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Pressure Dependence of the Elastic Constants of NaCl at Low Temperatures

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The paper presents the pressure derivatives of single-crystal NaCl in the temperature range of 180°–300°K. The data have been used to calculate the mode Grüneisen parameters. We have also predicted the shock-velocity and the particle-velocity relationship using the ultrasonic data at 300°K.

INTRODUCTION

In recent years there has been a considerable amount of work in the area of pressure dependence of elastic constants of solids with a view to understand the nature of solid-state binding and in certain cases to evaluate the equation of state. Following the work of Lazarus[1] many people have repeated the measurements on NaCl. Recently Bartels and Schuele[2] have reported the pressure derivatives of NaCl at 195° and 295°K and Bogardus[3] has measured the same in the high-temperature range of 25°–250°C. In the present study, we have carried on the measurements at the following temperatures: 300°, 261°, 222°, and 180°K. Our measurements are at temperatures which cover the range between the two temperature values of Bartels and Schuele.[2]

Table I. Comparison of zero-pressure adiabatic elastic constants with previous values (units: 10^{11} dyn/cm^2) at $T=300°$K.

Investigator	C_{11}^S	C_{12}^S	C_{44}^S
Present work	4.936	1.288	1.278
Bartels and Schuele	4.899	1.257	1.272
Lazarus	4.911	1.225	1.284

As an outside interest we have used our data on pressure derivatives to calculate the mode Grüneisen parameters. We have also predicted the shock-velocity and the particle-velocity relationship based on our data at 300°K.

EXPERIMENT AND DATA ANALYSIS

Ultrasonic velocities have been measured along preferred crystallographic directions in NaCl single crystals using the pulse interferrometric technique of Williams and Lamb.[4] Samples of the size $\frac{1}{2}$-in. cube were obtained from Semi-Elements, Inc. The samples were oriented in an x-ray diffractometer to better than 0.1°. The two opposite faces were carefully lapped and were made parallel to better than one part in 10^4. 10-MHz quartz transducers were used, and glycercine was found to be a good bonding material for runs below 260°K; for the 300°K run nonaq grease was used instead.

The pressure derivatives were obtained by measuring the transit times as a function of pressure at constant temperature. Four crystals were put in the pressure vessel and the transit times sere measured simultaneously. Although a three-crystal assembly is necessary if the self-consistent method of Cook[5] is to be used to analyze the data, the fourth crystal was used for additional check.

A gas-pressure system was used with helium as the transmitting medium and the maximum pressure applied was about 4 kbar. The pressure vessel was placed in a low-temperature chamber manufactured by Delta Design, Inc. With liquid nitrogen as a coolant, this chamber provides temperatures from 77° to 300°K controlled to 0.1°.

We have used the procedure of Cook[5] to analyze our data. According to this technique, by making simultaneous measurements of three independent elastic constants as function of pressure at a given temperature, one can self-consistently calculate the effective elastic constants at any pressure without assuming the linearity of any kind. We are indeed aware of the redundancy of using this procedure to evaluate the linear pressure derivatives using the data at low pressures. However, this technique is powerful in detecting any nonlinearities. The details of this analysis are extensively presented by Ghafelehbashi *et al.*[6] in a recent paper.

TABLE II. Pressure derivatives of second-order elastic constants of NaCl at room temperature.

Investigator	$(\partial B^S/\partial P)_T$	$(\partial C_{11}{}^S/\partial P)_T$	$(\partial C_{12}{}^S/\partial P)_T$	$(\partial C_{44}/\partial P)_T$
Present work	5.274	11.830	1.197	0.370
Bartels and Schuele	5.27	11.66	2.08	0.37
Lazarus	6.05	12.23	2.96	0.27

TABLE III. Adiabatic and isothermal elastic constants for NaCl as a function of pressure (units: P, bar; elastic constants, 10^{11} dyn/cm^2; T, °Kelvin). *Note*: Superscript s means adiabatic and T means isothermal values of the constants and B is the bulk modulus.

