

Thermal conductivity under pressure and through phase transitions in solid alkali halides. I.  
Experimental results for KCl, KBr, KI, RbCl, RbBr and RbI

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1985 J. Phys. C: Solid State Phys. 18 3943

(<http://iopscience.iop.org/0022-3719/18/20/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 130.54.110.71

This content was downloaded on 08/12/2014 at 07:48

Please note that [terms and conditions apply](#).

# Thermal conductivity under pressure and through phase transitions in solid alkali halides: I. Experimental results for KCl, KBr, KI, RbCl, RbBr and RbI

Per Andersson

Department of Physics, University of Umeå, S-901 87 Umeå, Sweden

Received 28 December 1983

**Abstract.** The thermal conductivity,  $\lambda$ , of polycrystalline KCl, KBr, KI, RbCl, RbBr and RbI has been measured at temperatures ( $T$ ) from 100–400 K and at pressures ( $P$ ) up to about 2.6 GPa, using the transient hot-wire method. Extensive results were obtained for  $\lambda(T, P)$  of both the low-pressure (NaCl-type) and high-pressure (CsCl-type) phases. There was generally good agreement with previous results for  $\lambda(P)$  at room temperature, the decrease of  $\lambda$  through the phase transition and  $\lambda(T)$  at atmospheric pressure. The heat capacity per unit volume was also measured simultaneously but for technical reasons data could be obtained only near room temperature. Corresponding values of specific heat capacity were in good agreement with previous work over the whole pressure range.

## 1. Introduction

This work was undertaken to investigate the effect of crystal structure on the pressure ( $P$ ) and temperature ( $T$ ) dependences of thermal conductivity,  $\lambda$ , for insulating solids; in particular the alkali halides. We have chosen here to study the potassium halides KCl, KBr and KI, and the rubidium halides RbCl, RbBr and RI. Under normal conditions these substances have the NaCl- or B1-type crystal structure, but they transform under moderate pressures to the CsCl- or B2-type structure. The transition pressures are about 0.5 GPa and 2 GPa for the rubidium and potassium halides, respectively. In our piston-cylinder-type of high-pressure apparatus we can measure conveniently the pressure dependence of  $\lambda$  for the two types of phases as well as the change of  $\lambda$  at the B1  $\rightarrow$  B2 transition. The thermal conductivity through the phase transition and well into the high-pressure phase has previously been measured only for KCl and RbCl (Dzhavadov and Krotov 1978) and for RbBr (Averkin *et al* 1976).

All previous measurements of the temperature dependence of  $\lambda$  have been made at zero pressure. In this study we give isobaric results for phases I (B1-type structure) and II (B2-type structure) of the various alkali halides. This enables a comparison to be made between the temperature dependences of  $\lambda$  for two phases of the same substance.

In insulating solids the heat transport is governed by phonons. For alkali halides the contribution to  $\lambda$  is mainly due to acoustic phonons, but the effect of optic phonons may

be important, especially when the ionic mass ratio is near unity. In a previous paper (Gerlich and Andersson 1982) from our laboratory we reported results for CsCl, CsBr and CsI.

In this paper (part I) we present extensive experimental results for the various substances and comparison with other work. In the following paper (part II) the results are analysed and compared with theory.

## 2. Experimental

The thermal conductivity,  $\lambda$ , was measured using the transient hot-wire method. Details of the method and of the general experimental arrangements have been given elsewhere (Ross *et al* 1977, 1979). The hot-wire was a nickel wire, 0.1 mm in diameter, which was installed as a circular loop between two pre-compacted plates of the specimen in the Teflon-lined pressure cell. The whole assembly was loaded into a piston-cylinder apparatus, and pressure was generated by a hydraulic press. The temperature was controlled by either heating or cooling the whole massive pressure vessel.

The materials used were powders of  $\geq 99.5\%$  purity. They were dried at 200 °C for 24 h, and then compacted in a steel die under a pressure of 0.1 GPa to form polycrystalline plates 39 mm in diameter and 8 mm thick. Care was taken to prevent absorption of moisture on the plates.

The measurements were generally carried out either as isobaric runs at various pressures in the temperature range 100–400 K, or as isothermal runs at room temperature in the pressure range up to about 2.6 GPa. For some of the substances isothermal runs were also carried out at temperatures below or above room temperature. To ensure good thermal contact between the hot wire and the specimen a minimum pressure of  $\geq 0.1$  GPa was used.

The accuracy was estimated as  $\pm 3\%$ , except at the lowest temperatures where a limit of  $\pm 5\%$  must be given.

