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# The minimum thermal conductivity of alkali halides

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**Abstract.** A phenomenological theory has been used to calculate the minimum thermal conductivity for 17 alkali halides with the NaCl structure in the temperature range 1–1200 K. The shortest mean free path has been chosen to be either the nearest-neighbour distance or the phonon wavelength. The calculations show that minimum thermal conductivity is difficult to obtain in alkali halides with the possible exceptions of LiF, NaBr, NaI, KI and RbF.

## 1. Introduction

In a simple model the thermal conductivity  $\lambda$  can be written

$$\lambda = \frac{1}{3Vk_{\text{B}}T^2} \sum_{q,j} [\hbar\omega(\mathbf{q}, j)]^2 N_0(\mathbf{q}, j) [N_0(\mathbf{q}, j) + 1] v(\mathbf{q}, j) l(\mathbf{q}, j) \quad (1)$$

where  $\omega(\mathbf{q}, j)$  is the frequency of the phonon with wave-vector  $\mathbf{q}$  and branch index  $j$ ,  $v$  is the group velocity,  $l$  is the mean free path and  $N_0$  is the thermal equilibrium distribution. The sum is taken over the whole first Brillouin zone.

When the temperature is raised, the three-phonon scattering increases and the mean free path of a phonon is shortened. There must be a shortest mean free path, however, since it cannot be shorter than the distance between the atoms. This leads to a departure from the  $T^{-1}$ -dependence at high temperatures and the thermal conductivity tends towards a minimum value. A high scattering rate may of course also be caused by defect scattering, isotope scattering, etc. Minimum thermal conductivity has been observed in glasses [1] where the phonons are scattered by the disorder in the structure. It has also been seen in some crystals [2, 3].

The minimum thermal conductivity has been treated phenomenologically by applying equation (1) with some choice of the shortest mean free path  $l$  [1, 4]. Two obvious choices are the nearest-neighbour distance  $r_0$  and the wavelength  $l_{\text{wl}}$  of the phonon.

Taking the shortest mean free path equal to the nearest-neighbour distance is thought to correspond to hopping conduction between localised states [4]. A recently published paper states that there are very few localised states even in such a strongly disordered structure as a glass [5]. This indicates that hopping between localised states cannot be the major mechanism for heat conduction in these crystals and  $l = r_0$  might not be a good choice.

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The shortest mean free path equal to a wavelength corresponds to the limit where the phonon concept becomes invalid. This choice has been successfully applied to quartz and some other materials [1]. Note, however, that the optic phonons are treated in a different way in [1].

We shall in this paper improve the phenomenological calculations made previously by using a realistic dispersion relation. All phonons are assumed to be scattered in some way so strongly that they all have the shortest possible mean free path. We would like to stress the fact that this is a phenomenological approach which has not been justified by any microscopic theory. Its validity is given by its capability of explaining the magnitude of the observed minimum thermal conductivity [1, 6].

A microscopic theory which may explain the minimum thermal conductivity has been proposed in [7]. It is rather complicated and has not yet been applied to a real crystal.

## 2. Calculations and results

We calculated the dispersion relations from a deformation dipole (DD) model with only nearest-neighbour short-range forces included. We used the room-temperature input data given in [8]. The dispersion relations were calculated for 152 evenly distributed points in one-fortyeighth of the first Brillouin zone. In order to obtain an accurate low-temperature behaviour, we replaced the 10 points closest to the  $\Gamma$  point with succeedinglly denser meshes.