P	B^s	B^T	$C_{11}{}^s$	$C_{11}{}^T$	$C_{12}{}^s$	$C_{12}{}^T$	C_{44}	Δ[a]	λ[b]
				$T=300$°K					
0	2.5036	2.3663	4.9356	4.7983	1.2876	1.1503	1.2781	0.05799	1.000000
350	2.5216	2.3846	4.9766	4.8396	1.2941	1.1571	1.2795	0.05743	1.000491
680	2.5385	2.4018	5.0169	4.8803	1.2992	1.1625	1.2806	0.05690	1.000951
975	2.5533	2.4171	5.0505	4.9143	1.3046	1.1684	1.2817	0.05643	1.001360
1450	2.5781	2.4421	5.1063	4.9703	1.3140	1.1781	1.2834	0.05567	1.002012
1925	2.6031	2.4676	5.1633	5.0278	1.3231	1.1875	1.2853	0.05492	1.002659
2470	2.6311	2.4961	5.2289	5.0940	1.3321	1.1972	1.2874	0.05405	1.003393
2950	2.6607	2.5261	5.2878	5.1532	1.3471	1.2125	1.2891	0.05328	1.004033
2500	2.6873	2.5534	5.3468	5.2130	1.3575	1.2237	1.2910	0.05240	1.004758
				$T=261$°K					
0	2.5462	2.4264	5.0826	4.9628	1.2780	1.1582	1.2897	0.04940	1.000000
555	2.5737	2.4542	5.1502	5.0307	1.2854	1.1660	1.2919	0.04867	1.000758
815	2.5875	2.4682	5.1804	5.0611	1.2910	1.1717	1.2929	0.04833	1.001110
1055	2.6008	2.4817	5.2096	5.0904	1.2965	1.1773	1.2937	0.04801	1.001433
1495	2.6240	2.5052	5.2619	5.1431	1.3050	1.1862	1.2952	0.04744	1.002022
2010	2.6506	2.5322	5.3210	5.2026	1.3155	1.1971	1.2969	0.04676	1.002705
2505	2.6762	2.5583	5.3811	5.2631	1.3238	1.2058	1.2987	0.04611	1.003355
3007	2.7053	2.5877	5.4432	5.3256	1.3564	1.2188	1.3008	0.04545	1.004008
3500	2.7285	2.6115	5.5007	5.3837	1.3424	1.2254	1.3023	0.04480	1.004643
4030	2.7557	2.6393	5.5610	5.4446	1.3530	1.2366	1.3041	0.04411	1.005319
				$T=222$°K					
0	2.5869	2.4885	5.2378	5.1395	1.2614	1.1631	1.3024	0.03951	1.00000
368	2.5960	2.4983	5.2724	5.1746	1.2578	1.1601	1.3036	0.03914	1.00049
698	2.6132	2.5156	5.3093	5.2117	1.2652	1.1676	1.3047	0.03880	1.00093
1010	2.6290	2.5315	5.3468	5.2494	1.2700	1.1726	1.3057	0.03848	1.00134
1507	2.6555	2.5583	5.4056	5.3084	1.2804	1.1832	1.3073	0.03798	1.00199
1995	2.6804	2.5836	5.4612	5.3644	1.2900	1.1932	1.3090	0.03748	1.00262
2525	2.7077	2.6113	5.5248	5.4283	1.2992	1.2028	1.3105	0.03694	1.00331
2960	2.7316	2.6354	5.5727	5.4765	1.3110	1.2149	1.3118	0.03650	1.00386
3475	2.7562	2.6605	5.6383	5.5426	1.3127	1.2170	1.3132	0.03597	1.00451
4005	2.7874	2.6920	5.6931	5.5978	1.3345	1.2391	1.3149	0.03543	1.00518
				$T=180$°K					
0	2.6238	2.5481	5.3887	5.3130	1.2414	1.1656	1.3143	0.02973	1.00000
385	2.6436	2.5682	5.4341	5.3586	1.2484	1.1729	1.3146	0.02939	1.00050
735	2.6648	2.5895	5.4776	5.4023	1.2584	1.1831	1.3131	0.02908	1.00095
1080	2.6781	2.6032	5.5141	5.4391	1.2601	1.1852	1.3181	0.02879	1.00139
1565	2.7015	2.6270	5.5677	5.4932	1.2684	1.1939	1.3201	0.02837	1.00201
2043	2.7228	2.6488	5.6184	5.5444	1.2751	1.2010	1.3225	0.02796	1.00262
2555	2.7456	2.6721	5.6729	5.5994	1.2819	1.2084	1.3257	0.02751	1.00326
3120	2.7748	2.7018	5.7396	5.6666	1.2924	1.2194	1.3254	0.02703	1.00396
3675	2.7985	2.7261	5.7998	5.7274	1.2979	1.2256	1.3273	0.02655	1.00465
4252	2.8281	2.7563	5.8650	5.7932	1.3097	1.2379	1.3248	0.02605	1.00535

[a] Δ is conversion factor from adiabatic to isothermal.