The transient hot-wire method also yields data for the heat capacity per unit volume,  $\rho c_p$ , where  $\rho$  is the mass density. As previously described (Ross *et al* 1979), the method uses a fitting procedure to calculate both  $\lambda$  and  $\rho c_p$  from measured values of the temperature rise of the hot wire. However, when the thermal diffusivity  $a$  ( $= \lambda / \rho c_p$ ) is large, reliable values of  $\rho c_p$  cannot be obtained. The reason for this is that the fitting procedure must employ the quantity  $at/r^2$ , where  $t$  is the time after initiation of the temperature rise and  $r$  is the radius of the hot wire. The fitted value of  $\rho c_p$  is mainly determined from measurements of temperature rise at small (i.e. short-time) values of  $at/r^2$ . The fitted value of  $\lambda$  is mainly determined from measurements at large values of  $at/r^2$ . With our equipment, the first measurement of temperature rise is made a short time (1 ms) after the beginning of the temperature rise. At this time, the quantity  $at/r^2$  will not be 'small' if  $a$  is sufficiently large. When this situation arises, reliable values of  $\rho c_p$  cannot be obtained using our method. The determination of  $\lambda$  is not adversely affected by large values of  $a$ .

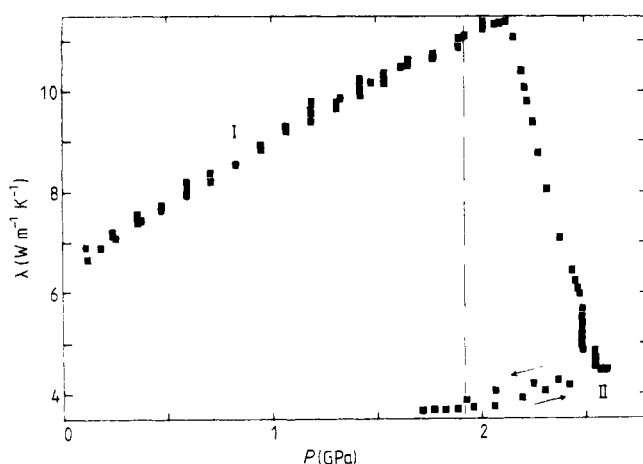
For the alkali halides, it turns out that  $\rho c_p$  can be measured reliably at room temperature. This is indicated by comparison with literature values for  $c_p$  at atmospheric pressure where agreement is generally within 5% (table 4). However, at low temperatures ( $T \leq 150$  K)  $a$  was sufficiently large that reliable values of  $\rho c_p$  could not be obtained. We therefore present only data for  $\rho c_p(P)$  at room temperature, where the inaccuracy is estimated as  $\pm 10\%$ .

### 3. Results and comparison with previous work

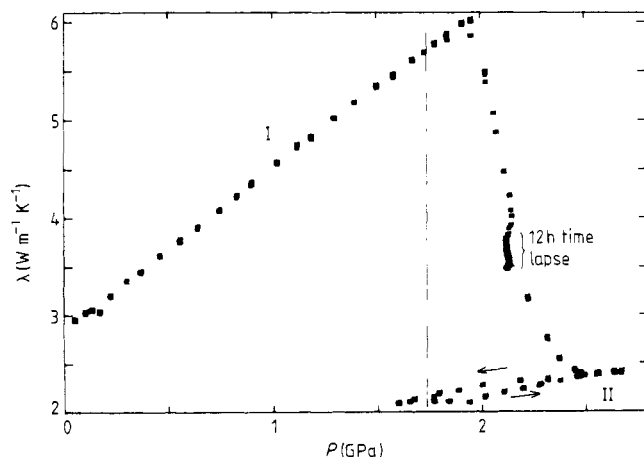
#### 3.1. Pressure dependence of thermal conductivity

Figures 1–6 show room temperature results for  $\lambda(P)$  for the six alkali halides studied. For a given substance and phase the results can be represented by straight lines of the form  $\lambda = A + BP$ , where  $A$  and  $B$  are constants. The corresponding numerical information is shown in table 1. In addition, the table also shows results for a few isothermal runs carried out for temperatures above and below room temperature.

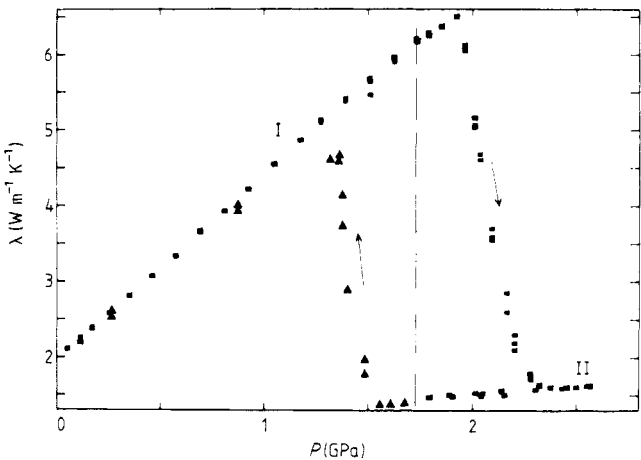
The measurements were carried out using the following general scheme. Starting at the minimum pressure  $\geq 0.1$  GPa, data were obtained at selected pressures. The pressure was first increased monotonically until the I  $\rightarrow$  II transition had taken place, i.e. until



