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Thermal Conductivity and Heat Capacity of Solid NaBr Under Pressure

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Using the transient hot-wire method, measurements were made for solid NaBr of both the thermal conductivity and the heat capacity per unit volume. The measurements were performed in the temperature range 100 to 400 K and at pressures up to 2 GPa. An adiabatic compression technique allowed the determination of the thermal expansivity as a function of pressure at room temperature. The heat capacity did not vary with pressure. Analysis of the thermal conductivity data showed that it can be described adequately by the Leibfried-Schlömann formula. For temperatures up to 400 K only acoustic modes needed to be taken into account. A small contribution of optic modes to the heat transport might be apparent at the highest temperatures.

KEY WORDS: heat capacity; high pressure; sodium bromide (NaBr); thermal conductivity; thermal expansivity.

1. INTRODUCTION

The simple crystal structure and ionic bonding of the alkali halides make them very suitable candidates for the study of the effects of pressure on thermal conductivity. Most of the alkali halides have already been investigated. However, no high-pressure thermal conductivity data exist for NaBr. The mass ratio in this compound is rather high ($\sigma = 3.48$) and therefore the optical branches of the phonon dispersion spectra are well separated from the acoustical ones. In these circumstances it may be assumed that the contributions to thermal conductivity are mainly from acoustic phonons and the effect of optic phonons is small [1]. This

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question has been investigated previously by this laboratory for other alkali halides [2–4]. The present study allows a further test of this assumption.

2. EXPERIMENTAL

We used the transient hot-wire method to measure simultaneously both the thermal conductivity, λ, and the heat capacity per unit volume, ρc_p, where ρ is the mass density. Details of the method have been given elsewhere [5, 6].

The hot wire was a nickel wire, 0.1 mm in diameter, which 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.

The material used was powder of $\gtrsim 99.5\%$ purity, obtained from Merck, West Germany. It was 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. The plates were then mounted in the Teflon cell under air atmosphere but with minimum time lapse to minimize water absorption, as NaBr is fairly hygroscopic.

In order to assess the amount of moisture collected accidentally with this rather simple method of sample preparation, as well as its effect on results, another cell was also made. This time the material was dried in a vacuum oven before and after compaction. The mounting of the experimental cell was performed in an argon atmosphere glove box in the presence of P_2O_5. Storage of the plates and transportation of the pressure cell from the glove box to the piston cylinder apparatus were made in a vacuum desiccator, again in the presence of P_2O_5. The water content in this second sample was monitored by means of differential scanning calorimetry, both before and after the run. No water was detected. The conductivity results from the two runs agreed within the experimental error, which showed that the water content in the first sample had a negligible effect on the thermal conductivity.

Measurements were made in the temperature range 100 to 400 K and at pressures up to 2 GPa. Over these ranges NaBr has only a single phase [7]. The inaccuracy in λ was estimated as $\pm 5\%$. The accuracy in the determination of ρc_p, when using the transient hot-wire method, is highly dependent on the thermal diffusivity of the material under investigation [3]. It was found in the case of NaBr that the error in ρc_p at relatively low temperatures was quite high, and no data for ρc_p are presented for those cases. We present only data for $\rho c_p(P)$ at room temperature, where the inaccuracy is estimated as $\pm 10\%$. Below room temperature we used atmospheric literature values of $\rho c_p(T)$ and determined $\lambda(T)$ using a one-parameter fit, instead of the ordinary two-parameter $(\lambda, \rho c_p)$ fit. It should be noted that in our experience [3] even a large error in ρc_p does not adversely affect the determination of λ.

The same cell and experimental arrangement were also used to measure the thermal expansivity α $[= V^{-1}(\partial V/\partial T)_P]$ of the sample as a function of the pressure at room temperature. Very simply this was done as follows [8]: a load cell in series with the piston was used to monitor the pressure inside the cell with the aid of a pressure versus load calibration curve. The pressure inside the cell was raised rapidly by ~0.2 GPa to obtain an approximately adiabatic compression. A data acquisition system was used to obtain subsequent simultaneous readings of the load cell and thermocouple output. About 50 points were accumulated in ~7 s. A typical set of data obtained is shown in Fig. 1. The equation

$$\alpha = \frac{\rho c_p}{T}\left(\frac{\partial T}{\partial P}\right)_S$$

was used to calculate the thermal expansivity at the average pressure at which the adiabatic compression took place.

