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A revised pressure scale for NaCl is proposed as an update for the 30-year-old work of Decker. An alternative approach to the analysis is utilized in conjunction with more recent data. The zero-Kelvin compression curve is parameterized using local basis functions (splines) and constrained by accurate pressure-volume-temperature data. Thermal pressures are estimated within a quasiharmonic framework using a volume-dependent Grüneisen parameter and the Debye thermal energy. In the pressure regime extending to 5 GPa uncertainties in pressure (based on measured volumes) are estimated to be less than 1%. Uncertainty increases to 1.5% at 10 GPa and 3% at 25 GPa. The largest contribution to systematic uncertainty at the highest pressures is the lack of knowledge of the volume dependence of the Grüneisen parameter. Misfit of other calculated thermodynamic properties with respect to data is relatively small. On the basis of the current analysis, pressures determined using the older Decker calibration are low. Along the 300 K isotherm, apparent errors in the Decker scale are as large as -3% (-0.3 GPa at 10 GPa, -0.47 GPa near 18 GPa, and -0.37 GPa at 25 GPa). At higher temperatures the apparent errors are smaller. At 1100 K and 20 GPa the error is -0.2 GPa. © *1999 American Institute of Physics.* [S0021-8979(99)01922-2]

INTRODUCTION

A series of papers by Decker[1–3] offered calculations for the equation of state of NaCl as ''a temporary practical pressure scale.'' In order to construct a calibration, Decker represented the ionic interaction potentials using both inverse power law and exponential terms. Nearest neighbor and second nearest neighbor interactions were included. He assumed that thermal effects were entirely quasiharmonic, characterized by a volume-dependent Grüneisen parameter. The Debye model served to represent vibrational thermal energy. Coefficients for dipole–dipole and dipole–quadrupole attractive terms were based on atomic polarizabilities applying the Mayer formula.[4] Other model parameters were constrained using 1 bar data (the ambient pressure bulk modulus and volumes as functions of temperature). Extant high-pressure compression data[5–7] were shown to agree with the theoretical model almost within his estimated uncertainties (1% below 5 GPa, 1.7% to 10 GPa and 2.4% to 20 GPa).

In situations where volumes are determined by x-ray diffraction (i.e., in large-volume, multi-anvil experiments), the Decker scale remains a pressure calibration standard of choice (see, for example, Ref. 8). Furthermore, the (secondary) ruby scale is tied to the Decker scale since Piermarini *et al.*[9] calibrated ruby fluorescence wavelength shifts to 20 GPa against NaCl volumes determined by x-ray diffraction. The ultrahigh pressure ruby calibrations[10,11] use a functional representation that forces a match to the Piermarini *et al.* pressure derivative at low pressure. A reassessment of Decker's approximately 30-year-old work in light of more recent data is therefore appropriate.

PRIOR EQUATION OF STATE STUDIES OF NaCl

Fritz *et al.*[7] reported Hugoniot data and a calculated 300 K isotherm to 30 GPa. These results have not been superceded and represent the only primary pressure-volume data (based on an absolute determination of pressure) beyond 3 GPa. Additional articles, extending the range and accuracy of NaCl pressure-volume-temperature (PVT) data were published subsequent to Decker's analysis. Here data traceable to absolute determinations of pressure (force/unit area) are noted. Spetzler, Sammis, and O'Connell[12] reported adiabatic elastic constants to 0.8 GPa and 800 K. These accurate data provide strong constraints on the initial derivatives of volume with respect to pressure and temperature. One bar sound velocities to nearly 800 K[13] have validated the work of Spetzler, Sammis, and O'Connell. Hart and Greenwood[14] reported pressure derivatives of the adiabatic bulk modulus to 1.5 GPa at room temperature. On the basis of length measurements of a 1-m-long crystal, Chhabildas and Ruoff[15] reported the pressure dependence of the bulk modulus to 0.7 GPa. An innovative experiment by Boehler and Kennedy[16] gave PVT data with small absolute uncertainties in pressure (0.4%) and in volume change (0.7%). These data span a range from ambient conditions to 500 °C and 3.1 GPa. Boehler[17] reported measurements of $(\partial T/\partial P)_s$ for NaCl to 5 GPa and 800 °C. One bar data to 1200 °C for thermal expansivities[18] and constant pressure heat capacities[19] have apparently not been remeasured since Decker's work.

Birch[20] proposed an eulerian finite strain equation of state for NaCl that was optimized with respect to the high-pressure data of Boehler and Kennedy[16] and Fritz *et al.*[7] His 25 °C isotherm gave a root-mean-square (rms) misfit of 5 MPa relative to the Boehler and Kennedy data. In contrast, Decker's equation of state has a rms misfit 34 MPa. In the regime of pressure and temperature explored by the Boehler

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and Kennedy data,[16] Birch found that thermal pressure was proportional to thermal energy. This provided high-pressure validation of Decker's assumptions of quasiharmonic thermal behavior.

Near the maximum pressure for the NaCl calibration (30 GPa), the isothermal equation of state given by Birch differs by more than 1 GPa from that given by Decker. The source of this discrepancy is worth noting. Fritz et al.[7] reported two fits to the primary NaCl shock-velocity (U_s)-particle velocity (U_p) data. A quadratic form was required to adequately represent the lowest pressure data. An isotherm based on that fit, given in their Table III, extended to a maximum pressure of 25 GPa. At higher pressure and in a regime of extrapolation, Fritz et al. recommended a linear U_s-U_p representation; their Table IV gave a preferred isotherm from 20 to 30 GPa. Birch's Table VI, which extends to a pressure of 30 GPa, lists densities that exactly match values calculated using the (low pressure) quadratic representation (Fritz provided both Birch and this author with computer generated tables that extend to 32 GPa for both the linear and quadratic representations). Near 30 GPa pressures differ by over 1 GPa at constant volume between the linear and quadratic forms. Decker used neither isothermal table in his analysis. Instead, he compared his equation of state at elevated pressure against the Hugoniot PVT states (with calculated temperatures) given by Fritz et al.[7]

