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HIGH TEMPERATURE AND HIGH PRESSURE EQUATIONS OF STATE

Final Report

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Headquarters
Defense Nuclear Agency
Washington, D. C. 20305

California Institute of Technology
Seismological Laboratory
Pasadena, California

Contract No. DASA 01-70-C-0021

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Abstract

A program of investigation of theoretical equations of state, and ultrasonic measurements to 10 kbar and 800°K is described. The theoretical work summarized includes: reduction and analysis of shock wave data for rocks and minerals, formulation of complete p-V-T equations of state for calculating high pressure and high temperature Hugoniots, release adiabats, and isotherms, and the examination of the empirical relations between bulk modulus and compressional velocity and density. The application of Kröner's theory of random aggregates to the prediction of rock elastic properties using single-crystal elastic constant data is discussed. Ultrasonic elasticity measurements on single crystal spinel ($MgAl_2O_4$) at ambient conditions, and on rock salt (NaCl) to pressures of 10 kbar and 800°K are also summarized.

1. Introduction

Equations of state, or constitutive equations, provide a complete mechanical as well as thermodynamic description of material. An equation of state relates stress or pressure, strain or density, and one or more thermodynamic variables, such as internal energy, or temperature, for a specific material. Equations of state for earth materials are necessary for the calculation of intense stress-wave propagation and seismic coupling resulting from explosions or impacts on, or within, the earth's crust. Because of the wide range of dynamic pressures which are induced within the vicinity of a nuclear explosion, the equations of state which are of interest will describe the response of a medium over a range of conditions from thousands of kilobars and tens of thousands of degrees down to a fraction of a bar and ambient temperature; the latter conditions correspond to large distances from the disturbance.

The present program which is a continuation of a previous program summarized by Ahrens (1970) has been theoretically concerned with equations of state of earth materials under the wide range of dynamic pressures and, to a lesser degree, with gathering some ultrasonic data at high temperatures (800°K) and moderate pressures (10 kbar) for some earth materials.

The theoretical phase of our program has concentrated in the following areas:

(a) Analysis of the increasing quantity of shock wave data for silicates and silicate-bearing rocks.

(b) Formulation and application of a complete and thermodynamically consistent p-V-T equation of state suitable for calculating Hugoniots, adiabats, and isotherms at very high compressions and temperatures. This class of equations of state are based on finite strain theory as carried out to the fourth-order term in Helmholtz free energy.

(c) Formulation of systematic relationships between the bulk modulus and compressional velocity with density for a variety of minerals and oxides.

(d) Preparation of several topical reviews on: equations of state and strength of material data pertinent to seismic coupling and, ultrasonic and dynamic and static pressure-volume data for rocks and minerals.

In the experimental phase of our program, we carried out high pressure and high temperature measurements on the elastic properties of rock salt. In addition, some high quality ultrasonic data on the elastic properties of the mineral, spinel were obtained.

2. Research Results

The papers which resulted from research fully and partially supported under this contract were:

1. Application of the Fourth-Order Anharmonic Theory to Prediction of equations of State at High Compressions and Temperatures, submitted to Physics of the Earth and Planetary Interiors. T. J. Ahrens and L. Thomsen.
2. On the Effects of Pressure upon Rock Elasticity, submitted to Physics of the Earth and Planetary Interiors, L. Thomsen.
3. Elastic Properties of Minerals, R. C. Liebermann and E. Schreiber, Transactions, American Geophysical Union, 52, 142-147, 1971.
4. Static and Dynamic Compression of Earth Materials, T. J. Ahrens and T. Takahahsi, Transactions, American Geophysical Union, 52, 147-153, 1971.
5. Recent Progress in the Study of Dynamic Rock Properties Pertinent to Predicting Seismic Coupling, T. J. Ahrens, submitted to Proceedings, 1970 ARPA Seismic Coupling Symposium.
6. On the Elasticity of Polycrystals and Rocks, L. Thomsen, J. Geophys. Res., in press, 1972.
7. The Bulk Modulus-Volume Relationship for Oxides, D. L. Anderson and O. L. Anderson, J. Geophys. Res., 75, 3494-3500, 1970.
8. Velocity-Density Relations, D. L. Anderson, J. Geophys. Res., 75, 1623-1624, 1970.
9. Revised Shock-Wave Equations of State of High-Pressure Phase of Rocks and Minerals, G. F. Davies and D. L. Anderson, J. Geophys. Res., 76, 2617-2627, 1971.
10. Shock Wave Equations of State of Minerals, T. J. Ahrens, Proceedings, International School of Physics, Enrico Fermi, in press, 1972.

