terms of a power series of P as

$$K(P) = -V\left(\frac{dP}{dV}\right)_s$$

$$= K_0 + K_0'P + \frac{1}{2}K_0''P^2 \quad (9)$$

where $K_0'' = \{(\partial^2 K/\partial P^2)_s\}_{P=0}$ is the coefficient of the first-order nonlinear term in the bulk modulus.

Integration of equation 9 in the same manner as *Murnaghan* [1944] shows that

$$\ln\left[\frac{x_2}{x_1}\left(\frac{P - x_1}{P - x_2}\right)\right] = \ln\left(\frac{\rho}{\rho_0}\right)^{\xi} \quad (10)$$

where

$$\xi = [(K_0')^2 - 2K_0K_0'']^{1/2} \quad (11)$$

and

$$x_1, x_2 = -(K_0'/K_0'') \pm (\xi/K_0'') \quad (12)$$

Rewriting equation 10, the 'second-order Murnaghan equation of state' is found as

$$P = [x_1(1 - Z^{\xi})]/[1 - (x_1/x_2)Z^{\xi}] \quad (13)$$

where the coefficients ξ, x_1, and x_2 are given by equations 11 and 12 respectively, and $Z = (V_0/V) = (\rho/\rho_0)$.

Similarly, the 'second-order Birch equation of state' may be found as

$$P = (3K_0/2)y^5[(y^2 - 1) + b_1(y^2 - 1)^2 + b_2(y^2 - 1)^3] \quad (14)$$

where

$$b_1 = 3/4(K_0' - 4) \quad (15)$$

and

$$b_2 = 1/24[143 + 9(K_0' - 7)K_0' + 9K_0K_0''] \quad (16)$$

and

$$y = (V_0/V)^{1/3} = (\rho/\rho_0)^{1/3}$$

as before.

Based on these second-order equations of state, the corresponding expressions for the $\phi(P)$ are:

$$\phi(P)_{\text{Murnaghan}} = \phi_0\left[1 + \left(\frac{K_0'}{K_0}\right)P + \left(\frac{K_0''}{2K_0}\right)P^2\right]\left[\frac{x_1}{x_2}\left(\frac{P - x_2}{P - x_1}\right)\right]^{1/\xi} \quad (17)$$

and

$$\phi(P)_{\text{Birch}} = \frac{\phi_0}{3}\{3y^4[1 + 2b_1(y^2 - 1) + 3b_2(y^2 - 1)^2 + \frac{5}{y^3}(P/K_0)]\} \quad (18)$$

These last two equations are new and account for the first-order nonlinear behavior of the bulk modulus with pressure. Their usefulness arises from the fact that all the parameters can be evaluated from either the quantities determined from ultrasonic measurements at modest-pressure range or from low-pressure ultrasonic data combined with high-pressure compression data (after the appropriate thermodynamic transformation).

TABLE 1. Comparison of Volume and the Seismic Parameter ϕ as a Function of Pressure (for $m = 4$)

(P/K_0)	$(V/V_0)_B$	$(V/V_0)_M$	$(\phi/\phi_0)_B$	$(\phi/\phi_0)_M$
0.000	1.000	1.000	1.000	1.000
0.020	0.981	0.981	1.059	1.059
0.040	0.964	0.964	1.115	1.118
0.060	0.948	0.948	1.169	1.175
0.080	0.933	0.933	1.222	1.231
0.100	0.919	0.919	1.272	1.287
0.120	0.906	0.907	1.322	1.342
0.140	0.894	0.895	1.369	1.396
0.160	0.883	0.884	1.416	1.449
0.180	0.872	0.873	1.462	1.502
0.200	0.862	0.863	1.506	1.554
0.220	0.852	0.854	1.550	1.606
0.240	0.843	0.845	1.593	1.657
0.260	0.835	0.837	1.634	1.707
0.280	0.826	0.829	1.675	1.757
0.300	0.818	0.821	1.716	1.806
0.320	0.811	0.814	1.755	1.855
0.340	0.803	0.807	1.795	1.904
0.360	0.796	0.800	1.833	1.952
0.380	0.789	0.794	1.871	2.000
0.400	0.783	0.788	1.908	2.048
0.420	0.776	0.782	1.945	2.095
0.440	0.770	0.776	1.981	2.141
0.460	0.765	0.770	2.017	2.188
0.480	0.759	0.765	2.052	2.234
0.500	0.753	0.760	2.087	2.280
0.600	0.728	0.736	2.255	2.504
0.700	0.706	0.716	2.414	2.722
0.800	0.687	0.699	2.566	2.934
0.900	0.669	0.683	2.712	3.141
1.000	0.653	0.669	2.853	3.344
1.500	0.592	0.615	3.491	4.304
2.000	0.549	0.577	4.054	5.196
2.500	0.516	0.549	4.566	6.040
3.000	0.490	0.527	5.039	6.846

TABLE 2. Comparison of Volume and the Seismic Parameter ϕ as a Function of Pressure (for $m = 5$)

