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Thermal Conductivity of Solid NaF Under High Pressure

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The thermal conductivity (λ) of solid NaF has been measured over the temperature (T) range 100–350 K and at pressures (P) up to 2.5 GPa, using the transient hot-wire method. Results for $\lambda(T,P)$ could be described to a good approximation by the Leibfried-Schlömann formula. It was found that the isochoric temperature derivative of the thermal resistivity W ($= \lambda^{-1}$) increased systematically with the mass ratio for the B1-type phases of the sodium and potassium halides.

KEY WORDS: high pressure; sodium fluoride (NaF); thermal conductivity; transient hot-wire method.

1. INTRODUCTION

The alkali halides are of special interest and importance in the study of the thermal conductivity (λ) of crystals under pressure, because of the relatively simple crystal structures involved. Investigations of λ under pressure (P) have already been made for a number of alkali halides [1], although in some instances the data were restricted to room temperature. This was the case in the only previous measurement of $\lambda(P)$ for NaF, by Alm and Bäckström [2]. In the present investigation of this substance we have measured the variation of λ with both pressure and temperature (T), which permits a more detailed comparison between theory and experiment.

NaF has the NaCl or B1 type of crystal structure over the pressure range of our equipment, and the same is true for the other sodium halides. These have recently been investigated in our laboratory, yielding data for

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$\lambda(T,P)$ for NaCl [3], NaBr [4], and NaI [3]. Although the crystal structure remains the same, what varies through the sodium halides is the mass ratio σ. This quantity has the value 1.21 for NaF, 1.54 for NaCl, 3.48 for NaBr, and 5.52 for NaI. As is well known, the mass ratio affects the separation in energy of the acoustic and optic modes in a crystal of diatomic basis, and this in turn should influence the relative influence of acoustic and optic phonons in the heat transport process. Data now available for the sodium halides provide the opportunity to analyze the variation of λ with the mass ratio. In particular, the substance of the present investigation (NaF) has a mass ratio rather close to the ideal value $\sigma = 1.00$, at which the optic modes would be a smooth continuation of the acoustic modes in an extended zone scheme.

2. EXPERIMENTAL

We used the transient hot-wire method to measure the thermal conductivity, λ. Details of the method and of the general experimental arrangements have been given elsewhere [5, 6]. The Ni hot wire, 0.1 mm in diameter, was installed as a circular loop between two precompacted 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 and it was measured using a chromel–alumel thermocouple in contact with the specimen.

The material used was powder of $\gtrsim 99.5\%$ purity, obtained from Merck, West Germany. It was dried at 200°C for 24 h in a vacuum oven and then compacted in a steel die under a pressure of 0.1 GPa to form polycrystalline plates. Mounting of the experimental cell was performed in an argon-atmosphere glove box in the presence of P_2O_5. We used two different samples for the experiments.

The measurements were carried out either as isobaric runs at various pressures in the temperature range 100–300 K or as isothermal runs up to about 2.5 GPa. To ensure good thermal contact between the hot wire and the specimen, a minimum pressure $\gtrsim 0.2$ GPa was used. The inaccuracy in λ was estimated as $\pm 5\%$.

The transient hot-wire method also yields data for the heat capacity per unit volume, ρc_p, where c_p is the specific heat capacity and ρ is the mass density. As discussed in a previous paper [7], due to the high values of the thermal diffusivity of the alkali halides, reliable values of ρc_p cannot be obtained for these materials at relatively low temperatures. It was found in the case of NaF that the error in ρc_p was high even at room temperature, and therefore no data for ρc_p are presented.