Since NaCl is the prototype ionic solid, substantial effort has been directed at understanding contributions to its thermodynamics. Nonquasiharmonic contributions to thermal pressure for NaCl have been extensively investigated. A positive trend to C_V, the constant-volume specific heat at high temperature, has been associated with an explicit anharmonic correction.[21,22] However, values for the temperature-dependent bulk modulus used in these earlier analyses are not supported by more recent data. In the current analysis less anharmonicity is apparent in the high temperature specific heat data. Enck and Dommel[18] suggested that the nonlinearity in their measurements of the coefficient of thermal expansion at high temperature was a consequence of the thermodynamics of Schottky defects. Wang and Reeber[23] recently reviewed the extensive literature on this idea. In order for defects to make a significant contribution to thermal expansion in the modest regime of temperature extending to 1200 K, an energy of formation substantially lower than measured is required.

CONSTRUCTION OF A NEW NaCl PRESSURE SCALE

The current work departs from Decker's analysis in that an arbitrary functional form is not imposed on the underlying ionic interaction potential. Rather, the volume potential necessary in a quasiharmonic model is directly determined from the primary data. Three sets of PVT data underlie the calibration. These are thermal expansivities,[18] the Boehler and Kennedy data,[16] and the shock wave Hugoniot data of Fritz et al.[7] The resulting model is compared against additional data sets.

Pressure is separated into a static (zero-Kelvin) compression component and a thermal component

$$P(V,T) = P_0(V) + P_{thermal}(V,T), \tag{1}$$

where the static pressure is given by the first volume derivative of the free energy

$$P_0 = -dF/dV(T=0) \tag{2}$$

and thermal pressure is given in the Mie–Grüneisen form

$$P_{thermal} = (\gamma/V)E_{vib}(T/\theta), \tag{3}$$

where γ, the Grüneisen parameter, is assumed temperature independent. E_{vib}, the Debye energy, is a function of T/θ and the volume dependence of θ, the Debye temperature, is given by

$$d \ln \theta / d \ln V = -\gamma. \tag{4}$$

Thermal pressure is subtracted from each measured high-pressure/high temperature data point. The locus of the resulting thermally corrected data then provides a representation of $P_0(V)$. Local basis functions (splines) are optimized with respect to these data under the side constraint that higher-order derivatives of $P_0(V)$ be minimized (using MATLAB function CSAPS). In order to achieve an overall smooth representation, lower weights were assigned to data near the two junctions between the three data sets. In the case of the shock wave data, Fritz et al.[7] suggested that the lowest pressure points might have larger systematic uncertainty as a result of residual strength effects. With definition of the zero-Kelvin compression curve in terms of spline coefficients and a Debye model for vibrational energy, all volume-dependent thermodynamic properties can be evaluated.

Prior utilization of shock wave data in the NaCl calibration has been thermodynamically inconsistent. Decker made comparisons against Hugoniot PVT states reported by Fritz et al. Birch used the 300 K isotherm of Fritz et al. that had been reduced from the Hugoniot states. The thermodynamic assumptions made by Fritz et al. differed from those used by either Decker or Birch. A consistent thermodynamic assumption underlies the analysis given here. Primary Hugoniot data (subscript h) are reduced to the zero-Kelvin compression curve

$$P_0 = P_h - \gamma/V(E_h - E_0), \tag{5}$$

where E_0 is energy along the zero-Kelvin compression curve and the Hugoniot energy is

$$E_h = P_h \Delta V / 2, \tag{6}$$

where ΔV is the volume change from the initial to final (shock) state. Since E_0 depends on the zero-Kelvin compression curve, iteration is necessary to define the curve on the basis of Hugoniot data.

In the current analysis, the Grüneisen parameter is assumed to be a temperature-independent function of volume (Fig. 1). In order to match 1 bar thermodynamic data at high temperature, γ is set constant in the expanded region. Under compression, the Grüneisen parameter is given a power-law volume dependence that satisfies available high-pressure thermodynamic data
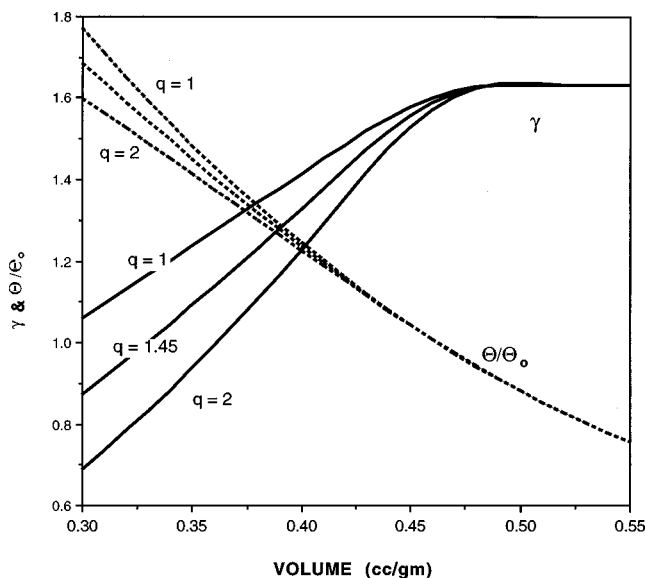
$$\gamma = \gamma_0 (V/V_0)^q. \tag{7}$$

FIG. 1. Volume dependence of the Grüneisen parameter (solid curves) and the Debye temperature θ/θ_0 (dashed curves). The upper curve for γ represents a power-law exponent of 1 at high pressure. The middle curve has $q = 1.45$. The lower curve has $q = 2$. For expanded volumes at high temperature, γ is assumed constant.

