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ELASTIC CONSTANTS OF FLUORIDES OF GROUPS IA AND IIA

Office of Technical Consultants
San Diego, California
December 1968

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ELASTIC CONSTANTS OF FLUORIDES OF GROUPS IA AND IIA

By K.C. Crouch, R.B. Rayment, and G.W. Marks

PROBLEM

Determine the elastic constants of lithium fluoride, sodium fluoride, calcium fluoride, strontium fluoride, and barium fluoride from room temperature to liquid-nitrogen temperatures.

RESULTS

1. Adiabatic elastic constants of the above-listed cubic crystals were determined over the stated temperature range.

2. Elastic-anisotropy factors, adiabatic compressibilities, and thermoelastances were evaluated from the elastic-constant data.

3. Results were compared with those of other investigators. Some conclusions were drawn concerning the mechanical data and structure.

RECOMMENDATION

1. Determine the elastic constants of certain crystals from liquid-helium temperatures up to the melting point, at atmospheric and higher pressures. Apply modern theoretical developments to the interpretation of the results.

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INTRODUCTION

Knowledge of the mechanical properties of solids is important not only because of possible application to engineering problems but also because of their intrinsic interest. The variation of the elastic constants of crystals with temperature and pressure, when correlated with other physical properties, yields an insight into the nature of ionic, atomic, and molecular binding forces. After comparison of experimental values with those calculated theoretically, a critical examination of underlying assumptions on which the theory was founded can be made.

For reviews of older work on theory, experimental methods, and results, the reader is referred to Bergman[1] and to Huntington.[2]

In recent years, a large number of investigations have been made concerning the physical properties of the alkali and alkaline-earth halides. This extensive investigation rests on the facts that good crystals of all or nearly all these compounds can be grown, they are cubic and of simple ionic arrangement, and they have only three elastic constants. In general, it is easier to interpret results and apply theory to these groups of crystals than to others of more complex structure or of lower symmetry.

Determinations of elastic constants at room temperature and at lower temperatures have been made for many of these halides. Not much work at higher temperatures has been done, largely because of experimental difficulties. Data are needed from 0°K to the melting points, at atmospheric and at higher pressures.

In this study the elastances of the fluorides LiF, NaF, CaF_2, SrF_2, and BaF_2 were determined from liquid-nitrogen temperatures to ambient temperature by means of the pulse-echo technique for the measurement of sound velocity. For initial comparison, values of the constants c_{11}, c_{12}, and c_{44} for these five fluorides, as presented by various investigators, are given in table 1. References are listed in the fifth column of this table. Some of our results are a little lower than those of others, for which we have no adequate explanation.

TABLE 1. COMPARISON OF MEASURED VALUES OF ELASTIC CONSTANTS AT ROOM TEMPERATURE (Continued on page 6).

Crystal	Elastic Constants, 10^{11} dynes/cm^2			Source*
	c_{11}	c_{12}	c_{44}	
LiF	9.74	4.04	5.54	3
	11.9	4.58	5.42	4
	11.77	4.33	6.28	5
	11.335	4.76	6.35	6
	10.86	3.724	6.28	this work

*See *REFERENCES*.

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1. See *REFERENCES* at end of report.

TABLE 1 (Continued).

Crystal	Elastic Constants, 10^{11} dynes/cm^2			Source*
	c_{11}	c_{12}	c_{44}	
NaF	9.70	2.56	2.80	7
	9.70	2.43	2.81	6
	9.70	2.38	2.822	8
	9.33	2.105	2.840	this work
CaF$_2$	16.44	5.02	3.47	5
	16.4	4.47	3.38	9
	16.4	5.3	3.370	10
	16.357	4.401	3.392	11
	16.494	4.462	3.380	12
	16.12	3.948	3.251	this work
SrF$_2$	12.35	4.305	3.128	13
	12.16	4.298	2.993	this work
BaF$_2$	8.915	4.002	2.535	14
	9.01	4.03	2.49	7
	9.122	4.148	2.551	11
	8.85	4.112	2.498	this work

*See *REFERENCES*.

THEORY

Sound Velocities

For an isometric crystal, sound velocities, elastic constants, and density are related as follows:[15]

1. Sound propagation is in the [100] direction:

$$\rho v_1^2 = c_{11} \tag{1}$$

$$\rho v_2^2 = \rho v_3^2 = c_{44} \tag{2}$$

v_1 is the velocity of the longitudinally polarized wave, v_2 and v_3 are the velocities of the shear waves, c_{ij} are the elastic constants, and ρ is the density of the crystal. The particle displacement for the transverse waves can be in any direction lying in the plane perpendicular to the direction of travel of the wave.

2. Sound propagation is in the [110] direction:

$$\rho v_1^2 = \tfrac{1}{2}(c_{11} + c_{12}) + c_{44} \tag{3}$$

$$\rho v_2^2 = \tfrac{1}{2}(c_{11} - c_{12}) \tag{4}$$

and

$$\rho v_3^2 = c_{44} \tag{5}$$

The particle displacement for v_2 is in the plane of the (110) face; that is, the wave is polarized parallel to the [110] direction. The particle displacement for v_3 is perpendicular to the (110) face; that is, the wave is polarized parallel to the [001] direction.

3. Sound propagation is in the [111] direction:

$$\rho v_1^2 = \tfrac{1}{3}(c_{11} + 2c_{12} + 4c_{44}) \tag{6}$$

and

$$\rho v_2^2 = \rho v_3^2 = \tfrac{1}{3}(c_{11} - c_{12} + c_{44}) \tag{7}$$

Again the particle displacement for the transverse waves can be in any direction lying in the plane perpendicular to the direction of travel of the wave.

It is observed from these equations that at least three sound-velocity measurements must be made on an isometric crystal to determine the elastic constants.

The condition that a material be elastically isotropic is that[2,16]

$$c_{11} - c_{12} = 2c_{44} \tag{8}$$

so that $2c_{44}/(c_{11}-c_{12})$ is equal to unity. The anisotropy factor A, which expresses the deviation from unity of a cubic crystal, is then given by

$$A = 2c_{44}/(c_{11} - c_{12}) \tag{9}$$

This is the square of the ratio of velocities of shear waves propagating in the [100] and [110] directions.

c' and c'' are defined by the relationships:

$$c' = (c_{11} + c_{12} - 2c_{44})/2 \tag{10}$$

$$c'' = (c_{11} - c_{12})/2 \tag{11}$$

The adiabatic compressibility is given by

$$\beta_s = 3/(c_{11} + 2c_{12}) \tag{12}$$

Atomic Arrangement

We briefly review the structure of the fluorides studied in this investigation.[17] Some pertinent data are given in table 2. LiF and NaF have the sodium chloride type of ionic arrangement whereas CaF_2, SrF_2, and BaF_2 have the fluorite structure. In the NaCl type there are eight cation-anion contacts per stoichiometric molecule and vice versa; in the fluorite type, however, each cation is surrounded by eight anions at the corners of an enclosing cube, whereas an anion is at the center of a regular tetrahedron of cations. In the [100] and [110] directions in LiF and NaF, planes are populated with both anions and cations. For the other fluorides, planes of anions and cations alternate in the [100] direction whereas in the [110] direction the planes are populated with both anions and cations. There are alternate layers of cations only and anions only in the [111] direction for both types of atomic arrangement.

TABLE 2. STRUCTURAL DATA FOR CERTAIN FLUORIDES OF CRYSTAL CLASS O_h^5.

Ionic Radii, angstroms	Li^+	Na^+	Ca^{++}	Sr^{++}	Ba^{++}	F^-
	0.60	0.95	0.99	1.13	1.35	1.36
Radius Ratio	Li^+/F^-	Na^+/F^-	Ca^{++}/F^-	Sr^{++}/F^-	Ba^{++}/F^-	
	0.441	0.699	0.728	0.831	0.993	
Interionic Distance, angstroms	LiF	NaF	CaF_2	SrF_2	BaF_2	
	2.009	2.307	2.36	2.50	2.68	

Li^+ has a very small ionic radius (table 2); this leads to marked differences in the properties of Li compounds from those of the other alkali metals of the same structure type. Because of the small radius ratio in LiF each anion approaches contact not only with the Li^+ ions but also with other anions. This causes the repulsive forces to be larger than they would be for either anion-cation or anion-anion contact alone. Thus equilibrium is established with a cation-anion distance larger than twice the radius of the anion. In view of the above we can expect the elastic properties of LiF to be quite different from those of NaF, and this is found to be the case.

EXPERIMENTAL PROCEDURE

For the experimental determination of sound velocities in the fluoride crystals, the pulse-echo method described by Redin was employed.[18] However, it was necessary to make some modifications in instrument settings and procedure. These are given in the appendix. Briefly the method consists in propagating a short pulse of sound, generated by a piezoelectric transducer down a cylindrical crystal specimen of known orientation. Either the generating transducer or a receiver on the opposite end of the specimen picks up the reflected waves, which are then observed on a cathode-ray oscilloscope. Thus the transit time of the pulse can be determined.

Reagent-grade crystals of the fluorides for this investigation were obtained commercially.* Requirements were that they be single crystals machined to right-circular cylinders coaxial with a specified crystallographic direction to within ±2°. These directions were [100], [110], and [111]. Lengths of crystals were ½, ¾, and 1 inch, and diameters were ¾ and ⅝ inch. The end surfaces of each crystal were rendered plane-parallel to within 1 mil. Crystals were stored over a desiccant when not in use.

