

Measurement of the *B1-B2* transition pressure in NaCl at high temperatures

Xiaoyuan Li* and Raymond Jeanloz

Department of Geology and Geophysics, University of California, Berkeley, California 94720

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The phase boundary and kinetics of the *B1-B2* transition in NaCl are documented between 298 and 670 K by visual observation into an externally heated diamond cell. We find an equilibrium (reversed) transition pressure $P_{tr}=26.8$ GPa at room temperature, with a Clapeyron slope $dP_{tr}/dT = -8.9$ MPa/K at elevated temperatures; the corresponding entropy change is 7.4 J/mol K. An apparent activation energy of 5.3 kJ/mol is obtained from the observed decrease in transition hysteresis with temperature. Previous determinations of the NaCl *B1-B2* transition pressure have been biased upward by 3 GPa or more due to kinetic hindrances. Extrapolating our results to 0 K, however, we find good agreement ($\sim 12\%$ difference) with the transition pressure derived from *ab initio* pseudopotential calculations.

INTRODUCTION

The transformation from *B1* (NaCl-type) to *B2* (CsCl-type) structures is the best documented phase transition occurring in alkali halides and alkaline-earth chalcogenides under pressure.¹ In a pioneering study, Bassett and co-workers demonstrated that NaCl transforms to the *B2* structure upon static compression to about 30 GPa at room temperature.² This convincingly demonstrated that the high-pressure transformation previously documented for NaCl by shock-wave (Hugoniot) measurements is due to the *B1-B2* transition.^{3,4} Furthermore, Bassett *et al.* noted that the transition occurs at pressures as low as 24 GPa under shock loading. As temperatures in the shock experiments were estimated to about 1000 K higher than in the static experiments, they concluded that the pressure-temperature (*P-T*) Clapeyron slope of the phase boundary must be negative. In comparison, the Clapeyron slopes for *B1-B2* transitions are found to be nearly zero or somewhat positive for most other alkali halides.^{1,2,5} The positive entropy change (ΔS_{tr}) implied by the negative Clapeyron slope for the NaCl transformation, and the trend of ΔS_{tr} for the *B1-B2* transition among halides has been discussed by several authors.^{2,5-7,8}

The 30-GPa *B1-B2* transition in NaCl has been tentatively proposed as a fixed point for pressure calibration.⁹ This may be warranted, given the large number of experiments in which the transition has been observed,¹⁰ but as mentioned in Ref. 9 and as documented in subsequent work the NaCl transition exhibits considerable hysteresis. In particular, x-ray diffraction studies on NaCl show that the *B1* and *B2* phases persist metastably over a ~ 10 -GPa interval with increasing and decreasing pressure at room temperature.^{11,12} The resulting uncertainty in the equilibrium (reversed) phase boundary precludes the use of this transition as a reliable fixed point: the 30 GPa value observed with increasing pressure is subject to kinetically induced variations from one experiment to another. Thus, a better determination of the equilibrium transition pressure would be useful for calibration purposes.

Recent *ab initio* calculations provide an additional motivation for accurately determining the equilibrium *B1-B2* boundary in NaCl.^{8,13} For example, Froyen and Cohen obtain a transition pressure of 27 GPa (static-lattice value) using the pseudopotential approach.¹³ Given the remarkable agreement between observed and calculated transition pressures for other systems,¹⁴ as well as the large hysteresis found experimentally for NaCl, it could be argued that the theoretical value for the *B1-B2* transition is at least as reliable as the experimentally measured pressure. Moreover, a quantitative comparison between the theoretical and experimental transition pressures requires that the Clapeyron slope be sufficiently well known to extrapolate observations to 0 K. To date, no direct measurement of the *B1-B2* Clapeyron slope has been published for NaCl, and the estimate based on comparing shock-wave and static measurements is subject to considerable uncertainty.⁹

The present study was carried out to measure the coexistence field between the *B1* and *B2* phases of NaCl as a function of temperature. Our purpose was threefold: (i) to document the hysteresis and hence the kinetics of the phase transition; (ii) to use this information to derive an equilibrium phase boundary; (iii) from the phase boundary to derive reliable values for the Clapeyron slope (or ΔS_{tr}) and the 0-K transition pressure. To our knowledge, this study involves the highest pressures to which transition kinetics and a Clapeyron slope of a polymorphic transformation have so far been determined by direct, *in situ* observation.