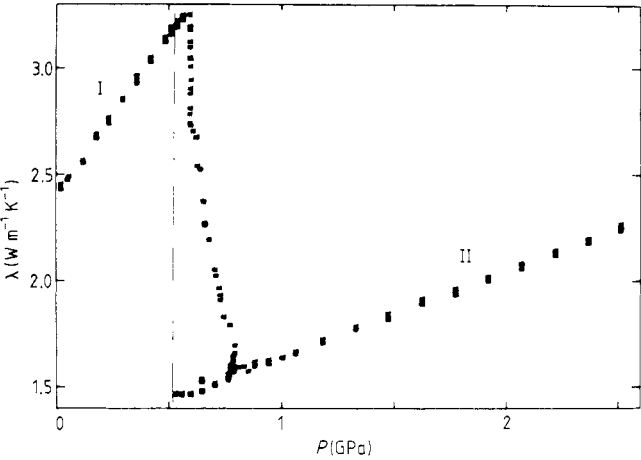
**Figure 1.** Isothermal pressure dependence of  $\lambda$  for KCl at 292 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).



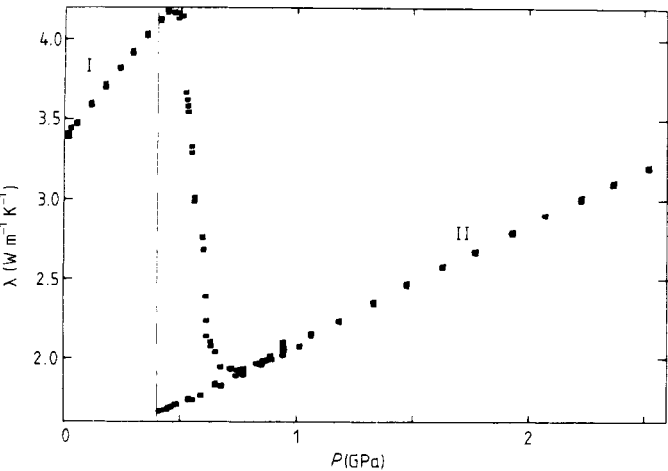
**Figure 2.** Isothermal pressure dependence of  $\lambda$  for KBr at 296 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).



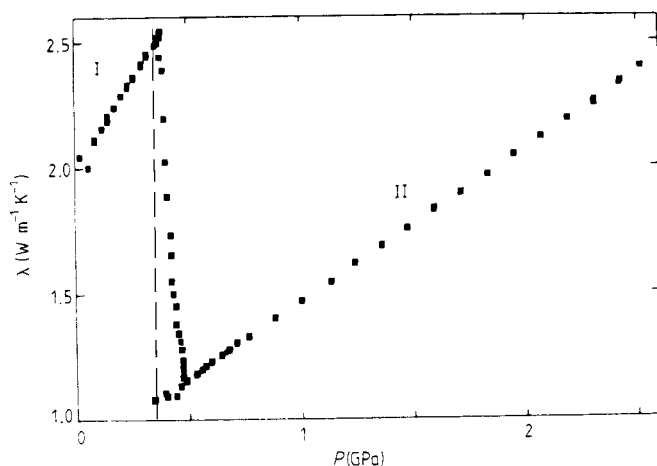
**Figure 3.** Isothermal pressure dependence of  $\lambda$  for KI at 295 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).



**Figure 4.** Isothermal pressure dependence of  $\lambda$  for RbCl at 294 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).



**Figure 5.** Isothermal pressure dependence of  $\lambda$  for RbBr at 294 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).



**Figure 6.** Isothermal pressure dependence of  $\lambda$  for RbI at 296 K. The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).

the measured values of  $\lambda$  again clearly started to increase on pressurisation, at which point the transition was assumed to be complete (see figure 2). Pressure was then decreased to about the equilibrium transition or somewhat below, but avoiding the reverse transition II  $\rightarrow$  I. This was followed by an increase of pressure up to the maximum available, which for the present set-up is about 2.7 GPa. The aim was to determine

**Table 1.** Isothermal pressure dependence of thermal conductivity,  $\lambda$ , fitted to equations of the form  $\lambda = A + BP$ . For phase II, note that  $A$  is an extrapolated value of  $\lambda$  for  $P = 0$ .