Each crystal was checked for coincidence of the cylinder axis with the specified crystallographic direction by the Laue back-reflection technique prior to sound-velocity measurements.[19,20] All crystals, including those which had required reorientation by machining of the end faces, were annealed for 24 hours at 400°C before sound-velocity measurements were made.

Transducers and receivers were ½-inch-diameter X-cut and Y-cut quartz crystals, gold-plated over chromium plate on both faces, and had a fundamental resonance frequency of 10 MHz within ±1 percent. These were also purchased commercially.**

The specimen holder for sound-velocity measurements from liquid-nitrogen temperatures to room temperature has been described.[21] In this holder the crystal is completely enclosed, so that the sample is protected from condensed moisture and ice. Plating of the cylindrical wall of the crystal was unnecessary, since a grounded silver sleeve provided sufficient shielding.

For measurement of low temperatures, copper-constantan thermocouples referenced at the ice point (0°C) and calibrated at the boiling point of liquid nitrogen (77.4°K) were used.

Further details concerning the experimental procedures are given in the appendix.

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*Harshaw Chemical Company, Cleveland, Ohio, and Valpey Corporation, Newport Beach, California

**Valpey Corporation, Newport Beach, California

RESULTS AND DISCUSSION

Elastic Constants

Measured values of sound velocity versus temperature for the fluoride crystals investigated are depicted in figures 1 to 5. Direction of propagation and wave type are given in the captions. The velocity of the longitudinal wave is always higher than that of the corresponding shear wave. Insofar as can be determined from the experimental data, the relationship between velocity and temperature is a linear one, the velocity declining with temperature rise (density decrease).

Values of the thermal expansion α *(T)* as a function of temperature, which are required in correcting for changes in path length and density between 90° and 300°K, are given by Riano for LiF and NaF.[22] Values for CaF_2 were obtained from the International Critical Tables.[23] Since the room-temperature values of α *(T)* for SrF_2 and BaF_2 differ from the value for CaF_2 by 3 and 10 percent, respectively, and since the trio have the same crystal structure, it was assumed

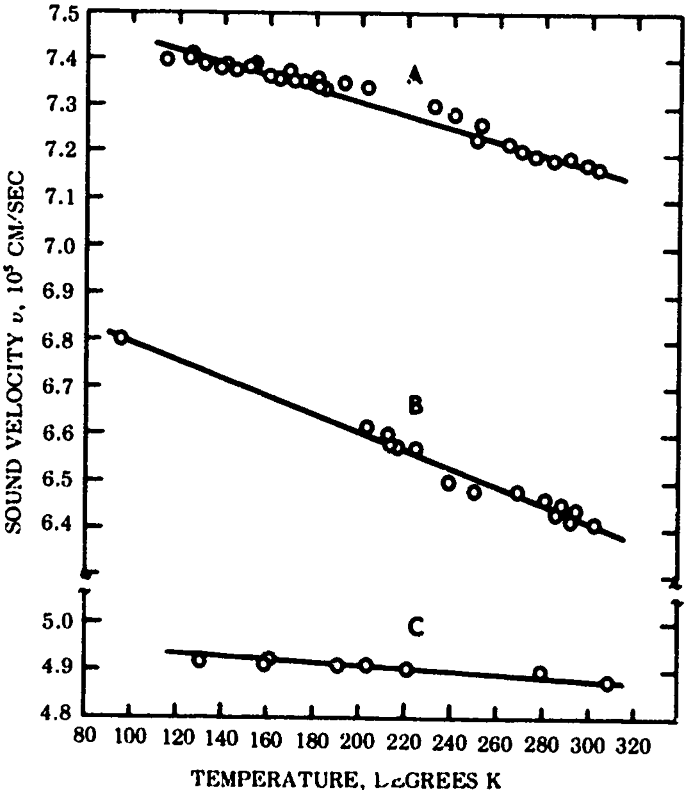

Figure 1. Variation of sound velocities with temperature in lithium fluoride (LiF): (A)[110] longitudinal, (B)[100] longitudinal, and (C)[100] shear waves.

that the temperature dependence of α(T) is the same; that is, the α(T) versus T curves are parallel. The expansion coefficients for SrF_2 and BaF_2 were then computed from those of CaF_2 by multiplying the latter by the ratio of the room-temperature values for the two crystals.

Densities of LiF and NaF at 0°, -79°, and -184°C were determined by Henglein.[24] Densities of representative crystals used in this work were measured at room temperature. Since densities at room temperature were known and the expansion coefficients had been estimated for lower temperatures, the densities were then calculated for these same temperatures. Such a procedure was sufficiently accurate for this investigation.

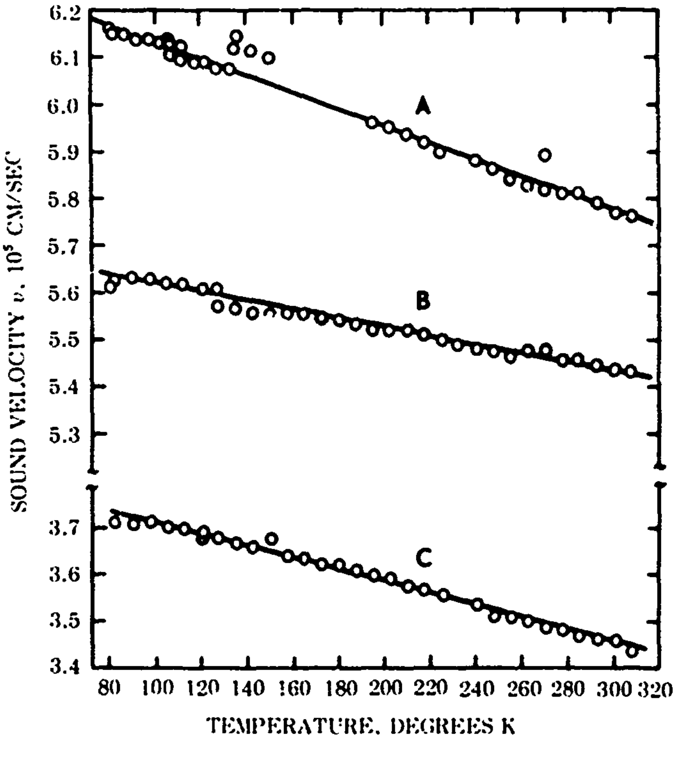

Figure 2. Variation of sound velocities with temperature in sodium fluoride (NaF): (A) [100] longitudinal, (B) [111] longitudinal, and (C) [111] shear waves.

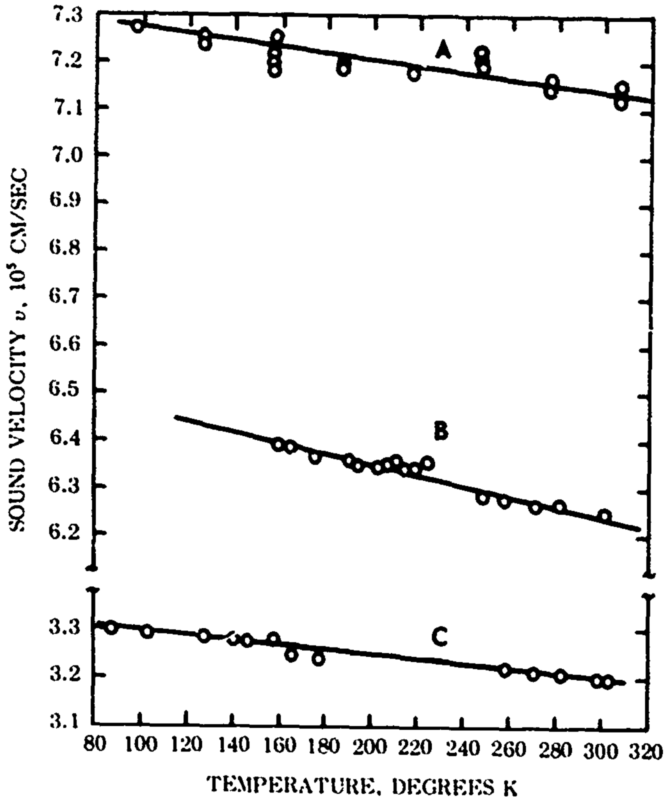

Figure 3. Variation of sound velocities with temperature in calcium fluoride (CaF$_2$): (A) [100] longitudinal, (B) [111] longitudinal, and (C) [100] shear waves.

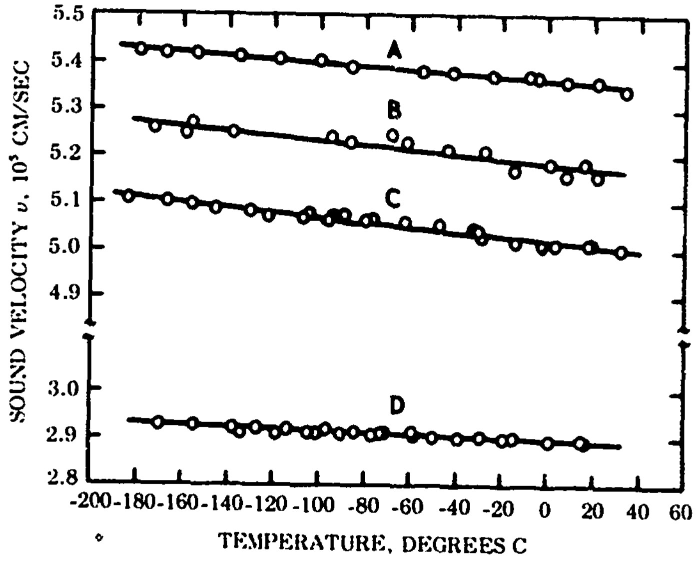

Figure 4. Variation of sound velocities with temperature in strontium fluoride (SrF$_2$): (A) [100] longitudinal, (B) [110] longitudinal, (C) [111] longitudinal, and (D) [111] shear waves.