EXPERIMENTAL PROCEDURE

Polycrystalline NaCl of 99.99% purity (obtained from Malinckrodt Inc.) was loaded in a Mao-Bell-type diamond cell¹⁵ with a gasket made of Inconel X-750 (250- μ m original thickness). We used type-I diamonds of $\frac{1}{4}$ ct. nominal weight and with matched, 8-sided culets 350 μ m in dimension. High temperature is achieved by a two-part external heater that is illustrated in Fig. 1. The heater

parts surround each diamond and are separated by the gasket, which is cut ~ 2 -cm long (i.e., the entire diameter of the diamond-cell cylinder) so as to enhance the heat transfer to the sample. Each heating element is a Pt-wound resistance heater consisting of 0.25-mm-diam platinum wire embedded in a high-temperature ceramic adhesive¹⁶ to form a disk about 20 mm in diameter and 1 mm thick. Up to 3 amps are supplied to the heater from a transformer, without any further power stabilization. With the arrangement shown in Fig. 1, sample temperatures in excess of 400 °C can be achieved throughout the 10^{11} Pa range in our diamond cell.

A ceramic-insulated Pt-(Pt-10 at. % Rh) thermocouple (0.12 mm diam) passing through one of the heating elements is used to determine the temperature of the sample (Fig. 1). This external thermocouple has been calibrated against an internal thermocouple (25 μ m diam) at zero pressure. The junction of the internal thermocouple was embedded in NaCl contained in the gasket and with the diamonds lightly clamped together in order to reproduce the thermal transfer characteristics of the sample volume at elevated pressures and temperatures. The calibration results (Fig. 2) indicate that the sample temperature is up to 320 K cooler than the external thermocouple at the peak temperatures used in this study. This calibration is supported by *in situ* observations of the melting points of In (429 K) and Bi (544 K) contained within the gasketed diamond cell at zero pressure. Based on our calibrations and on observations of temperature stability over periods of several hours, we estimate that our sample temperatures are known to within about 5 K.

In our experiments, pressure is calibrated by the ruby fluorescence technique.¹⁷ Fine-grained ruby powder (5000 ppm Cr concentration, $\lesssim 5$ μ m dimension) is distributed across the top of our sample in a small quantity (ruby to sample volume ratio $\lesssim 5\%$). The fluorescence is excited by a 13-mW He-Cd laser and is recorded using a system

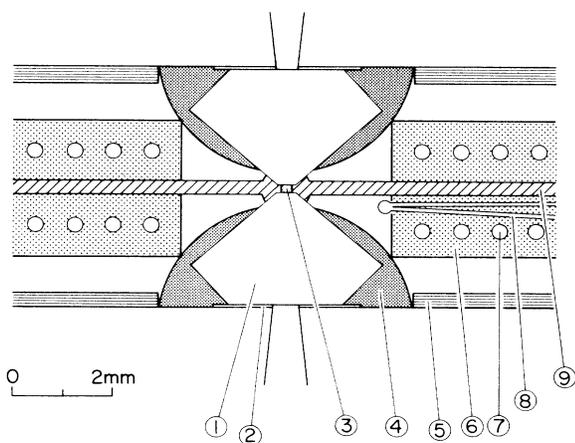


FIG. 1. Experimental assembly: (1) Diamond; (2) Zr foil; (3) sample; (4) high-temperature ceramic adhesive (Ref. 16); (5) mica-sheet insulation; (6) and (7) ceramic adhesive (Ref. 16) and Pt wire making up heater; (8) external thermocouple; (9) gasket.

