation occurred first in the sample with larger grain size and thickness. After initiation the transformation in each sample proceeded to completion in less than 1 min. The II-I transformation rates were measurably slower at higher pressures towards the equilibrium pressure as observed by decreasing the pressure from equilibrium conditions.

IV. DISCUSSION

The accuracy of calibrating initiation pressures in solid-media depends on the reproducibility of the initiation pressure and its relationship to the equilibrium pressure. Each of these properties relies on the fun-

damental transformation characteristics of the calibrant. In the present investigation on bismuth, the I–II initiation pressure was kinetic dependent and a fixed-pressure initiation hysteresis could not be measured even with the unusually slow pressurization rates employed. Also, the usual assumption that the equilibrium pressure is centered between the initiation pressures of the forward and reverse transformations was experimentally shown to be invalid for the bismuth I–II point. The interpretation of hysteresis phenomena given by Jeffery et al.[4] does not explain the present data for bismuth and, more generally, does not justify the existence of an initiation pressure hysteresis within which neither the forward nor the reverse transformation can take place. In the following discussion the characteristics of the initiation pressures are related to fixed-point pressure calibration according to the theory of nucleation in condensed systems.[8] Some thermodynamic and kinetic principles of phase changes are briefly stated to describe the experimental initiation pressures and to resolve the nature of initiation pressure hysteresis phenomena. All of the present data are explained, the strain and kinetic dependences of initiation are distinguished, the existence and properties of a real strain hysteresis of the initiation pressures is established, and the calibration pressure consistent with the present investigation is indicated for the bismuth I–II transformation in solid media.

A. Strain Dependence of Initiation

Thermodynamic equilibrium between a low-pressure phase I and a polymorphic high-pressure phase II is defined as the equality of the respective Gibbs volume free energy denoted as $G_V{}^I(P)$ and $G_V{}^{II}(P)$ at constant temperature. For the transformation of one phase to the other, ΔG_V is negative in sign at pressures within the thermodynamic stability field of the new phase and is positive elsewhere. The formation or nucleation of a new phase from the matrix of the original phase additionally involves the surface free-energy change ΔG_S that is associated with the formation of an interface between the two phases, and the elastic free-energy change ΔG_E that is caused by the volume change accompanying the nucleation. Nucleation specifically depends on the geometry and crystalline orientation of the nuclei and is heterogeneous, but the salient features of the phase change relevant to pressure calibration are illustrated by considering the forward transformation with homogeneous nucleation of a cubically shaped nucleus of phase II so that the total free-energy change is expressed by

$$\Delta G = l^3(\Delta G_v + E) + 6l^2\sigma, \qquad (1)$$

where l is the edge length of a cubic nucleus, $\Delta G_v = (G_V{}^{II} - G_V{}^I)/V_{II}$ is the volume free-energy difference between phase II and phase I per unit volume of the new phase, V_{II} is the molar volume of phase II,

E is the elastic strain energy of the nucleus and surrounding matrix per unit volume of the new phase, and σ is the surface free energy per unit area of the interface between the two phases. Nucleation of phase II is impossible below or at the equilibrium pressure since $\Delta G_v \geq 0$ and the elastic and surface free-energy changes are always positive for mechanical-type strain. Above the equilibrium pressure, embryos become stable nuclei only when the total ΔG is negative so that nucleus formation leads to a decrease in the total free energy of the system. For systems involving a fluid phase the volume change of transformation can be accomodated without the buildup of strain so that $E = 0$, and nucleation can consequently occur at pressures immediately above the equilibrium pressure. For condensed systems, however, the volume change must be accomodated by strain in the nuclei and surrounding matrix of the original phase so that there is a pressure range above equilibrium within which nucleation of the forward transformation is not thermodynamically allowed even though ΔG_v is negative. The elastic strain energy E_{I-II} is a strain barrier to initiation of the transformation, and the pressure range above the equilibrium pressure P_{eq} that is necessary to make $|\Delta G_v| = E_{I-II}$ represents the part of the initiation pressure hysteresis due to the forward transformation. Assuming that molar volumes are constant over a relatively small pressure range, then $\Delta G_v = (\Delta V/V_{II})\Delta P$, and the following expression is obtained for the pressure interval within which the forward transformation cannot take place:

$$\text{Forward hysteresis} = (P_{I-II} - P_{eq}) = (V_{II}/\Delta V)E_{I-II}, \qquad (2)$$

where the molar volume difference $\Delta V = (V_I - V_{II}) > 0$. The same principles apply analogously to the reverse transformation so that

$$\text{Reverse hysteresis} = (P_{eq} - P_{II-I}) = (V_I/\Delta V)E_{II-I}, \qquad (3)$$

and the total initiation pressure hysteresis due to transformation strain can be expressed as

$$\text{Total hysteresis} = (V_{II}E_{I-II} + V_I E_{II-I})/\Delta V, \qquad (4)$$

where E_{I-II} and E_{II-I} are the strain/volume for the forward and reverse transformations in the up and down pressure directions, respectively. Analogously there is an initiation hysteresis with respect to temperature.