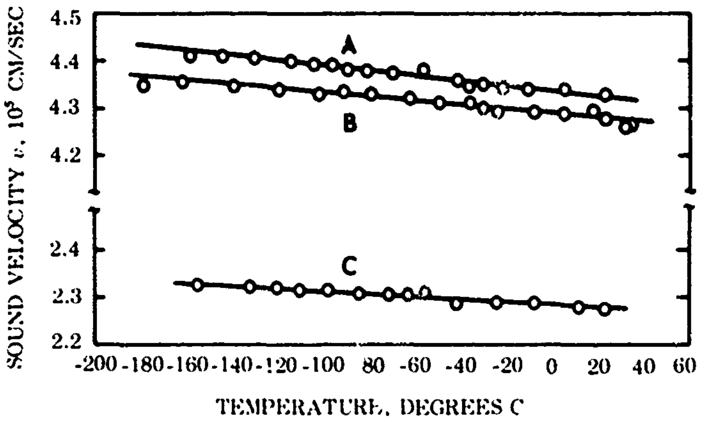

Figure 5. Variation of sound velocities with temperature in barium fluoride (BaF_2). (A) [111] longitudinal, (B) [100] longitudinal, and (C) [100] shear waves.

Elastances were computed by use of equations (1) to (7), velocities having been taken from the smoothed curves of figures 1 to 5. Data are presented in table 3 and plotted in figures 6 to 10. Most of the curves are nonlinear. All decline with rise in temperature except the c_{12} curve for NaF, which rises.

TABLE 3. ELASTIC CONSTANTS OF CERTAIN FLUORIDES AT LOW TEMPERATURES (Continued through page 18).

Temperatures, degrees Kelvin	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
			LiF		
120	12.22	4.235	6.531	1.636	0.145
130	12.14	4.205	6.518	1.643	0.146
140	12.06	4.179	6.503	1.650	0.147
150	11.99	4.150	6.489	1.655	0.148
160	11.91	4.120	6.476	1.663	0.149
170	11.83	4.092	6.462	1.670	0.150
180	11.75	4.064	6.448	1.678	0.151
190	11.68	4.035	6.433	1.683	0.152
200	11.60	4.005	6.420	1.691	0.153
210	11.53	3.977	6.405	1.696	0.154
220	11.45	3.950	6.381	1.702	0.155
230	11.38	3.920	6.378	1.710	0.156
240	11.31	3.893	6.363	1.716	0.157
250	11.23	3.865	6.350	1.724	0.158
260	11.15	3.837	6.337	1.733	0.159
270	11.08	3.808	6.321	1.738	0.160
280	11.01	3.780	6.307	1.745	0.161
290	10.93	3.750	6.293	1.753	0.163
300	10.86	3.724	6.280	1.760	0.164

TABLE 3 (Continued).

Temperature, degrees Kelvin	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
	NaF				
90	10.75	1.972	3.024	0.689	0.204
100	10.68	1.978	3.013	0.692	0.205
110	10.60	1.985	3.002	0.697	0.206
120	10.53	1.990	2.993	0.701	0.207
130	10.46	1.998	2.983	0.705	0.208
140	10.39	2.003	2.972	0.709	0.208
150	10.32	2.01	2.965	0.714	0.209
160	10.25	2.017	2.955	0.718	0.210
170	10.18	2.022	2.947	0.722	0.211
180	10.11	2.030	2.938	0.727	0.212
190	10.04	2.037	2.930	0.732	0.213
200	9.98	2.042	2.920	0.736	0.213
210	9.91	2.050	2.912	0.741	0.214
220	9.85	2.055	2.902	0.745	0.215
230	9.78	2.060	2.895	0.750	0.216
240	9.72	2.068	2.888	0.755	0.217
250	9.65	2.074	2.880	0.760	0.217
260	9.59	2.080	2.870	0.764	0.218
270	9.52	2.088	2.862	0.770	0.219
280	9.460	2.093	2.855	0.775	0.220
290	9.40	2.100	2.848	0.780	0.221
300	9.33	2.105	2.840	0.786	0.222

TABLE 3 (Continued).

Temperature, degrees Kelvin	Elastic Contents, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
	CaF$_2$				
90	16.91	–	3.480	–	–
100	16.89	–	3.471	–	–
110	16.86	–	3.460	–	–
120	16.83	4.557	3.450	0.562	0.116
130	16.79	4.523	3.440	0.561	0.116
140	16.76	4.490	3.428	0.559	0.117
150	16.73	4.455	3.418	0.557	0.117
160	16.69	4.422	3.409	0.556	0.117
170	16.65	4.390	3.400	0.555	0.118
180	16.62	4.355	3.388	0.552	0.118
190	16.58	4.321	3.377	0.551	0.119
200	16.54	4.287	3.365	0.549	0.119
210	16.50	4.255	3.352	0.547	0.120
220	16.46	4.220	3.342	0.546	0.120
230	16.41	4.186	3.330	0.545	0.121
240	16.37	4.150	3.320	0.543	0.122
250	16.33	4.117	3.307	0.542	0.122
260	16.29	4.082	3.296	0.540	0.123
270	16.25	4.048	3.285	0.538	0.123
280	16.21	4.015	3.275	0.537	0.124
290	16.16	3.982	3.262	0.536	0.124
300	16.12	3.948	3.251	0.534	0.125

TABLE 3 (Continued).

Temperature, degrees Kelvin	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
			SrF_2		
90	12.53	4.527	3.232	0.808	0.139
100	12.52	4.518	3.223	0.806	0.139
110	12.51	4.508	3.212	0.803	0.139
120	12.49	4.500	3.202	0.802	0.140
130	12.48	4.490	3.192	0.799	0.140
140	12.47	4.480	3.181	0.796	0.140
150	12.45	4.470	3.170	0.794	0.140
160	12.43	4.460	3.158	0.792	0.141
170	12.42	4.449	3.147	0.790	0.141
180	12.40	4.438	3.135	0.788	0.141
190	12.38	4.428	3.123	0.786	0.141
200	12.36	4.417	3.111	0.784	0.142
210	12.35	4.405	3.100	0.781	0.142
220	12.33	4.393	3.088	0.778	0.142
230	12.30	4.382	3.075	0.777	0.142
240	12.28	4.370	3.062	0.774	0.143
250	12.26	4.359	3.050	0.772	0.143
260	12.24	4.347	3.038	0.770	0.143
270	12.22	4.340	3.025	0.768	0.144
280	12.20	4.322	3.012	0.765	0.144
290	12.18	4.310	3.002	0.763	0.144
300	12.16	4.298	2.993	0.761	0.145

TABLE 3 (Continued).

Temperature, degrees Kelvin	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor *A*	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
			BaF_2		
100	9.23	4.352	2.648	1.086	0.167
110	9.22	4.342	2.641	1.083	0.168
120	9.20	4.332	2.636	1.083	0.168
130	9.18	4.321	2.629	1.082	0.168
140	9.17	4.310	2.622	1.079	0.169
150	9.15	4.302	2.617	1.080	0.169
160	9.14	4.291	2.608	1.076	0.169
170	9.12	4.280	2.601	1.075	0.170
180	9.10	4.268	2.595	1.074	0.170
190	9.08	4.255	2.588	1.073	0.171
200	9.06	4.242	2.580	1.071	0.171
210	9.04	4.230	2.572	1.069	0.171
220	9.02	4.218	2.565	1.068	0.172
230	9.00	4.205	2.557	1.067	0.172
240	8.98	4.190	2.548	1.064	0.173
250	8.96	4.178	2.540	1.062	0.173
260	8.94	4.165	2.532	1.061	0.174
270	8.91	4.150	2.523	1.060	0.174
280	8.89	4.138	2.515	1.059	0.175
290	8.87	4.126	2.507	1.057	0.175
300	8.85	4.112	2.498	1.054	0.176