Substance and phase	$T$ (K)	$A$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	$B$ ( $\text{W m}^{-1} \text{K}^{-1} \text{GPa}^{-1}$ )	$P$ (GPa)
KCl(I)	292	6.52	2.37	0–1.9
KCl(I)	397	4.16	1.83	0–1.2
KCl(II)	292	2.20	0.86	1.9–2.6
KBr(I)	105	10.0	4.06	0–1.2
KBr(I)	296	2.81	1.64	0–1.7
KBr(I)	414	1.77	1.15	0–1.2
KBr(II)	296	1.26	0.44	1.7–2.7
KI(I)	295	1.96	2.45	0–1.8
KI(II)	295	1.04	0.24	1.8–2.6
RbCl(I)	294	2.41	1.49	0–0.5
RbCl(II)	294	1.23	0.41	0.5–2.5
RbBr(I)	294	3.38	1.81	0–0.4
RbBr(II)	294	1.33	0.75	0.4–2.5
RbI(I)	243	2.60	1.64	0–0.4
RbI(I)	296	1.98	1.42	0–0.4
RbI(I)	359	1.52	1.00	0–0.4
RbI(II)	243	1.08	0.70	0.4–1.5
RbI(II)	296	0.86	0.60	0.4–1.5
RbI(II)	359	0.68	0.49	0.4–1.5

**Table 2.** Room temperature values of pressure coefficient of  $\lambda$ ,  $s = (1/\lambda_0)(\partial\lambda/\partial P)_T$ , for phases I and II and change of  $\lambda$  through I  $\rightarrow$  II phase transition. (Comparison with previous work.) Note that  $s = B/A$ , where  $\lambda = A + BP$  (table 1).

Substance	Phase I		Phase transition		Phase II		References
	$P$ (GPa)	$s$ (GPa <sup>-1</sup> )	$P_u$ (GPa)†	$(\lambda_{II}/\lambda_I)_{P=P_u}$	$P$ (GPa)	$s$ (GPa <sup>-1</sup> )	
KCl	0-1.9	0.36	1.93	0.35	1.9-2.6	0.39	This work
	0-1.9	0.33					Alm and Bäckström (1974)
	0-1	0.47					Seleznev <i>et al</i> (1976)
	0-1.9	0.32	1.93	0.40	1.9-3.2	0.17	Dzhavadov and Krotov (1978)
KBr	0-1.7	0.58	1.74	0.36	1.7-2.7	0.35	This work
KI	0-1.8	1.25	1.73	0.23	1.8-2.6	0.23	This work
	0-1	1.05					Seleznev <i>et al</i> (1976)
RbCl	0-0.5	0.62	0.52	0.45	0.5-2.5	0.33	This work
	0-0.5	0.64		0.46	0.5-2.7	0.21	Dzhavadov and Krotov (1978)
RbBr	0-0.4	0.54	0.40	0.40	0.4-2.5	0.57	This work
	0-0.4	0.68		0.44	0.4-1.0	0.47	Averkin <i>et al</i> (1976)
RbI	0-0.4	0.72	0.36	0.43	0.4-2.5	0.70	This work

† The transition pressures,  $P_u$ , are from Pistorius (1976).

accurately the change of  $\lambda$  at the transition and to obtain reliable values for  $\lambda$  in phase II over a pressure range as wide as possible.

In the case of the potassium halides the transitions were invariably very sluggish and occurred over a pressure range of about 0.5 GPa. Keeping the specimen for 12 h at a pressure about 0.2 GPa above that required to initiate the transition did not result in its completion (figure 2).

The equilibrium transition pressures for the six alkali halides as given by Pistorius (1976) are shown as vertical broken lines. These transitions are known to be sluggish (Pistorius 1964, 1965). On depressurisation the II  $\rightarrow$  I transitions took place at pressures well below the equilibrium pressures thus showing pronounced hysteresis (see results for KI, figure 3). It was also found that the initial values of  $\lambda$  for the low-pressure phases were recovered on depressurisation (e.g. figure 3).

Table 2 shows a comparison with previous work for the pressure coefficient of  $\lambda$ ,  $s = (1/\lambda_0)(\partial\lambda/\partial P)_T$ , for phases I and II and for the change of  $\lambda$  through the phase transition. For the pressure coefficients, agreement is within 20% for the low-pressure phases, but larger differences are found for the high-pressure phases. There is good agreement for the observed changes of  $\lambda$  through the phase transition. Data for the temperature dependence of  $s$  could be obtained for the K halides since we made isobaric runs at pressures of 0.1 and 1.2 GPa. The quantity  $s$  increased linearly with  $T$  in all cases with results for  $[s(300\text{ K})]^{-1} (ds/dT)$  of  $1.9 \times 10^{-3}\text{ K}^{-1}$ ,  $1.5 \times 10^{-3}\text{ K}^{-1}$  and  $1.2 \times 10^{-3}\text{ K}^{-1}$  for KCl, KBr and KI respectively.