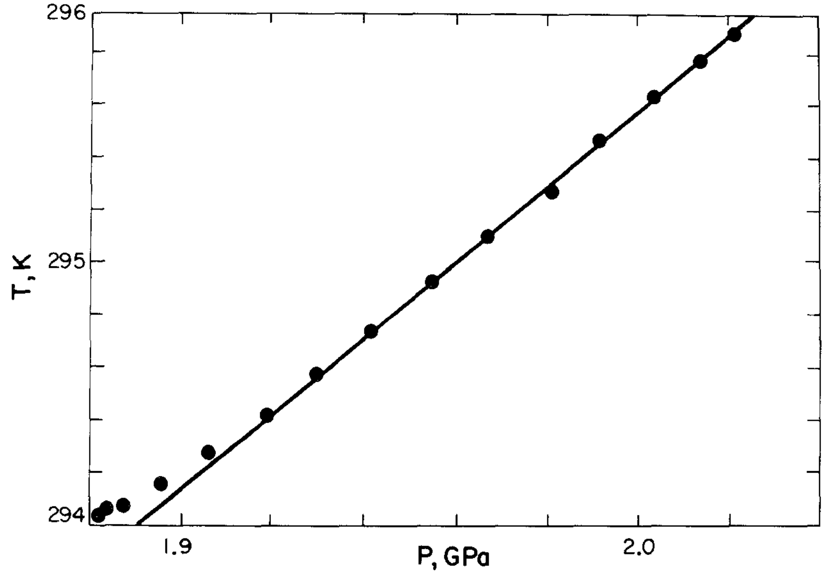

Fig. 1. Temperature versus pressure during an adiabatic compression run.

3. RESULTS AND COMPARISON WITH PREVIOUS WORK

3.1. Thermal Conductivity

Figure 2 shows results for $\lambda(P)$ from one isothermal pressure run. Equivalent numerical information from several isothermal runs at about room temperature is given in Table I.

The thermal resistivity $W(T) = 1/\lambda(T)$ is shown in Fig. 3. The isobars shown are made up of more than a thousand experimental points obtained by the automatic data collection system. The corresponding smoothed data at selected temperature are shown in Table II.

A kink can be seen at about 300 K on the 0.2-GPa isobar. This was absent on a subsequent run and is attributed to bad thermal contact at this relatively low pressure. The kink disappeared at higher pressures.

Using the data from these three isobars at 0.2, 1.0, and 2.0 GPa, we fitted equations of the form $\lambda = A + BP$ for various temperatures. We found that the value of $s = B/A$ does not vary significantly with temperature, its average value being 0.53 GPa^{-1}. The results for the thermal resistivity at zero pressure ($=1/A$) are given in Table II and also shown as a dashed line in Fig. 3. This figure also shows the values obtained by Eucken and Kuhn [9] at 83 and 273 K in 1928 as well as the data obtained by Petrov et al. [10].

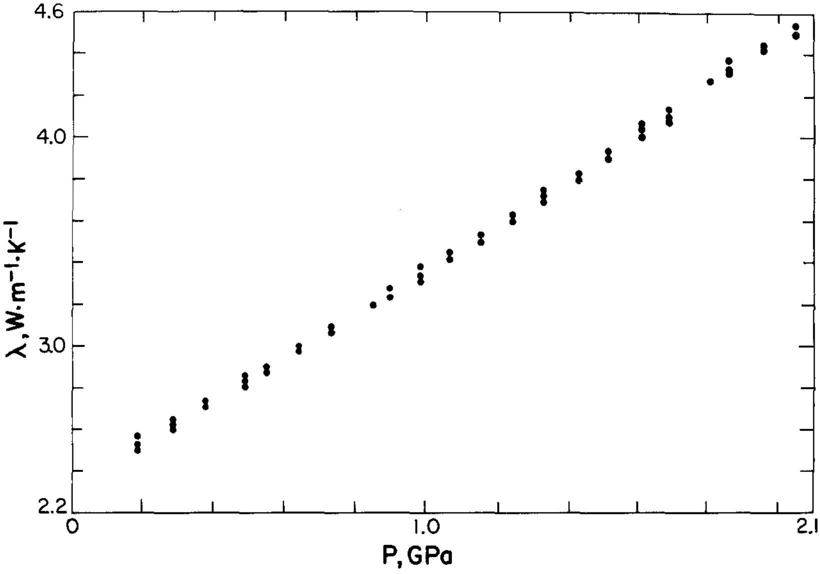

Fig. 2. Thermal conductivity of NaBr as a function of pressure at 293 K.