Smoothing splines are used to join expanded and compressed behavior. Three curves for γ are plotted, corresponding to $q = 1$, 1.45, and 2 in the compressed regime. The associated variation of the Debye temperature [using Eq. (4)] is also plotted in Fig. 1 as θ/θ_0 (where θ_0 is the Debye temperature under ambient conditions).

The fundamentally different volume dependence of the Grüneisen parameter in regimes of compression and expansion can be rationalized on the basis of the underlying volume potential. Coulomb and inductive forces dominate in the attractive region of the potential (high temperature expanded states) while short-range repulsive forces dominate in compression. Since γ is controlled by high order derivatives of the potential as a function of volume, γ need not exhibit identical behavior through the entire range of volume.

In analysis of shock wave data, the power-law exponent for γ is usually assumed to be equal to 1 with some experimental justification.[24] In the pressure regime below 5 GPa static high-pressure work indicates that q values for many different solids typically lie between 1 and 2.[25,26] Approximations for the Grüneisen parameter derived from the volume potential[27–29] are not inconsistent with the trends exhibited by the power-law parameterization. However, there is no compelling justification to rely on any empirical or theoretical extrapolation in the absence of measurement.

An optimal value for q (giving a minimum in the misfit to the Boehler and Kennedy data) was found to be approximately 1.45. Thus, in a regime of moderate pressure $\gamma(V)$ is reasonably constrained by data. However, values for γ, required to reduce the highest pressure shock wave data, are necessarily based on extrapolation. Both the standard shock wave assumption of $q = 1$ and a substantially larger value of $q = 2$ are shown in Fig. 1. These extremal values of q are considered later in a sensitivity test. Uncertainty in γ at high

FIG. 2. (a) Experimental data reduced to the zero-Kelvin isotherm and a spline representation of the data (solid line). Squares are the Hugoniot data. Filled circles are the PVT data by Boehler and Kennedy. Open circles are the thermal expansion data. (b) Deviations of data plotted in (a) relative to the spline representation. The same symbols as in (a) are used.

pressure contributes the largest formal uncertainty to the current calibration.

In Fig. 2(a) the static pressure points for all three primary PVT data sets and the spline representation are shown. Deviations of data from the fit are shown in Fig. 2(b). An expanded plot in Fig. 3 shows both the Boehler and Kennedy pressures measured along eight isotherms and the thermally corrected pressures. The success of the thermal correction in placing all data on a common curve gives general support for the models of E_{vib} and γ. In Fig. 4, the integral of the zero-Kelvin curve is shown. This is the volume potential underlying the thermodynamic description of NaCl. It shows asymmetry about the potential minimum as expected on the basis of the earlier discussion. Properties along the zero-Kelvin curve are given in Table I. Pressures as a function of volume and temperature are calculated and listed in Table II. This table can be replicated using the quasiharmonic thermal

FIG. 3. The primary PVT data of Boehler and Kennedy (open circles) and reduced to zero-Kelvin curve (filled circles).

TABLE I. Properties of NaCl on the zero-Kelvin compression curve.

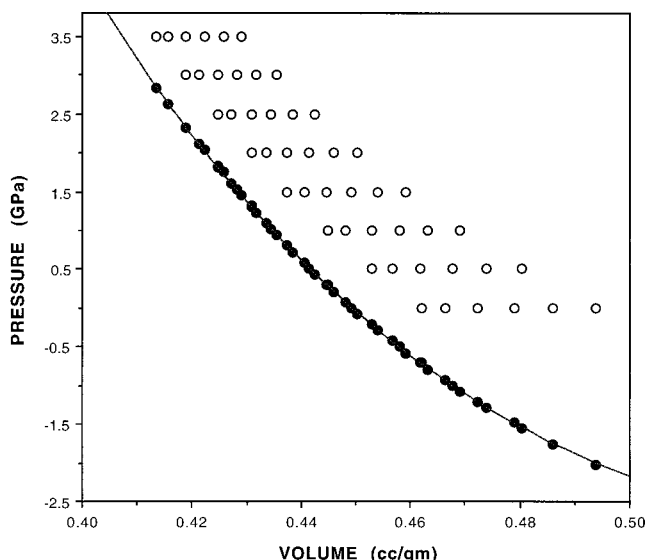| V(cc/gm)	P(GPa)	K_T(GPa)	K'	γ	θ
0.3143	23.12	112.61	2.69	0.93	446
0.3256	19.33	101.76	3.01	0.98	431
0.3369	16.03	91.44	3.25	1.03	417
0.3482	13.17	81.82	3.48	1.08	402
0.3595	10.70	72.95	3.70	1.13	388
0.3709	8.57	64.88	3.85	1.19	375
0.3822	6.73	57.71	3.95	1.24	361
0.3935	5.14	51.28	4.19	1.29	348
0.4048	3.77	45.35	4.47	1.35	336
0.4161	2.60	39.98	4.64	1.40	323
0.4274	1.59	35.41	4.27	1.46	311
0.4387	0.71	31.64	4.59	1.51	299
0.4500	−0.05	27.77	5.68	1.55	288
0.4613	−0.69	23.93	6.05	1.59	277
0.4726	−1.23	20.61	6.44	1.62	266
0.4839	−1.68	17.52	7.29	1.63	256
0.4953	−2.05	14.66	8.10	1.63	247
0.5066	−2.35	12.16	8.41	1.63	238
0.5179	−2.59	10.12	8.06	1.63	229
0.5292	−2.80	8.62	6.50	1.63	221
0.5405	−2.97	7.76	3.16	1.63	214

model [Eqs. (1–4)] with parameters based on a spline interpolation (MATLAB function SPLINE) of entries in Table I.

