

Heat Capacities and Grüneisen Parameters for NaF and NaBr below 25 K

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Abstract

Heat capacities of NaF and NaBr have been measured from 2 K to around 20 K. Limiting values of the Debye temperature Θ_0^c of 488 ± 2 K (NaF) and 224.6 ± 1 K (NaBr) agree with Θ_0^{el} within experimental errors. Values of the Grüneisen parameter $\gamma(T)$ lie between 0.9 and 1.1 in the range below 20 K.

Introduction

Arising from thermal expansion measurements on the alkali halides (White and Collins 1973) at low temperatures there was a need for heat capacity data on sodium fluoride and sodium bromide. In the case of NaF there are C_p data from 0.1 to 15 K (Harrison *et al.* 1968) but these give a value of the Debye characteristic temperature, $\Theta_0^c = 466 \pm 5$ K below 15 K, which does not agree with that calculated from elastic constants, $\Theta_0^{el} = 492 \pm 2$ K (Lewis *et al.* 1967) and 497 ± 5 K (Vallin *et al.* 1966). In the case of NaBr, the heat capacity data of Gardner and Taylor (1964) extend only down to 7 K.

Experimental Details

Heat capacity measurements were made over the range 2–25 K using the calorimeter and methods described previously (Birch 1975). The temperatures were measured with a germanium thermometer calibrated (r.m.s. error of 0.6 mK) by the thermometry group of the National Measurement Laboratory against the NML magnetic scale (see e.g. Besley and Kemp 1977).

The NaF and NaBr samples were both optical quality single-crystal cylinders from Harshaw Chemical Co. of Ohio (see White and Collins 1973); the masses of NaF and NaBr were respectively 40.78 and 45.79 g. The heat capacity of the addenda (heater, thermometer and MgO cylinder) amounted to about 10% of the total in the case of NaF and about 4% in the case of NaBr.

Heat Capacities and Debye Temperatures

The measured values of C_p (Table 1) were used to calculate values for the equivalent Debye temperature $\Theta_D(T)$, and the results are shown in Fig. 1. From graphs of $C_p T^{-3}$ versus T^2 (or by extrapolation of $\Theta_D(T)$ versus T^2) we obtain the following limiting values of the Debye temperature:

$$\Theta_0^c = 488 \pm 2 \text{ K for NaF} \quad \text{and} \quad 224.6 \pm 1 \text{ K for NaBr.}$$

Table 1. Measured heat capacities for NaF and NaBr

<i>T</i> (K)	<i>C_p</i> (mJ mol ⁻¹ K ⁻¹)	<i>T</i> (K)	<i>C_p</i> (mJ mol ⁻¹ K ⁻¹)	<i>T</i> (K)	<i>C_p</i> (mJ mol ⁻¹ K ⁻¹)
<i>(a) Results for NaF</i>					
2.308	0.413	7.506	14.27	13.144	77.0
2.636	0.615	7.718	15.44	13.378	81.6
2.750	0.705	7.934	16.59	13.620	85.8
2.975	0.893	8.185	18.02	13.769	88.9
3.084	0.996	8.412	20.05	14.175	98.2
3.614	1.588	8.639	21.59	14.433	102.4
3.850	1.922	8.886	23.36	14.688	107.8
3.966	2.106	9.329	27.09	14.806	110.3
4.090	2.280	9.851	31.76	15.234	121.1
4.215	2.504	10.106	34.17	15.754	136.3
4.342	2.742	10.196	35.40	16.012	143.9
4.470	2.957	10.432	37.52	16.019	145.0
5.193	4.605	10.641	39.59	16.574	162.2
5.530	5.60	11.510	51.5	18.494	230.0
6.330	8.46	11.702	53.0	18.798	243.5
6.352	8.56	12.219	61.7	19.112	254.8
6.653	9.64	12.395	63.4	19.419	266.9
6.718	10.06	12.590	66.7	19.733	280.9
6.858	10.87	13.029	74.1	20.05	296.7
<i>(b) Results for NaBr</i>					
2.666	6.48	5.125	49.3	15.948	2326.4
2.735	7.09	5.295	54.6	16.129	2413.1
2.767	7.16	7.423	164.0	16.138	2360.6
2.893	8.38	8.621	263.4	16.314	2530.0
2.893	8.26	9.055	323.4	16.498	2558.0
3.013	9.33	10.121	484.5	16.679	2691.3
3.087	10.33	11.808	849.8	17.349	3011.6
3.293	12.44	11.940	883.3	17.543	3093.4
3.434	13.95	12.255	946.5	17.702	3116.6
3.556	15.57	12.450	1013.6	18.060	3330.7
3.709	17.87	13.115	1190.9	18.536	3642.3
3.997	21.94	13.368	1256.3	18.698	3731.6
4.023	22.76	14.921	1878.6	18.873	3840.2
4.376	29.41	15.167	1952.7	19.260	3946.2
4.551	32.50	15.348	2071.3	19.390	3856.5
4.717	36.76	15.674	2214.5		
4.877	40.69	15.886	2316.6		