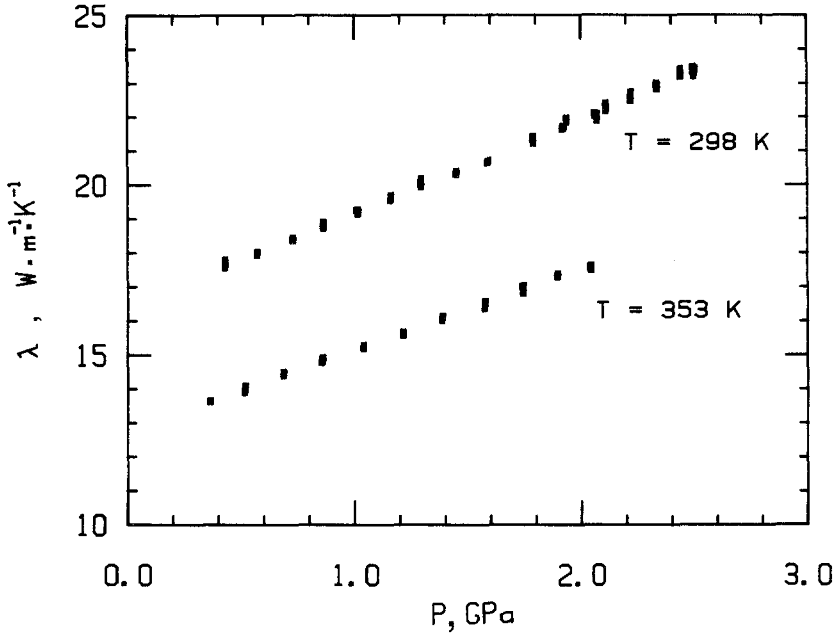

Fig. 1. Thermal conductivity (λ) of NaF plotted against pressure (P) along isotherms.

3. RESULTS AND COMPARISON WITH PREVIOUS WORK

Figure 1 shows results for $\lambda(P)$ from two isothermal pressure runs. The results can be represented by a straight line of the form $\lambda = A + BP$. The values of the quantities A and B together with that of $\lambda^{-1}(\partial\lambda/\partial P)_T = B/A$, from this and previous work, are given in Table I. Our value of B/A at room temperature is 38% higher than that of Alm and Bäckström [2].

The data given in Table I provide, at $P = 0$, the value of λ ($= A$) and the pressure derivative s ($= B/A$) for the particular isotherms stated. In

Table I. Isothermal Pressure Dependence of the Thermal Conductivity, λ, of NaF Fitted to Equations of the Form $\lambda = A + BP$, Where λ Is in $W \cdot m^{-1} \cdot K^{-1}$ and P is in GPa

	A ($W \cdot m^{-1} \cdot K^{-1}$)	B ($W \cdot m^{-1} \cdot K^{-1} \cdot GPa^{-1}$)	B/A (GPa^{-1})	T (K)	P (GPa)
This work	16.5	2.73	0.165	298	0–2.6
This work	12.82	2.33	0.182	353	0–2.1
Alm and Bäckström [2]			0.12	300	0–3