Table I. Isothermal Pressure Dependence of the Thermal Conductivity, λ, of NaBr 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 ($W \cdot m^{-1} \cdot K^{-1} \cdot GPa^{-1}$)	T (K)	P (GPa)
2.27	1.085	295	0–2.0

Our results disagree with that of Eucken and Kuhn at 83 K but agree well with their value at 273 K. Eucken and Kuhn used a linear flow method using polycrystalline samples. It is possible that their boundary conditions were not satisfied at low temperatures.

Our thermal resistivity results are 20–25% higher than those of Petrov et al. [10]. They used a linear heat flow method [11] and single crystalline samples which were transparent to infrared radiation, thus having a substantial radiative component in their observed thermal conductivity. Although Petrov et al. tried to minimize this effect and correct for it, it is

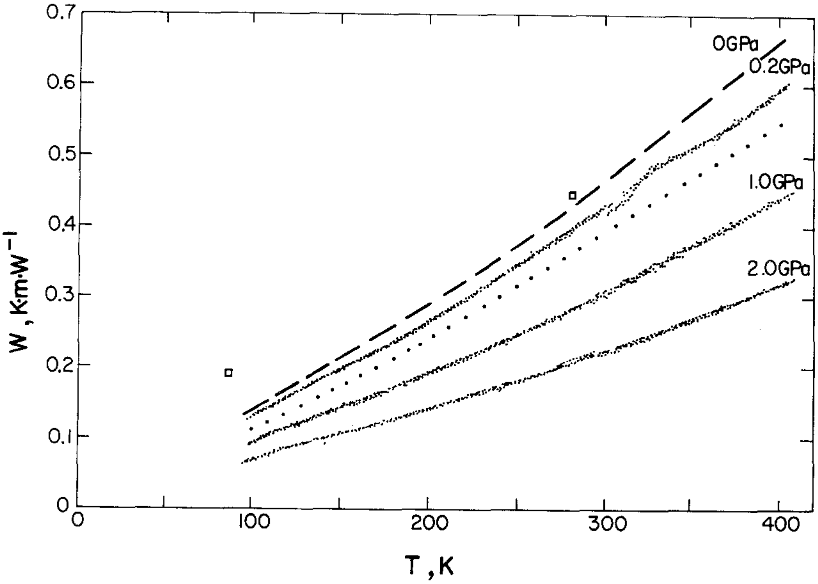

Fig. 3. Isobaric thermal resistivity of NaBr as a function of temperature. For comparison with previous work, our results at 0.2 GPa were extrapolated to zero pressure and are represented by the dashed line. (□) Eucken and Kuhn [9]; (●) Petrov et al. [10].

Table II. Isobaric Temperature Dependence of the Thermal Resistivity ($K \cdot m^{-1} \cdot W^{-1}$) for NaBr (Smoothed Values)[a]

	T(K)						
P (GPa)	100	150	200	250	300	350	400
0	0.139	0.215	0.287	0.376	0.469	0.564	0.665
0.2	0.126	0.192	0.259	0.337	0.418	0.503	0.592
1.0	0.093	0.143	0.192	0.248	0.307	0.373	0.440
2.0	0.069	0.104	0.142	0.181	0.222	0.270	0.318

[a] The values at zero pressure are by extrapolation.

possible that this is one cause of the observed discrepancy in results. At the lowest temperatures our values of W might be somewhat high due to grain boundary scattering of phonons in our polycrystalline samples.

3.2. Heat Capacity

We found that the room temperature value of ρc_p was independent of pressure (Fig. 4). Using density and compressibility data [7], we found that the corresponding specific heat capacity, c_p, decreased slightly