UNCERTAINTIES IN THE NEW NaCl PRESSURE SCALE

Random error can be partially accounted for on the basis of PVT data scatter relative to the proposed calibration. The data of Boehler and Kennedy have a rms misfit of 10 MPa. This is approximately comparable with their estimated uncertainties of 0.4% in pressure and 0.7% in volume. Hugoniot data have a standard error (2σ) of about 1% (110 MPa) at 10 GPa and 1.4% (350 MPa) near 25 GPa. When the power-law exponent for the volume dependence of γ is changed from the optimal value of 1.45, misfits to the Boehler and Kennedy data increase by 50% for both $q=1$ and
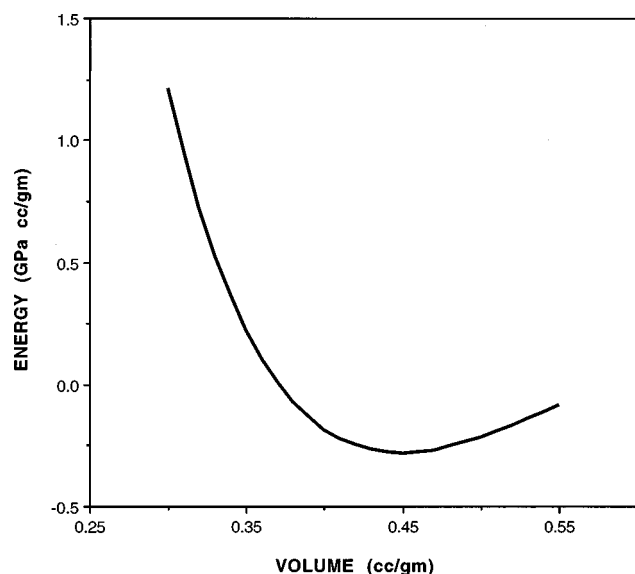

FIG. 4. The volume potential implicit in the zero-Kelvin compression curve. The zero of the energy scale was arbitrarily chosen for figure.

$q=2$ while the Hugoniot data are equally well fit. On this basis, uncertainties based on random error of measurement are estimated to expand with pressure (~0.5% at 5 GPa, 1% at 10 GPa, 1.5% at 25 GPa).

A test of the sensitivity of the derived equation of state on the assumed volume dependence of the Grüneisen parameter is given in Fig. 5. The 300 K isotherm based on $q=1.45$ is taken as the standard. New zero-Kelvin curves, based on $q=1$ and $q=2$, were calculated. The resulting 300 K isotherms were subtracted from the standard. At low pressure the equation of state is nearly insensitive to q. Above 10 GPa, where only Hugoniot data constrain the calibration and where thermal pressures become significant, systematic deviations increase. On the basis of Fig. 5, uncertainties of 100 MPa at 10 GPa and 600 MPa at 25 GPa are assigned. Thus, the uncertain behavior of γ at the highest pressures is a significant source of systematic error.

Under the assumption that errors associated with data scatter and uncertain γ values are uncorrelated, the current analysis leads to an estimated uncertainty in the pressure calibration of 0.5% at 5 GPa, 1.5% at 10 GPa and 3% at 25 GPa.

COMPARISONS WITH OTHER THERMODYNAMIC DATA

Additional tests of the NaCl calibration are made using 1 bar data at high temperature and data extending to a few GPa. Derivatives of the equation of state were evaluated numerically to obtain K_T, the bulk modulus at constant temperature, and α, the thermal expansivity. Constant volume heat capacities C_V follow from the Debye model. The Grüneisen parameter, the ratio K_s/K_T and constant pressure to constant volume specific heats, C_p/C_V, are then calculated.

In Figs. 6–9 1 bar, high temperature data are considered. At all temperatures, the adiabatic bulk modulus agrees within 1% (Fig. 6). The maximum 2.5% deviation of model specific

TABLE II. Equation of state for NaCl. Temperature (Kelvin) are given across the top of the table. Volumes and volume compressions are given in the first two columns. All other entries are pressures (GPa) at the specified volume and temperature.