[b] $\lambda = L(0)/L(P)$ (the ratio of length at pressure $=0$ to pressure $=P$).

TABLE IV. Pressure derivatives of adiabatic and isothermal elastic constants for NaCl.

T (°K)	$(\partial B^s/\partial P)_T$	$(\partial B^T/\partial P)_T$	$(\partial C_{11}{}^s/\partial P)_T$	$(\partial C_{11}{}^T/\partial P)_T$	$(\partial C_{12}{}^s/\partial P)_T$	$(\partial C_{12}{}^T/\partial P)_T$	$(\partial C\ /\partial P)_T$
300	5.274	5.369	11.830	11.925	1.997	2.092	0.370
261	5.240	5.324	11.892	11.976	1.914	1.998	0.355
222	5.111	5.180	11.563	11.633	1.859	1.929	0.312
180	4.728	4.822	11.110	11.204	1.536	1.631	0.340

RESULTS

We present our data in a series of tables, Table I–VIII. We have given both the pure adiabatic and the pure isothermal pressure derivatives. The plots of the elastic constants as a function of pressure at $T=300°\mathrm{K}$ are given in Figs. 1–4. In Fig. 5, we have plotted the temperature variation of the pressure derivatives along with the data of Bartels and Schuele[2] at 195° and 295°K. The derivatives themselves are good within 5%. The variation, however, is outside the error. All the derivatives decrease very slowly with decreasing temperature and a rather "strange" behavior is exhibited below about 190°K; $\partial C_{11}/\partial P$ and $\partial C_{12}/\partial P$ go down, while $\partial C_{44}/\partial P$ starts going up. Bogardus[3] has reported that

$$[\partial C_{11}/\partial P]_{523°\mathrm{K}} < [\partial C_{11}/\partial P]_{300°\mathrm{K}}$$

while

$$[\partial C_{44}/\partial P]_{523°\mathrm{K}} > [\partial C_{44}/\partial P]_{300°\mathrm{K}}.$$

It appears that the variation does not strictly follow the simple quasi-harmonic behavior. In a recent paper Ghafelehbashi *et al.*[6] also reported a minimum around 200°K in the variation of $[\partial C_{44}/\partial P]$ with temperature for RbCl, for example. At this point we can only say that more work is indeed needed in a wide range of low temperatures. Such an effort is underway in our laboratory.

We have also calculated the mode Grüneisen parameters by using Slater's relation and our pressure-derivative data. The detailed analysis of the computation of macroscopic Grüneisen parameter and its temperature dependence will be dealt with in a future article on that subject covering other alkali halides.

Ruoff[7] has developed an equation of state, based on the bulk modulus variation with pressure of the form

$$B^s = B_0{}^s + B_0{}^{s\prime} P + B_0{}^{s\prime\prime}(p^2/2),$$

TABLE V. Grüneisen γ_i for several modes of vibrations using relation $\gamma_i = -\frac{1}{6} + (B^T/2C_i)(\partial C_i/\partial P)_T$, where C_i are the elastic constants and B^T is isothermal bulk modulus.

			NaCl			
Direction of propagation	γ_L (Longt.)[a]	γ_L[b]	γ_{T_1} (shear)[a]	γ_{T_1}[b]	γ_{T_2} (shear)[a]	γ_{T_2}[b]
			$T=300°\mathrm{K}$			
100	2.669	2.62	0.176	0.17	0.176	0.17
110	1.796	1.78	0.176	0.17	3.021	2.91
111	1.455	1.45	1.283	2.20	2.283	2.20
			$T=261°\mathrm{K}$			
100	2.672	···	0.167	···	0.167	···
110	1.803	···	0.167	···	3.015	···
111	1.458	···	2.293	···	2.293	···
			$T=222°\mathrm{K}$			
100	2.580	···	0.131	···	0.131	···
110	1.753	···	0.131	···	2.860	···
111	1.423	···	2.190	···	2.190	···
			$T=180°\mathrm{K}$			
100	2.460	···	0.163	···	0.163	···
110	1.666	···	0.163	···	2.774	···
111	1.342	···	2.146	···	2.146	···

[a] Present work.

