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Elastic Constants of RbF from 300 to 4.2 K[*]

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The adiabatic elastic constants have been measured in single crystals of rubidium fluoride over the temperature range of 300 to 4.2 K to investigate a discrepancy with neutron scattering data. The values of the elastic constants at 0 K, extrapolated from 4.2 K, are $C_{11}=6.527$, $C_{44}=0.952$, and $C_{12}=1.255$ in units of 10^{11} dyn/cm^2. The Debye characteristic temperature at 0 K (Θ_D) as calculated from the elastic constants is $\Theta_D=221.0$ K. A summary of Debye temperature values calculated from elastic constant data at 0 K is presented for all previously measured face-centered-cubic alkali halides.

INTRODUCTION

Recently Raunio and Rolandson[1] have obtained the phonon dispersion relations for RbF by using inelastic scattering of thermal neutrons. The elastic constants of RbF were calculated at 80 K by utilizing the dispersion curves for small wave vectors. A comparison of these elastic constants with those obtained from an extrapolation of Haussühl's[2] room-temperature thermoelastic constants showed acceptable agreement for C_{44} and C_{12} but not for C_{11}.

Because of the large discrepancy in the two calculated values of C_{11}, we have measured the temperature dependence of the elastic constants of RbF from 300 to 4.2 K.

EXPERIMENTAL

The single-crystal specimens used in these measurements were approximately cylindrical with a diameter of 1.6 cm and a length of 2.5 cm. The crystals were obtained from Semi-Elements Inc. with the end faces of one crystal oriented perpendicular to the [100] axis and the end faces of the other oriented perpendicular to the [110] axis. The orientations were checked in this laboratory by means of x-ray Laue backreflections. Since RbF is extremely hygroscopic, preparation of the crystal was accomplished in a helium atmosphere. The crystals were aligned to within 1° of the desired directions. The end faces were polished parallel to within ±0.001 cm.

Because of the symmetry of a cubic crystal, there are only three independent elastic constants: C_{11}, C_{44}, and C_{12}.[3] To obtain C_{11} and C_{44} one simply measures the velocities (V) of 10-MHz longitudinal and transverse sound waves propagated in the [100] direction. Then if the density ρ is known, the following relations may be used: $C_{11} = \rho V_L^2$ and $C_{44} = \rho V_T^2$. To obtain C_{12}, one measures the velocity (V'_T) of a transverse wave propagated along the [110] direction with its particle motion polarized perpendicular to the [001] direction giving $C' = \rho(V'_T)^2 = \frac{1}{2}(C_{11} - C_{12})$. One can also determine C_{44} by measuring the velocity (V''_T) of a transverse wave propagated along the [110] direction with its particle motion polarized parallel to the [001] direction and using the relation $C_{44} = \rho(V''_T)^2$.

The method employed to measure the sound velocities in the crystals was the well-known pulse-echo technique. The equipment has been described in an earlier publication.[4]

The bond between the crystal and transducer was Non-Aq stopcock grease for the temperature range of 160 to 300 K. For measurements between 160 and 80 K, an organic mixture of 5-parts ethyl ether, 6-parts pentane, and 2-parts ethyl alcohol

TABLE I. Elastic constants C_{11}, C_{12}, C_{44}, and $2\rho(V'_T)^2$ propagated in the [110] direction with the particle motion polarized perpendicular to the [001] direction in units of 10^{11} dyn/cm^2, densities ρ in units of g/cm^3, and compressibilities K in units of 10^{-12} cm^2/dyn as a function of temperature in units of K for rubidium fluoride.