11. Equation of State of NaCl: Ultrasonic Measurements to 8 kbar and 800°K and Static Lattice Theory, H. Spetzler, C. G. Sammis, and R. J. O'Connell, submitted to <u>The Journal of the Physics and Chemistry of Solids</u>, 1972.

12. Quasi-Harmonic Finite Strain Equation of State, G. F. Davies, to be submitted for publication, 1972.

The significant results we obtained (and reported in these papers) are summarized in the following discussions:

A. Formulation of Equations of State and Theoretical Analysis of Experimental Data

Using a revised value for the relation between the zero-pressure seismic parameter, $\Phi_o = \left(\frac{\partial p}{\partial \rho}\right)_s$, density ρ_o, and mean atomic weight, M, given by

$$\rho_o\ (g/cm^3) = 0.0492\ M\ \phi_o^{1/3} \qquad (1)$$

where p is pressure, ρ is density and s is entropy, Davies and Anderson (paper 2) reduced the high-pressure shock wave data for a series of 19 rocks and minerals to adiabatic conditions. In a revision of an earlier paper (Ahrens <u>et al</u>., 1969) they found that the adiabats could be fit using a Birch-Murnaghan equation. This equation predicts a smooth increase of Φ with increasing density (or pressure).

The resulting adiabats are derived from the shock wave data using a Mie-Gruneisen equation of state. In equation (1) Φ_o is given in units of $(km/sec)^2$. For three iron-rich minerals the emprical equation

$$\rho_o(g/cm^3) = 0.051\ M\phi^{1/3} \qquad (2)$$

for the relation of density and seismic parameter at zero pressure was applied. The resulting p-ρ equations of state are observed to be roughly parallel in the log $(\rho/\overline{M})$ versus log ϕ plane (Figure 1).

Upon examining the relation of bulk modulus and density (actually specific volume) Anderson and Anderson (paper 7) found that the product of bulk modulus and specific volume for different classes of oxides is found to be effectively a constant for a given set of structures and coordination numbers. A second useful result in an empirical relation has been found between the reduced Madelung constant, and the ionic packing in a lattice. This result, when applied with knowledge of the bulk modulus, can be used for calculating theoretical equations of state in materials having potentials of the essentially ionic type.

A large volume of both ultrasonic and shock wave data describing the elastic constants and p-V-T equation of state have been reported in the literature for single crystals and monomineralic samples. Thomsen in a series of two papers (2 and 6) has examined the application of Kröner's (1967) theory to prediction of the elastic constants and equation of state of polycrystalline materials and rocks (composed of more than one mineral) in terms of the elastic moduli of the individual crystal species. In the case of polymineralic rocks, the lack of complete data make tests of Kröner's perfectly disordered aggregate theory versus the more common, but empirical, Reuss-Voigt-Hill average, difficult. However, the Kröner theory provides a self-consistent framework for extrapolation of near-zero pressure data to high pressure (paper 2). In the case of a highly porous aggregate this theory appears to describe the available data well (Figure 2). It is in this context that the theory will probably be most useful in predicting elastic properties of porous rocks on the basis of their composition