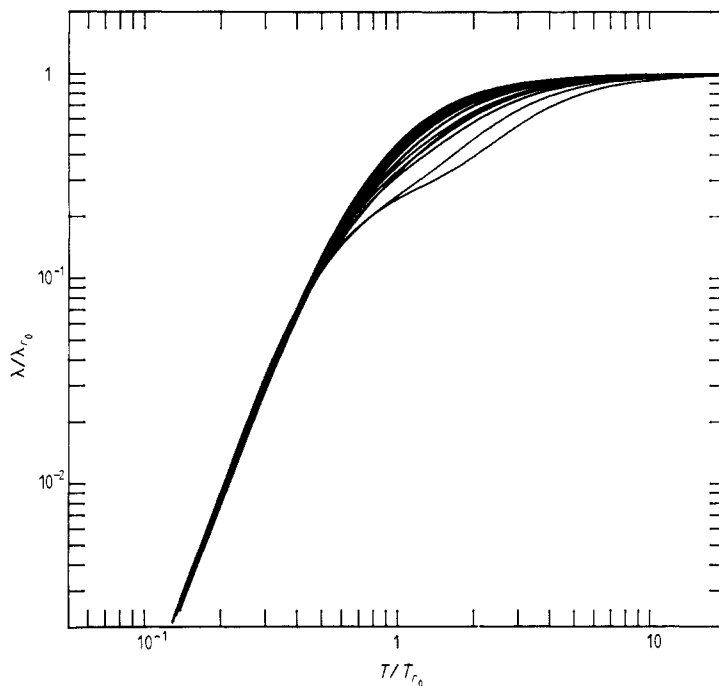
The result when  $l = r_0$  is used in equation (1) is shown in figure 1. All 17 alkali halides with the NaCl structure have been plotted in the same figure after scaling the temperature with  $T_{r_0}$  and the thermal conductivity with  $\lambda_{r_0}$ .  $T_{r_0}$  and  $\lambda_{r_0}$  are found in table 1. At high temperatures the minimum thermal conductivity tends towards a constant value  $\lambda_{r_0}$  which has been taken to equal the calculated  $\lambda$ -value at 1200 K. At low temperatures, we have a  $T^3$ -dependence which can be obtained from equation (1) if a Debye model is assumed. The crossover between the extrapolated  $T^3$ -dependence and the high-temperature value determines  $T_{r_0}$ . With this scaling, the results for nearly all crystals fall on the same curve.

The results which do not follow the universal curve are for the crystals that have a gap between the acoustic and optic branches. They are LiI, LiBr, CsF, LiCl, NaI, RbF, NaBr, KI and RbCl, listed in order of decreasing gap. In crystals with a large gap the acoustic branches have been excited at  $T_{r_0}$  but not the optic branches and the minimum thermal conductivity tends towards a constant value. At somewhat higher temperatures the optic branches become excited and we obtain an increase in the minimum thermal conductivity. This effect is most pronounced in LiI and LiBr which are the lowest and next-lowest curves, respectively, in figure 1. The effect resembles the plateau that one finds in glasses at low temperatures but there are other explanations suggested for the origin of this plateau [17, 18].

Figure 2 gives the result with  $l = l_{w1}$ . The scaling factors  $T_{w1}$  and  $\lambda_{w1}$  are found in table 1. The main difference from figure 1 is that we now have a  $T^2$ -dependence at low temperatures. Since glasses have this  $T^2$ -dependence, this might favour the wavelength as the better choice. We also see that  $\lambda_{w1}$  is greater than  $\lambda_{r_0}$  by a factor of approximately 3. This was expected since  $l_{w1}$  can never be shorter than  $r_0$ .

We have also calculated the volume dependence of the minimum thermal conductivity. It is usually expressed by the Bridgman parameter

$$g = -[\partial(\ln \lambda)/\partial(\ln V)]_T. \quad (2)$$



**Figure 1.** Minimum thermal conductivity of alkali halides with the NaCl structure. The shortest mean free path is equal to the nearest-neighbour distance. The scaling factors  $\lambda_{r_0}$  and  $T_{r_0}$  are found in table 1.