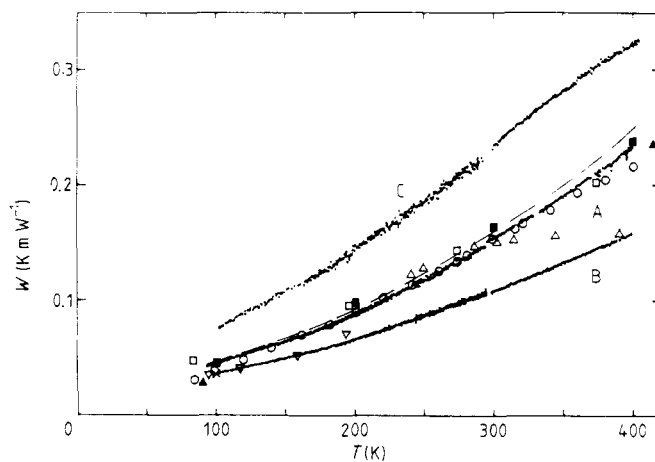
**Table 3.** Isobaric temperature dependence of thermal resistivity in  $\text{K m W}^{-1}$  (smoothed values). Zero-pressure values are by extrapolation.

Substance and phase	$P$ (GPa)	$T$ (K)						
		100	150	200	250	300	350	400
KCl(I)	0	0.046	0.066	0.093	0.123	0.162	0.202	0.250
KCl(I)	0.13	0.045	0.064	0.089	0.118	0.154	0.191	0.236
KCl(I)	1.2	0.036	0.050	0.067	0.087	0.109	0.133	0.160
KCl(II)	2.6	0.075	0.108	0.145	0.186	0.234	0.282	0.324
KBr(I)	0	0.096	0.148	0.208	0.284	0.363	0.456	0.538
KBr(I)	0.12	0.092	0.140	0.197	0.267	0.339	0.423	0.500
KBr(I)	1.2	0.065	0.096	0.132	0.173	0.212	0.256	0.306
KBr(II)	2.6	0.139	0.205	0.271	0.347	0.420	0.495	0.557
KI(I)	0	0.110	0.190	0.279	0.388	0.524	0.681	0.830
KI(I)	0.12	0.100	0.170	0.248	0.345	0.462	0.595	0.728
KI(I)	1.2	0.056	0.087	0.124	0.173	0.224	0.278	0.346
KI(II)	2.1	0.214	0.323	0.433	0.560	0.672	—	—
RbCl(I)	0	0.122	0.184	0.250	0.334	0.429	0.528	0.643
RbCl(I)	0.30	0.108	0.160	0.216	0.285	0.362	0.440	0.530
RbCl(II)	1.5	0.180	0.270	0.357	0.457	0.553	0.641	0.726
RbBr(I)	0	0.082	0.125	0.173	0.240	0.310	0.402	0.485
RbBr(I)	0.30	0.074	0.111	0.152	0.209	0.267	0.342	0.409
RbBr(II)	1.5	0.123	0.183	0.249	0.329	0.409	0.496	0.585
RbI(I)	0	0.137	0.205	0.292	0.399	0.519	0.647	0.795
RbI(I)	0.30	0.119	0.175	0.247	0.333	0.427	0.525	0.636
RbI(II)	1.5	0.151	0.242	0.342	0.461	0.579	0.698	0.822

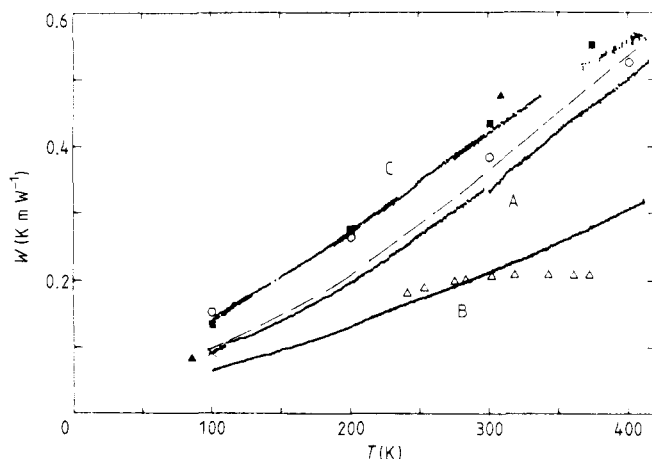


### 3.2. Temperature dependence of thermal resistivity

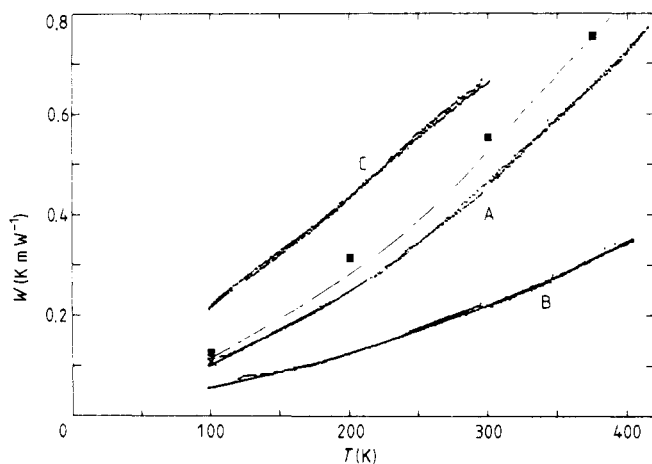
The results for the isobaric runs are conveniently presented and discussed in terms of the thermal resistivity  $W (=1/\lambda)$ . Figures 7–12 include our results for  $W(T)$ . We obtained a large number of data points, and cooling and heating gave the same results. Corresponding smoothed data at selected temperatures are shown in table 3. Our low-pressure isobaric results can be compared with previous work at zero pressure, which was mainly on single crystals. To simplify this comparison we have extrapolated our low-pressure conductivity data to atmospheric pressure. To do this extrapolation we used