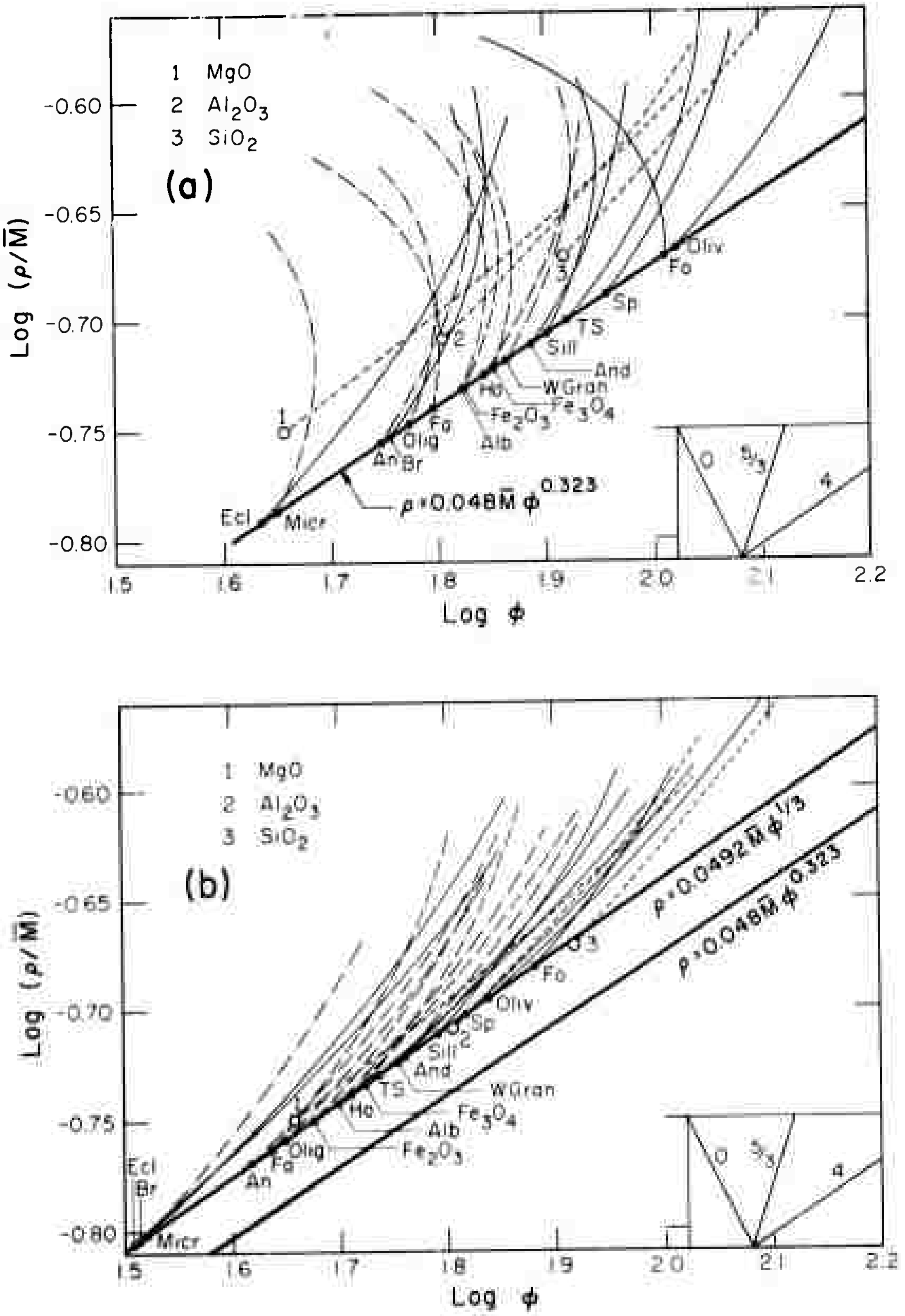

Fig. 1. Log ϕ versus log $(\rho/\bar{M})$ for adiabats of 17 high-pressure shock-induced phases. (a) zero-pressure constraint on adiabats given by $\rho = 0.048\ M\ \phi^{0.323}$ as previously used by Ahrens et al. (1969). Short dashed curves, oxides; long-dashed curves, iron-rich compounds, dash-dot curves, rocks containing feldspars. (b) zero-pressure constraint on adiabats given by Eqn. 2. Symbols for rocks and minerals are identified in Table 1 (after Davies and Anderson, 1971, paper 9).