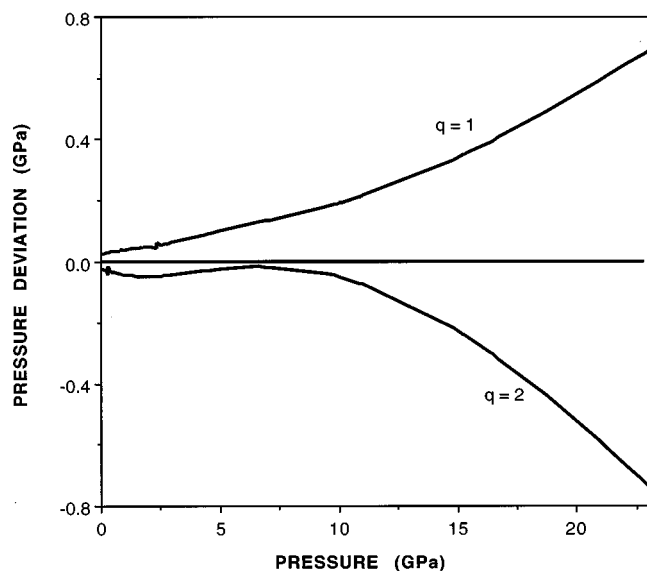| Volume (cc/gm)	$(V_0-V)/V_0$	300	400	500	600	700	800	900	1000	1100	1200
0.3143	0.3197	23.68	23.91	24.15	24.40	24.64	24.89	25.14	25.39	25.64	25.90
0.3166	0.3147	22.88	23.11	23.36	23.60	23.85	24.10	24.35	24.60	24.85	25.11
0.3188	0.3100	22.10	22.34	22.58	22.83	23.08	23.33	23.58	23.83	24.09	24.34
0.3211	0.3050	21.35	21.59	21.83	22.08	22.33	22.58	22.83	23.08	23.34	23.59
0.3233	0.3002	20.62	20.85	21.10	21.35	21.60	21.85	22.10	22.36	22.61	22.87
0.3256	0.2952	19.90	20.14	20.39	20.64	20.89	21.14	21.39	21.65	21.90	22.16
0.3279	0.2903	19.21	19.45	19.69	19.94	20.20	20.45	20.70	20.96	21.22	21.47
0.3301	0.2855	18.53	18.77	19.02	19.27	19.52	19.78	20.03	20.29	20.55	20.80
0.3324	0.2805	17.87	18.12	18.37	18.62	18.87	19.13	19.38	19.64	19.90	20.16
0.3347	0.2755	17.24	17.48	17.73	17.98	18.24	18.49	18.75	19.01	19.27	19.53
0.3369	0.2708	16.62	16.86	17.11	17.36	17.62	17.88	18.14	18.39	18.65	18.91
0.3392	0.2658	16.01	16.26	16.51	16.76	17.02	17.28	17.54	17.80	18.06	18.32
0.3414	0.2610	15.43	15.67	15.93	16.18	16.44	16.70	16.96	17.22	17.48	17.74
0.3437	0.2561	14.86	15.11	15.36	15.62	15.87	16.13	16.39	16.66	16.92	17.18
0.3460	0.2511	14.31	14.55	14.81	15.07	15.33	15.59	15.85	16.11	16.37	16.63
0.3482	0.2463	13.77	14.02	14.27	14.53	14.79	15.05	15.32	15.58	15.84	16.10
0.3505	0.2413	13.25	13.50	13.75	14.01	14.27	14.54	14.80	15.06	15.33	15.59
0.3528	0.2364	12.74	12.99	13.25	13.51	13.77	14.03	14.30	14.56	14.83	15.09
0.3550	0.2316	12.25	12.50	12.76	13.02	13.28	13.55	13.81	14.08	14.34	14.61
0.3573	0.2266	11.78	12.03	12.29	12.55	12.81	13.07	13.34	13.61	13.87	14.14
0.3595	0.2219	11.31	11.56	11.82	12.09	12.35	12.62	12.88	13.15	13.42	13.68
0.3618	0.2169	10.86	11.12	11.38	11.64	11.90	12.17	12.44	12.71	12.97	13.24
0.3641	0.2119	10.43	10.68	10.94	11.21	11.47	11.74	12.01	12.27	12.54	12.81
0.3663	0.2071	10.00	10.26	10.52	10.78	11.05	11.32	11.59	11.86	12.13	12.40
0.3686	0.2022	9.59	9.85	10.11	10.38	10.64	10.91	11.18	11.45	11.72	11.99
0.3709	0.1972	9.19	9.45	9.71	9.98	10.25	10.52	10.79	11.06	11.33	11.60
0.3731	0.1924	8.81	9.06	9.33	9.60	9.86	10.13	10.41	10.68	10.95	11.22
0.3754	0.1874	8.43	8.69	8.95	9.22	9.49	9.76	10.03	10.31	10.58	10.85
0.3776	0.1827	8.06	8.32	8.59	8.86	9.13	9.40	9.67	9.95	10.22	10.49
0.3799	0.1777	7.71	7.97	8.24	8.51	8.78	9.05	9.33	9.60	9.87	10.15
0.3822	0.1727	7.37	7.63	7.90	8.17	8.44	8.71	8.99	9.26	9.54	9.81
0.3844	0.1680	7.03	7.30	7.56	7.84	8.11	8.38	8.66	8.93	9.21	9.48
0.3867	0.1630	6.71	6.97	7.24	7.51	7.79	8.06	8.34	8.61	8.89	9.17
0.3889	0.1582	6.39	6.66	6.93	7.20	7.48	7.75	8.03	8.31	8.58	8.86
0.3912	0.1532	6.09	6.35	6.63	6.90	7.17	7.45	7.73	8.01	8.28	8.56
0.3935	0.1483	5.79	6.06	6.33	6.61	6.88	7.16	7.44	7.72	7.99	8.27
0.3957	0.1435	5.50	5.77	6.04	6.32	6.60	6.88	7.15	7.43	7.71	7.99
0.4003	0.1336	4.95	5.22	5.50	5.78	6.06	6.33	6.62	6.90	7.18	7.46
0.4048	0.1238	4.44	4.71	4.99	5.26	5.55	5.83	6.11	6.39	6.67	6.96
0.4093	0.1141	3.95	4.22	4.50	4.78	5.07	5.35	5.63	5.92	6.20	6.49
0.4138	0.1043	3.49	3.77	4.05	4.33	4.62	4.90	5.19	5.47	5.76	6.04
0.4184	0.0944	3.07	3.34	3.62	3.91	4.19	4.48	4.77	5.05	5.34	5.63
0.4229	0.0846	2.66	2.94	3.22	3.51	3.80	4.08	4.37	4.66	4.95	5.24
0.4274	0.0749	2.28	2.56	2.85	3.13	3.42	3.71	4.00	4.29	4.58	4.87
0.4319	0.0652	1.92	2.20	2.49	2.78	3.07	3.36	3.65	3.94	4.23	4.52
0.4364	0.0554	1.58	1.86	2.15	2.44	2.73	3.02	3.31	3.60	3.89	4.19
0.4432	0.0407	1.10	1.39	1.68	1.97	2.26	2.55	2.84	3.13	3.43	3.72
0.4500	0.0260	0.67	0.95	1.24	1.53	1.82	2.12	2.41	2.70	3.00	3.29
0.4568	0.0113	0.27	0.56	0.85	1.14	1.43	1.72	2.01	2.31	2.60	2.90
0.4613	0.0015	0.03	0.32	0.60	0.89	1.19	1.48	1.77	2.06	2.36	2.65
0.4636	−0.0035	−0.09	0.20	0.49	0.78	1.07	1.36	1.65	1.95	2.24	2.53
0.4681	−0.0132		−0.02	0.27	0.56	0.85	1.14	1.43	1.72	2.01	2.31
0.4726	−0.0229			0.06	0.35	0.64	0.93	1.22	1.51	1.80	2.09
0.4772	−0.0329			−0.13	0.15	0.44	0.73	1.02	1.31	1.60	1.89
0.4817	−0.0426				−0.03	0.25	0.54	0.83	1.11	1.40	1.69
0.4862	−0.0524					0.08	0.36	0.65	0.93	1.22	1.50
0.4930	−0.0671					−0.16	0.12	0.40	0.68	0.96	1.25
0.4988	−0.0818						−0.10	0.17	0.45	0.73	1.01
0.5088	−0.1013							−0.09	0.18	0.46	0.73
0.5179	−0.1210								−0.05	0.22	0.48
0.5269	−0.1405									0.01	0.27
0.5360	−0.1602									−0.18	0.08
0.5405	−0.1699										−0.01