Thus the origin of initiation pressure hysteresis phenomena is the elastic free-energy change of nucleation. The strain energy associated with the volume change of the forward and reverse transformations prevents nucleation in the thermodynamic stability field of the new phase and determines a real pressure and temperature hysteresis of initiation. The size of the initiation hysteresis is determined by the atomic

volume of each phase and the strain energy of nucleation of each transformation. Since the forward and reverse hysteresis depend on asymmetrical parameters, there is little justification for the *a priori* assumption that the equilibrium pressure is centered within the initiation pressure hysteresis. An analytic expression and comparison of the strain energies for nucleation of the forward and reverse transformations is beyond the scope of the present work since E depends[9] not only on the shape and size of the nucleus and on the elastic moduli of each phase, but also on the distribution of strain between nucleus and matrix and on the coherent or incoherent nature of the interface between the phases. Using the present data for bismuth the limiting relationship $E_{I-II} \leq 0.3 \, E_{II-I}$ is obtained by taking 0.17 kbar as the largest value for ΔP_{I-II}, 0.54 kbar as the smallest value for ΔP_{II-I}, and $V_{II}/V_{I} \approx 0.94$. The forward hysteresis and consequently E_{I-II}/E_{II-I} are probably even smaller in view of the kinetic dependence of the I–II transformation, even with the very slow pressurization rates employed. The specific behavior exhibited by a given transformation is of course different for different materials, depending on the variety of parameters mentioned. Nevertheless the present interpretation of hysteresis phenomena provides some qualitative information pertinent to fixed-point pressure calibration with other calibrant transformations.

Equations (2) and (3) show that the initiation pressures referred to the equilibrium pressure are determined by the relative values of $V_{II}E_{I-II}$ and $V_{I}E_{II-I}$ for first-order polymorphic transformations. The atomic volumes are an asymmetrical parameter that favors $(P_{I-II} - P_{eq}) < (P_{eq} - P_{II-I})$ since the forward transformation (up pressure direction) is always accompanied by a volume decrease, whereas the reverse transformation always undergoes a volume increase. While it cannot be concluded *a priori* that the smaller strain energy is always associated with the transformation that undergoes the volume decrease, several qualitative considerations suggest that this correlation might be valid. The strain energy can be considered from the point of view of the atomic displacements from the normal lattice positions that would be occupied in the unstrained single-phase state, with the strain energy varying as the square of the displacements. For a transformation with a volume decrease the atoms are displaced by coulomb forces, but for a transformation with a volume increase the strain is effected by stronger repulsive forces of the atoms and the strain also probably extends over larger atomic distances. Furthermore, the formation of nuclei with a volume increase is resisted not only by the atomic repulsion energy but by the additional constraint that the volume expansion must take place against the external confining pressure. From this elementary reasoning it is inferred for other polymorphic calibrants that the strain energy is probably smaller for the

forward transformation and that the equilibrium pressure might be toward the high-pressure side of the strain hysteresis of initiation in general.

The dependence of the strain hysteresis on the transformation volume change suggests that there should be little or no strain hysteresis associated with second-order transformations, i.e., transformations in which there is no volume discontinuity between the phases as a function either of pressure or temperature. In the first place, it is the existence of a volume change that gives rise to a strain hysteresis of initiation. Also, experimental measurements of the Curie points of ferromagnets and second-order ferroelectrics are reproducible with little or no temperature hysteresis when slow heating and cooling rates are employed. In Eq. (4) the strain energies per unit volume depend on ΔV, and if the strain energy is proportional to the square of the strain then one would expect the magnitude of the strain hysteresis to be directly proportional to the transformation volume change. This relationship is in agreement with the relative absence of strain hysteresis for transformations in which there is no volume change, but otherwise the correlation appears to have questionable value for comparing different first-order transformations. The magnitude of the strain hysteresis depends on other parameters besides ΔV, and the kinetic dependence of nucleation must also be considered. If the relative contribution of strain and kinetics is not known for initiation, then one cannot be certain that the measured initiation pressure interval represents the true strain hysteresis. This is particularly true, for example, when comparing at room temperature a series of elements such as bismuth, thallium, and barium that have progressively higher melting points.