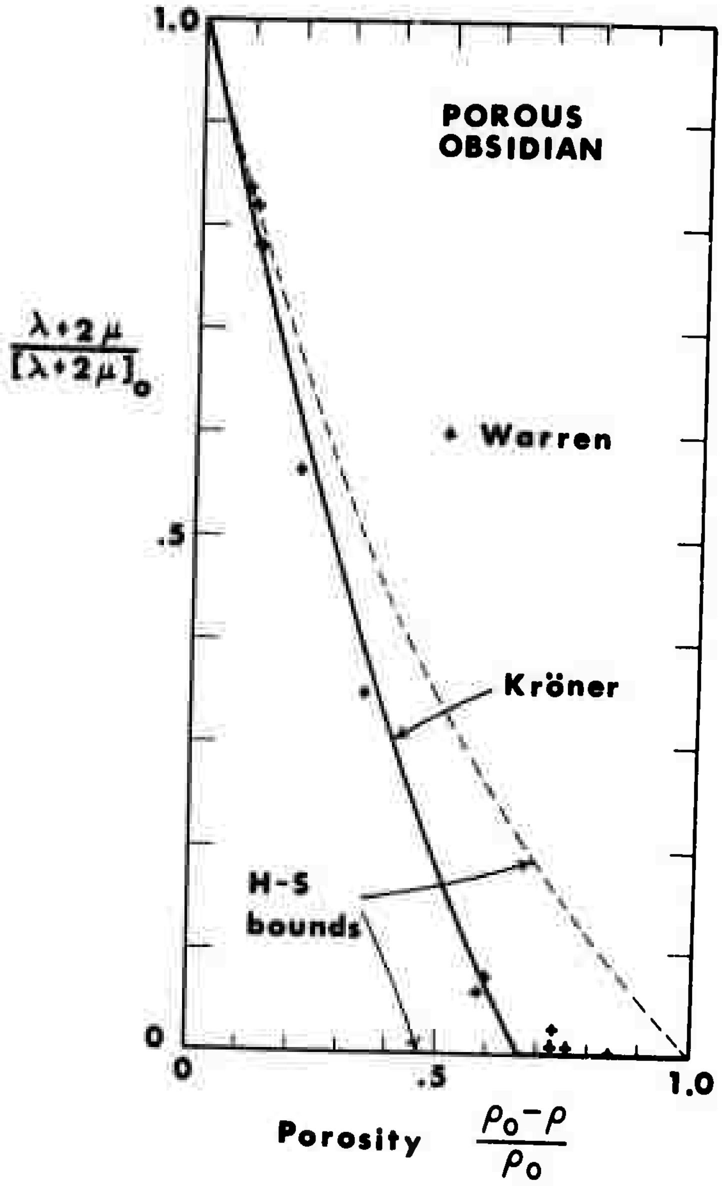

Figure 2. Normalized modulus $\lambda + 2\mu = K + 4\mu/3$ for porous obsidian; data from Warren (1969), theory after Kroner and Hashin-Shtrikman. Agreement with Kroner's theory is similar for shear modulus μ (after Thomsen, 1972).

and density alone.

Recent progress in the study of dynamic yielding of solid and porous rocks, the effect of water on the equation of state and very high pressure equations of state was reviewed by Ahrens (paper 5) at the 1970 ARPA Symposium. New Hugoniot data, both above and below the Hugoniot elastic limit was compared with hydrostatic compression data. These comparisons indicate that appreciable stress differences, comparable to those existing at the dynamic yield point, are supportable by rocks, such as sandstone, limestone and granite above the dynamic yield point. The quasi-static failure tests which have recently been reported provide data which closely satisfy a Prager-Drucker-type yield surface. In particular, the one-dimensional stress tests for a series of porous and non-porous rocks indicate sensitivity of fracture stress and dynamic (Young's) modulus on strain rate. Of special importance is the observation that water affects the dynamic flow, and resulting stress waves from underground explosions because of steam formation. Water strongly affects the phenomenon of block sliding which takes place after the initial shock has propagated through an initially competent rock. This mechanism is believed to represent the dominant process limiting shear stresses at late times in the flow around explosions in originally strong rocks. He also notes that at high shock pressures a series of shock-induced phase transitions involving changes of from 10 to 60% in density takes place in silicate minerals. These phase changes account for most of the compression which occurs in the first megabar of pressure in solid rocks. As a result of these transitions the release adiabats upon initial unloading from Hugoinot states are considerably steeper in the stress-density plane than the corresponding Rayleigh lines and give rise to appreciable intrinsic shock attenuation.

8.