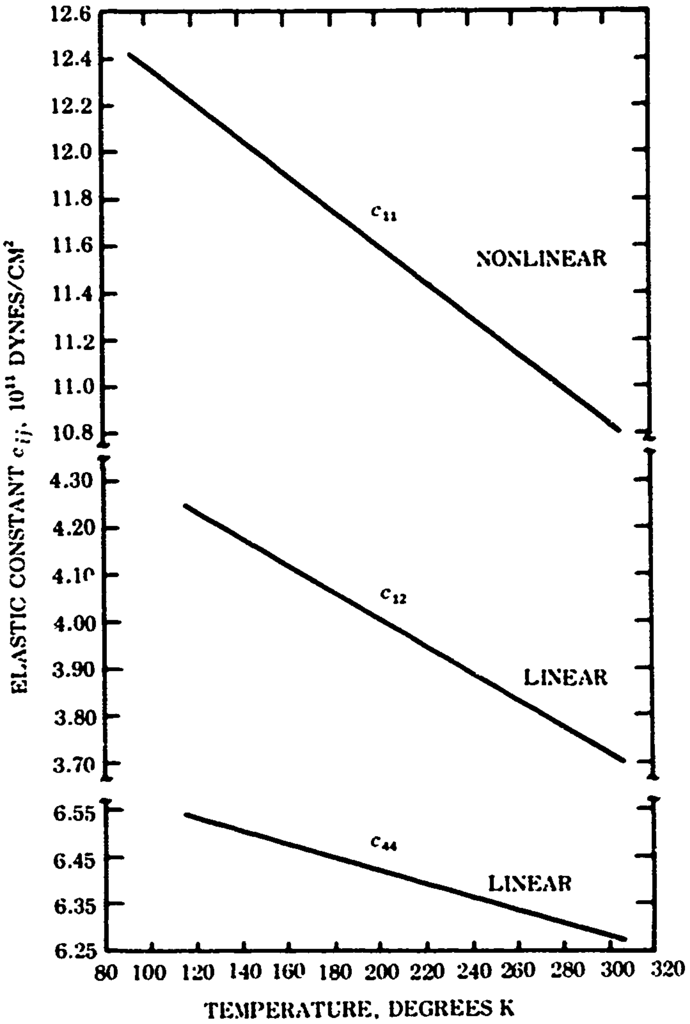

Figure 6. Temperature dependence of the elastic constants c_{11}, c_{12}, and c_{44} of lithium fluoride (LiF).

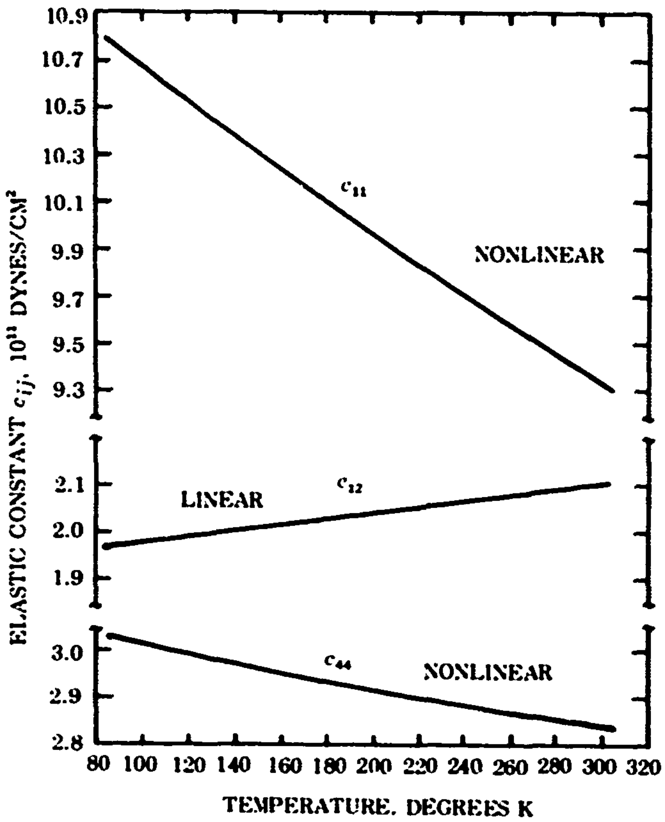

Figure 7. Temperature dependence of the elastic constants c_{11}, c_{12}, and c_{44} of sodium fluoride (NaF).

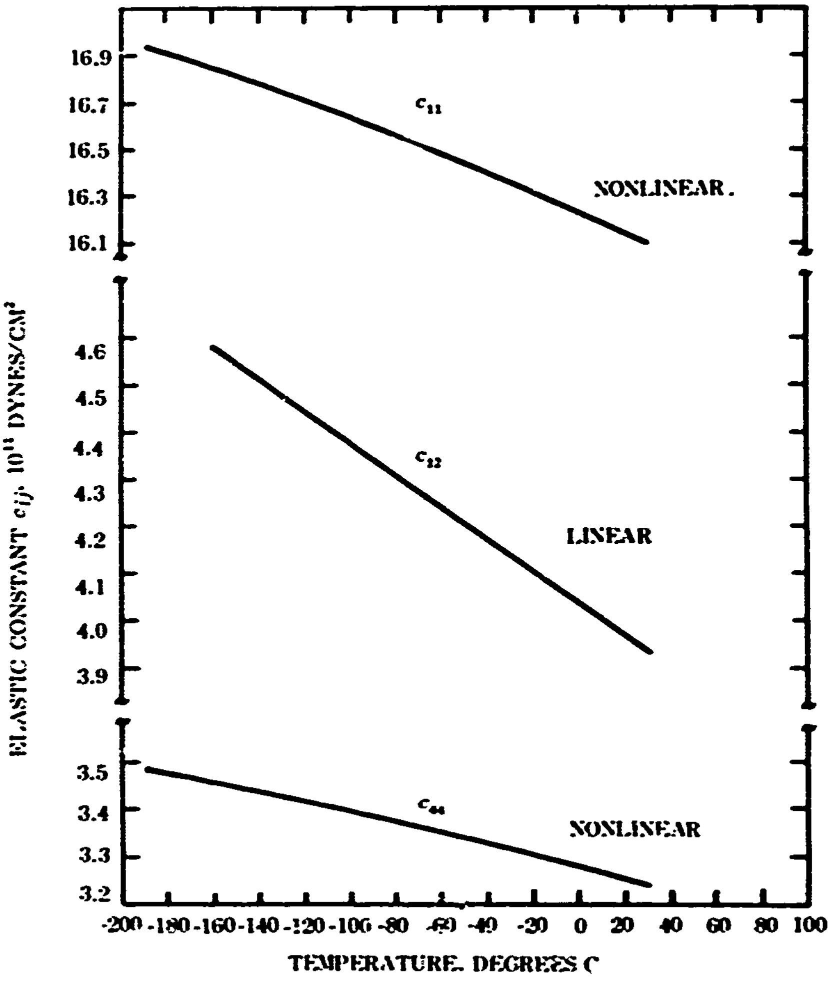

Figure 8. Temperature dependence of the elastic constants c_{11}, c_{12}, and c_{44} of calcium fluoride (CaF$_2$).

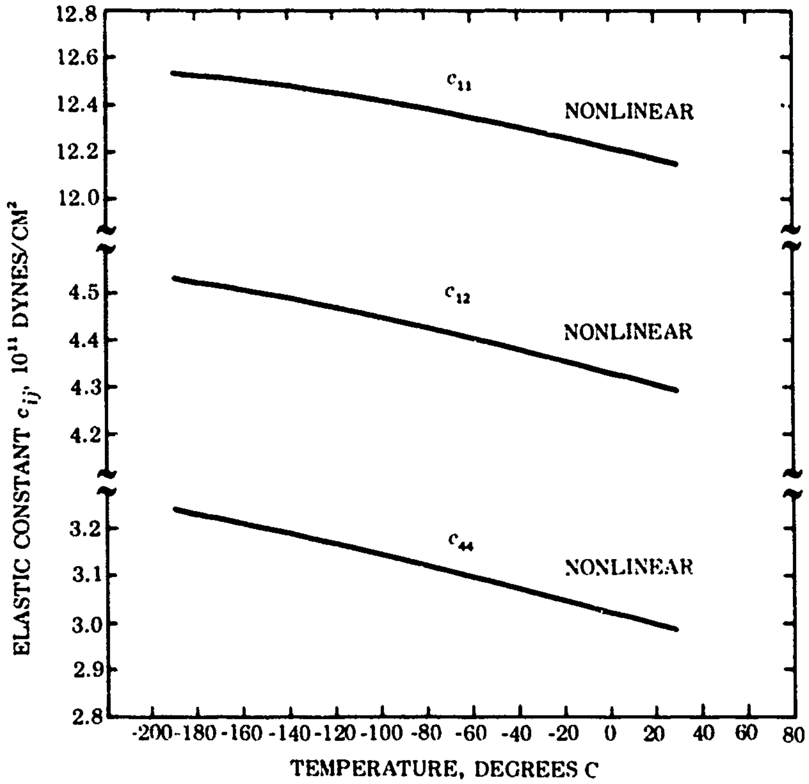

Figure 9. Temperature dependence of the elastic constants c_{11}, c_{12}, and c_{44} of strontium fluoride (SrF_2).