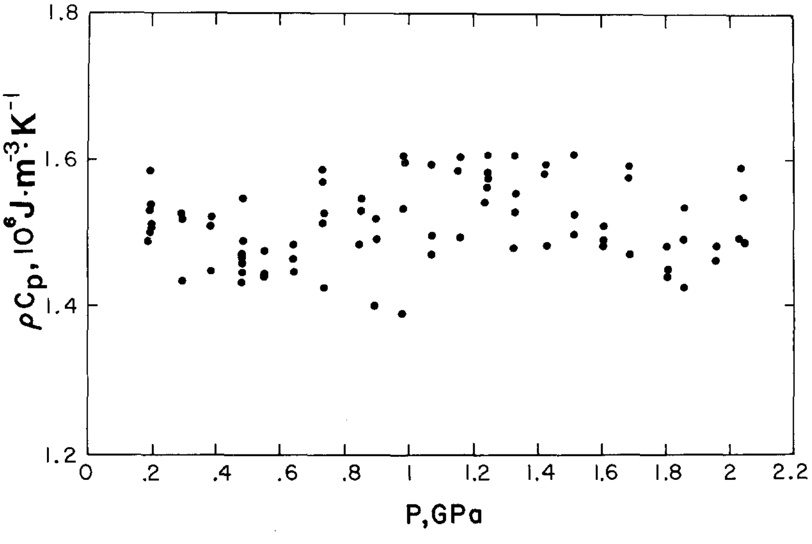

Fig. 4. Heat capacity per unit volume of NaBr as a function of pressure at 293 K.

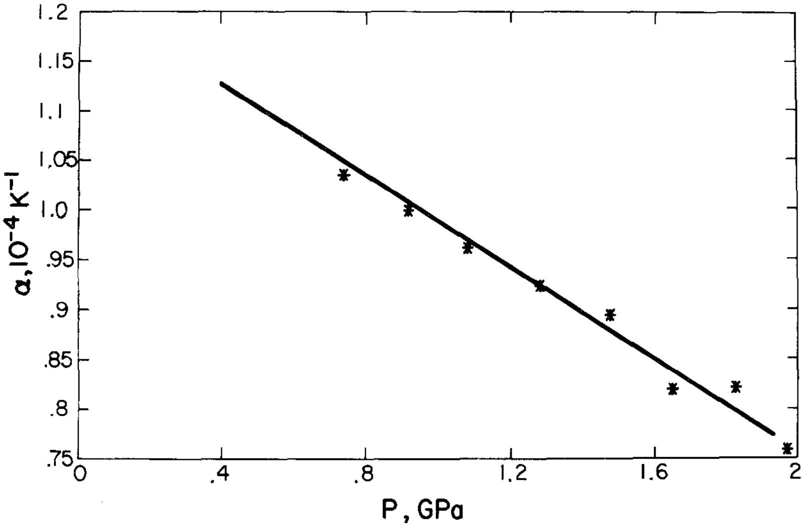

Fig. 5. Thermal expansivity of NaBr as a function of pressure. The solid curve is a straight line fitted to the experimental points.

(0–10%) up to 2 GPa. The low-pressure value of c_p was equal to 471 J · kg^{-1} · K^{-1}. The literature value is 497 J · kg^{-1} · K^{-1} [12], so agreement is within 5%.

3.3. Thermal Expansivity

Figure 5 shows the values of the thermal expansivity of NaBr, plotted as a function of pressure. The solid line is a first-order polynomial least-squares fit to the data. Equivalent numerical information is given in Table III, where comparison of the "recommended" value at ambient

Table III. Thermal Expansivity, α, of NaBr, Fitted to an Equation of the Form $\alpha = D + EP$, Where α Is in K^{-1} and P Is in GPa

	D	E	$(\partial\kappa_T/\partial T)_P$	P
	(10−4 K^{-1})	(10^{-4} GPa^{-1}·K^{-1})	(10^{-4} GPa^{-1}·K^{-1})	(GPa)
This work	1.22	−0.231	0.231[a]	0–2
Touloukian et al. [13]	1.248	—		Atmosphere
Landolt-Börnstein [14]			0.251	

[a] Calculated using $\left(\frac{\partial\alpha}{\partial P}\right)_T = -\left(\frac{\partial\kappa_T}{\partial T}\right)_P$.

pressure, obtained from Touloukian et al. [13], is given. Our value differs from Touloukian's by less than 5%.

There are no existing data in the literature concerning the variation of the thermal expansivity of NaBr with pressure. Thus no direct comparison of our results with those of others is possible. It is, however, possible to use the following thermodynamic identity:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \kappa_{\mathrm{T}}}{\partial T}\right)_P$$

where κ_{T} is the isothermal compressibility.

A value for the temperature derivative of the compressibility of NaBr was calculated from elastic constant data given by Landolt-Börnstein [14]. Table III also shows the value deduced from our measured values of $\alpha(P)$. As can be seen, the agreement between the two values is rather good.