In 1970, a fourth-order finite strain equation of state which self-consistently treated the thermal properties of solids was first described by Thomsen (1970). One important merit of this theory is that the Gruneisen parameter (γ) which is so vital in adequately describing high pressure Hugoniots and release adiabats for solids is explicitly given as a function of volume in terms of other thermodynamic properties and the value of γ at ambient conditions. The theory, originally derived in order to describe p-V-T equations of state, has later been extended so as to describe shear moduli by Thomsen (1972). A major disadvantage of the finite strain approach is that the definition of strain is not unambiguous. Originally Thomsen derived an equation of state by expanding the Helmholtz free-energy in terms of the Lagrangian strain parameter η,

$$\eta = \frac{1}{2}\left[\left(\frac{V}{\tilde{V}}\right)^{2/3} - 1\right] \tag{3}$$

where $\tilde{V}$ is the volume of the solid in the rest state (at 0°K with the effect of zero-point vibrational energy removed). This theory was briefly summarized in our previous Final Report (Ahrens, 1970). More recently Davies (paper 12) derived another, more general, and probably equivalent form of the equation of state using strain measures such as

$$e = \left[(V/V_o)^{1/3} - 1\right] \tag{4}$$

$$\varepsilon = \frac{1}{2}\left[1 - (V/V_o)^{-2/3}\right] \tag{5}$$

where, rather than relative to the rest state, the standard volume is taken, more conveniently, under ambient conditions. Because of the above mentioned ambiguity in the definition of the finite strain the various finite strain theories begin to diverge from each other at compressions $V/V_o \lesssim 0.7$. In spite of this drawback, because of the potential usefulness of finite strain theory in generating theoretical Hugoniots, isotherms, and release adiabats for a wide class of both initially solid, and porous materials using low-pressure ultrasonic and thermodynamic data, Ahrens and Thomsen (paper 1) exhaustively tested its applicability for 17 metals, compounds, and minerals. The materials studied were all cubic (crystal structure) and ones for which good elastic constant, thermodynamic and shock wave data were available. Ultrasonic values of the bulk modulus, K, its pressure derivative $K' = dK/dP$ and in some cases, the second pressure derivative of bulk modulus $K'' = dK'/dP$ was employed in the analysis.

They concluded that the fourth order anharmonic theory is adequate to predict P(V) for the metals to compressions of $(\Delta V/V_o)_{max} \approx 0.3$, and in a few cases to much greater compression. For ionic compounds, the maximum compression is generally smaller, and more erratic within each group of halides. The uncertainties associated with the two covalent compounds, MgO and BeO, make generalizations for this class hazardous. Experimental resolution of the experimental uncertainties in the parameters K_o' and $K_o''K_o$ will, eventually allow a more definitive test of the fourth order theory for this class of materials. The purely thermal contributions to the pressure seem to be well described for the metals up to their melting points and for MgO to temperatures almost three times the Debye temperature. However, the description of the free energy function as a function of temperature can be improved by using a more refined model for the specific heat (Kieffer and Kamb, 1971). The elastic moduli are described well to compressions of perhaps 0.2, although the data is very limited.

On this basis, they concluded that the anharmonic theory is probably adequate to describe the elasticity of all cubic minerals to compressions of $V/V_o \cong 0.7$.

B. Ultrasonic Measurements

Although some measurements of the elasticity of single crystal spinel were carried out by R. J. O'Connell summarized in Table 2, our major effort was concentrated on a very complete study of rock salt at high temperatures and pressures. The work reported in (paper 11) represents the first (elasticity) measurements of this material at simultaneously high pressure and temperature. Of particular interest are the pressure dependence of the derivative (dK_T/dP) and d^2K_T/dP^2 which were both measured for the first time (Fig. 3). The complete reduction of the ultrasonic data in terms of a p-V-T equation of state permitted calculating the variation of the Gruneisen parameter as a function of volume and temperature Fig. 4. As can be seen in the figure, γ is nearly independent of temperature, at constant volume, as is assumed, in the commonly employed Mie-Gruneisen equation of state.