The interpretation of hysteresis phenomena given by Jeffery *et al.*[4] does not define a hysteresis of the nuclei since their criterion for nuclei growth can be satisfied by kinetic time at pressures 1 bar from equilibrium. The important distinctions with the present interpretation are that the origin of the hysteresis is the elastic free-energy change associated with the transformation volume change, and the transformation pressure is additionally a function of kinetic time. The measurements of Davidson and Lee[1] do not represent a true sample hysteresis, as a kinetic dependence of initiation was reported. It should be noted that Bridgman attached no importance to initiation pressures in his studies of polymorphic transitions.[2] His experimental procedure was concerned with adjustments of pressure and sample composition to reach the equilibrium pressure after a transformation initiated rather than with the initiation pressures per se.[3]

B. Kinetic Dependence of Initiation

Nucleation is not instantaneous at pressures above the initiation pressure hysteresis because of the kinetics associated with the formation of the minimum

size cluster of atoms required for a nucleus of the new phase to be stable. The total free energy of formation of the new phase passes through a maximum ΔG^* as a function of the size of the embryos, and in the usual manner the coordinates of the maximum are found from Eq. (1) to be

$$l^* = -4\sigma/(\Delta G_v + E) \qquad (5)$$

$$\Delta G^* = 32\sigma^3/(\Delta G_v + E)^2, \qquad (6)$$

where l^* is the edge length of the minimum critical size cluster of atoms required for the formation of stable nuclei, the free energy of formation of the critical size nucleus ΔG^* is the thermodynamic barrier to nucleation, and E and σ are considered independent of the size, shape, and crystalline orientation of the nucleus. For thermally activated nucleation the critical size of a nucleus is attained by the kinetic addition of atoms that must reach and cross the boundary between the two phases by diffusion, so even at pressures when $|\Delta G_v| > E$ the initiation of the transformation is a function of kinetic time and the nucleation rate. For example, if atomic movement across the nucleus/matrix interface is associated with an activation energy ΔG_m, then according to classical nucleation theory the steady-state rate of homogeneous nucleation per unit volume I at constant temperature and pressure can be expressed as

$$I = Nv_0 \exp[-(\Delta G^* + \Delta G_m)/kT], \qquad (7)$$

where N is the number of atoms of phase I per unit volume, v_0 is the fundamental jump frequency, and ΔG_m is often denoted as the kinetic barrier to nucleation. The nucleation behavior as a function of pressure P above the upper boundary P_{I-II} of the strain hysteresis can be shown qualitatively from the pressure variation of l^*, ΔG^*, and I with the approximation that the changes in σ and E by pressure are negligible. Expanding ΔG_v in a Taylor series expansion about P_{I-II}, retaining terms to first order, and substituting into Eq. (5) gives

$$l^*(P) = 4\sigma(V_{II}/\Delta V)[1/(P - P_{I-II})], \qquad (8)$$

where $\Delta V = (V_I - V_{II}) > 0$, so that the size of the critical nucleus decreases for increasing pressures above the strain hysteresis. Analogously from Eq. (6)

$$\Delta G^*(P) = 32\sigma^3(V_{II}/\Delta V)^2[1/(P - P_{I-II})^2] \qquad (9)$$

and the free energy of formation of the critical size nucleus also decreases with increasing pressure. In Eq. (7) the exponential factors are the significant terms that determine the pressure variation of the nucleation rate. For nonthermally activated nucleation, e.g., shear or displacive transformations, atomic diffusion is not involved and $\Delta G_m \approx 0$. For thermally activated nucleation only short-range diffusion is involved in one-component systems and it can be inferred from the results of self-diffusion studies that

ΔG_m is invariant for small pressure changes. Since ΔG^* decreases inversely with the square of the pressure difference, the nucleation rate depends primarily on ΔG^* and is faster for higher pressures above the strain hysteresis.