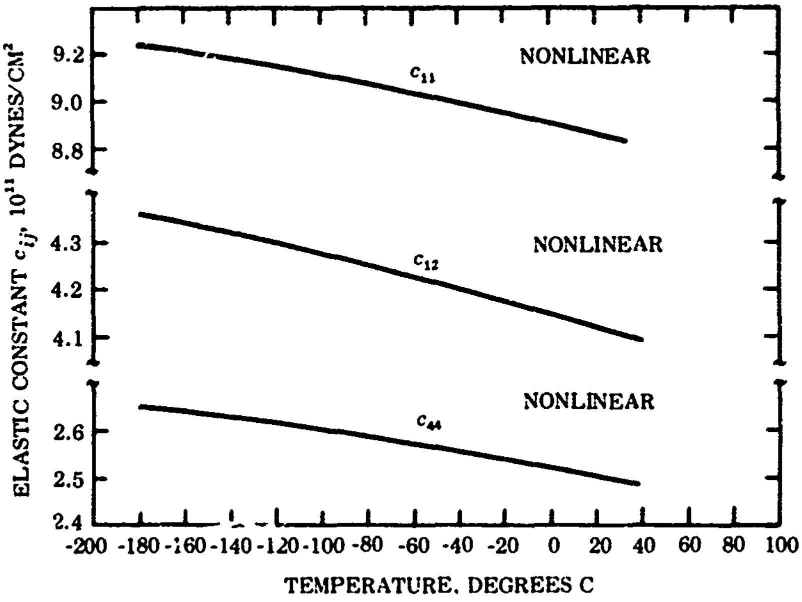

Figure 10. Temperature dependence of the elastic constants c_{11}, c_{12}, and c_{44} of barium fluoride (BaF_2).

c_{11} and c_{12} for NaF from room temperature to 500°C and c_{44} from room temperature to 800°C have been evaluated from data given by Nikaranov and Stepanov and values are listed in table 4.[25] Their values at 290°K as compared to ours are $c_{11} = 9.431, 9.40$; $c_{12} = 2.038, 2.100$; $c_{44} = 2.829, 2.848$ ($\times 10^{11}$dynes/cm^2), which is very good agreement indeed.

TABLE 4. ELASTIC CONSTANTS OF NaF AT HIGH TEMPERATURES.

Temperature, degrees Kelvin	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
	c_{11}	c_{12}	c_{44}		
293	9.431	2.038	2.829	0.761	0.223
323	9.300	2.014	2.807	0.773	0.229
373	8.963	1.894	2.773	0.785	0.235
423	8.713	1.876	2.735	0.800	0.241
473	8.446	1.843	2.701	0.818	0.247
523	8.196	1.811	2.665	0.835	0.254
573	7.872	1.669	2.633	0.849	0.268
623	7.629	1.633	2.598	0.867	0.275
673	7.382	1.590	2.563	0.885	0.284
723	7.079	1.461	2.528	0.900	0.300
773	6.843	1.418	2.494	0.919	0.310
823	–	–	2.460	–	–
873	–	–	2.425	–	–
923	–	–	2.393	–	–
973	–	–	2.356	–	–
1023	–	–	2.322	–	–
1073	–	–	2.288	–	–
			Extrapolated Data		
0	11.372	2.669	3.036	0.698	0.180
1265	4.523	1.007	2.152	1.224	0.459

Elastic constants for CaF_2 and SrF_2 at very low temperatures are given in tables 5 and 6, respectively. Where values overlap with ours, good agreement is found except for Huffman and Norwood's values of c_{12} for CaF_2, which are about 20 percent higher. However, their values for c_{12} are also higher than those of other investigators. The upward trend in the magnitudes of the constants as the temperature is lowered continues until absolute zero is approached, a region where the constants change very little.

TABLE 5. ELASTIC CONSTANTS OF CaF_2 AT LOW TEMPERATURES.

Temperature, degrees Kelvin	Density ρ, g/cm^3	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
		c_{11}	c_{12}	c_{44}		
4.2	3.2107	17.4	5.6	3.593	0.61	0.10
20	3.2107	17.4	5.4	3.593	0.60	0.11
40	3.2106	17.3	5.5	3.586	0.61	0.11
60	3.2102	17.3	5.3	3.576	0.60	0.11
80	3.2094	17.2	5.3	3.562	0.60	0.11
100	3.2081	17.1	5.4	3.548	0.61	0.11
120	3.2063	17.0	5.3	3.533	0.60	0.11
140	3.2042	16.9	5.5	3.518	0.62	0.11
160	3.2017	16.8	5.4	3.506	0.62	0.11
180	3.1991	16.7	5.5	3.487	0.62	0.11
200	3.1962	16.6	5.7	3.465	0.64	0.11
220	3.1931	16.5	5.6	3.449	0.63	0.11
240	3.1898	16.5	5.6	3.429	0.63	0.11
260	3.1864	16.4	5.7	3.409	0.64	0.11
280	3.1830	16.4	5.4	3.390	0.62	0.11
300	3.1795	16.4	5.3	3.370	0.61	0.11

TABLE 6. ELASTIC CONSTANTS OF SrF_2 AT LOW TEMPERATURES.

Temperature, degrees Kelvin	Density ρ, g/cm^3	Elastic Constants, 10^{11} dynes/cm^2			Elastic Anisotropy Factor A	Adiabatic Compressibility β_s, 10^{-11} cm^2/dyne
		c_{11}	c_{12}	c_{44}		
4.2	4.321	12.87	4.748	3.308	0.815	0.134
20	4.321	12.88	4.747	3.308	0.813	0.134
40	4.320	12.86	4.736	3.304	0.813	0.134
60	4.320	12.85	4.716	3.297	0.811	0.135
80	4.319	12.82	4.695	3.291	0.810	0.135
100	4.316	12.79	4.664	3.280	0.807	0.136
120	4.314	12.75	4.626	3.264	0.804	0.136
140	4.311	12.71	4.592	3.250	0.801	0.137
160	4.308	12.66	4.554	3.235	0.798	0.138
180	4.304	12.62	4.251	3.219	0.795	0.138
200	4.300	12.58	4.485	3.205	0.792	0.139
220	4.295	12.53	4.446	3.191	0.789	0.140
240	4.290	12.48	4.410	3.176	0.787	0.141
260	4.286	12.44	4.376	3.161	0.784	0.142
280	4.281	12.39	4.342	3.144	0.781	0.142
300	4.277	12.35	4.305	3.128	0.778	0.143

Adiabatic Compressibility β_S

Compressibilities were calculated by use of equation (12) and are given in tables 3 to 6. The increase in magnitude with rise in temperature is small. Apparently there is correlation between the ratio of the radii of the cations and the ratio of the compressibilities. This observation is illustrated in table 7 for crystals at 300°K. The greater the radius of the cation ($R_M{}^+$ or $R_M{}^{++}$), the greater the compressibility.

TABLE 7. CORRELATION BETWEEN RATIO OF COMPRESSIBILITIES AND RATIO OF RADII OF CATIONS AT 300°K.

Crystal	$R_M{}^+/R_{Li}{}^+$	β/β_{LiF}
LiF	1.00	1.00
NaF	1.58	1.35
Crystal	$R_M{}^{++}/R_{Ca}{}^{++}$	β/β_{CaF_2}
CaF_2	1.00	1.00
SrF_2	1.14	1.16
BaF_2	1.36	1.41

Anisotropy Factor *A*

Values of this constant are also given in tables 3 to 6. This factor rises with temperature for LiF and NaF but declines with temperature for the other fluorides. Only for LiF and BaF_2 are the anisotropy factors greater than 1. In fact, the values for BaF_2 are so nearly unity that this crystal might be expected to behave very much like an isotropic solid under certain experimental conditions. However, the Cauchy relations for cubic crystals ($c_{12} = c_{44}$; $c_{11} = 3c_{44}$) do not hold for any of these fluorides.

Thermoelastic Constants

Rate of change of elastic-stiffness coefficients with temperature can best be studied, perhaps, by an examination of the thermoelastic constants. The thermoelastic constant τ_{ij}, at a stated temperature t, is defined by the relation[6]

$$\tau_{ij} = d \log c_{ij}/dt = (1/c_{ij})\,(dc_{ij}/dt) \tag{13}$$

Obviously a thermoelastic-constant-versus-temperature curve can be deduced from an elastance-versus-temperature curve by determining the slope of the latter at a series of points. Although such a procedure appears to be sufficiently straightforward, actually it is not always easy to determine accurately the slopes of such curves, for often the curvature is small. For example, refer to the elastance curves for NaF in figure 7.

Corresponding to equations (3) and (4), respectively,

$$\tau' = (\tau_{11} + \tau_{12} + 2\tau_{44})/2 \tag{14}$$

$$\tau'' = (\tau_{11} - \tau_{12})/2 \tag{15}$$

Since $\rho v_{100}^2 = c_{11}$

then $$(2/v_{100})\,(dv_{100}/dT) + (1/\rho)(d\rho/dT) = (1/c_{11})\,(dc_{11}/dT) \tag{16}$$

$$\tau_{11}$$

Also, since

$$\rho v_{100}^2 = (c_{11} + c_{12} + 2c_{44})/2 = c' \tag{17}$$

then $$(2/v_{110})\,(dv_{110}/dT) + (1/\rho)\,(d\rho/dT) = (1/c')\,(dc'/dT) \tag{18}$$

$$= \tau'$$

Equations (16) and (18) show the relation of the velocity and density-temperature coefficients to the corresponding thermoelastances.

$$(\tau'/\tau_{11}) = \frac{(2/v_{110})\,(dv_{110}/dT) + (1/\rho)\,(d\rho/dT)}{(2/v_{100})\,(dv_{100}/dT) + (1/\rho)\,(d\rho/dT)} \tag{19}$$

Over a small temperature range in which the change in density can be ignored

$$\frac{(1/v_{110})\,(dv_{110}/dT)}{(1/v_{100})\,(dv_{100}/dT)} \cong \tau'/\tau_{11} \tag{20}$$

that is, τ'/τ_{11} is the ratio of longitudinal-velocity-temperature coefficients in the [110] and [100] directions.