T	C_{11}	C_{12}	C_{44}	ρ	K	$2\rho(V'_T)^2$ $=C_{11}-C_{12}$
300	5.509	1.449	0.9239	3.8434	0.3568	4.060
295	5.529	1.447	0.9245	3.8452	0.3562	4.082
280	5.586	1.432	0.9263	3.8508	0.3550	4.154
260	5.666	1.416	0.9289	3.8582	0.3530	4.250
240	5.745	1.398	0.9312	3.8655	0.3512	4.347
220	5.825	1.383	0.9339	3.8728	0.3492	4.442
200	5.903	1.364	0.9361	3.8801	0.3476	4.539
180	5.984	1.352	0.9387	3.8872	0.3453	4.632
160	6.064	1.336	0.9411	3.8941	0.3434	4.728
140	6.143	1.321	0.9437	3.9009	0.3415	4.822
120	6.222	1.304	0.9461	3.9073	0.3398	4.918
100	6.301	1.289	0.9485	3.9134	0.3379	5.012
80	6.381	1.272	0.9503	3.9188	0.3361	5.109
60	6.460	1.257	0.9515	3.9234	0.3343	5.203
40	6.511	1.255	0.9520	3.9266	0.3326	5.256
20	6.527	1.255	0.9520	3.9282	0.3320	5.272
4.2	6.527	1.255	0.9520	3.9284	0.3320	5.272

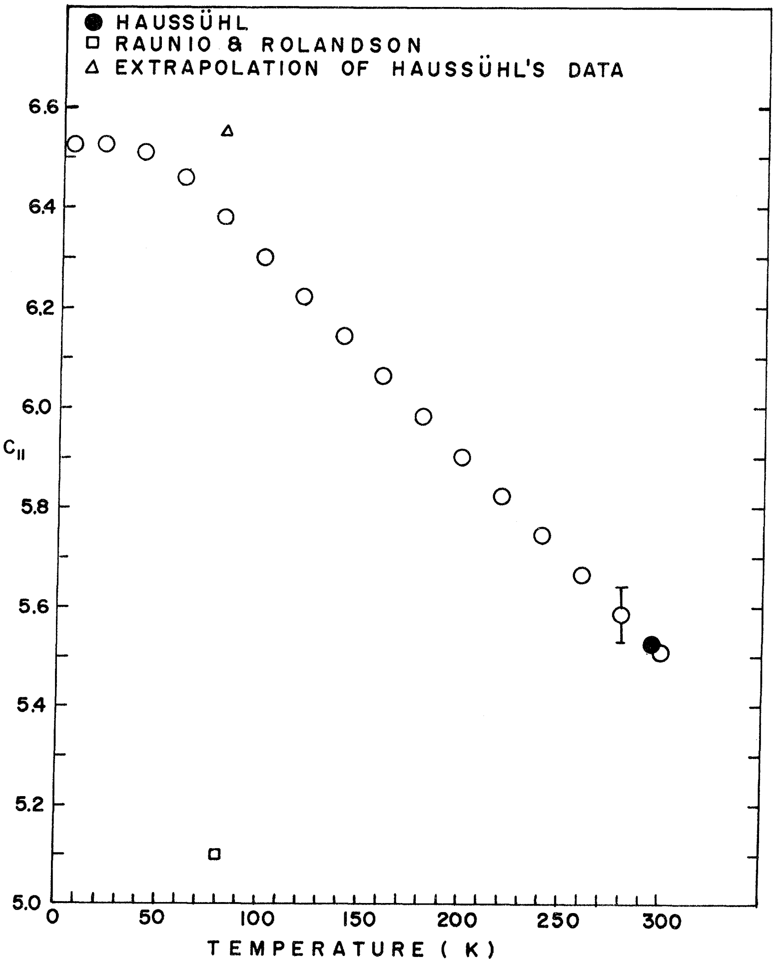

FIG. 1. The elastic constant C_{11} of RbF in units of 10^{11} dyn/cm^2 as a function of temperature in units of K.