The kinetic data of the type shown in Fig. 3 were the result of experiments that were designed to specifically test the initiation of the bismuth I–II transformation under simultaneous isothermal/isobaric conditions. The waiting periods that were observed prior to isothermal/isobaric initiation of the transformation are the kinetic times required to form sufficient nuclei of bismuth II to give a measurable alteration of the relative resistance of the sample and are a reflection of the nucleation rate. If fractional transformation is proportional to the fractional resistance change between all phase I and all phase II, the measurement sensitivity corresponded to the detection of about the initial 0.03% transformation. The shorter waiting periods at higher pressures above the strain hysteresis are due to the kinetic times required to attain the same extent of fractional transformation. This behavior is the result of faster nucleation rates at higher pressures. The large pressure coefficient of the waiting periods is due to the exponential dependence of the nucleation rate on ΔG^* and is the reason for the appearance of a fixed initiation pressure for the magnitude of the pressurization rates generally employed. The relatively small change in pressure necessary to make nucleation of bismuth II observable diminishes the kinetic dependence of initiation and is advantageous for the reproducibility of fixed-point pressure calibration.

The kinetic behavior observed for the bismuth I–II transformation conforms to the thermodynamic and kinetic characteristics of phase changes as a first-order transformation with a thermally activated nucleation and growth mechanism. Nucleation and growth are also ascribed to the II–I transformation, but the elastic free-energy change of nucleation may have a more dominant influence on nucleation because of the increase of volume associated with this phase change. The dependence of nucleation on E_{II-I} is probably the principal cause of the large underpressurization observed for initiation of the transformation and also is likely responsible for the variation of the initiation pressure on cycling since E_{II-I} depends, among other things, on the past history of the sample. It seems unlikely that the lack of reproducibility of the II–I initiation pressure is due to remnant bismuth I left from incompletion of the previous transformation since long kinetic times were allowed at large overpressurizations of the I–II transformation before II–I initiation was measured. Once stable nuclei were formed, the transformation ran to completion rapidly because of the large underpressurization of the equilibrium pressure.

When interpreting pressure data from the behavior

of solid-solid transitions, it is important to recognize that the initiation pressures depend on the type[10] of transformation mechanism and that sluggish nucleation kinetics may prevent measurements of the true strain hysteresis in practical experimental times. The sluggish nucleation and growth kinetics of thallium and barium at room temperature and of bismuth I–II at cryogenic temperatures are inherently due in some measure to the large temperature departure from the melting points and the relative lack of thermal kT for the transformations. In these cases it is probably not valid to assume that the nucleation kinetics are rapidly reduced by small changes in pressure (as noted earlier for bismuth I–II at 25 C) because of the stronger dependence of chemical kinetics on temperature. In first-order reconstructive transformations thermal energy and kinetic time are involved in the breakage of bonds and the rearrangement of atoms to form the new structure. An extreme example of the combined effects of strain and kinetics in such a case is the quartz–coesite transition for which about 60 kbar above equilibrium conditions at 450 C are required to form coesite without nucleating agents.[11] For displacive and martensite-type transformations the nucleation kinetics are usually rapid but the latter are usually associated with large strain hysteresis. The kinetics of second-order transformations also depend on the type of transformation, generally being fast for ferromagnetic and ferroelectric Curie points and slow for order–disorder transformations. As fixed-point pressure calibrants, second-order displacive or Curie point transformations are desirable from the standpoints of little or no strain hysteresis and fast nucleation kinetics.

The transformation characteristics of initiation are evident from the previous discussion. The strain energy associated with the volume change of the forward and reverse transformations determines a strain hysteresis of initiation. The strain hysteresis of the initiation pressures is expressed by Eq. (4). Outside of the strain hysteresis, initiation depends on the particular chemical kinetics involved in the formation and growth of the critical size nucleus. The initiation of a transformation can take place at various pressures rather than at a single-valued initiation pressure, with faster kinetics associated with pressures farther from the strain hysteresis. If the transformation nucleates easily then initiation occurs close to the boundary of the strain hysteresis. In this case if the elastic strain energy of nucleation is small then initiation may also closely correspond to the equilibrium pressure. When the nucleation kinetics are sluggish then the measured initiation pressure interval represents only an apparent hysteresis. When the elastic strain energy of nucleation is large then there is no close correspondence of initiation and equilibrium.