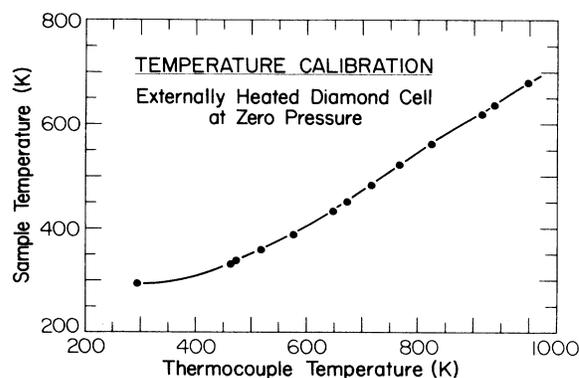


FIG. 2. Correlation between sample temperature (measured by a thermocouple in the sample area at $P=0$) and the temperature at the external thermocouple.

described elsewhere.¹⁸ To correct for the temperature-induced shift in the frequency of the R_1 line we use the expression of Powell *et al.*:¹⁹

$$\Delta\tilde{\nu} = a (T/T_D)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx. \quad (1)$$

With $a = -177$ cm^{-1} and $T_D = 450$ K, this equation yields temperature shifts in good agreement with those observed at zero pressure by Powell and co-workers on ruby with 5000 and 11 000 ppm Cr, and with shifts observed by Shimomura *et al.*²⁰ on ruby with 7000 ppm Cr. The latter authors also showed that the effect of pressure on the temperature shift is negligibly small to at least 4 GPa. Therefore, we feel, justified in using (1) for the present experiments.

In each run, pressure is applied first to about 10 GPa, and then the temperature is raised. The maximum and minimum pressures in the sample are typically between 9.6 and 12.9 GPa before heating. In many cases the highest pressures occur near the sample-gasket boundary (~ 50 – 100 μ m from the center of the sample) due to inhomogeneous deformation of the sample and gasket during loading. Once the desired temperature is reached, pressure is slowly increased (~ 1 GPa/min) and the sample is simultaneously observed by transmitted-light microscopy. The pressure-induced B2 phase appears first in the form of distinct grains located in the region of highest pressure. Owing to the mismatch in indices of refraction of the two phases, the partial transformation of the NaCl is readily observed by a change in its texture.^{2,10} With increasing pressure, the partially converted region spreads out across the sample. Pressure is measured wherever a ruby grain lies on the boundary between this partially converted region and the entirely unconverted region. In this way, we measure the pressure P_{B1-B2} corresponding to the initiation of the transformation (first appearance of the new phase). As the sample is further converted to the high-pressure phase, the small ($\lesssim 2$ μ m), initially-formed crystals coalesce and recrystallize into larger (~ 10 μ m) grains with increasing pressure. Well above the transition pressure (e.g., at 35.4 GPa for a temperature of 373 K) the grain boundaries are no longer discerned in the sam-

ple; we interpret this as meaning that the $B1$ phase has totally disappeared. After complete conversion, the pressure is slowly unloaded (~ 1 GPa/min) and the $B1$ phase reappears as distinct grains in the region of lowest pressure. As before, we determine the pressure P_{B2-B1} at the initiation of the (back) transformation. This pressure occurs along the boundary between the high-pressure region of pure $B2$ phase and the lower-pressure region containing both $B1$ and $B2$ phases. During the measurements, the pressure gradient in the cell is typically 0.009 GPa/ μm . It produces a pressure difference of less than 0.045 GPa on one ruby grain. This difference is far smaller than the uncertainty in our pressure measurements ($\gtrsim 0.5$ GPa: Table I). As each measurement is done by focusing the laser beam on only one ruby grain, the values of P_{B1-B2} and P_{B2-B1} are not affected by the pressure gradient at the present precision.

RESULTS AND DISCUSSION

Our experimental results are summarized in Table I and Fig. 3. The derivation of the $B1$ - $B2$ phase boundary and coexistence curves is described in the following paragraphs. Before entering that discussion, however, we note that our room-temperature observations are in good agreement with the x-ray diffraction measurements of Sato-Sorensen¹¹ and of Heinz and Jeanloz,¹² as well as with the qualitative result given by Mao *et al.*⁹ for the $B1$ - $B2$ transition of NaCl. The region of metastability for the two phases is 6.9 ± 0.7 GPa at room temperature, and we find an apparent transition pressure of 30 GPa on loading; this agrees well with the results of previous studies.^{2,10} Also we find that the hysteresis pressure, defined as

$$P_{\text{hyst}}(T) = \frac{1}{2}[P_{B1-B2}(T) - P_{B2-B1}(T)],$$

decreases with increasing temperature just as has been found for the $B1$ - $B2$ transition in the K and Rb halides.^{21,22} Although it might appear that P_{hyst} is roughly inversely proportional to temperature in our experiments, we show below that our data are more compatible with a simple kinetic model containing a stronger temperature dependence.