4. DISCUSSION

4.1. Absolute Value of λ

The thermal conductivity of insulators at temperatures comparable or higher than their Debye temperature is given, strictly at constant volume, by the Leibfried-Schlömann formula. Assuming contributions from acoustic phonons only, and three phonon scattering processes, the thermal conductivity for the NaCl structure may be expressed by [1]

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

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, 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. B is a constant whose value is somewhat uncertain [15–17] but has been taken by Slack [1] to be equal to $3.04 \times 10^4\ \mathrm{W \cdot m^{-2} \cdot K^{-3}}$ $(\mathrm{g\ atom})^{-1}$. If optical phonons do also contribute to the thermal transport, $\tilde{\theta}_{\infty}$ and $\tilde{\gamma}_{\infty}$ are replaced by their respective values calculated for the whole phonon spectrum, θ_{∞} and γ_{∞}.

The values of $\tilde{\theta}_{\infty}$ and θ_{∞} were obtained from Slack [1] and from Reid et al. [18], respectively. Both $\tilde{\gamma}_\infty$ and γ_∞ were assumed to be equal to the room-temperature thermodynamic Grüneisen parameter

$$\gamma_{\text{th}} = \frac{\alpha B_{\text{s}}}{\rho c_{\text{p}}}$$

where B_{s} is the adiabatic bulk modulus.

We calculated γ_{th} from the thermal expansivity [13], adiabatic bulk modulus [14], and specific heat capacity [12] and assuming that $\rho = 3.203\ \text{g} \cdot \text{cm}^{-3}$. In Table IV we have given the value of the thermal conductivity at room temperature calculated using Eq. (1) for the case of either acoustic phonons only or all phonons contributing to the thermal conduction. It is evident from the comparison with the measured value that most of the heat transport in NaBr at room temperature is by means of acoustic phonons. This ought to be expected in view of the large mass ratio of this compound. The phonon dispersion curves have been measured by Reid et al. [18]. There it can be seen that the optic phonon modes are quite separate from the acoustic ones. So at relatively low temperatures one expects heat to be transferred by acoustic phonons, while very little acoustic phonon scattering is caused by optic phonons due to the large energy separation between the two types of dispersion curves. On the other hand, not all the optic branches have a small dispersion so it is possible that, when excited, some heat will be transferred by them.

4.2. Density Dependence of λ, *g*; Density and Temperature Dependence of *g*

The density dependence of the thermal conductivity can be discussed if one formally differentiates λ with respect to density as is done by Slack [1].

$$g = \left(\frac{\partial \ln \lambda}{\partial \ln \rho}\right)_T = B_{\text{T}} \left(\frac{\partial \ln \lambda}{\partial P}\right)_T = 3\gamma + 2q - \frac{1}{3} \tag{2}$$

Table IV. Calculated and Measured Values of the Thermal Conductivity of NaBr at Zero Pressure and 294 K

						$\lambda\ (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$		
$\bar{M}$ (g atom)	B_{S} (GPa)	δ (10^{-10} m)	$\tilde{\theta}_\infty$ (K)	θ_∞ (K)	γ_{th}	Acoustic phonons only	Acoustic and optic phonons	Measured
41.44	20.4	2.986	150	218	1.60	2.64	8.10	2.27

where we have assumed that

$$\gamma = \left(\frac{\partial \ln \theta}{\partial \ln \rho}\right)_T = B_T\left(\frac{\partial \ln \theta}{\partial P}\right)_T$$

and where

$$q = -\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_T = -B_T\left(\frac{\partial \ln \gamma}{\partial P}\right)$$

The quantity q is usually called the second Grüneisen parameter.

Using $\gamma = \gamma_{\text{th}} = \alpha B_s/\rho c_p$ and $B_s = B_T(1 + \alpha\gamma_{\text{th}} T)$, where B_T is the isothermal bulk modulus, we find

$$\gamma = \frac{\alpha B_T}{\rho c_p - B_T \alpha^2 T}$$

The latter equation was used to calculate γ at various pressures from our measured values of α and ρc_p. The pressure variation of B_T was obtained from Vaidya and Kennedy [7]. The values of γ are shown in Fig. 6.