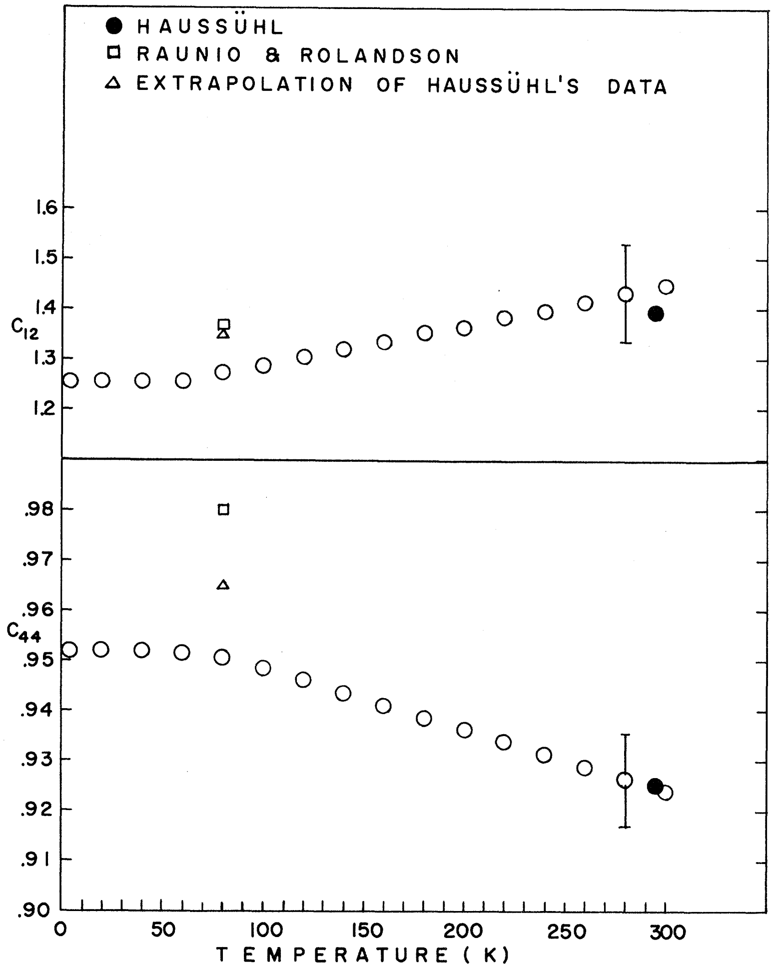

FIG. 2. The elastic constants C_{12} and C_{44} of RbF in units of 10^{11} dyn/cm^2 as a function of temperature in units of K.

was used as a binder. For measurements below 80 K dried natural gas was the binder.

The temperature measurements were made with a copper-constantan thermocouple in contact with the specimen. The emf measurements were taken with a Leeds and Northrup six-dial potentiometer. The crystals were cooled at a rate of approximately 10 K/h.

RESULTS AND DISCUSSION

In order to calculate the elastic constants of RbF as a function of temperature, it is necessary to know the temperature dependence of the crystals length and density. There are no data available on the temperature dependence of these properties. The density at 298.16 K has been calculated from the x-ray-measured lattice constants and found to be $\rho = 3.8440$ g/cm^3.[5] The linear expansion coefficient at 233.7 K was obtained from the volume expansion coefficient (9.5×10^{-5} K^{-1}) given by Huggins.[6] The temperature dependence of the linear expansion coefficient and consequently the density were obtained by using the well-known Grüneisen relationship[7] and the theoretical values of the temperature-dependent specific heat of RbF as given by Karo.[8]

To account for the thickness of the binder, a correction was made in the measured echo round-trip times. A correction of 0.04 μ sec was subtracted from times for transverse waves and 0.03μ sec was subtracted from times for longitudinal waves.[9]

Table I gives the values of the elastic constants, the calculated densities, and the compressibilities as calculated from $\beta = 3/(C_{11} + 2C_{12})$.

The estimated possible error for C_{11}, C_{44}, and $C' = \frac{1}{2}(C_{11} - C_{12})$ at 4.2 K is ±1%. Figures 1 and

TABLE II. The experimental elastic constants at 4.2 K compared to theoretical calculations at 0 K for RbF in units of 10^{11} dyn/cm^2.