The data in Fig. 2 and the kinetic nature of the bismuth I–II transformation are not in agreement with the recommendation of Jeffery et al.[4] that 26.2 kbar be utilized to calibrate the initiation of this transformation in solid-media pressure systems. The separation between the I–II initiation pressure and the 25.4 kbar equilibrium pressure was only 0.22 kbar with the slow pressurization rate. In the kinetic holding experiments, I–II initiation was observed 0.17 kbar from the equilibrium pressure. Furthermore the kinetic dependence of nucleation can be expected to be diminished in solid pressure media when compared to the nucleation kinetics that obtain under hydrostatic conditions. It is known that grinding, crushing, or scratching a solid reactant creates nucleation sites in the parent phase, reduces or removes induction periods, and in general facilitates the nucleation rate of the new phase. A solid pressure medium produces such an effect on a calibrant sample and would cause an initiation pressure to be closer rather than farther from equilibrium. Therefore in solid pressure media the equilibrium pressure of 25.4 kbar serves as a more accurate calibration point than 26.2 kbar for initiation of the bismuth I–II transformation. Although initiation of a transformation cannot take place at the equilibrium pressure if a volume change is associated with the transformation, the elastic strain energy for the case of bismuth I–II initiation must be of such a low value that the equilibrium pressure is a satisfactory approximation for solid pressure media within the realm of pressure gradients and pressurization rates. The same result cannot be stated a priori to hold for other calibrant transformations however, since the elastic strain energies of nucleation are not known theoretically, the relative initiation and equilibrium pressures have not been measured hydrostatically, and the kinetic dependence of nucleation might not be overcome completely by solid pressure media. Hydrostatic pressure experiments that relate to these considerations for bismuth, thallium, and barium are planned.

C. Sample Effects on Initiation and Equilibrium

For solid-state transformations it is general experience that the transformation characteristics are influenced by the character of the sample. Such behavior is understandable by virtue of the factors involved in the nucleation and growth of a new phase and should pertain accordingly to the initiation and equilibrium pressures of calibrant transformations. Even though microstructure and thickness were not independently separated between the bismuth samples examined in the present investigation, both parameters probably exhibit an influence on the transformation behavior. Solid-state nucleation is heterogeneous and is favored by irregularities in the microstructure, e.g., at boundaries between the grains or at lattice dislocations within the grains. The anisotropy-induced deforma-

tion caused by compression, both inter- and intra-grain, is greater in a sample with larger thickness and the creation of additional nucleation sites enhances initiation of the transformation. Davidson and Lee[1] concluded that the bismuth I–II transformation pressure and transformation rate are structure insensitive with respect to the presence of grain boundaries and associated localized plastic deformation. An effect of microstructure is indicated, however, by their observation that the transformation did not initiate simultaneously in single-crystal and polycrystal samples. Also the influence of grain boundaries on the transformation may have been overshadowed by the relatively large 0.43-cm thickness of their samples. The creation of nucleation sites within the grains by anisotropy-induced deformation would result in the appearance of the transformation with equal facility within the grains and at the grain boundaries. Jeffery et al.[4] suggested that the transformation characteristics are influenced by the shape of the sample in solid pressure systems but their strip and cylindrical samples differed fivefold in diameter also. In the present investigation the shape of the two samples was identical but different transformation behavior was observed, showing that sample shape alone is not a unique parameter. In addition to microstructure and thickness, purity is another parameter that will influence the transformation behavior, and the individual effects of these parameters will be reported later. Heydemann[12] examined the bismuth I–II transformation using samples of different purity but the grain size was also different.

The transformation behavior represented in Figs. 2 and 3 is also informative with respect to the magnitude of the pressurization rate and the "sharpness" of the I–II transformation in solid-media apparatus. In view of the close proximity of the equilibrium and I–II initiation pressures, the accuracy of the pressure calibration should be evaluated in terms of the pressure increment employed in the pressurization procedure. The correlation of "sharpness" of the I–II transformation with uniformity of pressure must be considered in the context of kinetic time, character of the sample, and pressurization rate, since each of these factors influences sharpness in addition to the extent of the pressure gradients. For example, the lack of sharpness with a slow pressurization rate can in some cases be indicative of an accurate calibration inasmuch as completion of the transformation is more sluggish for pressures closer to equilibrium. On the other hand, any transformation can appear sharp with a sufficiently large pressurization rate so that the experimental observation of a sharp transformation within a short period of time can in some instances actually be a manifestation of overdriving the transformation and an inaccurate calibration.