Details of our analysis of the observed coexistence boundaries between the $B1$ and $B2$ phases are given elsewhere, but the combined equilibrium and kinetic aspects

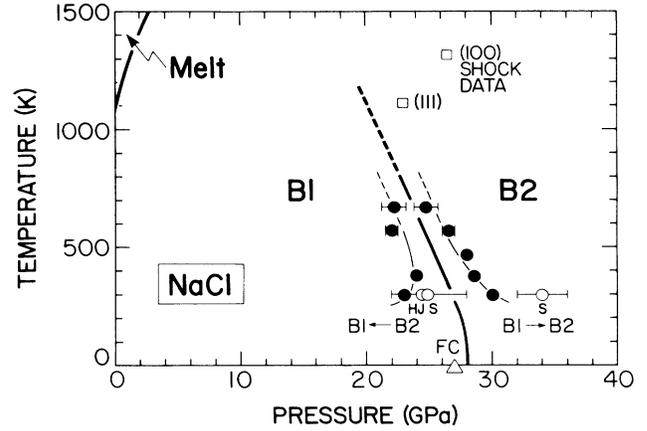


FIG. 3. Summary of the present experimental results (solid points with error bars) on the pressure-temperature phase diagram of NaCl. The best-fit coexistence curves (P_{B1-B2} , P_{B2-B1} shown by thin lines) and $B1$ - $B2$ equilibrium phase boundary (P_{tr} , heavy curve) are obtained from the analysis described in the text. For comparison, coexistence pressures from Ref. 11 (S) and Ref. 12 (HJ) are shown as open points, the $B1$ - $B2$ transition pressures derived from shock data (Ref. 4) are given as open squares ([100] and [111] are shock-propagation directions in single crystals), and the transition pressure obtained from *ab initio* calculations are shown by the open triangle (FC, Ref. 13). The melting curve is from Ref. 35.

are described briefly as follows.^{23,24} The entropy change across the transformation, ΔS_{tr} , is treated in the harmonic approximation and only vibrational contributions to the entropy are considered. Integrating the Clapeyron equation, we find to a high degree of approximation that the equilibrium transition pressure is given as a function of temperature by

$$P_{\text{tr}}(T) = P_{\text{tr}}^0 + \frac{1}{\Delta V_{\text{tr}}} \left[F \left(\frac{\hbar \bar{\omega}_1}{kT} \right) - F \left(\frac{\hbar \bar{\omega}_2}{kT} \right) \right], \quad (2)$$

where the volumes of the two phases (subscripts 1 and 2) are taken to be constant along the Clapeyron curve (the volume change on transformation $\Delta V_{\text{tr}} = \text{const}$).²³ The free-energy functions F depend on the vibrational spectra of the two phases, but for our purposes only average fre-

TABLE I. $B1$ - $B2$ transition pressures for NaCl.

Temperature T (K)	Observed coexistence pressure		Equilibrium transition pressure P_{tr} (GPa) ^c
	P_{B1-B2} (GPa) ^a	P_{B2-B1} (GPa) ^b	
298 ± 0.2	30.0 ± 0.5	23.1 ± 0.5	26.6 ± 0.5
373 ± 5.0	28.6 ± 0.5	24.0 ± 0.5	26.3 ± 0.5
473 ± 5.0	28.1 ± 0.5		$(26.0 \pm 0.8)^d$
573 ± 5.0	26.6 ± 0.6	22.1 ± 0.6	24.4 ± 0.6
673 ± 5.0	24.8 ± 0.9	22.2 ± 0.9	23.5 ± 0.9

^aAppearance of $B2$ phase in $B1$ phase on increasing pressure.

^bAppearance of $B1$ phase in $B2$ phase on decreasing pressure.