**Figure 7.** Isobaric temperature dependence of thermal resistivity of KCl: A, I (0.1 GPa); B, I (1.2 GPa); C, II (2.6 GPa). Our results at 0.1 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\square$ , Eucken (1911);  $\blacktriangle$ , Joffé (1956);  $\triangle$ , McCarthy and Ballard (1960);  $\times$ , Walker (1963);  $\circ$ , Devyatkov and Smirnov (1963a);  $\nabla$ , Taylor *et al* (1965);  $\blacksquare$ , Petrov *et al* (1974).



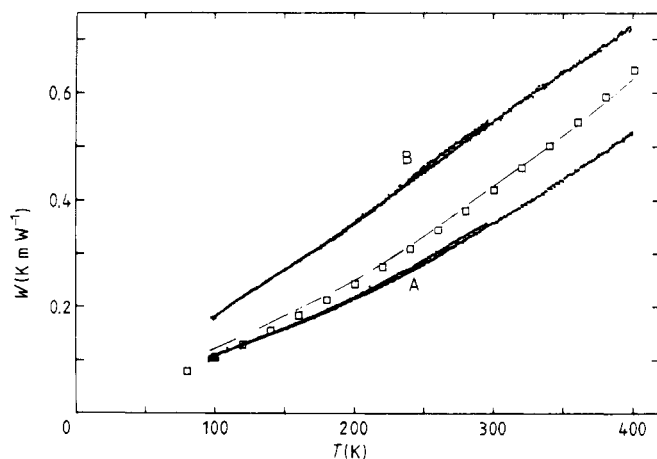
**Figure 8.** Isobaric temperature dependence of thermal resistivity for KBr: A, I (0.1 GPa); B, I (1.2 GPa); C, II (2.6 GPa). Our results at 0.1 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\blacktriangle$ , Joffé (1956);  $\triangle$ , McCarthy and Ballard (1960);  $\times$ , Walker (1963);  $\circ$ , Devyatkov and Smirnov (1963b);  $\blacksquare$ , Petrov *et al* (1974).



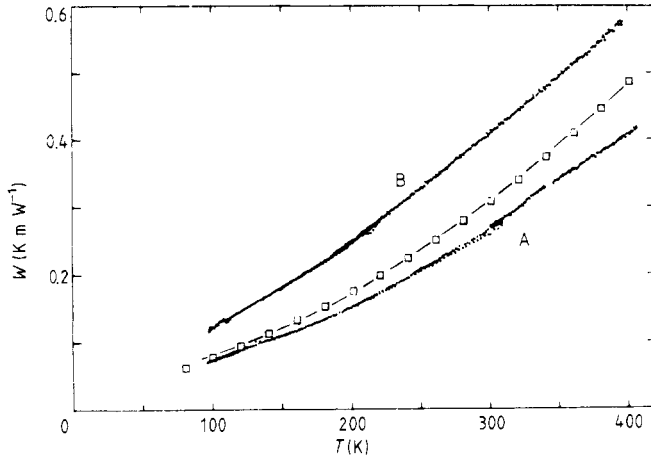
**Figure 9.** Isobaric temperature dependence of thermal resistivity for KI: A, I (0.1 GPa); B, I (1.2 GPa); C, II (2.6 GPa). Our results at 0.1 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\times$ , Walker (1963);  $\blacksquare$ , Petrov *et al* (1974).

our measured values of  $s(T)$  for the K halides (see above). For the Rb halides, where only one isobar was measured for phase I, we used our measured values of  $s$  at room temperature and assumed a value  $[s(300\text{ K})]^{-1}(ds/dT) = 1.5 \times 10^{-3}\text{ K}^{-1}$  which was the average value for the K halides. The results are shown as broken curves in figures 7–12 and are also given in table 3.