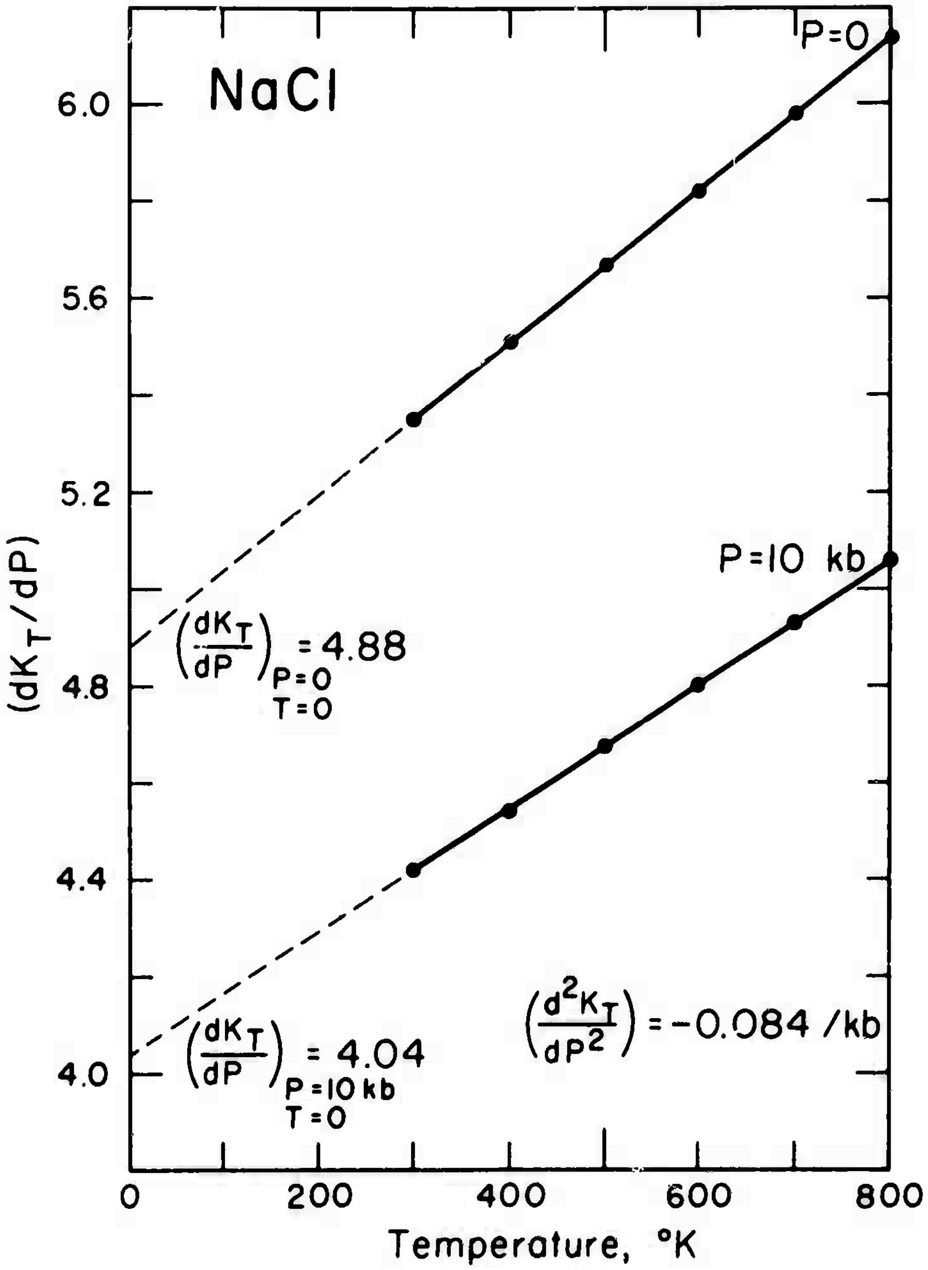

Figure 3. $(\partial K_T/\partial P)$ versus temperature at 0, and 10 kbar from the ultrasonic measurements on NaCl of Spetzler et al. 1972, paper 11).