FIG. 5. Sensitivity of model pressures on the assumed volume dependence of the Grüneisen parameter. The equation of state for NaCl using the power-law exponent $q=1.45$ is taken as the standard. Two curves represent deviations from the standard as a result of $q=1$ and $q=2$.
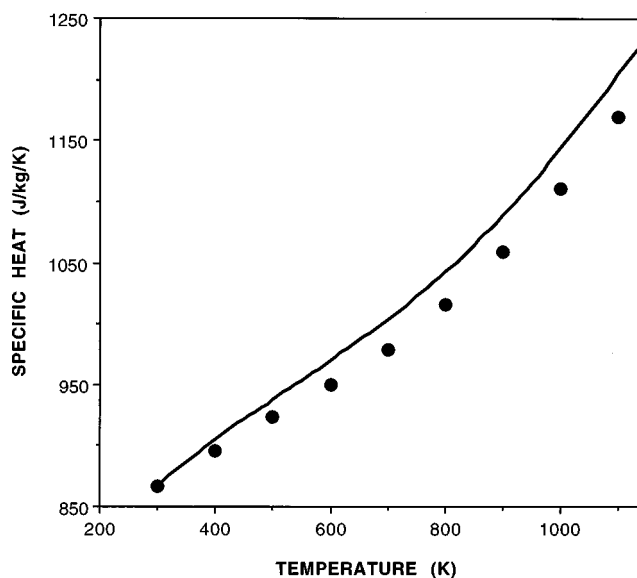

FIG. 7. Comparisons of the model specific heat at constant volume as a function of temperature at 1 bar. Filled circles are from the JANF Tables. The solid line is the model prediction.

heats from measurement (Fig. 7) could be interpreted either as an indication of a small (negative) anharmonic contribution, or as a defect in the current model parameterization, or as a slight error in measurement. The 1 bar thermal expansivities nearly match experiment (Fig. 8). The thermodynamic Grüneisen parameter ($\gamma = \alpha V C_p / K_s$) (plotted in Fig. 9) is nearly temperature independent and almost matches the quasiharmonic γ used to construct the calibration. The small difference between the derived and quasiharmonic γ is likely due to the accumulation of numerical error.

High-pressure data are plotted in Figs. 10, 11, and 12. In Fig. 10, the adiabatic bulk modulus at 300 and at 800 K to 1

GPa is matched to within 2%. The adiabatic temperature changes ($\partial T/\partial P_s = T\gamma/K_s$) measured by Boehler[17] to 5 GPa and to 1100 K are plotted Fig. 11. At 300 K the data are in accord with the model. A systematic offset of about 20% at high pressure and elevated temperature argues that Boehler's $\partial T/\partial P_s$ data are not wholly consistent with the PVT data of Boehler and Kennedy. Boehler[17] proposed a value for q, the power-law exponent of γ, of 2 in order to fit the data shown in Fig. 11. However, γ and K_s are not thermodynamically independent. Within the context of the current quasiharmonic analysis, K_s changes in proportion with γ such that $\partial T/\partial P_s$ is independent of the exponent q. If the PVT data are not in error, systematic bias in the $\partial T/\partial P_s$ measurements must be considered.

FIG. 6. Comparisons of the model adiabatic bulk modulus as a function of temperature at 1 bar. Filled circles are from Spetzler, Sammis, and O'Connell. Asterisks are from Yamamoto and co-workers. Solid lines are model predictions.
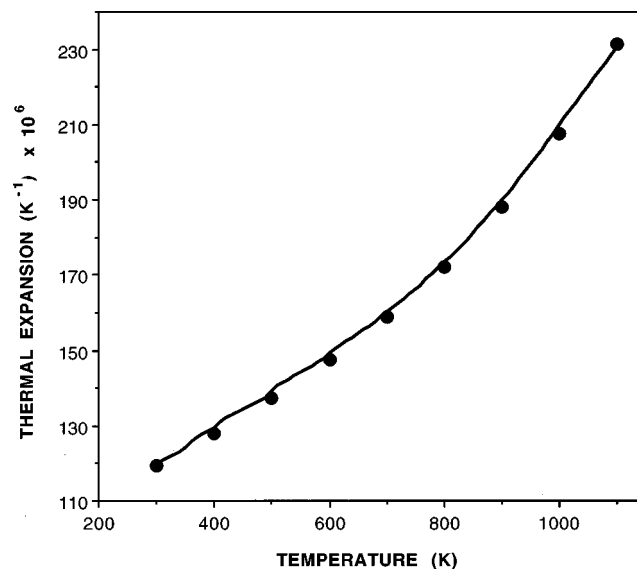