Source	C_{11}	C_{12}	C_{44}
Experiment	6.527	1.255	0.952
Krishnan and Roy (Ref. 10)	5.400	1.300	1.300
Karo (Ref. 8)	5.140	1.320	1.320
Dick (Ref. 11)	5.680	0.511	1.690

TABLE III. Debye temperatures in units of K calculated from elastic constants for the fcc alkali halides with the ionic radii given in angstrom units.

Halide	F	Cl	Br	I
Alkali	($R=1.33$)	($R=1.81$)	($R=1.96$)	($R=2.19$)
Li ($R=0.68$)	734[a] 734.4[d] 734.1[f]	427.7[b] 429[e]	276.6[c]	
Na ($R=0.98$)	496.2[g] 491.5[e]	321[h] 321.9[j] 322[l] 322.3[n] 322[o] 321.2[e] 321.7[p]	224.6[e]	167.3[i] 167.6[k] 167.9[m]
K ($R=1.33$)	327[q] 335.9[e]	234[r] 236[u] 237.1[x] 236.3[z]	171.7[s] 172.8[v]	129[t] 131[w] 131.5[y] 130.9[aa]
Rb ($R=1.48$)	221.0[bb] 222.0[dd]	168[cc] 171[ee] 168.9[e]	136.5[e]	108[e]

[a] Briscoe and Squire (Ref. 20) using method of Betts *et al.* (Ref. 17).

[b] Marshall *et al.* (Ref. 4) using method of Betts *et al.* (Ref. 17).

[c] Marshall and Cleavelin (Ref. 21) using method of Betts *et al.* (Ref. 17).

[d] Recalculation by Alers and Neighbours (Ref. 22) of data of Briscoe and Squire (Ref. 20) using method of de Launay (Ref. 18).

[e] Lewis *et al.* (Ref. 16) using method of de Launey (Ref. 18).

[f] Recalculation by Alers and Neighbours (Ref. 22) of data of Briscoe and Squire (Ref. 20) using numerical integration.

[g] Vallin *et al.* (Ref. 23) using method of Betts *et al.* (Ref. 17).

[h] Recalculation by Alers and Neighbours (Ref. 22) of data of Overton and Swim (Ref. 24) using method of Betts *et al.* (Ref. 17).

[i] Claytor and Marshall (Ref. 25) using method of Betts *et al.* (Ref. 17).

[j] Recalculation by Alers and Neighbours (Ref. 22) of data of Overton and Swim (Ref. 24) using numerical integration.

[k] Claytor and Marshall (Ref. 25) using method of de Launay (Ref. 18).

[l] Recalculation by de Launay (Ref. 18) of data of Overton and Swim (Ref. 24).

[m] Recalculation by Martin (Ref. 26) of data of Claytor and Marshall (Ref. 25) using revised thermal expansion data and method of de Launay (Ref. 18).

[n] Recalculation by Fugate and Schuele (Ref. 27) of data of Overton and Swim (Ref. 24).

[o] Fugate and Schuele (Ref. 27) using numerical integration.

[p] Recalculation by Lewis *et al.* (Ref. 16) of data of Fugate and Schuele (Ref. 27) using method of de Launay (Ref. 18).

[q] Marshall and Miller (Ref. 28) using method of Betts *et al.* (Ref. 17).

[r] Norwood and Briscoe (Ref. 29) using method of Betts *et al.* (Ref. 17).

[s] Recalculation by Alers and Neighbours (Ref. 22) of data of Galt (Ref. 30) using method of Betts *et al.* (Ref. 17).

[t] Norwood and Briscoe (Ref. 29) using method of Betts *et al.* (Ref. 17).

[u] Norwood and Briscoe (Ref. 29) using method of de Launay (Ref. 18).

[v] Recalculation by Alers and Neighbours (Ref. 22) of data of Galt (Ref. 30) using numerical integration.

[w] Norwood and Briscoe (Ref. 29) using method of de Launay (Ref. 18).

[x] Recalculation by Alers and Neighbours (Ref. 22) of data of Norwood and Briscoe (Ref. 29) using numerical integration.