^cDerived quantity: $P_{\text{tr}} = \frac{1}{2}(P_{B1-B2} + P_{B2-B1})$.

^dBased on $P_{B2-B1} = 23.9$ GPa obtained by interpolation.

quencies ($\bar{\omega}$) need be considered. Three parameters therefore define the equilibrium boundary; we take these to be the $T=0$ transition pressure P_{tr}^0 , the average vibrational frequency of the low-pressure phase $\bar{\omega}_1$, and the ratio of average vibrational frequencies $\bar{\omega}_2/\bar{\omega}_1$. As shown below, a more detailed treatment of the equilibrium boundary is not warranted by our data.

In order to apply (2), our measurements of the coexistence pressures, P_{B1-B2} and P_{B2-B1} , must be extrapolated to obtain equilibrium transition pressures. We do this with reference to a simple nucleation and growth model of the transition kinetics.²⁵ Our coexistence curves (Fig. 3) correspond roughly to contours of constant amount of transformation observed over a time period that is the same at each temperature. Assuming that the kinetics are growth limited in our experiments (this is supported by our microscopic observations of recrystallization and grain growth), the coexistence curves represent the interplay between the activation (free) energy of transformation Δg^\pm and the thermodynamic driving force ΔG corresponding to the overpressure (or underpressure) at each temperature. Thus, the rate parameter

$$\kappa = \kappa_0 \exp \left[\frac{-\Delta g^\pm}{kT} \right] \left[1 - \exp \left[\frac{-\Delta G}{kT} \right] \right] \quad (3)$$

is taken to be constant for all of our experiments (κ_0 is a constant).

It could be argued that a nucleation and growth model is inappropriate for the B1-B2 transition, given the prior suggestions that a mechanical instability or shear mechanism may be involved.^{2,4,21,26,27} We note, however, that according to lattice dynamical models both B1 and B2 structures are found to be mechanically unstable with respect to each other, when taken to sufficiently high or low pressures (respectively) beyond the equilibrium boundary.^{7,8} Given that both phases can become mechanically unstable and that a large overdriving is apparently required to induce such mechanical instability, we expect only a small contribution to ΔG that is symmetric with respect to overpressure and underpressure. Thus, we base our analysis on the assumption that the thermodynamic driving force at a given temperature is

$$\Delta G = |\Delta V_{\text{tr}}[P - P_{\text{tr}}(T)]| ,$$

which ignores contributions from mechanical instabilities (see also Ref. 13).

To a first approximation, we find that the coexistence curves are symmetric about the equilibrium transformation boundary according to this kinetic model. The major source of asymmetry in the nucleation and growth analysis for pressure-induced transformations arise from the activation volume ΔV^\pm , which increases Δg^\pm on the high- (relative to the low-) pressure side of the transition (assuming $\Delta V^\pm > 0$). We consider this to be a small effect that cannot be resolved in the present study.²³

The result of our kinetic model is that ΔG is given by the positive quantity $-\Delta V_{\text{tr}}P_{\text{hyst}}$ at each temperature and the equilibrium transition pressure is located at

$$P_{\text{tr}}(T) = \frac{1}{2}[P_{B1-B2}(T) + P_{B2-B1}(T)] ,$$

as listed in Table I. Figure 4 illustrates that our data are compatible with such a model in that (3) is satisfied; in particular, our measurements do not support $P_{\text{hyst}} \propto T^{-1}$ (i.e., $\Delta g_\pm = 0$). We derive an apparent activation energy of 5.3 kJ/mol for the B-1-B2 transformation of NaCl, which is comparable in magnitude to estimates for this transition among other alkali halides.^{21,22,27} We emphasize, however, that the numerical value for Δg^\pm is subject to corrections due to our simplifying assumptions in the kinetic analysis. We expect these corrections to be small, but they cannot be quantitatively determined at present. Also, the coexistence curves (shown explicitly in Fig. 3) cannot be extrapolated to low temperatures because our kinetic formalism does not include quantum-statistical effects.²⁸