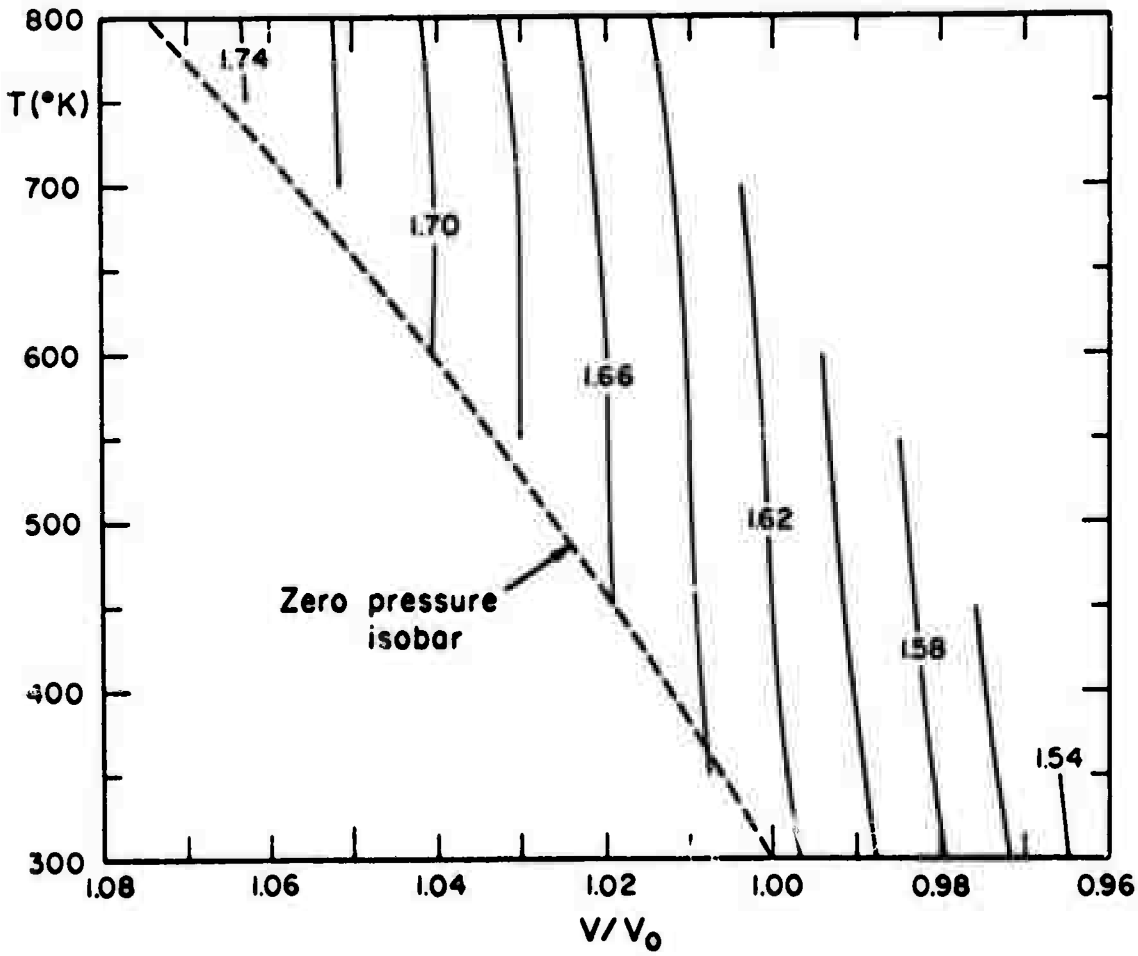

Figure 4. Contours of the Gruneisen function $\gamma(V,T)$ over the volume and temperature range of the ultrasonic measurements for NaCl. The dashed line shows the zero pressure isobar (after Spetzler *et al.*, 1972, paper 11).

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TABLE 1. Parameters of the "ambient" adiabats derived using the "original" and "revised" seismic equations of state