[y] Recalculation by Alers and Neighbours (Ref. 22) of data of Norwood and Briscoe (Ref. 29) using numerical integration.

[z] Value quoted by Lewis *et al.* (Ref. 16) from Norwood and Briscoe (Ref. 29) using method of de Launay (Ref. 18).

[aa] Value quoted by Lewis *et al.* (Ref. 16) from Norwood and Briscoe (Ref. 29) using method of de Launay (Ref. 18).

[bb] Present work using method of Betts *et al.* (Ref. 17).

[cc] Marshall *et al.* (Ref. 4) using method of Betts *et al.* (Ref. 17).

[dd] Present work using method of de Launay (Ref. 18).

[ee] Marshall *et al.* (Ref. 4) using method of de Launay (Ref. 18).

2 show the temperature dependence of the elastic constants.

The elastic constants of RbF have been measured at room temperature by Haussühl.[2] His values are $C_{11}=5.525$, $C_{44}=0.925$, $C_{12}=1.395$, and $2C'=4.130$ (units of 10^{11} dyn/cm^2 will be used throughout). Raunio and Rolandson[1] have used the phonon dispersion relations from inelastic scattering of thermal neutrons to calculate the elastic constants at 80 K. Their results gave $C_{11}=5.1$, $C_{44}=0.98$, and $C_{12}=1.37$. They compared these values with the extrapolated values of Haussühl's room-temperature thermoelastic constants, which gave $C_{11}=6.55$, $C_{44}=0.965$, and $C_{12}=1.35$. These values are plotted in Fig. 1. This shows a serious disagreement in the values of C_{11} as calculated by the two methods. Raunio calculated his values of C_{11} from the slopes of four branches [100]LA, [100]TA, [111]LA, and [111]TA, obtaining two values of C_{11} which were consistent (5.05 and 5.12).

Because of the large disagreement in C_{11} there was some question concerning whether Haussühl's extrapolated values were incorrect at 80 K or whether perhaps the dispersion for small wave vectors in RbF might be more pronounced than in other alkali halides. Our results indicate that perhaps both of these statements are probably correct.

The experimental values for the elastic constants

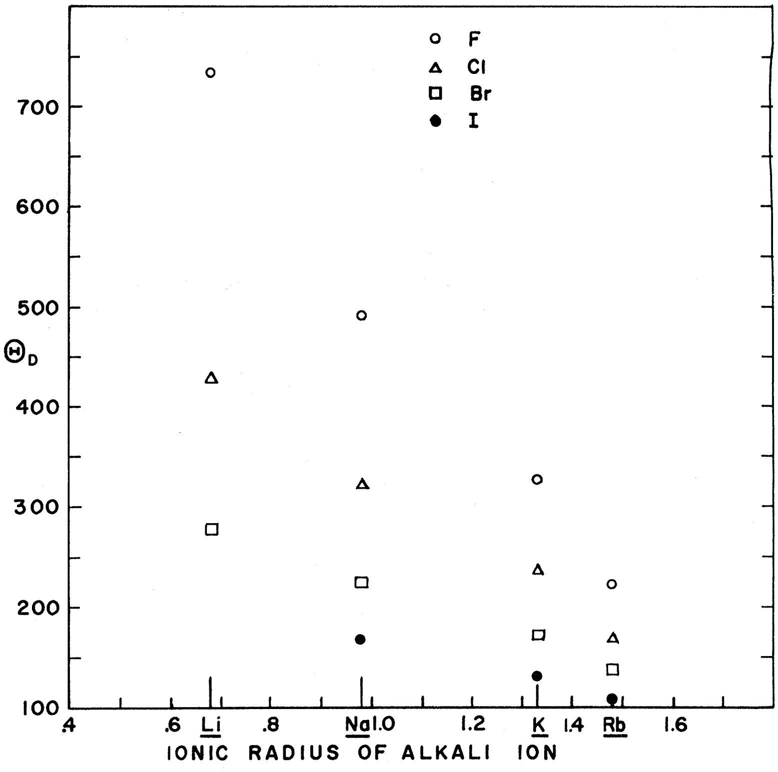

FIG. 3. The Debye temperatures at 0 K of fcc alkali halides in units of K as a function of the ionic radii of the alkali ion in angstrom units.

at low temperatures are compared to various theoretical calculations[8,10,11] in Table II. The agreement in general is not so good as is the case for other alkali halides.