In [19], we describe how to calculate the phonon dispersion relation at different volumes. A small volume change does not alter the shape of the curves in figures 1 and 2 and hence it suffices to give the volume dependence of the scaling factors. These are  $g_{r_0}$  and  $t_{r_0}$  for figure 1 and correspondingly for figure 2. The definition of  $t$  is similar to that of  $g$ :

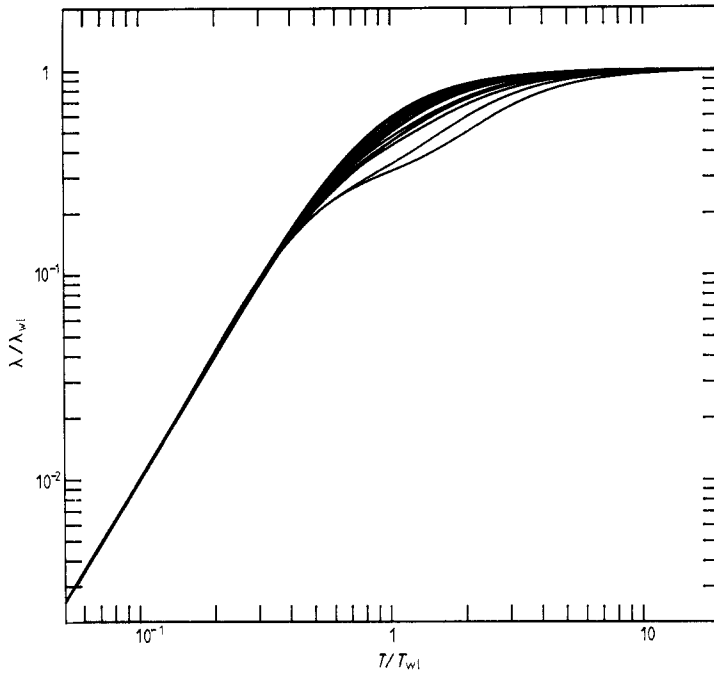
$$t_{r_0} = -[\partial(\ln T_{r_0})/\partial(\ln V)]_T. \quad (3)$$

In table 2, we give values of  $g_{r_0}$ ,  $t_{r_0}$ ,  $g_{w_1}$  and  $t_{w_1}$  for 10 alkali halides. The calculated  $g$ -values are very low compared with the  $g$ -values measured at room temperature ( $g = 5$ – $10$ ). The reason for this is that the experiments are performed under conditions where three-phonon scattering processes give important contributions to the  $g$ -value [19]. In our calculation of the minimum thermal conductivity, we have assumed that these scattering processes have reached a maximum and that the mean free path is the shortest possible. This mean free path scales with the lattice constant and adds, in principle, only a constant of value  $\frac{1}{3}$  to the  $g$ -value.

With  $l = r_0$  in equation (1), we can take  $r_0$  outside the summation over  $\mathbf{q}$ -vectors. This is not possible when  $l = l_{w_1}$ . In the latter case, phonons in the neighbourhood of  $\Gamma$  will be more important in the summation over  $\mathbf{q}$  than in the first case. However, we do not expect any greater differences between  $g_{r_0}$  and  $g_{w_1}$  since the relative numbers of long-wavelength phonons is small at high temperatures. This is also seen to be the case in table 2. It is more difficult to predict relationships between  $t_{r_0}$  and  $t_{w_1}$  but it can be seen in table 2 that the values are very close except for RbCl.

**Table 1.**  $T_{r_0}$  and  $\lambda_{r_0}$  are the scaling factors in figure 1 and  $T_{w_1}$  and  $\lambda_{w_1}$  are the scaling factors in figure 2.  $\lambda_{mp}$  is the thermal conductivity of the solid at the melting point  $T_{mp}$ , extrapolated from room-temperature values.  $\lambda_L$  is the measured thermal conductivity in the liquid phase just above the melting point.