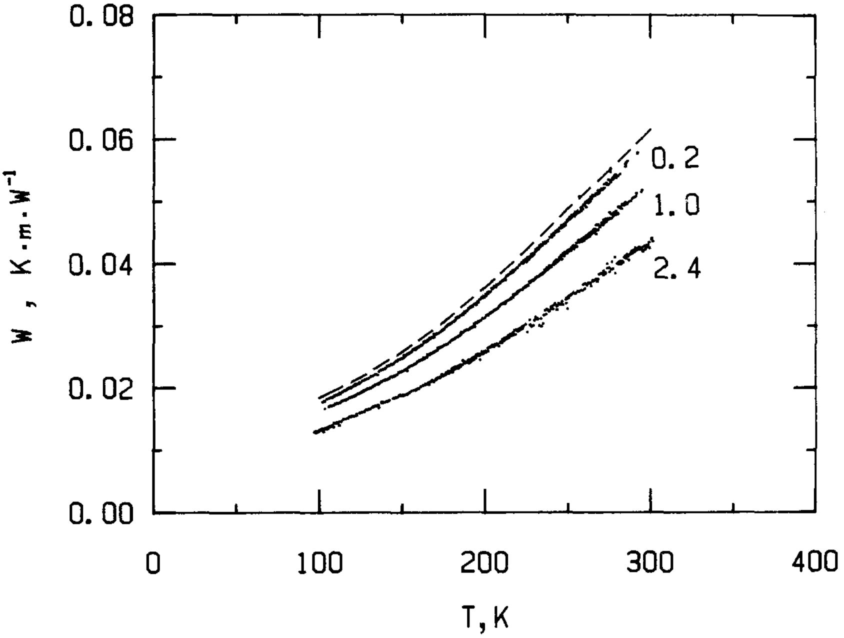

Fig. 2. Thermal resistivity (W) of NaF plotted against temperature (T) along isobars. The numbers are pressures in GPa. The dashed line referring to zero pressure was obtained by extrapolation.

order to obtain similar data over the whole range of temperatures, we compared the measured values of λ along the three isobars at pressures of 0.2, 1.0, and 2.4 GPa, shown in Fig. 2. We assumed that λ varied linearly with P at all temperatures. The resulting values of thermal resistivity W as a function of temperature at zero pressure obtained by extrapolation are given in Table II. They are also represented by the dashed line in Fig. 3, where we make a comparison with the results of previous workers [8–10]. As can be seen the values from this work agree very well with those of Petrov et al. [8], and the agreement with the work of Smirnov et al. [9] is reasonable. The values given by Walker [10] show poor agreement with ours above 200 K.

4. DISCUSSION

4.1. The Absolute Value of λ

The thermal conductivity of insulators at temperatures comparable to or higher than their Debye temperatures is given, strictly at constant

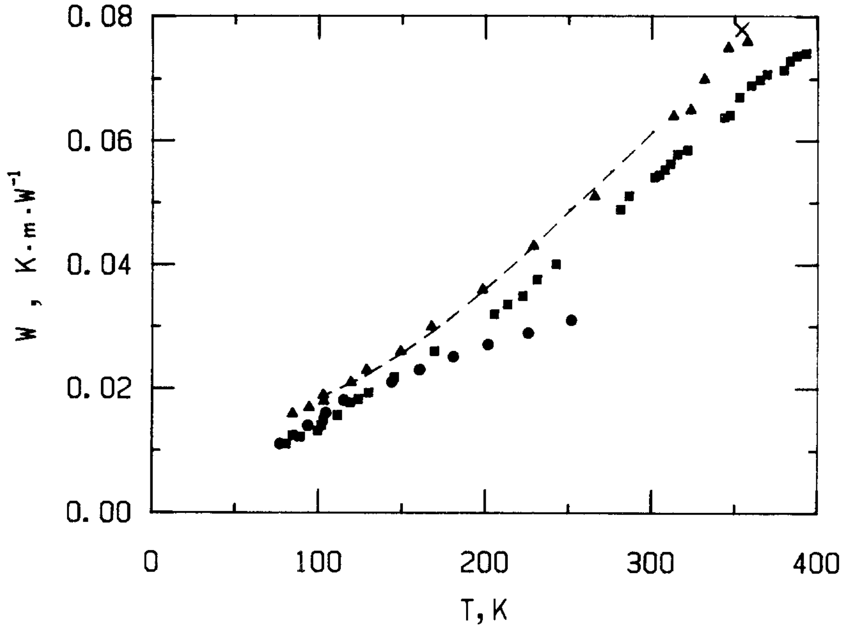

Fig. 3. Thermal resistivity of NaF plotted against temperature (T) at zero pressure compared with previous work. (– – –) Present work (by extrapolation from the isobars); (X) present work (by extrapolation of the 353 K isotherm); (▲) Petrov et al. [8]; (■) Smirnov [9]; (●) Walker [10].