We deduced a value for q by plotting $\ln \gamma$ vs $\ln \rho$, using density data [7]. A straight line was fitted to the data points. In Table V we give the value of q as well as the extrapolated value of γ at zero pressure. We have included for comparison the values of Roberts and Ruppin [19]. As can be

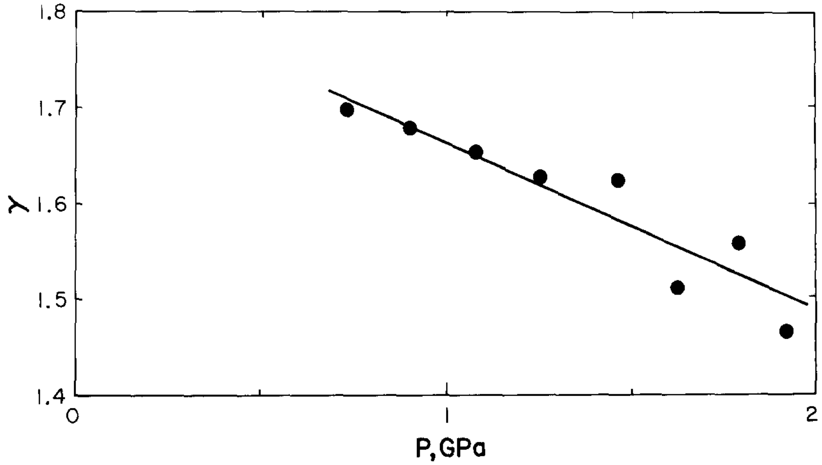

Fig. 6. Grüneisen parameter of NaBr as a function of pressure. The solid curve is a straight line fitted to the experimental points.

Table V. Values of the Density Derivative of the Thermal Conductivity, g

			$P=0$ GPa		$P=2$ GPa	
	$\gamma(P=0)$	q	g calculated	g measured	g calculated	g measured
This work	1.84	2.8	10.8	9.7	9.7	7.0
Roberts and Ruppin [19]	1.64	1.75	8.1		7.4	

seen from Table V, although our γ value is in reasonable agreement with theirs, there is a substantial difference between the q values. Table V also contains the values obtained for g at $P=0$ and $P=2$ GPa from Eq. (2) using our values for γ and q and those by Roberts and Ruppin. The same table contains the values for g that we obtained from our 294 K isotherm, by plotting $\ln \lambda$ vs $\ln \rho$ and using density data [7]. The agreement between the calculated and the measured values for g indicates that the Leibfried-Schlömann formula can describe fairly satisfactorily the pressure variation of the thermal conductivity of NaBr. As this formula was derived for a solid in which the main source of resistance to heat transport is three phonon acoustic interactions, this agreement would indicate that indeed these processes are responsible for the thermal resistivity of NaBr. It should be pointed out, however, that the γ and q calculated by us from measurements contains contributions from all vibration modes, both acoustic and optic. A proper calculation should include only the acoustic γ and q. As no high-pressure data exist concerning the behavior of the acoustic phonon dispersion curves, this is not possible at this stage. In view of these considerations, the agreement between calculated and measured g should be looked upon with caution.

We can calculate g at zero pressure as a function of temperature, using our values for the pressure derivative of λ, $s=B/A$, together with the variation of the isothermal bulk modulus with temperature, calculated from elastic constant data [14]. The results thus obtained are given in Fig. 7. As can be seen, no clear variation of g with temperature is observed.

4.3. Isochoric Temperature Dependence of W $(=1/\lambda)$

From Eq. (1) we expect the thermal resistivity W to be proportional to T. All experimental curves in Fig. 3 are seen to curve slightly upward. However, the Leibfried-Schlömann formula applies strictly to isochoric conditions. It has been observed previously that $W(T)$ measured at con-