Whereas the initiation hysteresis represents trans-

formation reversal of the initiation pressures, the region of indifference represents transformation reversal across the equilibrium pressure when both phases are simultaneously present in the sample. In the latter case the transformations reverse over a much smaller pressure range since there is no nucleation problem. The 0.06-kbar region of indifference measured for the sample with smaller grain size and thickness is about the same as that reported by Bridgman.[3] The value of about 0.03 kbar for the sample with larger grain size and thickness is the smallest reported to date, but Bridgman made no special attempt to determine the smallest width of the region per se. The important consideration for pressure calibration is the reproducibility of the center of the region of indifference. Within the experimental uncertainty caused by small temperature variations, the center of the region of indifference was essentially the same for the two samples. The larger region of indifference that was measured for the thinner sample was probably due partially to the very slow transformation rates exhibited by this sample, but nevertheless the width of the region must also be a real function of the microstructure, purity, and thickness of the sample. The effect of these sample parameters on the width of the region and on the reproducibility of the equilibrium pressure will be reported subsequently.

V. CONCLUSIONS

It is concluded that the bismuth I–II and II–I transformations take place by a thermally activated nucleation and growth mechanism with kinetic dependent nucleation of the I–II transformation and a large strain energy of nucleation for the II–I transformation. For these transformations the equilibrium pressure is asymmetrically located toward the high-pressure side of the initiation pressure interval. The I–II transformation initiates within 0.17 kbar of the equilibrium pressure. The initiation pressures and the region of indifference depend on the microstructural and dimensional properties of the sample.

For all solid–solid polymorphic transformations it is concluded that the origin of initiation hysteresis phenomena is the elastic free-energy change of nucleation. The strain energy associated with the volume change of the forward and reverse transformations prevents nucleation in the thermodynamic stability field of the new phase and causes a real strain hysteresis of initiation with respect to pressure or temperature. Outside of the strain hysteresis the initiation pressure depends on the chemical kinetics involved in the formation and growth of the new phase. Both the strain and kinetic dependences of the initiation pressures are important in the interpretation of solid–solid transformation behavior. Initiation occurs close to the boundary of the strain hysteresis if the nucleation kinetics are rapid. If at the same time the strain

energy of nucleation is small then the initiation pressure may represent a good approximation of the equilibrium pressure. It is concluded that second-order displacive and Curie point transformations have desirable characteristics as fixed-point calibrants from the standpoints of little or no strain hysteresis of initiation and rapid initiation kinetics. For pressure calibration in solid-media apparatus it is concluded that the interpretation of hysteresis phenomena presented by Jeffery et al.[4] is not complete, and that the initiation of the bismuth I-II transformation should be calibrated with the equilibrium pressure rather than with 26.2 kbar.

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Parametric Studies of the Iodine Photodissociation Laser*

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Experimental data for the iodine photodissociation laser are presented over the following ranges of operating conditions: CF_3I pressure, 0.4–500 Torr; argon pressures, 5–200 Torr; and flash energy, 225–1764 J. Peak powers of 400 W and optimal gains of 45 dB/m were observed. The experimental results for CF_3I pressures less than 200 Torr and for the first 25 μsec of lasing action are within 10% of the predictions from a four-level kinetic model of the laser. These results indicate the utility of kinetic models for describing pumping, radiative, and collisional processes.

INTRODUCTION

Laser emission has been observed at 1.315 μ from the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ magnetic-dipole transition in atomic iodine after flash photolysis of CF_3I, CH_3I, and other alkyl and fluoroiodides.[1–6] In a previous article,[7] a simple kinetic rate equation model, useful for predicting population inversions and laser outputs, was presented. The model includes pumping, radiative, and collisional effects and correctly predicts the dependence of the output on reactant pressure and flashlamp parameters. A reasonable fit with Polack's data on peak output powers[3] was achieved. In this paper experimental data on the iodine laser is reported and compared with more extensive results from the model.

EXPERIMENTAL APPARATUS

A schematic of the experimental iodine laser apparatus is shown in Fig. 1. The one-meter long, 10-mm-i.d. quartz laser tube has Vitresoil quartz windows attached at Brewster's angle. Two gold-surfaced, spherical concave mirrors form the resonant cavity. A linear xenon flash lamp, with an average pulse rise time of 20 μsec and pulse width (FWHH) of 150 μsec, is employed. The flash lamp and laser tube are placed at the two foci of a polished elliptical reflector. Two commercial helium–neon lasers are provided for optical alignment of the resonant cavity.

An 18-μf foil capacitor, charged by a 15-kV power supply, delivers up to 1764 J to the flash lamp. The minimum energy input for the system is 225 J. A triggered spark gap prevents premature firing of the lamp while the capacitor is being charged. Two 30-kV trigger modules simultaneously ionize the lamp, actuate the spark gap, and trigger an oscilloscope trace.

Up to 4% of the laser beam's energy is deflected by a quartz flat through a one meter Jarrell–Ash grating spectrometer to either a germanium diode or