Values for the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} for the five fluorides investigated, over the temperature range 100° to 300°K, were deduced from the elastance-versus-temperature curves of figures 6 to 10. Plotted points in figures 11 to 15 indicate values of the corresponding elastic-constant curves at which the slopes were determined. These figures show that:

1. Curves for LiF, CaF_2, and SrF_2 are roughly linear and decline with temperature rise.

2. The τ_{11} and τ_{44} curves for NaF show maxima. All remaining curves decline monotonically with increase in temperature.

3. Values of τ_{12} for NaF are positive; all other values for these fluorides are negative.

4. The order of the constants is as follows:

LiF: $\tau_{12} < \tau_{11} < \tau_{44}$;
NaF: $\tau_{11} < \tau_{44} < \tau_{12}$;
CaF_2: $\tau_{12} < \tau_{44} < \tau_{11}$;
SrF_2 and BaF_2: $\tau_{44} < \tau_{12} < \tau_{11}$.

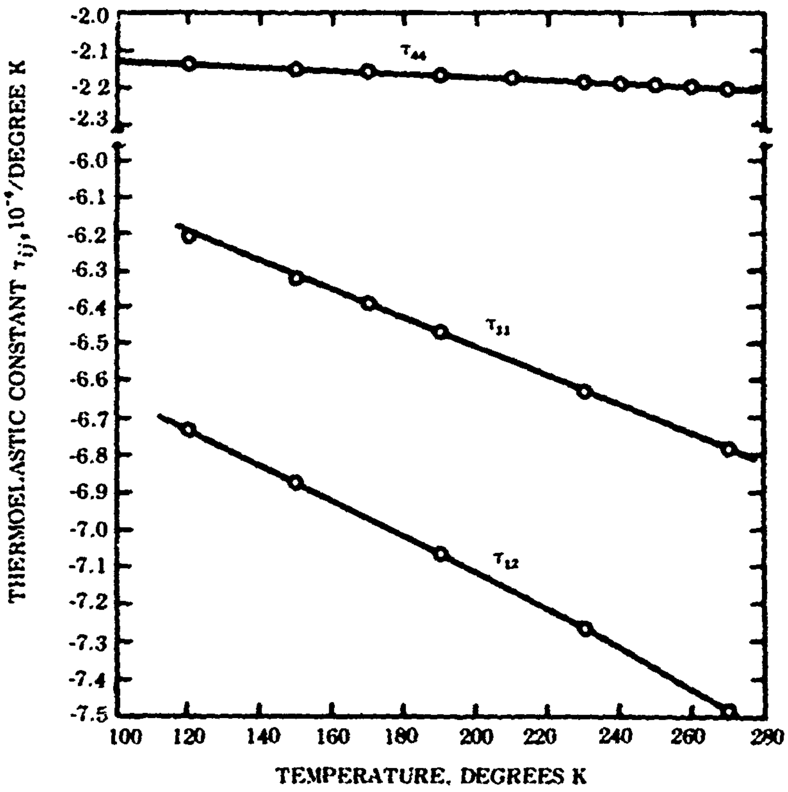

Figure 11. Variation of the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} of lithium fluoride (LiF) with temperature in degrees Kelvin.

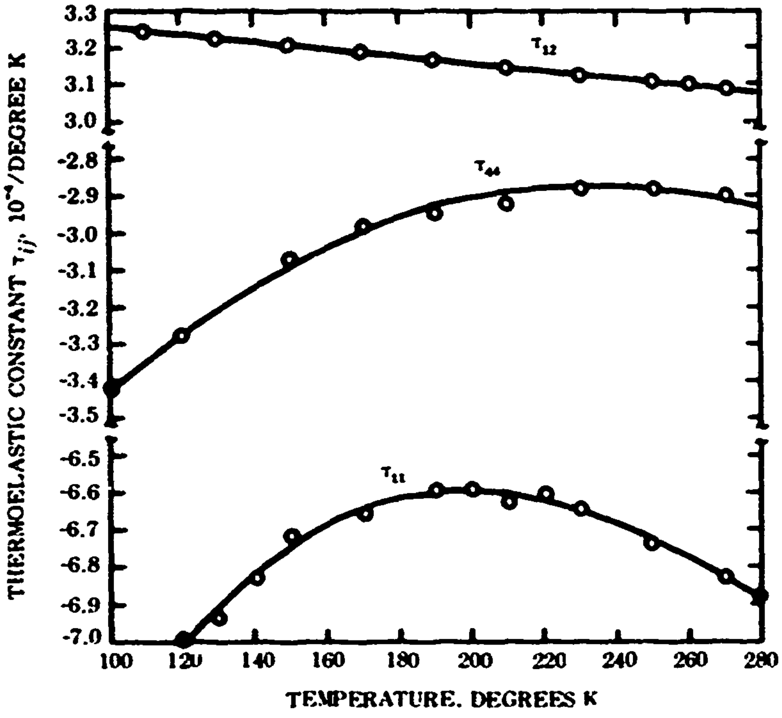

Figure 12. Variation of the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} of sodium fluoride (NaF) with temperature in degrees Kelvin.

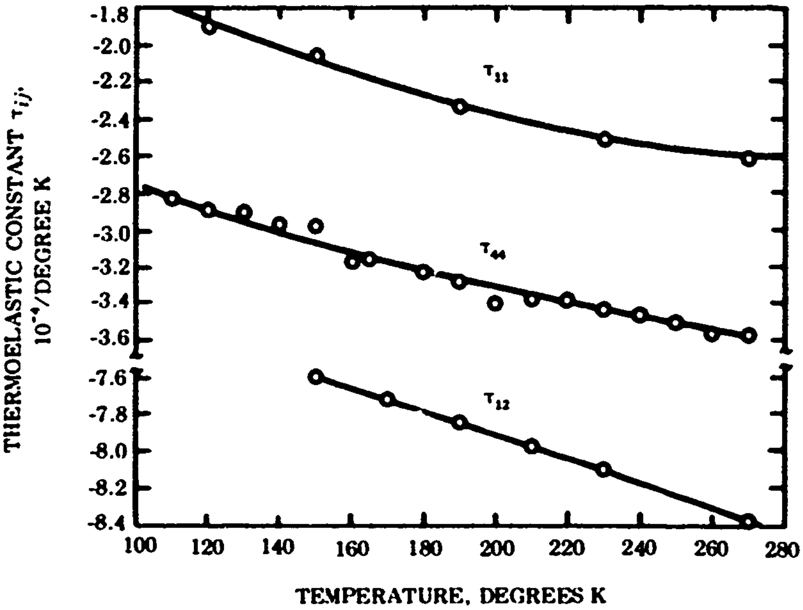

Figure 13. Variation of the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} of calcium fluoride (CaF_2) with temperature in degrees Kelvin.

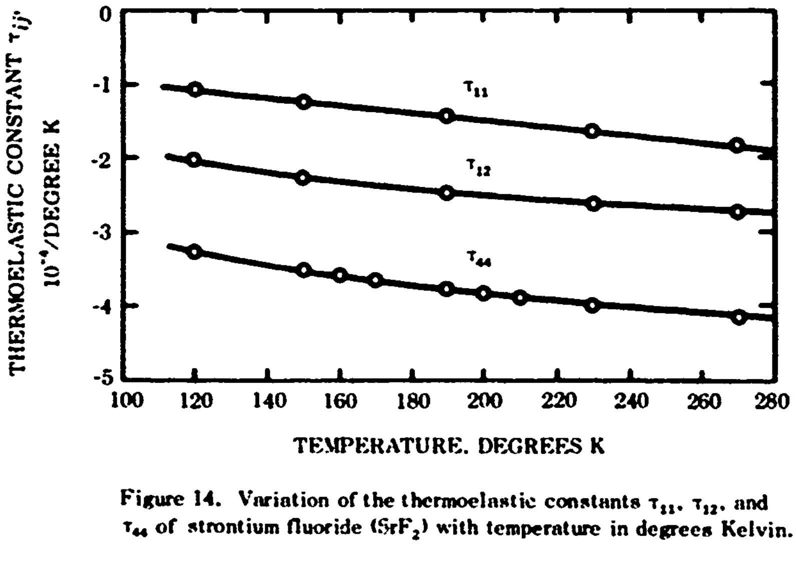

Figure 14. Variation of the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} of strontium fluoride (SrF_2) with temperature in degrees Kelvin.