Crystal	$T_{r_0}$ (K)	$\lambda_{r_0}$ (W m <sup>-1</sup> K <sup>-1</sup> )	$T_{w_1}$ (K)	$\lambda_{w_1}$ (W m <sup>-1</sup> K <sup>-1</sup> )	$\lambda_{mp}$ (W m <sup>-1</sup> K <sup>-1</sup> )	Reference	$T_{mp}$ (K)	$\lambda_L$ (W m <sup>-1</sup> K <sup>-1</sup> )	Reference
LiF	124	0.91	148	2.87	3.84	[9]	1118	1.73	[16]
LiCl	74	0.39	88	1.24	—	—	878	0.46	[16]
LiBr	51	0.27	62	0.86	—	—	823	0.39	[16]
LiI	37	0.19	45	0.60	—	—	722	—	—
NaF	93	0.56	110	1.76	3.85	[10]	1266	1.25	[1]
NaCl	59	0.28	70	0.90	1.66	[11]	1074	0.99	[1]
NaBr	40	0.18	48	0.57	0.63	[12]	1020	0.31	[1]
NaI	30	0.12	36	0.40	0.42	[11]	934	—	—
KF	62	0.28	73	0.92	1.69	[13]	1131	—	—
KCl	47	0.21	56	0.67	1.78	[14]	1043	0.80	[1]
KBr	33	0.13	40	0.44	0.82	[14]	1007	0.29	[1]
KI	25	0.09	30	0.31	0.60	[14]	954	0.23	[1]
RbF	43	0.18	49	0.57	0.63	[15]	1068	—	—
RbCl	32	0.12	37	0.39	0.71	[14]	991	—	—
RbBr	28	0.12	33	0.37	1.00	[14]	966	—	—
RbI	22	0.08	26	0.28	0.63	[14]	920	—	—
CsF	35	0.15	41	0.49	—	—	955	—	—



**Figure 2.** Minimum thermal conductivity of alkali halides with the NaCl structure. The shortest mean free path is equal to the phonon wavelength. The scaling factors  $\lambda_{wl}$  and  $T_{wl}$  are found in table 1.

**Table 2.**  $t_{r0}$ ,  $g_{r0}$ ,  $t_{wl}$  and  $g_{wl}$  are the volume dependences of  $T_{r0}$ ,  $\lambda_{r0}$ ,  $T_{wl}$  and  $\lambda_{wl}$ , respectively.  $\lambda_{wl}^{red}$  and  $\lambda_{mp}^{red}$  (in units of  $\text{W m}^{-1} \text{K}^{-1}$ ) are the corresponding quantities in table 1 reduced to the volume of the solid at the melting point.  $g_{300}$  is the experimental room-temperature value of  $g$  that has been used in the reduction in  $\lambda_{mp}^{red}$ .

Crystal	$t_{r0}$	$g_{r0}$	$t_{wl}$	$g_{wl}$	$\lambda_{wl}^{red}$	$g_{300}$	Reference	$\lambda_{mp}^{red}$
LiF	1.54	0.51	1.42	0.51	2.71	7.9	[9]	1.54
NaF	1.20	2.64	1.26	2.44	1.27	7.6	[10]	1.39
NaCl	0.68	1.78	0.69	1.97	0.71	7.4	[11]	0.67
NaBr	0.77	2.08	0.74	2.14	0.45	9.7	[12]	0.21
KCl	1.06	2.98	1.08	2.87	0.49	6.1	[20]	0.93
KBr	0.72	2.73	0.69	2.68	0.33	8.2	[20]	0.35
KI	0.58	2.64	0.64	2.65	0.24	15.8	[20]	0.12
RbCl	1.25	2.13	2.17	2.21	0.32	9.0	[20]	0.31
RbBr	0.47	2.32	0.59	2.41	0.30	7.1	[20]	0.53
RbI	0.52	2.99	0.64	2.96	0.22	7.5	[20]	0.33

### 3. Discussion

The minimum thermal conductivity in the alkali halides is most likely to be seen at high temperatures where the phonon scattering rate is high, but there are very few high-temperature measurements of the thermal conductivity in these crystals. In [21], high-

temperature values are reported for several alkali halides and they show a significant deviation from the  $T^{-1}$ -dependence. The deviation is not consistent with our calculations since in [21] a strong increase in the  $\lambda$ -values is obtained near the melting point whereas we obtain a constant value of the minimum thermal conductivity. The effect seen in [21] is probably not the minimum thermal conductivity but can instead be explained by radiative heat transport which has not been properly corrected for in the measurements.