Table 2. Characteristic values of NaF and NaBr at low temperatures

Values are listed for the density ρ , molar volume V , bulk modulus B_s , Debye temperatures Θ and Grüneisen parameters γ

Metal halide	$\rho(4\text{K})^{\text{A}}$ (g cm ⁻³)	$V(4\text{K})^{\text{A}}$ (cm ³)	$B_s(4\text{K})^{\text{A}}$ (GPa)	Θ_0^e (K)	Θ_0^{el} (K)	γ_0^{th}	γ_0^{el}
NaF	2.851	14.7	51.43	488 ± 2	491.5 ± 2.4	0.91	1.02
NaBr	3.299	31.2	22.57	224.6 ± 1	224.6 ± 1.2	0.99	1.13

^A Values from Lewis *et al.* (1967).

The above values for Θ_0^c agree within limits of error with the values of Θ_0^{el} calculated from elastic moduli given by Lewis *et al.* (1967) (see Table 2).

The scatter of the individual Θ_D values about the mean is less than $\frac{1}{2}\%$, corresponding to less than 1.5% in the values of C_p .

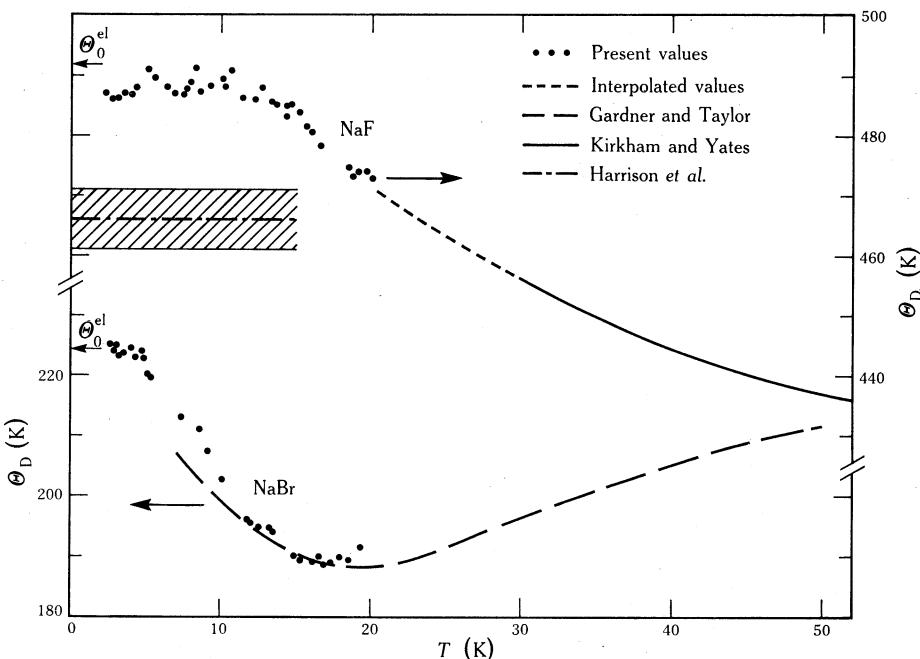


Fig. 1. Variation of the Debye temperature Θ_D with temperature T for NaBr and NaF. The present values (some being omitted for clarity) are plotted together with the results from Gardner and Taylor (1964), Kirkham and Yates (1968) and Harrison *et al.* (1968). The hatching on the data from Harrison *et al.* shows their estimated uncertainty of ± 5 K.