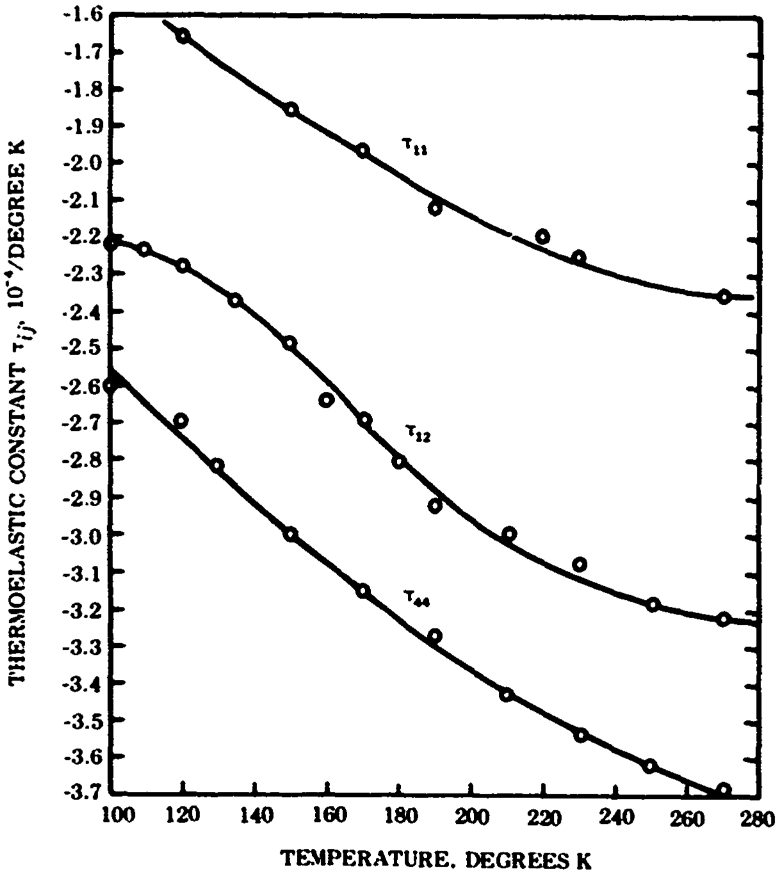

Figure 15. Variation of the thermoelastic constants τ_{11}, τ_{12}, and τ_{44} of barium fluoride (BaF_2) with temperature in degrees Kelvin.

Values of τ_{11} and τ_{44} for LiF and NaF at 0°C are compared with those of Haussühl in table 8.[4] His value of τ_{12} for LiF is omitted, since he states that it is uncertain because of the small experimentally measured value. Also, the sign of the constant could not be determined. Table 8 shows that results are in fair agreement. When the difficulties in deducing the thermoelastances are considered, the results agree about as well as can be expected.

TABLE 8. COMPARISON OF VALUES OF THERMOELASTANCES FOR LiF AND NaF AT 0°C.

Crystal	τ_{11}	τ_{12}	τ_{44}	Source
	10^{-4}/degree K			
LiF	-6.6	—	-2.8	Haussühl[4]
	-6.79	-7.5	-2.22	this work
NaF	-6.37	1.8	-2.1	Haussühl[4]
	-6.84	3.09	-2.91	this work

Further conclusions concerning the elastances can be drawn from the data of table 9 at the Kelvin temperatures of 130°, 200°, and 273°. τ_{11}, τ_{12}, and τ_{44} were taken from the curves of figures 11 to 15; τ', τ'', and τ'/τ_{11} were calculated by use of equations (14) and (15).

1. τ_{11} depends mainly on ionic arrangement and very little or not at all on the radius of the cation. At any one of the given temperatures, marked changes in numerical value occur only on passing from the NaCl type of structure to the fluorite type.

2. τ_{12} depends markedly on the radius of the cation. Not only are the numerical values for LiF and NaF very different, but values for LiF are positive, whereas those for NaF are negative.

3. τ_{44} tends to be a little higher numerically for the fluorite type of structure than for the NaCl type.

4. τ' tends to rise numerically with rise in temperature.

5. τ'/τ_{11} varies from one fluoride to the next but appears not to be temperature dependent.

The focusing tube for the X-ray beam had a single 0.5-mm pinhole. Film-to-specimen distance was 3.0 cm. A filter of 10-mil aluminum sheet, 2 inches in diameter, was placed at the center of the flat-plate camera to reduce fogging by scattered radiation. Blackening of weaker outer spots was reduced too severely if the filter was placed entirely over the film.

The procedure was first to mark each crystal on its cylindrical surface with two fiducial lines parallel to the axis of this surface and spaced 180° apart. The crystal could then be oriented in a specimen holder so that the plane of the fiducial lines was horizontal. Figure A1 shows the holder employed with a crystal in place for diffraction. A screw holds the crystal, which rests in a cylindrical trough, firmly in position. Mounted on the front of the holder is a linear piece of phosphor-bronze wire, which is parallel to the plane of the fiducial lines marked on the crystal. On exposure to X-rays this wire casts a shadow on the film which indicates the orientation of the crystal with respect to the diffraction pattern. A representative Laue back-reflection photograph is shown in figure A2.

Back-reflection diagrams were taken of both faces of each specimen to determine not only orientation but also whether these faces were plane-parallel and whether the crystal was a single one. If a specimen is a single crystal and the faces are plane-parallel, then the back-reflection diagrams from the faces will be identical provided the orientation in the crystal holder is the same in both cases. Patterns were analyzed by means of a Grenginger chart and a Wulff stereographic net as described in the literature.[19,20] Crystals showing misalignment greater than ±2° between cylinder axis and specified crystallographic direction were machined to the predetermined correction and again tested.

For orientation purposes the X-axis of all Y-cut quartz transducers was marked on one of the plated faces of these crystals by a diametrical line. Since the positions of the crystallographic axes in the fluoride crystals had been determined from X-ray photographs, it was then possible to orient the transducer correctly when necessary for mounting on the crystal face. As previously mentioned, this is required only when the direction of propagation of the plane-polarized transverse wave is in the [110] direction. For determination of velocity v_2, the X-axis of the transducer must be parallel to the [110] direction, and for determination of velocity v_3, parallel to the [001] direction.

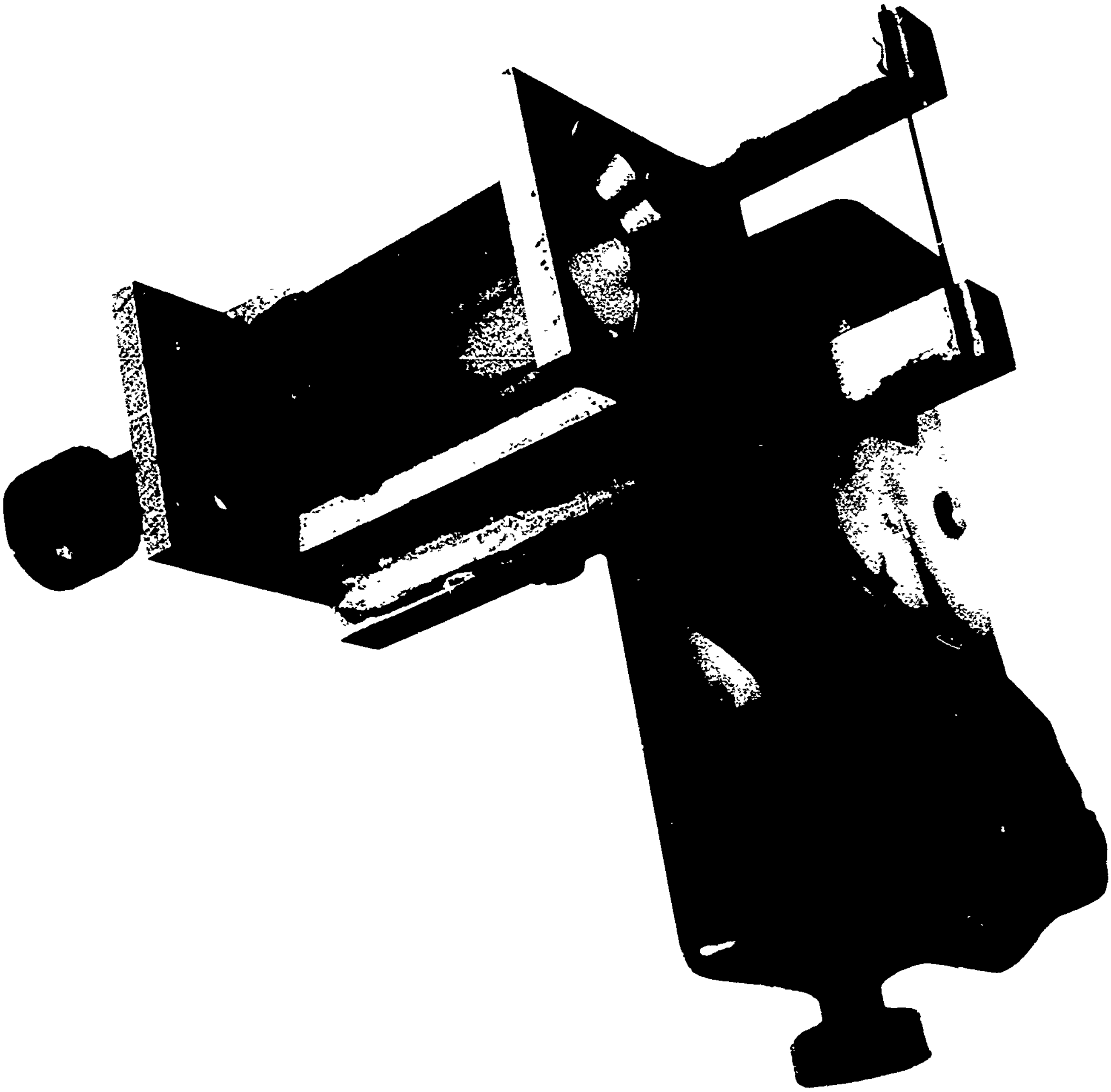

Figure A1. Specimen holder for Laue back-reflection X-ray diffraction.