	$\rho_o = 0.048\ \overline{M}\Phi^{.323}$					$\rho_o = 0.0492\ \overline{M}\Phi^{1/3}$				
	ρ_o (g/cm^3)	K_o (Mb)	ξ	K'_o	Φ_o (km/sec)^2	ρ_o (g/cm^3)	K_o (Mb)	ξ	K'_o	Φ_o (km/sec)^2
Forsterite (Fo)	4.31	4.425	2.22	1.05	103	4.18	3.186	0.88	2.83	76
Olivinite (Oliv)	4.58	4.840	0.86	2.85	106	4.28	2.961	0.48	3.35	69
Twin Sisters dunite (TS)	4.12	3.367	1.01	2.65	82	3.94	2.147	0.41	3.45	55
Hortonalite dunite (Ho)	4.75	3.319	1.22	2.37	70	4.59	2.366	0.65	3.14	52
Fayalite (Fa)	5.31	3.319	1.87	1.50	63	5.03	2.173	0.89	2.81	43
Hematite (Fe_2O_3)	5.96	3.991	1.52	1.98	67	5.70	2.727	0.83	2.89	48
Magnetite (Fe_3O_4)	6.30	4.488	1.66	1.79	71	6.11	3.225	0.94	2.74	53
Spinel (Sp)	4.19	3.819	1.06	2.59	91	4.03	2.646	0.53	3.29	65
Enstatite (Ens)	4.20	4.031	4.23	-1.64	96	3.93(c)	---	---	---	---
Bronzitite (Br)	3.74	2.117	1.14	2.48	57	3.33	1.086	0.49	3.34	33
Sillimanite (Sill)	4.00	3.187	1.40	2.33	80	3.94	2.435	0.82	2.91	62
Andalusite (And)	3.95	3.045	1.16	2.46	77	3.84	2.185	0.61	3.19	57
Anorthosite (An)	3.71	2.084	1.20	2.40	56	3.57	1.481	0.67	3.11	41
Oligoclase (Olig)	3.69	2.198	1.60	1.87	60	3.57	1.592	0.72	3.15	45
Albitite (Alb)	3.81	2.550	1.63	1.82	67	3.69	1.84	0.71	3.05	50
Microcline (Micr)	3.50	1.563	1.47	2.04	45	3.36	1.09	0.70	3.06	33
Westerly granite (WGr)	3.96	2.907	1.32	2.24	73	3.90	2.22	0.75	3.00	57
Eclogite (Ecl)	3.61	1.555	0.76	2.99	43	3.49	1.12	0.39	3.48	32
Periclase (MgO)	3.584(a)	1.628	0.11	3.85	45					
Corundum (Al_2O_3)	3.988(a)	2.551	-0.12	4.16	64					
Stishovite (SiO_2)	4.287(a)	3.546	0.66	3.12	83					
Wustite (FeO)	5.86(a, b)	---	---	---	30(b)					

TABLE 1. (continued)

	$\rho_o = 0.051\ \overline{M}\Phi^{1/3}$				
	ρ_o	K_o	ξ	K_o'	Φ_o
	(g/cm^3)	(Mb)	—	—	$(km/sec)^2$
Fayalite	4.82	1.65	0.67	3.10	34
Hematite	5.44	2.03	0.58	3.23	37
Magnetite	6.00	2.69	0.72	3.05	45

(a) Fixed density.

(b) Extrapolated from $Fe_{.95}O$ (Clark, 1966; Anderson, 1969).

(c) From hugoniot.

Table 2

Elastic Properties of Spinel ($MgO \cdot 2.6\ Al_2O_3$)

(R.J. O'Connell, private communication)

	Units	Value	$\left.\frac{\partial}{\partial T}\right)_{300°K,\ 0\ kb.}$ (°K^{-1})	$\left.\frac{\partial}{\partial P}\right)_{300°K,\ 0\ kb.}$ (kbar^{-1})	$\left.\frac{\partial^2}{\partial T \partial P}\right)_{300°K,\ 0\ kb}$ (°K^{-1} kbar^{-1})
α	°K^{-1}	1.62×10^{-5}	6.30×10^{-8}	-6.91×10^{-8}	—
C_P	erg/g°K	8.03×10^{6}	1.28×10^{4}	-5.24×10^{3}	—
* V_P	cm/sec	9.083×10^{5}	-38.31	441.4	-.025
† V_S	cm/sec	4.476×10^{5}	-25.03	33.18	.069.
K_S	dyne/cm^2	2.0191×10^{12}	-1.765×10^{8}	3.765×10^{9}	-5.7×10^{5}
K_T	dyne/cm^2	2.0081×10^{12}	-2.787×10^{8}	3.815×10^{9}	-3.5×10^{5}
C_{11}	dyne/cm^2	2.986×10^{12}	-3.00×10^{8}	4.389×10^{9}	-5.6×10^{5}
C_{12}	dyne/cm^2	1.5356×10^{12}	-1.01×10^{8}	3.452×10^{9}	-13.7×10^{5}
C_{44}	dyne/cm^2	1.5740×10^{12}	-0.99×10^{8}	0.826×10^{9}	0.8×10^{5}
ρ	g/cm^3	3.6193	-5.86×10^{-5}	1.80×10^{-3}	—

* V_P $\left[C_{11}/\rho\right]^{1/2}$

† V_S $\left[(C_{11}-C_{12})/2\rho\right]^{1/2}$