volume, by the Leibfried-Schlömann formula. Assuming contributions from acoustic phonons only, and three phonon scattering processes, the thermal conductivity may be expressed by [11]

$$\lambda = \frac{B n^{1/3} \delta \bar{M} \tilde{\theta}_{\infty}^{3}}{\tilde{\gamma}_{\infty}^{2} T} \tag{1}$$

where $\bar{M}$ is the average atomic weight, δ is the cube root of the average volume per atom, n is the number of atoms per primitive unit cell ($n = 2$ for the NaCl type of structure), and $\tilde{\theta}_{\infty}$ and $\tilde{\gamma}_{\infty}$ are the Debye temperature and Grüneisen parameter, respectively, in the high-temperature limit, evaluated over the spectrum of the acoustic phonons only. The value of the constant B is assumed to be 3.04×10^4 W·m^{-2}·K^{-3}·g-atom^{-1} [11]. If optic phonons also contribute fully to thermal transport, then $\tilde{\theta}_{\infty}$ and $\tilde{\gamma}_{\infty}$ would be expected to be replaced by their respective values (θ_{∞} and γ_{∞}) calculated for the whole phonon spectrum. The values of $\tilde{\theta}_{\infty}$ and θ_{∞} were taken from Slack [11]. We assumed both $\tilde{\gamma}_\infty$ and γ_∞ to be equal to the room-temperature thermodynamic Grüneisen parameter

$$\gamma_{\text{th}} = \frac{\alpha B_{\text{S}}}{\rho c_{\text{p}}} \tag{2}$$

where B_{S} is the adiabatic bulk modulus and α is the thermal expansivity. We calculated γ_{th} from data for thermal expansivity [12], adiabatic bulk modulus [13], specific heat capacity [14], and density [15]. In Table III, we have given the values of λ at room temperature calculated using Eq. (1) in the two cases of acoustic phonons, or all phonons taking part in the heat transport, as well as our measured conductivity value.

From Table III it can be seen that our measured value at 298 K lies between the two calculated values and close to that calculated assuming only acoustic phonons ($\lambda_{1,\text{calc}}$). We infer from this behavior that both acoustic and optic phonons contribute to the heat transport process, which is consistent with our analysis of $W(T)$ in the following subsection.

4.2. Density and Temperature Effects

We plotted the logarithm of thermal conductivity λ against the logarithm of density ρ, using the room temperature data for $\lambda(P)$ from Table I and tabulated data for ρ at 0, 0.5, 1.0, 1.5, 2.0, and 2.5 GPa from Ref. 15. Values for the quantity

$$g = \left(\frac{\partial \ln \lambda}{\partial \ln \rho}\right)_T \tag{3}$$

were then evaluated by finite differences. Figure 4 shows the resulting values of g as a function of pressure. As can be seen, g decreases with pressure. The theoretical prediction for g using Eq. (1) may be expressed as [11]

$$g = 3\gamma + 2q - \frac{1}{3} \tag{4}$$

Table II. Thermal Resistivity of NaF in $\text{K} \cdot \text{m} \cdot \text{W}^{-1}$[a]

T (K)								
100	125	150	175	200	225	250	275	300
0.0185	0.0217	0.0258	0.0306	0.0362	0.0422	0.0488	0.0550	0.0615

[a] Values are for zero pressure and were obtained by extrapolation.

Table III. Calculated and Measured Values of the Thermal Conductivity of NaF at Zero Pressure and Room Temperature

T (K)	$\bar{M}$ (g-atom)	B_S (GPa)	δ (10^{-10} m)	$\tilde{\theta}_\infty$ (K)	θ_∞ (K)	γ_{th}	$\lambda_{1,calc}$ ($W \cdot m^{-1} \cdot K^{-1}$), acoustic phonons only	$\lambda_{2,calc}$ ($W \cdot m^{-1} \cdot K^{-1}$), acoustic and optic phonons	λ_{meas} ($W \cdot m^{-1} \cdot K^{-1}$)
298	20.99	48.47	2.31	395	445	1.53	16.38	23.43	16.5