[b] Bartels, Ref. 2.

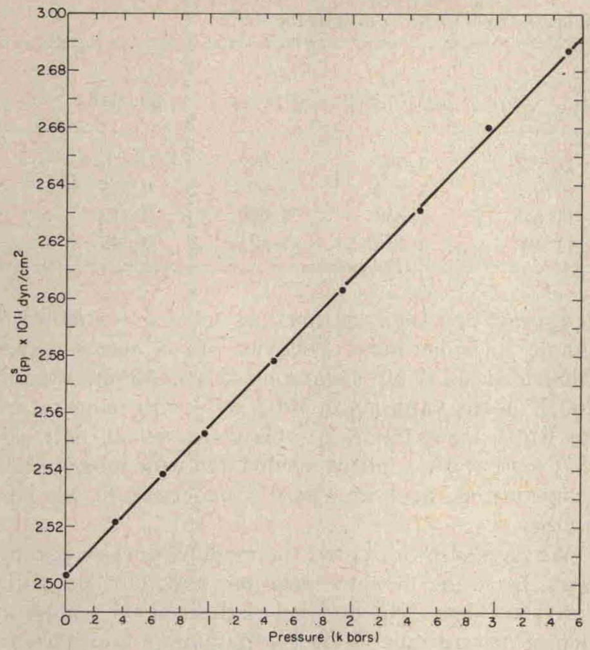

FIG. 1. Variation of the adiabatic elastic constant C_{11}^s as function of pressure at $T=300$°K.

where B_0^s, $B_0^{s\prime}$, and $B_0^{s\prime\prime}$ are the zero-pressure bulk modulus and its first and second pressure derivatives respectively. The resultant equation of state is then combined with the Rankine–Hugoniot conservation relations to obtain a Maclurin series for the shock-velocity versus the particle-velocity relationship

$$U_s = c + sU_p + s'U_p^2 + \cdots .$$

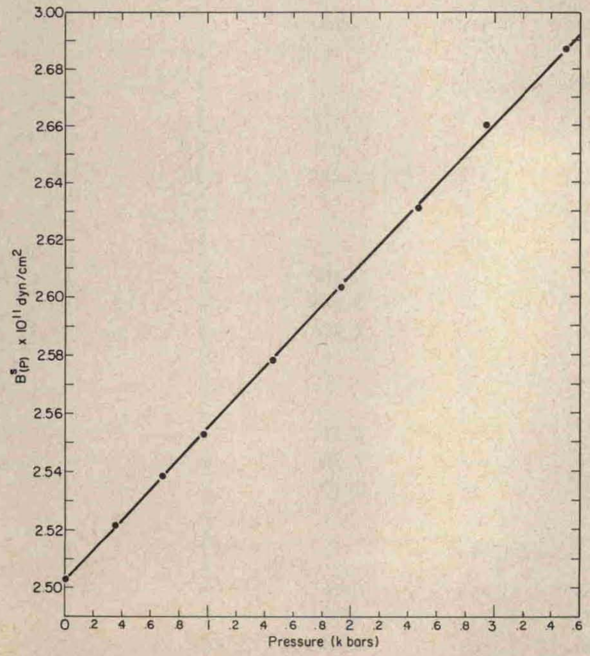

FIG. 2. Variation of the adiabatic bulk modulus, (B^S), as function of pressure at $T=300$°K.

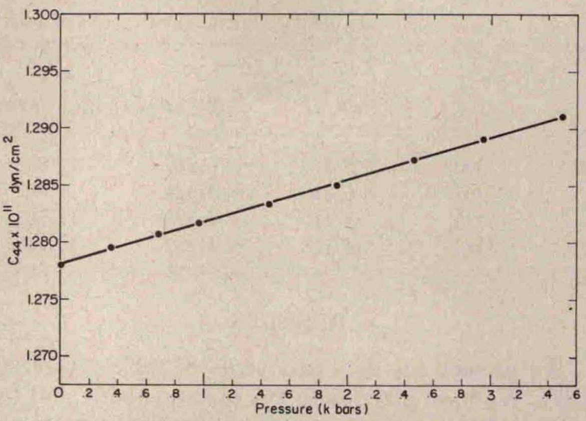

FIG. 3. Variation of the elastic constant C_{44} as function of pressure at $T=300$°K.