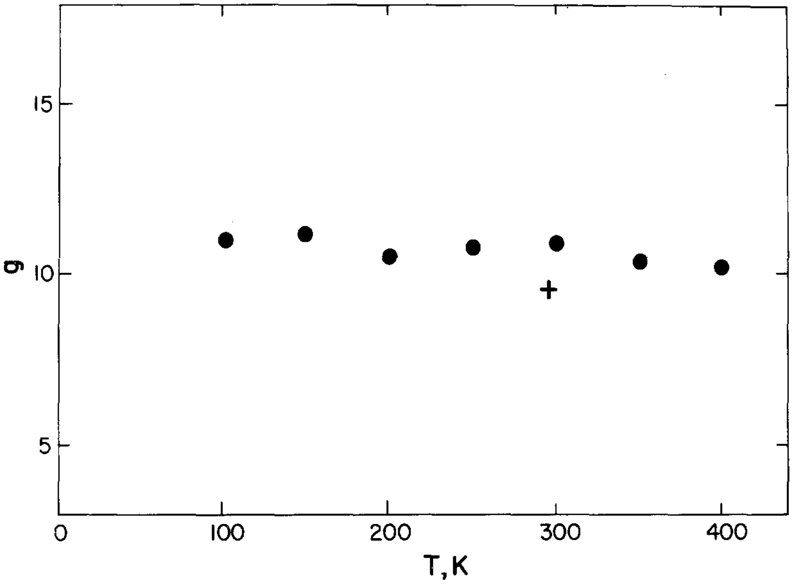

Fig. 7. Variation of g at zero pressure with temperature. Data for $s = B/A$ obtained (+) by direct measurements under isothermal conditions (Table I) and (●) indirectly from measurements under isobaric conditions. Data for $B_T(T)$ calculated from Ref. 14.

stant pressure will differ from $W(T)$ at constant volume [2, 20]. Since we have g as a function of temperature, we are able to reduce our constant-pressure thermal resistivity data to constant-volume data. The volume at $P = 0$ and $T = 0$ was chosen. For the reduction we used our extrapolated values of $W(T)$ at zero pressure (Table II) and our values of $g(T)$ (Fig. 7) together with $\alpha(T)$ as given by Touloukian et al. [13]. The results thus obtained are shown in Fig. 8. As can be seen, the isochoric curve is straight, except for a small downward bending at the highest temperatures. A comparison with the included isobaric curve at $P = 0$ shows that correction to constant volume is very important.

A straight line was fitted to the low-temperature points of the constant-volume curve. We also calculated the temperature derivative of W using Eq. (1) and the data in Table IV. The results are shown in Table VI, and they confirm further the observation that heat transport in this material takes place mainly through the acoustic phonons. The slight downward curvature of the isochoric curves is an indication of a further contribution to the thermal conductivity of NaBr. It is possible that at high

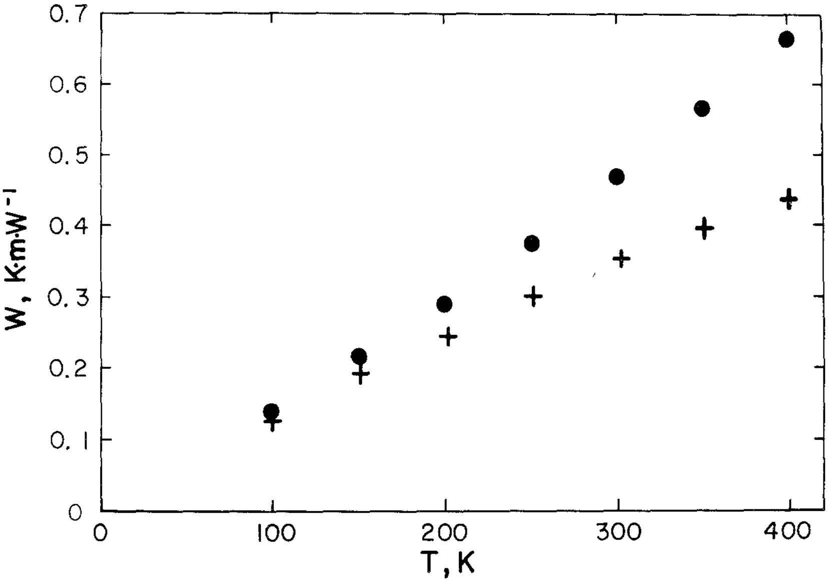

Fig. 8. Thermal resistivity of NaBr as a function of temperature. (+) Isochoric for volume at $P=0$ and $T=0$; (●) isobaric at $P=0$.

temperatures optic modes with substantial dispersion are excited and that they contribute more to heat conduction than to scattering of the acoustic phonons.

5. CONCLUSIONS

The thermal conductivity of NaBr can be described adequately by the Leibfried-Schlömann formula as a function of both pressure and temperature if only the acoustic modes are taken into account. A small contribution of the optic modes might be apparent at high temperatures.

Table VI. Temperature Derivative of Isochoric Thermal Resistivity

Caclulated (10^{-3} m · W^{-1})		
Acoustic phonons only	Acoustic and optic phonons	Measured (10^{-3} m · W^{-1})
1.29	0.409	1.04

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