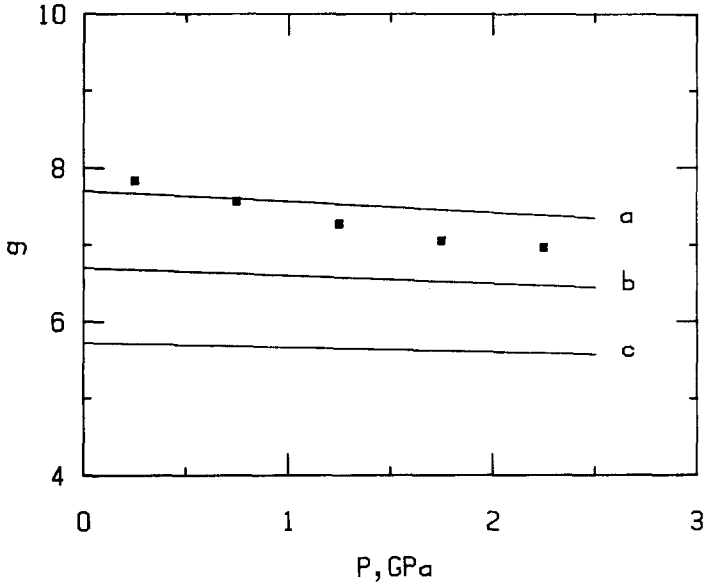

Fig. 4. The quantity g plotted against pressure (P) for NaF at room temperature; comparison between present experimental results and theoretical estimates. (■) Present results; (—) theoretical estimates for various values of q—(a) 1.72 [18], (b) 1.22 [17], and (c) 0.73 [16].

where we have assumed

$$\gamma = \left(\frac{\partial \ln \theta}{\partial \ln \rho}\right)_T = B_\mathrm{T}\left(\frac{\partial \ln \theta}{\partial p}\right)_T \tag{5}$$

and the second Grüneisen parameter

$$q = -\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_T = -B_\mathrm{T}\left(\frac{\partial \ln \gamma}{\partial P}\right)_T \tag{6}$$

B_T is the isothermal bulk modulus.

The volume dependence of g can be expressed as

$$g = 3\gamma_0(V/V_0)^q + 2q - \frac{1}{3} \tag{7}$$

where γ_0 is the Grüneisen parameter at zero pressure and V/V_0 is the relative volume at pressure P. We have calculated g at zero pressure and at 2 GPa using our calculated value for γ_th and different values of q obtained from the literature [16–18]. The quantity q was assumed to be independent of pressure, and V/V_0 was taken from Ref. 15. The results are shown in Fig. 4 and compared with our experimental values. As can be seen agreement is reasonable, although the experimental values of g vary somewhat more strongly with P than do the theoretical predictions. We infer from this comparison that the Liebfried-Schlömann formula provides a reasonably satisfactory description of the pressure variation of the thermal conductivity of NaF.

We have also calculated g at zero pressure as a function of temperature, using our values for the pressure derivative of λ, s ($= B/A$), and values of $B_T(T)$ calculated from elastic constant data [13]. The results thus obtained are shown in Fig. 5. We find $g \simeq 8$, almost independent of T. In order to provide a comparison with theory, we made a rough calculation of g at 100 K, using Eq. (4). According to White and Collins [19], γ is almost constant in the temperature range 100–300 K. To obtain $q(T)$ we used an expression derived by Bassett et al. [16],

$$q = 1 + (1 + T\alpha\gamma)\delta_S - B'_S + \gamma + T(\partial \ln \gamma/\partial T)_V \qquad (8)$$