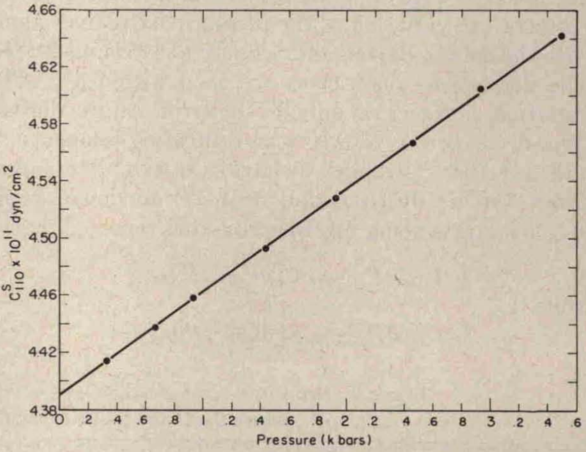

FIG. 4. Variation of the adiabatic elastic constant C_{110}^s as a function of pressure at $T=300$°K. $(C_{110}^s = C_{11}^s + C_{12}^s + 2C_{44})/2$.

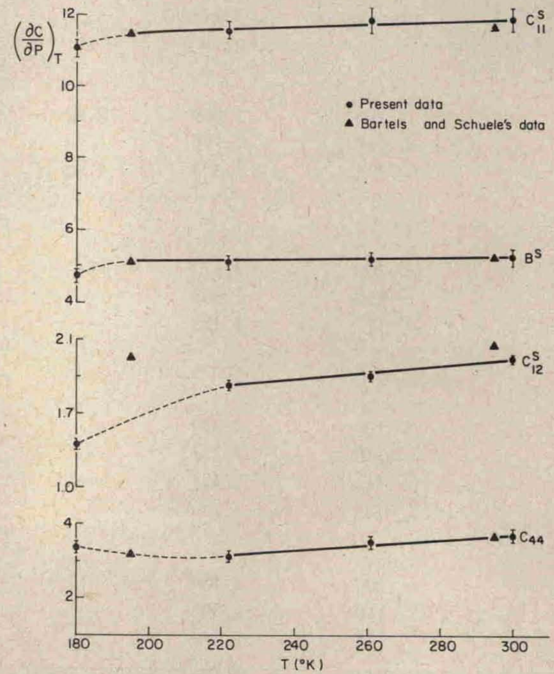

FIG. 5. Temperature variation of $(\partial C_{ij}^s/\partial P)_T$.

The coefficients c, s' can be evaluated in terms of the unshocked density and quantities available from ultrasonic data at high pressures:

$$c=(B_0{}^s/\rho_0)^{1/2},$$

$$s=(B_0{}^{s\prime}+1)/4,$$

and

$$s'=(24c)^{-1}[s(7-B_0{}^{s\prime}+4\gamma_0)+2B_0{}^sB_0{}^{s\prime\prime}].$$

c and s are evaluated using the ultrasonic data for $B_0{}^s$ and $B_0{}^{s\prime}$. $B_0{}^{s\prime\prime}$, however, is evaluated on the basis of empirical Born model. Assuming a potential energy of a system of N positive ions and N negative ions such as NaCl, to be

$$E=-N(Ae^2/r)+(B/r^n),$$

one can arrive at

$$2B_0{}^sB_0{}^{s\prime\prime}=-\tfrac{8}{9}(3B_0{}^{T\prime}-4).$$

Hence we evaluate s'. We obtain the following expression for U_s-U_p relationship

$$U_s=3.401+1.51347U_p+0.02378U_p{}^2.$$

Where U_s, U_p are expressed in km/sec. Fritz *et al.*[8] report the following linear fit of their shock experiment:

$$U_s=(3.528\pm0.012)+(1.343\pm0.009)U_p.$$

The agreement is rather good.

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