FIG. 8. Comparisons of the model thermal expansivities as a function of temperature at 1 bar. Filled circles are from Enck and Dommel. The solid line is the model prediction.
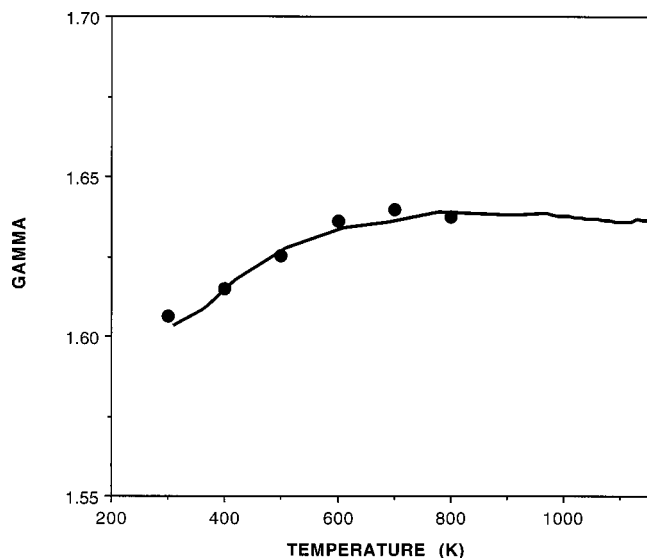
FIG. 9. Comparisons of the model Grüneisen parameter as a function of temperature at 1 bar. Filled circles are evaluated from the thermodynamic data as $\alpha K_s V/C_p$. The solid line is the model prediction.
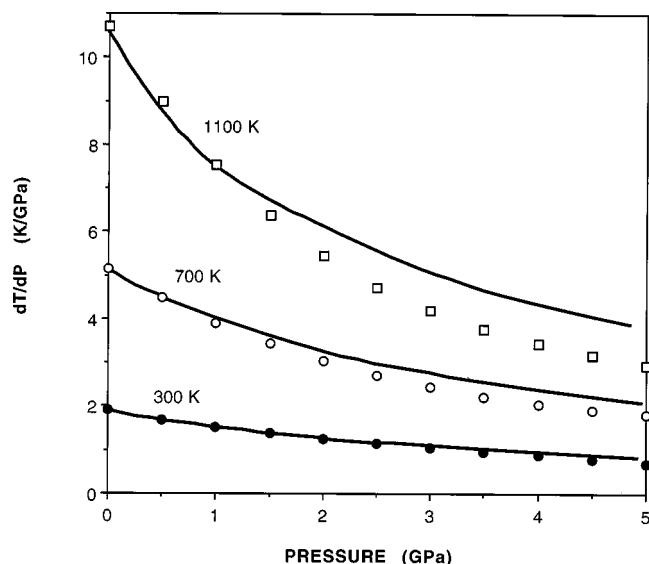

FIG. 11. Comparisons of the model with the dT/dPs measurements at 300, 500, and 1100 K from Boehler. Solid lines are model predictions.

The pressure derivative of the adiabatic bulk modulus ($K'=dK_s/dP$) shown in Fig. 12, representing a second derivative of the compression curve, is a most severe test of the current analysis. Joins between the three primary data sets are evident in this representation. Small discontinuities in the second derivative of the compression curve (implicit in the data) are observed at 0 GPa and at 3 GPa. Nonlinear systematic errors in measurements could rationalize this behavior, with little consequence for the pressure calibration. However, the nonmonotonic behavior shown in Fig. 12 makes detailed comparisons with experiment problematic.

Measured values of K' appear to lie on the appropriate trend suggested by a visual smoothing of the model. In the regime of large volumes, where the calibration depends en-

tirely on the thermal expansion data, K' has a maximum value near 8. Both K' and its derivative dK'/dP change significantly in the low-pressure regime to 5 GPa. Experimental determination of dK'/dP is an exacting task and the uncertainties in measurements are typically large. However, data shown in Fig. 12 are in reasonable accord with the predictions. With data extending to less than 1 GPa, Chhabildas and Ruoff[15] reported $dK'/dP=-1$ GPa^{-1} and Spetzler, Sammis, and O'Connell[12] gave a value of -0.9 GPa^{-1}. The experiment by Hart and Greenwood[14] extending to 1.5 GPa resulted in $dK'/dP=-0.34$ GPa^{-1}. The trend towards smaller values of dK'/dP for data obtained over a greater pressure range is in accord with the features of K' shown in Fig. 12.

FIG. 10. Comparisons of the model adiabatic bulk modulus at high pressure with 300 and 800 K data from Spetzler, Sammis, and O'Connell. Solid lines are model predictions.
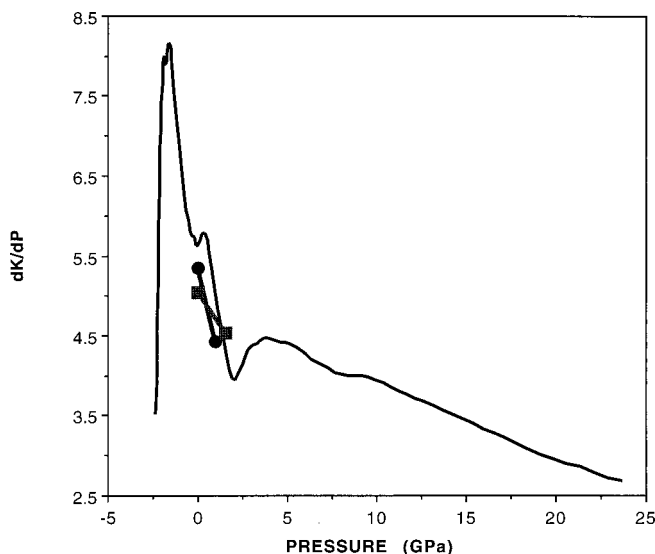