Three parameters are required to specify the equilibrium transition pressure from (2). At best our data only justify solving for two parameters, so we fix $\bar{\omega}_1$ independently. The reasons for doing this are that $\bar{\omega}_1$ can be calculated from the known thermodynamic properties of the B1 phase, and we have found that our solution is least sensitive to this parameter. Thus, we take a single-oscillator (Einstein) model for the free-energy functions and Eq. (2) becomes explicitly

$$P_{\text{tr}}(T) = P_{\text{tr}}^0 + \frac{6RT}{\Delta V_{\text{tr}}} \ln \left[\frac{1 - \exp(-\Theta_1/T)}{1 - \exp(-\Theta_2/T)} \right] , \quad (4)$$

which can be fitted to the data by least squares. In (4), R is the gas constant ΔV_{tr} is per formula mole, and Θ_1, Θ_2 are the characteristic temperatures for the oscillators. We take the latter to be related to the mean-squared vibrational frequency and the Debye temperature by²⁹

$$\Theta = \hbar \langle \omega^2 \rangle^{1/2} / k = \Theta_D \sqrt{3/5} .$$

The advantage of (4) is its simplicity for reducing data from high-pressure experiments. It goes beyond illustrative purposes, however, in that more elaborate models for the vibrational spectra yield transition boundaries that differ insignificantly from this simple formula within the resolution of the data (Fig. 6).²³

The Debye temperature for the B1 phase of NaCl is well constrained as a function of pressure,³⁰ but ΔV_{tr} is relatively poorly known. We take a value of $\Theta_1 = 393 \pm 11$ K at the transition, and associate a large uncertainty with

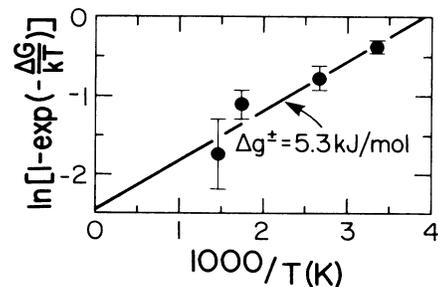


FIG. 4. Fit of the present experimental results to Eq. (3) in the text. An apparent activation energy is derived from the slope of the best-fit line.

the volume change based on the range of reported values:^{2,6,11,12} $\Delta V_{tr} = 0.83 \pm 0.20 \text{ cm}^3/\text{mol}$. The fit of (4) to our data is summarized in Fig. 5, and the best solution is shown in Fig. 6. We find a $T=0$ value of $P_{tr}^0 = 28.2 \text{ GPa}$ and a ratio of frequencies $\bar{\omega}_2/\bar{\omega}_1 \equiv \Theta_2/\Theta_1 = 0.86$. The latter corresponds to a high-temperature, harmonic value for the entropy change of $\Delta S_{tr} = 7.4 \text{ J/mol K}$ (Clapeyron slope $dP_{tr}/dT = -8.9 \text{ MPa/K}$), which is within the range quoted by Liu and Bassett.⁶ The precision for P_{tr}^0 and ΔS_{tr} is approximately $\sim 0.05 \text{ GPa}$ and $\sim 0.3 \text{ J/mol K}$, respectively, but the absolute uncertainties are much larger due to the uncertainty in ΔV_{tr} (Fig. 5). For comparison, a straight-line fit to the data in Fig. 6 yields a Clapeyron slope of -8.6 MPa/K .

As is evident from the equilibrium phase boundaries (shown in Figs. 3 and 6), previous estimates of the *B1-B2* transition pressure for NaCl have been too high. At room temperature we obtain a best-fit value of 26.8 GPa , as compared with the unreversed value of 30 GPa . Perhaps more surprising is the strong evidence from our measurements that the transition is overdriven by as much as 8 GPa under shock loading ([100] propagation). We note that the shock temperatures are validated by spectroradiometric measurements,³¹ and even in the most favorable [111] orientation the transition is overdriven by about 3 GPa along the Hugoniot. Our conclusion that the *B1-B2* transition is mildly sluggish on the timescale of shock experiments is in accord with detailed observations on several halides, however.³²