In an experiment on LiF [22], care was taken to correct for the radiative heat transport and it was found that, even with this correction,  $\lambda$  deviated from the  $T^{-1}$ -dependence near the melting point and had a constant value at the highest temperatures. We have corrected the thermal conductivity values in [22] from constant pressure to constant volume. With the experimental room-temperature  $g$ -value ( $g = 7.9$  [9]), we obtain  $\lambda = 7.64 \text{ W m}^{-1} \text{ K}^{-1}$  for the temperature-independent high-temperature value corrected to the volume at 300 K. If we use the calculated  $g$ -value ( $g = 0.51$ ) for the minimum thermal conductivity, we obtain from [22] a corrected high-temperature value of  $\lambda = 3.26 \text{ W m}^{-1} \text{ K}^{-1}$ . It is not possible to decide whether this corrected measurement really gives the minimum thermal conductivity or not. Assuming a  $g$ -value appropriate to minimum thermal conductivity gives a  $\lambda$ -value close to the calculated minimum whereas assuming a  $g$ -value equal to the measured room-temperature values gives a  $\lambda$ -value much higher than the minimum. We shall return to this experiment below.

Can three-phonon processes alone give rise to minimum thermal conductivity? To answer this question, we took the room temperature values from measurements on pure alkali halide crystals and calculated the thermal conductivity  $\lambda_{\text{mp}}$  at the melting point, assuming a  $T^{-1}$ -dependence. Note that  $\lambda_{\text{mp}}$  is not the thermal conductivity that would be found in an experiment performed at the melting point since we have not taken the thermal expansion into account. However,  $\lambda_{\text{mp}}$  is the proper quantity to use in a comparison with our calculations since both refer to the room-temperature volume.

Comparing  $\lambda_{\text{mp}}$  with the high-temperature values  $\lambda_{r_0}$  and  $\lambda_{w_1}$ , we find that  $\lambda_{\text{mp}}$  is much greater than  $\lambda_{r_0}$  and  $\lambda_{w_1}$  for most crystals. For NaBr, NaI and RbF,  $\lambda_{\text{mp}}$  is only slightly larger than  $\lambda_{w_1}$ . We conclude that, if the wavelength is the proper shortest mean free path to use, there is a possibility that some indications of the minimum thermal conductivity in NaBr, NaI and RbF are seen at high temperatures.

There have been attempts to reduce the thermal conductivity in KCl by mixing it with KBr [23]. The reduction was not great enough to give the minimum thermal conductivity. From our calculations it seems as if NaBr, NaI and RbF would be the most interesting crystals to manipulate in order to obtain increased phonon scattering.

Is there a possibility that increasing the pressure would be a way to obtain the minimum thermal conductivity? In view of the  $g$ -values given in table 2 the answer must be 'no'. Although the  $g$ -values are positive and the minimum thermal conductivity will increase with increasing pressure, this will not help us. Experimental  $g$ -values at room temperature usually lie in the range 5–10 for the alkali halides. This means that the 'normal' thermal conductivity at a particular temperature increases more rapidly than the minimum value and the difference between the two would increase. Note that this statement is valid for a particular temperature. Since the melting point of an alkali halide increases rapidly when pressure is applied, it might be possible to observe minimum thermal conductivity near the high-pressure melting point. However, we have made rough estimates which indicate that this will not happen since the increase in the melting point with pressure is too small.