Using Madelung's constant for the NaCl structure and the compressibility and nearest-neighbor distance at 0 K, we calculate the lattice energy[12] at 0 K for RbF to be $U_0 = -7.814 \times 10^5$ J/mole (−186.8 kcal/mole). The lattice energy has not been measured experimentally but our value can be compared to theoretically predicted values in the range of −184 to −189 kcal/mole.[13–15]

The elastic-anisotropy factor $A = 2\, C_{44}/(C_{11} - C_{12})$ which is equal to one for an isotropic material has been calculated at 300 and 4.2 K to be 0.455 and 0.361, respectively. These anisotropy factors can be compared with the anisotropy factors of other alkali halides.[16] One finds that RbF is the least anisotropic of the rubidium halides and the most anisotropic of the alkali fluorides. Furthermore, RbF becomes more anisotropic at low temperatures, as do all the alkali halides except the lithium halides. The Cauchy relation for cubic crystals $C_{12} = C_{44}$ is not satisfied as is the case with other alkali halides.[16] The failure of the Cauchy relation is represented by the nonzero values of $\Delta = C_{12} - C_{44}$ at 300 and 4.2 K, which were calculated to be 0.525 and 0.303, respectively.

The Debye temperature at 0 K (Θ_D) has been calculated from the elastic constants at 0 K by two methods. Using the Betts, Bhatia, and Wyman method,[17] we obtain a value of $\Theta_D = 221.0$ K. Using the method of de Launay,[18] the value obtained is $\Theta_D = 222.0$ K. These values of the Debye temperature can be compared to the values calculated from neutron data[19] of $\Theta_D = 242$ K and $\Theta_D = 222$ K and to the theoretical value calculated by Karo[8] of $\Theta_D = 231$ K. We present in Table III a summary of Debye temperatures calculated from elastic constant data at 0 K for all the face-centered-cubic (fcc) alkali halides except LiI and CsF, which to our knowledge have not yet been calculated from experimental data. We plot in Fig. 3 the Debye temperature for the various fcc alkali halides vs the ionic radii of the alkali ion. The qualitative pattern of the Debye temperatures allows us to predict an approximate value for LiI of $\Theta_D \simeq 200$ K.

SUMMARY

The elastic constants at 295 K are in good agreement with the room-temperature elastic constants of Haussühl. The elastic constants at 80 K found by extrapolating Haussühl's room-temperature data are consistently higher than the values found in the present work. The differences of 2.7% for C_{11}, 1.6% for C_{44}, and 6.1% for C_{12} at 80 K are not unreasonable for agreement between measured and extrapolated values. We find acceptable agreement between both ultrasonic experiments and the neutron scattering experiment in the calculation of C_{44} and C_{12}. The elastic constant C_{11} in the present experiment is 6.381, in reasonable agreement with the extrapolated value from Haussühl's data of 6.55 but in serious disagreement with the value of 5.1 calculated by Raunio and Rolandson from neutron scattering data. Raunio and Rolandson suggested as one possible explanation that the extrapolation of C_{11} from Haussühl's data might be incorrect. As an alternate explanation they point out that dispersion for small wave vectors is more pronounced in RbF than in the chlorides and could cause the calculated values of the elastic constants to be too small. Our measurements support the latter explanation. The present measurements complete the elastic-constant data at 0 K on the rubidium halides, leaving only LiI and CsF as the remaining unmeasured fcc alkali halides. A summary of the Debye temperature at 0 K calculated from measured elastic constants for all fcc alkali halides is presented in Table III, in which the dependence on ion size for both the alkali and the halide is clearly shown.

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