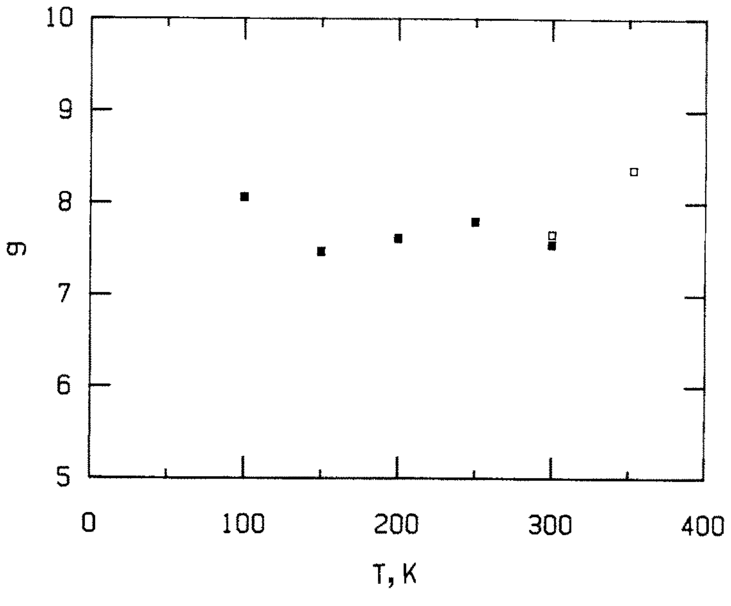

Fig. 5. The quantity g plotted against temperature (T) for NaF at zero pressure. Data for $s = B/A$ obtained (□) by direct measurement under isothermal conditions (Table I) and (■) indirectly from measurements under isobaric conditions. Data for $B_T(T)$ calculated from Ref. 13.

which is expressed in terms of experimentally available quantities. In this expression,

$$\delta_S = -\frac{1}{\alpha B_S}(\partial B_S/\partial T)_P \tag{9}$$

and

$$B'_S = (\partial B_S/\partial P)_T$$

The values of $(\partial B_S/\partial T)_P$ and $(\partial B_S/\partial P)_T$ were calculated using the temperature and pressure derivatives of adiabatic elastic constants obtained from Ref. 20. Assuming $(\partial B_S/\partial T)_P$ to be independent of temperature, we were able to calculate B_S at 100 K. We also assumed B'_S to be independent of temperature. The last term in Eq. (8) is negligible in the temperature range of the present work. The calculations gave us a value $q = 5.4$ at 100 K, and using this value in Eq. (4), g turned out to be about 15 at this temperature. This value of g is about twice our experimental value. We

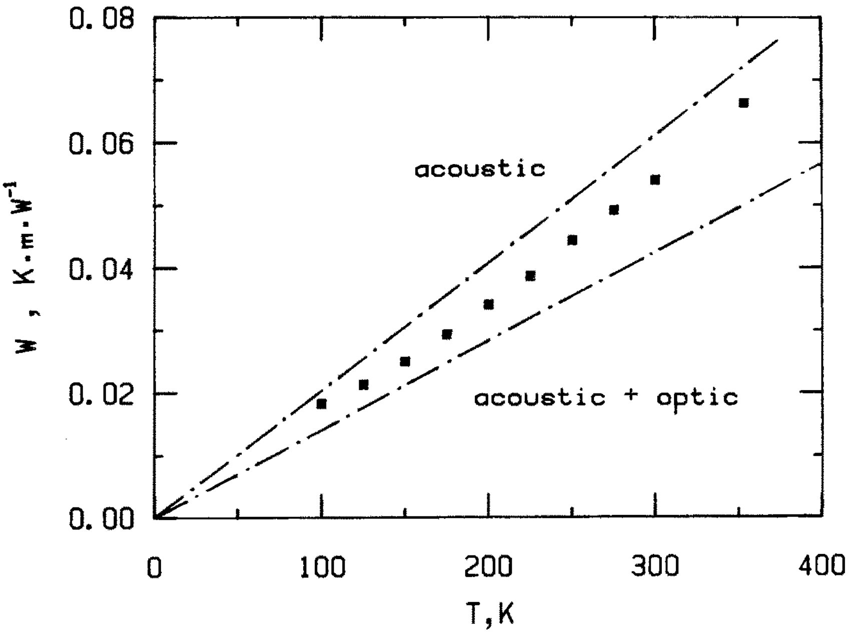

Fig. 6. Thermal resistivity (W) plotted against temperature (T) for NaF under isochoric conditions; comparison between experiment and theory. (■) Present experimental results; (–·–) theoretical predictions using Eq. (1) and assuming either acoustic only or acoustic + optic phonons.

doubt that this disagreement is significant in view of approximations in the theoretical estimate.