FIG. 12. Comparisons of the model pressure pressure of $K'=dK_s/dP$ at 300 K. Filled circles are from Spetzler, Sammis, and O'Connell. Filled squares are from Hart and Greenwood. The solid line is the model prediction.
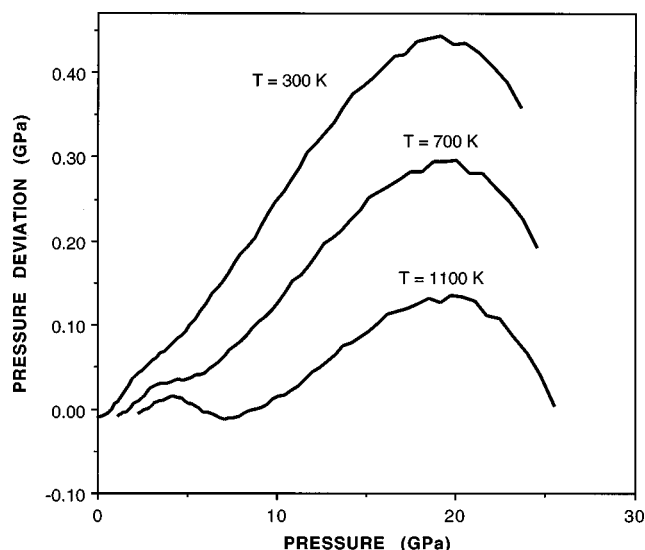
FIG. 13. Deviations at common volumes between the current equation of state for NaCl and the calibration of Decker at three different temperatures. Positive deviations correspond to the current calibration predicting higher pressures than the Decker scale.

COMPARISON OF THE CURRENT CALIBRATION WITH THE DECKER SCALE

The difference between the current equation of state for NaCl and that given by Decker is shown in Fig. 13 for isotherms at 300, 700, and 1100 K. At room temperature and at all pressures, Decker's work gives lower pressures for a given volume than suggested by the current analysis. At 300 K, the 0.3 GPa difference in pressure at 10 GPa (3%) lies on the edge of the mutual estimated uncertainties. At higher pressure, the deviation appears to reach a maximum value of 0.47 GPa near 18 GPa (2.5%) and to decrease to 0.37 GPa at 25 GPa (1.5%). Decker's isotherms at higher temperatures deviate less from the current work. The 1100 K isotherms are nearly identical to almost 10 GPa. At 20 GPa and 1100 K the deviation approaches 1%.

CONCLUSION

A recalibration of the NaCl pressure scale is accomplished using primary high-pressure data. A quasiharmonic analysis is shown to provide a thermodynamically consistent description of the measured properties over a wide range of temperature and pressure. The most compelling interpretation is that all data support a calibration that is systematically

at a higher pressure for a given volume than estimated using the Decker scale. At room temperature, the Decker scale is systematically in error by 3% at 10 GPa. If only the Hugoniot data gave evidence of a systematic error, it would be possible to invoke uncertainty in γ as an explanation. However, in the pressure regime to 3 GPa, the more accurate primary data of Boehler and Kennedy reinforce the deviation trend evident at still higher pressure.

[1] D. L. Decker, J. Appl. Phys. **36**, 157 (1965).
[2] D. L. Decker, J. Appl. Phys. **37**, 5012 (1966).
[3] D. L. Decker, J. Appl. Phys. **42**, 3239 (1971).
[4] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).
[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).
[6] H. G. Drickamer, R. W. Lynch, R. C. Clendenen, and E. A. Perez-Albuerne, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 19, pp. 135–228.
[7] J. N. Fritz, S. P. Marsh, W. J. Carter, and R. G. McQueen, in *Accurate Characterization of the High Pressure Environment*, edited by E. C. Lloyd (National Bureau of Standards, Washington, DC, 1972), Vol. 326, pp. 201–208.
[8] Y. Wang and D. J. Weidner, Geophys. Res. Lett. **21**, 895 (1994).
[9] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).
[10] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
[11] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).
[12] H. Spetzler, C. G. Sammis, and R. J. O'Connell, J. Phys. Chem. Solids **33**, 1727 (1972).
[13] S. Yamamoto, I. Ohno, and O. L. Anderson, J. Phys. Chem. Solids **48**, 143 (1987).
[14] S. Hart and P. H. Greenwood, Solid State Commun. **46**, 161 (1983).
[15] L. C. Chhabildas and A. L. Ruoff, J. Appl. Phys. **47**, 4182 (1976).
[16] R. Boehler and G. C. Kennedy, J. Phys. Chem. Solids **41**, 517 (1980).
[17] R. Boehler, J. Geophys. Res. **86**, 7159 (1981).
[18] F. D. Enck and J. G. Dommel, J. Appl. Phys. **36**, 839 (1965).
[19] D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed. (U.S. Department of Commerce, National Bureau of Standards, Washington DC, 1971), Vol. 37.
[20] F. Birch, J. Geophys. Res. **91**, 4949 (1986).
[21] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
[22] E. R. Cowley, J. Phys. Chem. **4**, 988 (1971).
[23] K. Wang and R. R. Reeber, Phys. Chem. Miner. **23**, 354 (1996).
[24] J. M. Brown and R. G. McQueen, J. Geophys. Res. **91**, 7485 (1986).
[25] R. Boehler and J. Ramakrishnan, J. Geophys. Res. **85**, 6996 (1980).
[26] R. Boehler, J. Geophys. Res. **87**, 5501 (1982).
[27] M. A. Barton and F. D. Stacey, Phys. Earth Planet. Inter. **39**, 167 (1985).
[28] F. Quareni and F. Mulargia, Geophys. J. **93**, 505 (1988).
[29] O. L. Anderson, H. Oda, A. Chopelas, and D. G. Isaak, Phys. Chem. Miner. **19**, 369 (1993).