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Thermal Conductivity and Heat Capacity of Solid Silver Bromide (AgBr) Under Pressure

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The thermal conductivity, λ, and the heat capacity per unit volume, ρc_p, have been measured for solid silver bromide (AgBr) using the transient hot-wire method. Measurements were made at temperatures in the range 100–400 K and at pressures up to 2 GPa. ρc_p was found to be independent of temperature and pressure over these ranges. λ of AgBr was found to be similar to that of AgCl, which was measured previously. For AgBr, only acoustic phonons needed to be taken into account up to 340 K, but optic phonons probably carried some heat at higher temperatures. The Leibfried-Schlömann (LS) formula could describe the ratio $\lambda(\mathrm{AgCl})/\lambda(\mathrm{AgBr})$, but not the ratio $\lambda(1\ \mathrm{GPa})/\lambda(0)$ for either substance. An empirical modification of the LS formula could describe the latter ratios but not the former. Further theoretical developments are required for understanding of $\lambda(P)$ for even such relatively simple substances as AgCl and AgBr.

KEY WORDS: heat capacity; high pressure; silver bromide (AgBr); silver chloride (AgCl); thermal conductivity.

1. INTRODUCTION

We recently [1] reported measurements of the thermal conductivity and heat capacity of solid AgCl under pressure. The present work is a report of similar measurements for AgBr. We shall examine, in particular, how well available theoretical models for the thermal conductivity can describe the relation between these two substances and the density dependence for each.

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2. EXPERIMENTAL DETAILS

We used the transient hot-wire method to measure simultaneously both the thermal conductivity, λ, and the heat capacity per unit volume, ρc_p. c_p is the specific heat capacity at constant pressure, and ρ is the mass density. Details of the method have been given elsewhere [2]. It will sometimes be convenient [3] to present and discuss results in terms of the thermal resistivity $r(=1/\lambda)$.

AgBr powder of 99.9% purity was compacted under a pressure of 0.3 GPa to form polycrystalline plates which were loaded into our high pressure cell [4]. During our experiments, the initially white, translucent plates darkened to a brown color. This probably occurred in the course of a temperature excursion from 300 to 400 K. However, there was no evidence that darkening of the sample affected our results. In [1], we found that deliberate darkening of our sample of AgCl (by exposure to light) did not affect the results, from which we inferred that there was a negligible radiative contribution to the total λ. It appears that AgBr is similar in this respect.

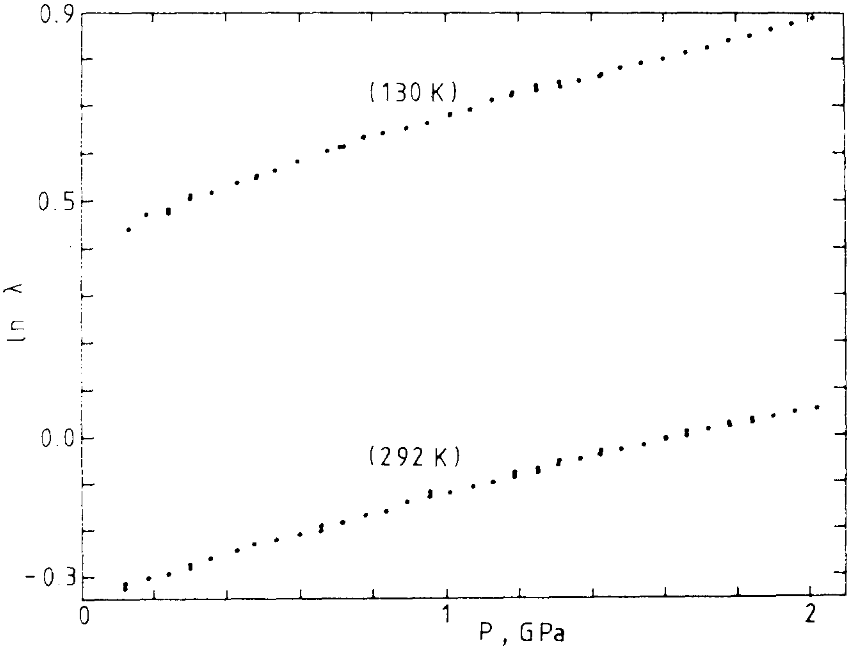

Fig. 1. Isothermal pressure dependence of the logarithm of thermal conductivity λ (in $W \cdot m^{-1} \cdot K^{-1}$), of AgBr. Temperature is given in parentheses.