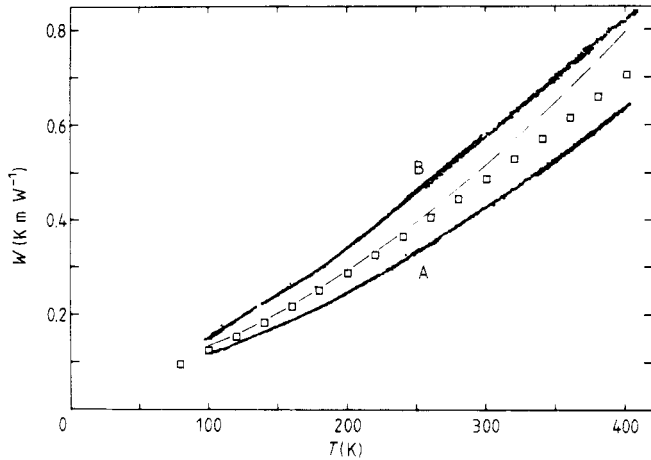
For KCl we find good agreement between our results and those of Petrov *et al* (1974). We also find reasonable agreement with the results of Eucken (1911) and Devyatkov and Smirnov (1963a) over most of the temperature range. However, at 400 K our results for the thermal resistivity are about 10% higher than those of Devyatkov and Smirnov (1963a). At 100 K our results for  $W$  are about 25% higher than those of Devyatkov and



**Figure 10.** Isobaric temperature dependence of thermal resistivity for RbCl: A, I (0.3 GPa); B, II (1.5 GPa). Our results at 0.3 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\square$ , Moore *et al* (1975).



**Figure 11.** Isobaric temperature dependence of thermal resistivity for RbBr: A, I (0.3 GPa); B, II (1.5 GPa). Our results at 0.3 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\square$ , Moore *et al* (1975).



**Figure 12.** Isobaric temperature dependence of thermal resistivity for RbI: A, I (0.3 GPa); B, II (1.5 GPa). Our results at 0.3 GPa were extrapolated to zero pressure and represented by the broken curve for comparison with previous work:  $\square$ , Moore *et al* (1975).

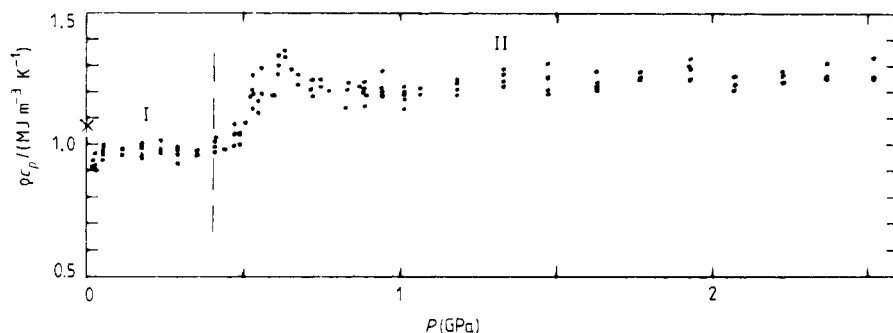
Smirnov (1963a), Taylor *et al* (1965) and Walker (1963). The results of McCarthy and Ballard (1960) on KCl (figure 7) and on KBr (figure 8) show exceptionally small temperature dependences of  $W$  in the temperature range 300–400 K, and they are, in our opinion, erroneous. For KBr our results for  $W$  at about 100 K agree within 10% with those of Joffé (1956) and Walker (1963) but over the whole temperature range are considerably lower than those of Petrov *et al* (1974). Our results are also lower than those of Devyatkova and Smirnov (1963b), except at  $T > 300$  K where agreement is reasonable. In the case of KI we find good agreement between our results and those of Petrov *et al* (1974) over the whole temperature range, and with those of Walker (1963) at about 100 K.

The thermal resistivity of RbCl, RbBr and RbI has been measured by Moore *et al* (1975) at zero pressure over the range 80–400 K. As can be seen from figures 10–12 our results agree well with theirs in the range above 200 K, except for RbI where our values are always higher, up to 13% at 400 K. At the lowest temperatures our observed values for  $W$  are generally higher than theirs, with differences at 100 K of 20%, 6% and 12% for RbCl, RbBr and RbI respectively.

To summarise, we find generally good agreement in the range 150–300 K between our results for  $W$  and those of previous work for the six alkali halides studied. However, at low temperatures our results are higher than those of most previous work for several of the substances. It is unlikely that this discrepancy is due to grain boundary scattering in our polycrystalline specimens since Moore *et al* (1975) found no difference between polycrystalline and single-crystal specimens of RbI near 100 K. At high temperatures contributions to the thermal conductivities from radiation might have introduced errors in the calculated lattice thermal conductivities from previous single-crystal experiments.

### 3.3. Pressure dependence of heat capacity

Figure 13 shows typical results for  $\rho c_p(P)$ , obtained for RbBr at room temperature. For all six alkali halides and within a given phase the results for  $\rho c_p$  are constant or increase slightly with pressure. At the I  $\rightarrow$  II transition an increase in  $\rho c_p$  is always observed.



**Figure 13.** Isothermal pressure dependence of heat capacity per unit volume for RbBr at 294 K.  $\times$ —using literature values of  $c_p$  (Clusius *et al* 1949) and  $\rho$  (Vaidya and Kennedy 1971). The vertical broken line indicates the equilibrium transition pressure (Pistorius 1976).