Grüneisen Parameters

Using the experimental values for the linear coefficients of thermal expansion α given by White and Collins (1973) we can now calculate values for the Grüneisen parameter

$$\gamma = 3\alpha B_s V/C_p,$$

where V is the molar volume and B_s is the adiabatic bulk modulus (see Table 2). The individual values of γ shown in Fig. 2 correspond to individual α values given in Table 1 of the paper by White and Collins. Values used for C_p above 20 K are from Kirkham and Yates (1968) for NaF and from Gardner and Taylor (1964) for NaBr. As well as individual values we can calculate average limiting values γ_0^{th} from the T^3 terms in the expressions ($T \ll \Theta_D$)

$$\alpha = bT^3 + cT^5 + \dots, \quad C_p = BT^3 + CT^5 + \dots.$$

White and Collins gave the coefficient values, for NaF, $b = (1.34 \pm 0.03) \times 10^{-11} \text{ K}^{-4}$ and, for NaBr, $b = (16.0 \pm 0.5) \times 10^{-11} \text{ K}^{-4}$, and these values together with $BT^3 = 2 \times 1944(T/\Theta_0)^3 \text{ J mol}^{-1} \text{ K}^{-1}$ lead to the results for γ_0^{th} given in Table 2 and shown hatched in Fig. 2.

The limiting values γ_0^{th} are significantly (10%) smaller than the values of γ_0^{el} calculated from the low temperature elastic stiffnesses (Lewis *et al.* 1967) and from an extrapolation to low temperature of the room-temperature pressure derivatives of the stiffnesses (Miller and Smith 1964; Roberts and Smith 1970). Reasons for the

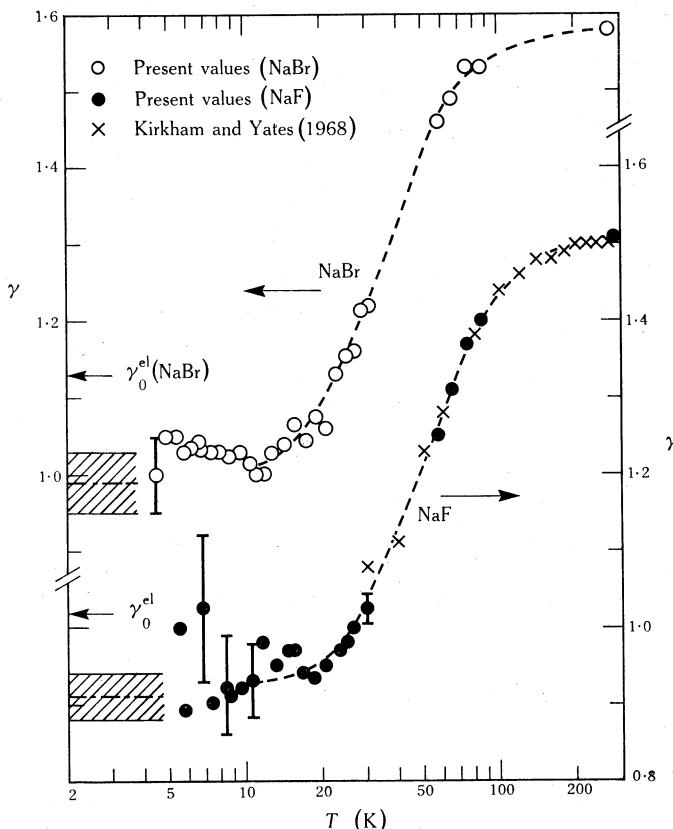


Fig. 2. Variation of the Grüneisen parameter $\gamma = 3\alpha B_0 V/C_p$ with temperature for NaBr and NaF. The results shown hatched are the limiting γ_0 values determined from experimental T^3 terms in α and C_p . Some points below 6 K (with relatively large error bars) have been omitted here for clarity.

discrepancy may lie with either set of measurements. Smith and his colleagues place a general estimate of 5% uncertainty on their pressure derivatives; extrapolation of the derivatives to low temperature reduces γ_0^{el} by 5% and could introduce a further uncertainty of a few per cent. On the other hand, errors in α are about $\pm 5\%$ near 10 K for NaF, which has a comparatively high Θ_D and correspondingly small expansion at low temperatures. Values of α for NaBr are an order of magnitude larger than those for NaF and errors are likely to be less than $\pm 1\%$ from 5 to 30 K.

Note that, for NaCl, low temperature measurements of elastic stiffnesses and their pressure derivatives lead to $\gamma_0^{\text{el}} = 1.06$, in agreement with thermal values determined by White and Collins (1973) and by Case and Swenson (1974). These thermal data show a clear minimum in $\gamma(T)$ for NaCl centred near $\Theta/20$ and about 5% deep. If

a similar shallow minimum exists for NaF and NaBr, then it follows that γ_0^{el} is approximately correct for NaF, and that $\gamma_0 \approx 1.07$ for NaBr. The thermal measurements clearly rule out a minimum of the size (40%) predicted in a calculation for NaF by Achar and Barsch (1971) (cf. the discussion in the paper by White and Collins 1973).

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