(P/K_0)	$(V/V_0)_B$	$(V/V_0)_M$	$(\phi/\phi_0)_B$	$(\phi/\phi_0)_M$
0.000	1.000	1.000	1.000	1.000
0.020	0.981	0.981	1.078	1.079
0.040	0.964	0.964	1.153	1.157
0.060	0.949	0.949	1.225	1.234
0.080	0.935	0.935	1.295	1.309
0.100	0.922	0.922	1.362	1.383
0.120	0.910	0.910	1.427	1.456
0.140	0.899	0.899	1.491	1.529
0.160	0.888	0.889	1.553	1.600
0.180	0.878	0.880	1.614	1.671
0.200	0.869	0.871	1.674	1.741
0.220	0.860	0.862	1.732	1.810
0.240	0.852	0.854	1.789	1.879
0.260	0.844	0.847	1.845	1.947
0.280	0.836	0.839	1.900	2.015
0.300	0.829	0.833	1.955	2.081
0.320	0.822	0.826	2.008	2.148
0.340	0.816	0.820	2.061	2.214
0.360	0.809	0.814	2.113	2.279
0.380	0.803	0.808	2.164	2.344
0.400	0.797	0.803	2.214	2.408
0.420	0.792	0.797	2.264	2.472
0.440	0.786	0.792	2.314	2.536
0.460	0.781	0.788	2.362	2.599
0.480	0.776	0.783	2.411	2.662
0.500	0.771	0.778	2.458	2.724
0.600	0.749	0.758	2.689	3.031
0.700	0.729	0.740	2.910	3.331
0.800	0.712	0.725	3.122	3.624
0.900	0.697	0.711	3.327	3.911
1.000	0.683	0.699	3.525	4.193
1.500	0.629	0.652	4.439	5.540
2.000	0.590	0.619	5.262	6.809
2.500	0.561	0.594	6.023	8.022
3.000	0.537	0.574	6.737	9.190

A form of the second-order Murnaghan equation of state, equation 13, has been presented earlier by *Ruoff* [1967] and by G. R. Barsch and Z. P. Chang ('Ultrasonic and static equation of state for cesium halides,' in *Accurate Characterization of the High-Pressure Environment*, unpublished manuscript, 1970). The equation of state given by Barsch and Chang is similar to equation 14 in this paper.

Crystalline solids undergoing compression without a phase change are characterized by $K(P)$ increasing monotonically with pressure and $K'(P)$ decreasing monotonically with pressure. The second condition requires that $K'' < 0$; such behavior was ultrasonically observed for three cesium halides [*Chang and Barsch*, 1967]. Because $K_0'' < 0$, equation 9 implies the existence of a finite pressure at which $K(P)$ becomes negative. Yet $K(P)$ cannot be negative, by the first law of thermodynamics. Use of the second-order Murnaghan equation of state to extrapolate density to high pressure leads to impossible results. Similarly, equation 17 should not be used to extrapolate the seismic $\phi(P)$. The Birch equation of state, which is a phenomenological equation based on a rapidly converging Taylor expansion of the interatomic potential, appears to describe experimental compression curves of solids more closely than any other equation of state yet known. For this reason, the ultrasonic method discussed here for calculating ϕ at high pressure is based on the use

TABLE 3. Comparison of Volume and the Seismic Parameter ϕ as a Function of Pressure (for $m = 6$)

(P/K_0)	$(V/V_0)_B$	$(V/V_0)_M$	$(\phi/\phi_0)_B$	$(\phi/\phi_0)_M$
0.000	1.000	1.000	1.000	1.000
0.020	0.981	0.981	1.097	1.099
0.040	0.965	0.965	1.189	1.196
0.060	0.950	0.950	1.278	1.292
0.080	0.936	0.937	1.363	1.386
0.100	0.924	0.925	1.445	1.479
0.120	0.913	0.914	1.525	1.571
0.140	0.902	0.903	1.602	1.662
0.160	0.892	0.894	1.677	1.752
0.180	0.883	0.885	1.751	1.841
0.200	0.875	0.877	1.823	1.929
0.220	0.866	0.869	1.893	2.016
0.240	0.859	0.862	1.962	2.103
0.260	0.851	0.855	2.029	2.189
0.280	0.844	0.848	2.096	2.274
0.300	0.838	0.842	2.161	2.358
0.320	0.831	0.836	2.225	2.442
0.340	0.825	0.831	2.289	2.526
0.360	0.819	0.826	2.351	2.609
0.380	0.814	0.820	2.413	2.691
0.400	0.808	0.815	2.473	2.773
0.420	0.803	0.811	2.533	2.854
0.440	0.798	0.806	2.592	2.935
0.460	0.793	0.802	2.651	3.015
0.480	0.789	0.798	2.709	3.095
0.500	0.784	0.794	2.766	3.175
0.600	0.764	0.775	3.043	3.567
0.700	0.746	0.760	3.308	3.951
0.800	0.730	0.746	3.562	4.327
0.900	0.716	0.734	3.807	4.697
1.000	0.703	0.723	4.044	5.061
1.500	0.653	0.681	5.141	6.813
2.000	0.617	0.652	6.130	8.478
2.500	0.589	0.630	7.045	10.079
3.000	0.567	0.612	7.905	11.631