The difference between the 'normal' and the 'minimum'  $g$ -values makes it more probable, however, that minimum thermal conductivity can be seen under isobaric

conditions than our isochoric calculations indicate. When the lattice is allowed to expand from room-temperature volume to the actual volume at the melting point, we obtain an appreciable decrease in  $\lambda_{\text{mp}}$  while the decrease in  $\lambda_{\text{wl}}$  is much less. This makes the difference between  $\lambda_{\text{mp}}$  and  $\lambda_{\text{wl}}$  smaller at the melting point than shown in table 1 since the latter refers to room-temperature volume. As an example, we reduce the values of  $\lambda_{\text{wl}}$  and  $\lambda_{\text{mp}}$  for LiF (with  $g$ -values quoted above) from room-temperature volume to the actual volume at the melting point. We obtained  $\lambda_{\text{wl}}^{\text{red}} = 2.71 \text{ W m}^{-1} \text{ K}^{-1}$  and  $\lambda_{\text{mp}}^{\text{red}} = 1.54 \text{ W m}^{-1} \text{ K}^{-1}$ . When referred to the correct volume, the value of the thermal conductivity at  $T_{\text{mp}}$  obtained by extrapolation of the room-temperature experimental value is lower than the calculated minimum thermal conductivity. This implies that the thermal conductivity values near the melting point obtained in [22] for LiF are minimum thermal conductivity values or at least very close to the minimum.

We have made corresponding corrections for all alkali halides in table 2. It is found that  $\lambda_{\text{wl}}^{\text{red}}$  is very close to  $\lambda_{\text{mp}}^{\text{red}}$  for most of these alkali halides, which implies that minimum thermal conductivity cannot be seen over any temperature range below the melting point. KCl turns out to be the crystal farthest away from the minimum value. For LiF, NaBr and KI we have  $\lambda_{\text{wl}}^{\text{red}} \approx 2\lambda_{\text{mp}}^{\text{red}}$ , which implies that minimum thermal conductivity may be seen for a small temperature range just below the melting point.

We summarise this discussion as follows. The experimental room-temperature values of the thermal conductivity are extrapolated to the melting point  $T_{\text{mp}}$ . However, these values refer to the room-temperature volume and consequently we use the experimental  $g$ -values at 300 K to correct the  $\lambda$ -values further to the volume at  $T_{\text{mp}}$ . The final value  $\lambda_{\text{mp}}^{\text{red}}$  obtained is the expected value of the thermal conductivity at  $T_{\text{mp}}$  due to ordinary three-phonon scattering. In the same way, we obtain  $\lambda_{\text{wl}}^{\text{red}}$  by correcting the calculated minimum thermal conductivity values at  $T_{\text{mp}}$  to the correct volume using the calculated  $g_{\text{wl}}$ -values. The condition for minimum thermal conductivity to be seen is that  $\lambda_{\text{mp}}^{\text{red}} < \lambda_{\text{wl}}^{\text{red}}$  in some temperature range below  $T_{\text{mp}}$ . This is the case for LiF, NaBr and KI.

It is also interesting to compare the high-temperature values with the thermal conductivity in the liquid phase (table 1). The disorder in a glass and that in a liquid are similar and the thermal conductivity due to phonon-like excitations is likely to be near the minimum thermal conductivity. The thermal conductivity  $\lambda_{\text{L}}$  of the liquid phase just above the melting point can be reduced by doping with foreign atoms and thus adding more scattering centres; so the  $\lambda_{\text{L}}$ -values are not minimum values. It is seen that  $\lambda_{\text{L}}$  has the same magnitude as  $\lambda_{r_0}$  and  $\lambda_{\text{wl}}$ . In most cases,  $\lambda_{\text{L}}$  lies between the calculated values, indicating that liquid alkali halides have a thermal conductivity close to the minimum thermal conductivity. However, we must remember that we have compared  $\lambda$ -values appropriate to different densities (alkali halides expand about 15–20% on melting) and we also know very little about phonons and other excitations in the liquid phase.

#### 4. Summary

The phenomenological theory shows that it is difficult to establish conditions under which an alkali halide crystal exhibits minimum thermal conductivity. The best conditions for observing minimum thermal conductivity are atmospheric pressure and temperatures near the melting point. Increasing the pressure would make it even more difficult to obtain minimum thermal conductivity. The most promising candidates for observing this effect are NaBr, NaI and RbF. When our calculated values are reduced from values for the room-temperature volume to the actual volume at the melting point, we find that



LiF and KI may also exhibit values of  $\lambda$  close to the minimum thermal conductivity at very high temperatures.

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