Fortuitously, the effect of kinetics in both static and dynamic experiments is to shift the transition pressure by about the same amount, so our values for the Clapeyron slope and entropy change on transformation are similar to those determined previously.⁶ A linear extrapolation of our Clapeyron curve to higher temperatures leads to a predicted triple point between *B1, B2* and melt phases at

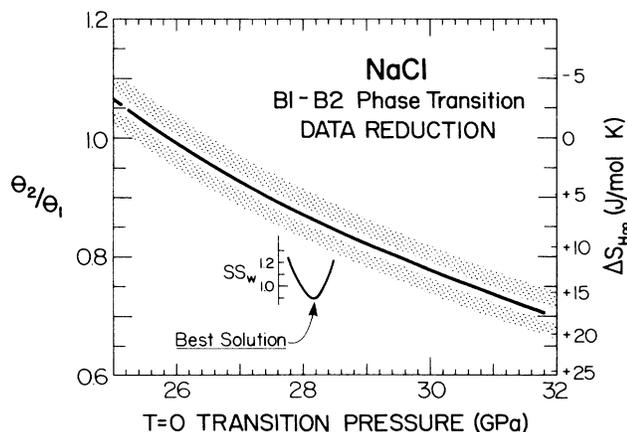


FIG. 5. Trade-off (bold curve) and uncertainties (shaded band) between the values of P_{tr}^0 and Θ_2/Θ_1 that best fit the data according to Eq. (4) in the text; the corresponding value for the high-temperature limit of harmonic entropy change is shown on the right. The best overall solution is given by the minimum in the weighted sum of squared deviations between observed and calculated transition pressures (SS_W , which is plotted over a limited range of P_{tr}^0).

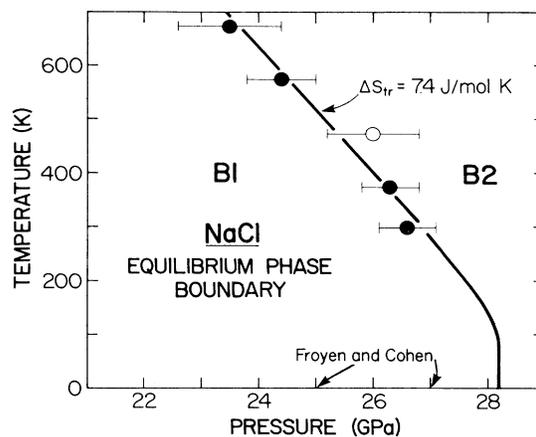


FIG. 6. Values of P_{tr} obtained in this study (open symbol is by interpolation: Table I) and the corresponding best-fit Clapeyron curve according to Eq. (4). A Debye model for Eq. (2) yields a phase boundary that is indistinguishable from the curve shown here (the difference is less than the width of the curve). The theoretical transition pressures obtained by Froyen and Cohen (Ref. 13) for the static lattice (27 GPa) and including zero-point vibrations (25 GPa) are shown at the bottom.

approximately 10 GPa and 2200 K . Such conditions are currently achievable in large-volume presses,³³ and a determination of the triple point would allow our analysis to be significantly extended. In particular, anharmonic contributions to ΔS_{tr} and the differential thermal expansions of *B1* and *B2* phases^{8,24,34} could be evaluated.

Our extrapolated value for the transition pressure at $T=0$ is in good agreement with the value predicted theoretically by Froyen and Cohen¹³ (Figs. 3 and 6): including zero-point corrections, the discrepancy is less than 3.5 GPa (12%). Thus, our experiments provide a significant validation of the pseudopotential calculations, although minor discrepancies remain. That the predicted transition pressure is lower than the observed value is consistent with the experimental equation of state for the *B2* phase being at a slightly larger volume than that obtained theoretically.¹² Also, the theoretical value for Θ_2/Θ_1 (0.88) is larger than the one determined in this study, which is understandable from the smaller volume that is predicted theoretically. Nevertheless, our analysis illustrates the importance of properly accounting for temperature corrections when comparing theoretical and experimental transition pressures. Without the use of our kinetic and equilibrium model in the data reduction, agreement between theory and experiment would have appeared to be significantly worse than it actually is.

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- *Also at: Department of Physics, Jilin University, Changchun, People's Republic of China.
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