From Eq. (1) we expect the thermal resistivity *W* to be proportional to *T*, although this prediction from the Leibfried-Schlömann formula applies strictly to isochoric conditions. Since we know $g(T)$, we can reduce our experimental isobaric data for *W* to isochoric conditions. The specific volume we chose was that pertaining to $T=0$ and $P=0$. For the reduction we used $W(T)$ at zero pressure from Table II, $g(T)$ as represented in Fig. 5, and $\alpha(T)$ given by Touloukian et al. [12]. The results are shown in Fig. 6. As can be seen the isochoric data fall on a straight line which can be extrapolated through the origin, and the slight upward curvature seen in the isobaric curves in Fig. 2 can thus be attributed to the effect of thermal expansion. The dot–dash lines in Fig. 6 represent the two cases of acoustic phonons only and both optic and acoustic phonons. The points representing the isochoric data lie between these two theoretical predictions.

We infer from this comparison of theory and experiment that both acoustic and optic modes need to be taken into account for the thermal conductivity of NaF and that, when this is done, the Leibfried-Schlömann

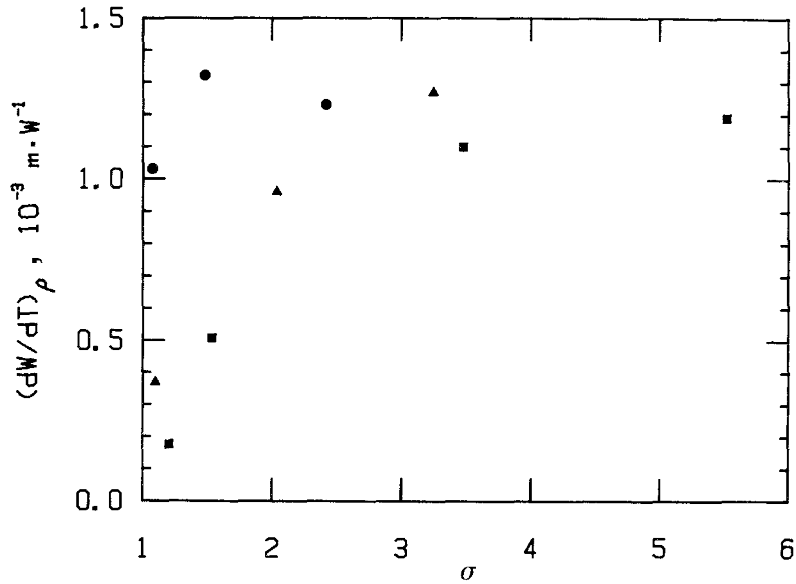

Fig. 7. Isochoric temperature derivative of thermal resistivity (*W*) plotted against mass ratio (σ) for B1-type phases of alkali halides. (■) Sodium halides: NaF (present work); NaCl [3]; NaBr [4]; NaI [3]. (▲) Potassium and (●) rubidium halides from Table 4 of Ref. 1.

formula provides a satisfactory description. Similar considerations apply [3] to NaCl and NaI. In the case of NaBr [4], it has been concluded that only the acoustic modes need to be considered in applying the Leibfried-Schlömann formula. Over the sodium halides as a group, we had expected to see the experimental values move closer to the theoretical prediction for acoustic + optic modes as the mass ratio approached unity, where the optic modes join smoothly with the acoustic modes. However, the present results for NaF ($\sigma = 1.21$) show in Fig. 6 that the experimental value is approximately midway between the theoretical predictions for acoustic only and acoustic + optic phonons. On the other hand, the acoustic-mode Debye temperature for NaF is about 400 K [11], so that optic phonons may not be extensively excited.

Despite the absence of the expected tendency in a comparison between theory and experiment, we do find a fairly clearly defined variation with mass ratio of the quantity $(\partial W/\partial T)_\rho$, which for NaF is the slope of the experimental line shown in Fig. 6. Data for $(\partial W/\partial T)_\rho$ vs σ for B1-type phases of alkali halides are shown in Fig. 7. As can be seen, a systematic increase in $(\partial W/\partial T)_\rho$ with σ can be established for the sodium and potassium halides.

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