Measurements were made at temperatures (T) in the range 100–400 K and at pressures (P) in the range 0.1–2 GPa. Over these ranges, AgBr has only a single phase [5] of NaCl-type of structure, like AgCl [1]. The inaccuracies were estimated as ±5% in λ and ±10% in ρc_p, but the imprecisions were much smaller.

3. RESULTS AND COMPARISON WITH PREVIOUS WORK

3.1. Thermal Conductivity

Our results for $\ln\lambda(P)$ are shown in Fig. 1, and for $r(T)$ in Fig. 2. Equivalent numerical information is presented in Tables I and II. It can be seen from Fig. 1 that $(\partial \ln\lambda/\partial P)_T$ was independent of T to a good approximation. Using our value for this derivative, our results can be compared with previous work at zero pressure. We find agreement within 7% with the result of McCarthy and Ballard [6] at about 310 K. Measure-

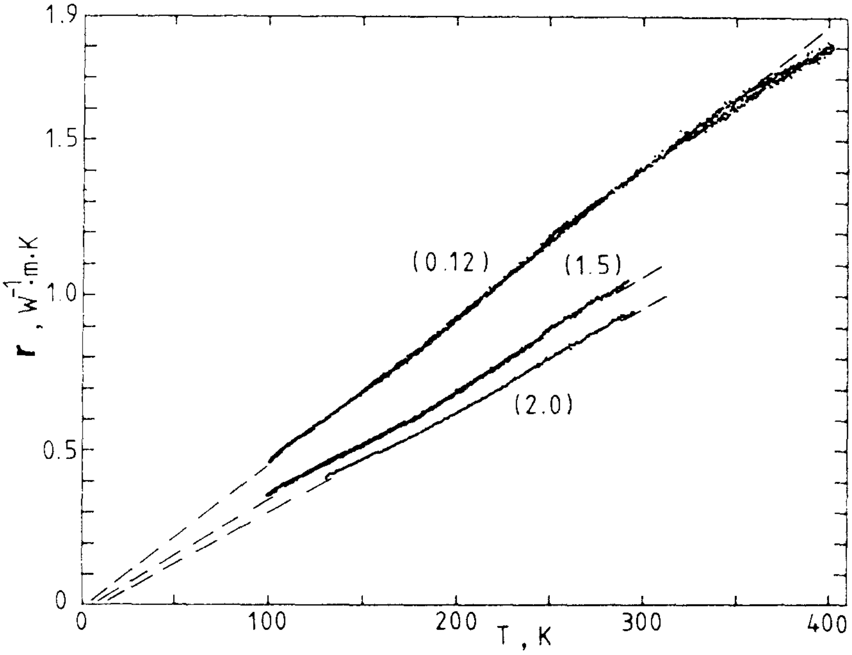

Fig. 2. Isobaric temperature dependence of thermal resistivity, r, of AgBr. Pressure in GPa is given in parentheses. Broken lines correspond to fitted equations (Table II) for $T < 340$ K.

Table I. Isothermal Pressure Dependence of Thermal Conductivity, λ, of AgBr Fitted to Equations of Form[a] $\lambda = D + EP$

D ($W \cdot m^{-1} \cdot K^{-1}$)	E ($W \cdot m^{-1} \cdot K^{-1}\, GPa^{-1}$)	T (K)	P (GPa)
0.705	0.179	292	0–2.0
1.520	0.448	130	0–2.0

[a] Where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and P is in GPa.