Using density and compressibility data (Vaidya and Kennedy 1971) we have calculated the specific heat capacity  $c_p(P)$  (table 4). As can be seen from the table, agreement with literature values at atmospheric pressures is generally within 5%. For  $c_p$  under pressure, no change could be detected over the pressure range of phase I for the Rb halides or of phase II for the K halides. Otherwise,  $c_p$  decreased with increasing pressure. Linear equations were fitted to the data and the coefficients are given in table 4. The change of  $c_p$  at the I  $\rightarrow$  II phase transition was small, and not more than 5% except for KI where a change of 10% was observed.

Dzhavadov and Krotov (1978) did not detect any change in  $c_p$  at the phase transition in KCl and RbCl. The total decrease in  $c_p$  which we observed up to 2.5 GPa was in the

**Table 4.** Room temperature pressure dependence of specific heat capacity,  $c_p$ , for phases I and II fitted to equations of form  $c_p \text{ (kJ kg}^{-1} \text{ K}^{-1}) = C + D P$ , and change of  $c_p$  through I  $\rightarrow$  II phase transition.

Substance	Phase I			Phase transition			Phase II		Literature value for $c_p$ at $P = 1 \text{ atm}^\ddagger$
	$C$	$D$	$P \text{ (GPa)}$	$P_t^\dagger \text{ (GPa)}$	$(c_{p,\text{II}}/c_{p,\text{I}})_{P=P_t}$	$C$	$D$	$P \text{ (GPa)}$	
KCl	0.680	-0.016	0-1.9	1.93	0.97	0.628	—	1.9-2.6	0.694
KBr	0.424	-0.014	0-1.7	1.74	1.00	0.399	—	1.7-2.7	0.439
KI	0.304	-0.017	0-1.8	1.73	1.10	0.303	—	1.8-2.6	0.318
RbCl	0.433	—	0-0.5	0.52	0.96	0.418	-0.006	0.5-2.5	0.428
RbBr	0.286	—	0-0.4	0.40	1.05	0.305	-0.009	0.4-2.5	0.318
RbI	0.246	—	0-0.4	0.36	1.02	0.252	-0.005	0.4-2.5	0.247

$^\dagger$  The transition pressures,  $P_t$ , are from Pistorius (1976).

$^\ddagger$  Values from Clusius *et al* (1949) except RbCl (Higashigaki and Chihara 1976).

range 0–8%. The total decrease found by Dzhavadov and Krotov for KCl and RbCl was within this range.

### Acknowledgments

The author wishes to thank Dr Russell G Ross and Dr Glen A Slack for many helpful and valuable discussions and suggestions when the manuscript was being prepared.

### References

- Alm O and Bäckström G 1974 *J. Phys. Chem. Solids* **35** 421  
Averkin A A, Logachev Yu A, Petrov A V, Seleznev V E and Tsyapkina N S 1976 *Sov. Phys.–Solid State* **18** 1853  
Clusius K, Goldmann J and Perlick A 1949 *Z. Naturf. a* **4** 424  
Devyatkova E D and Smirnov I A 1963a *Sov. Phys.–Solid State* **4** 1445  
—— 1963b *Sov. Phys.–Solid State* **4** 1836  
Dzhavadov L N and Krotov Yu I 1978 *Sov. Phys.–Solid State* **20** 379  
Eucken A 1911 *Ann Phys.* **34** 185  
Higashigaki Y and Chihara H 1976 *Bull. Chem. Soc. Japan* **49** 2089  
Gerlich D and Andersson P 1982 *J. Phys. C: Solid State Phys.* **15** 5211  
Joffé A F 1956 *Can. J. Phys.* **34** 1342  
McCarthy K A and Ballard S S 1960 *J. Appl. Phys.* **31** 1410  
Moore J P, Williams R K and Graves R S 1975 *Phys. Rev. B* **11** 3107  
Petrov A V, Tsyapkina N S and Logachev Yu A 1974 *Sov. Phys.–Solid State* **16** 39  
Pistorius C W F T 1964 *J. Phys. Chem. Solids* **25** 1477  
—— 1965 *J. Phys. Chem. Solids* **26** 1003  
—— 1976 *Prog. Solid State Chem.* **11** 1  
Ross R G, Andersson P and Bäckström G 1977 *High Temp.–High Pressures* **9** 87  
—— 1979 *Mol. Phys.* **38** 377  
Seleznev V E, Tsyapkina N S, Petrov A V, Averkin A A and Logachev Yu A 1976 *Sov. Phys.–Solid State* **18** 824  
Taylor A, Albers H R and Pohl R O 1965 *J. Appl. Phys.* **36** 2270  
Vaidya S N and Kennedy G C 1971 *J. Phys. Chem. Solids* **32** 951  
Walker C T 1963 *Phys. Rev.* **132** 1963