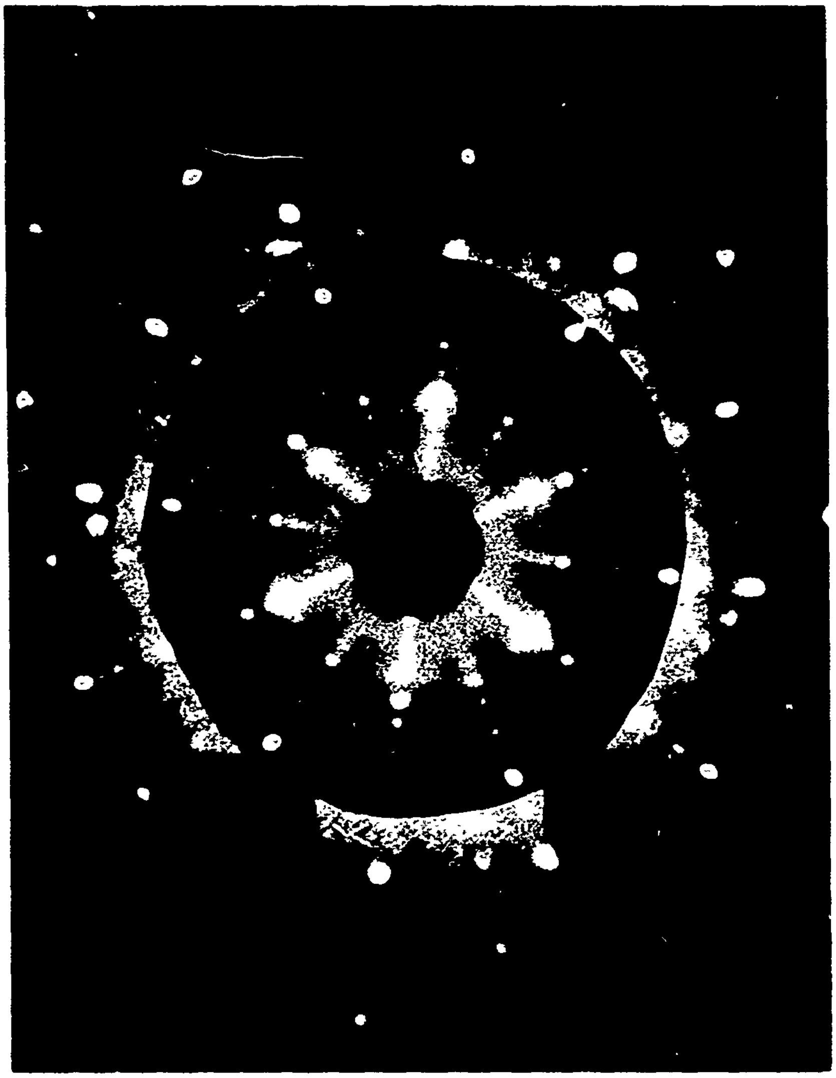

Figure A2. Laue back-reflection photograph, BaF_2, (100) face.

Polishing Technique

X-ray investigation by the method described showed that some of the crystals deviated more than the permissible ±2° from coincidence of the cylinder and crystallographic axes. The angle θ of the correction, which is the angle between the cylinder axis and the crystallographic axis, as determined by the back-reflection technique, is related to the correction Δ by

$$\Delta = D \tan \theta \tag{21}$$

where D is the diameter of the crystal.

Crystals to be corrected were properly oriented, and the distance was marked back from the face on the cylindrical surface at the point at which the maximum dimensional change was to be made. Usually both faces of such crystals needed correction. Faces also had to be rendered plane-parallel. If the required correction was small, it was made by hand, with number-400 silicon carbide paper on a glass plate. As polishing proceeded, the progress of the work was checked on a dial indicator.

When larger corrections were necessary, the crystal was placed in a special holder, then locked in a precision indexing head clamped to a drill press, and polished with a sanding disk mounted in the chuck. The faces of the holder were accurately parallel and the edges of the hole in which the crystal was fixed were perpendicular to the faces. The correction angle was set on the indexing head, the crystal having been correctly oriented. Finishing touches to the crystal were made by the first method.

Coupling Cements

No one cement was found suitable for binding quartz transducers to fluoride crystals over the entire range from liquid-nitrogen temperatures to room temperature. A number of oils, greases, low-molecular-weight alcohols, esters, etc., were tested for possible use as coupling cements. The range of usefulness of a substance as a bonding material was indicated by the appearance of the signal on the oscilloscope screen as the temperature was lowered, and the subsequent disappearance of the signal at a still lower temperature. However, some substances retained their usefulness as bonds down to the lowest temperature at which measurements were made, -178°C.

The range of a cement for a given kind of crystal was somewhat dependent on whether the transducers were X-cut or Y-cut.

The substances which proved most suitable were used subsequently in the work. The approximate temperature ranges over which they are applicable are given below:

1.2 Propane diol	-175° to -115°C
Methyl salicylate	-115° to -25°C
Phenyl salicylate	-25° to +35°C

If transit-time-versus-temperature data are taken for different lengths of crystal of the same type, the magnitudes of the observed velocities are not the same. This is the result of coupling-cement-transducer interference effects which are proportionately greater the shorter the crystal. The latter observation can be used to determine the required correction to the delay time, provided it is assumed that the absolute value of the correction is the same, irrespective of crystal length. It appears that this assumption is valid, provided that the faces of the crystals have been polished to the same degree, for it was found that for any given crystal the measured velocity was reproducible within the limits of experimental error. This means that the technique employed for forming the bonds yields concordant results.

If it is assumed that correction in delay time is independent of crystal length, the following procedure can be employed for determining the correction time t_c. t_c is that transit time which, when subtracted from the measured transit time, yields the actual delay time for the specimen. Let ℓ_1 and ℓ_2 be the lengths of two crystals of the same type where $\ell_1 > \ell_2$, t_{1m}, and t_{2m} are the corresponding measured transit times, and t_1 and t_2 are the time-delay times.

By assumption, then

$$t_1 = t_{1m} - t_c \tag{22}$$

and

$$t_2 = t_{2m} - t_c \tag{23}$$

By measurement $v_1 = v_2$,

$$v_1 = (\ell_1/t_1) = \ell_1/(t_{1m} - t_c) \tag{24}$$

$$v_2 = (\ell_2/t_2) = \ell_2/(t_{2m} - t_c) \tag{25}$$

so that

$$t_c = \frac{\ell_2\, t_{1m} - \ell_1\, t_{2m}}{\ell_2 - \ell_1} \tag{26}$$

and

$$v = \frac{\ell_2 - \ell_1}{t_{2m} - t_{1m}} \tag{27}$$

Three or more lengths of crystal should be used when this method is applied, and the results for different pairs compared. If the correction is found to be within the limits of experimental error, it can be neglected.

By way of example, studies on calcium fluoride crystals showed that the measured delay time was 0.2 percent too high.

Temperature Measurement

A copper-constantan thermocouple, with reference junction at the ice point, was used for determining the temperature of the fluoride crystal during the period in which sound-velocity measurements were made. Thermocouples were formed by heli-arc welding; those fabricated by other methods failed to yield reproducible results. The low-temperature junction was soft-soldered to one end of a strip of silver foil. The strip was wrapped around the middle of the crystal one and one half times with the thermocouple inside and then taped onto the crystal. Since the foil was also used as a grounding electrode, one lead of the thermocouple was grounded to the pulse-generating equipment.

Investigation showed that in the neighborhood of –160°C the temperature gradient along a 1-inch crystal was about 1.5°. When the experimental method employed is considered, some difference in the temperature of the crystal is to be expected before and after the transit time is determined on the oscilloscope. However, in no case did this difference exceed 0.5°C.

Possible Sources Of Error

Error in velocity determination is given by the following expression:

$$(dv)^2 = \left(\frac{\partial v}{\partial t}\right)^2 (dt)^2 + \left(\frac{\partial v}{\partial \ell}\right)^2 (d\ell)^2 \tag{28}$$

where dv, dt, and $d\ell$ are the absolute errors in the measurement of velocity, transit time, and sample length, respectively. Since $v = \ell / t$

$$(dv)^2 = \ell^2 t^{-4} (dt)^2 + t^{-2} (d\ell)^2 \tag{29}$$

The above equation is used to determine the absolute error in v, and the percentage error is then given by $100(dv/v)$.

Possible sources of error were as follows:

1. Instrumentation errors. According to Huntington, the use of ultrasonic pulses to determine sound velocity in a material and thus the elastic constant yields an internal accuracy generally of about 1 percent.[2] At present the technique appears to be the simplest and most accurate for general work. The chief error lies in the determination of the delay time. In this study it was found that repeated determinations of delay time for given experimental conditions lay within ±0.2 percent.

2. Deviation of the cylinder axis from the specified crystallographic direction. This possible source of error was largely eliminated by employing X-ray alignment technique and later machining the crystal to correspondence when necessary.

3. Thickness of bonding cements holding transducers to crystals. Investigation indicated that this source of error was small and that it lay within the experimental error of the velocity determination.

Roughly, the overall error in the determination of values of c_{11} and c_{44} was estimated to be about ±2 percent, and in the determination of the value of c_{12} about ±7 percent.

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13. ABSTRACT

Adiabatic elastic constants of certain cubic crystals – lithium fluoride, sodium fluoride, calcium fluoride, strontium fluoride, and barium fluoride – are determined over the room-to-liquid-nitrogen-temperature range. Elastic-anisotropy factors, adiabatic compressibilities, and thermoelastances are evaluated from the elastic constant data. Results are compared with those of other investigators.

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