Table II. Isobaric Temperature Dependence of Thermal Resistivity, r, of AgBr Fitted to Equations of Form[a] $r = F + GT$

F ($W^{-1} \cdot m \cdot K$)	G ($W^{-1} \cdot m$)	P (GPa)	T (K)
– 0.016	4.72×10^{-3}	0.12	100–340
0.370	3.58×10^{-3}	0.12	340–402
– 0.019	3.60×10^{-3}	1.5	99–292
– 0.035	3.33×10^{-3}	2.0	130–295

[a] Where r is in $W^{-1} \cdot m \cdot K$ and T is in K.

ments by Pochapsky [7] employed a nonstandard technique and yielded results for λ which were larger than ours by a factor of about 1.3. Pochapsky's results agreed at 273 K with the value due to Giacomini [8]. Bremer and Nölting [9] measured λ as a function of both temperature and pressure, but agreement with our work is poor. For example, the value of λ which they obtained at 0.1 GPa and 300 K is about 0.7 times our result. Moreover, they found that λ increased by a factor of about 1.5 between 18 MPa and 0.3 GPa near 300 K, whereas we found an increase by a factor 1.25 between 0 and 1 GPa (Table I). The results of Bremer and Nölting indicate a volume dependence of λ for AgBr which would be exceptionally large [10], and we conclude that there was a significant systematic error in their work.

3.2. Heat Capacity

Figure 3 shows our results for $\rho c_p(T)$ at 0.12 GPa. We found that ρc_p was independent of pressure up to 2 GPa at both 300 and 130 K. As a result, data for $\rho c_p(T)$ at 1.5 and 2 GPa were indistinguishable from those for 0.12 GPa and have not been shown.

Our results may be compared with previous work at zero pressure. We used the heat capacity measured by Eastman and Milner [11], a density [12] at 300 K of 6.476 $g \cdot cm^{-3}$, and "recommended values" [13] for thermal

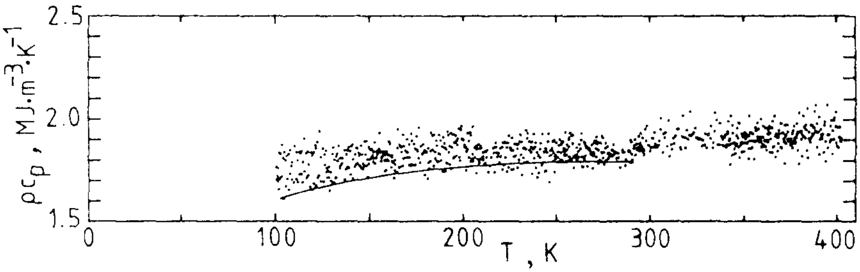

Fig. 3. Isobaric temperature dependence of heat capacity per unit volume, ρc_p, of AgBr at 0.12 GPa. Previous work [11–13] at atmospheric pressure shown by solid line.

expansion. The result is given in Fig. 3 and shows good agreement with our work.

4. DISCUSSION

The measured dispersion relation for AgBr [14] is similar to that for AgCl [15] in the sense that the velocity of optic phonons can be as large as that of acoustic phonons for both of these substances. We therefore expect the thermal properties of AgBr to be similar to those of AgCl [1]. Such similarity is indicated by, for example, the quantity $g = (\partial \ln \lambda / \partial \ln \rho)_T$, which had the value 8.9 for AgCl and 9.4 for AgBr, using the compressibilities measured by Loje and Schuele [12].

In [1], we found $r \propto T$ for AgCl up to 300 K, and Fig. 2 shows that the same is true for AgBr up to 340 K. For AgCl, the smaller value of dr/dT for $T > 300$ K was attributed to conduction of heat by optic phonons. A similar, but much less pronounced, effect is shown in Fig. 2 for AgBr, and we assume it was similarly due to conduction of heat by optic phonons. From the empirical analysis of Devyatkova and Smirnov [16], we had expected that r would increase more rapidly than proportional to T at the highest temperatures, since the mass ratio is < 2, due to a predominance of optic-acoustic scattering at such a small mass ratio. Our results showed otherwise, but we can see from Fig. 2 that the deviation from $r \propto T$ was small. For $T < 300$ K, we conclude that only acoustic phonons need to be taken into account for both AgBr and AgCl [1].

In [1], we concluded that the Leibfried-Schlömann (LS) formula [17] needed to be modified in order to adequately describe the pressure dependence of λ for AgCl. Two different modifications were tested. One modification involved multiplying the LS formula by an empirical factor [18], $(c_{11}/c_{44})^{0.6}$, where c_{11} and c_{44} are measured elastic constants. In the other modification, we assumed that a formula of LS type could be applied to each acoustic mode separately, and the result summed, with the relevant mode phonon velocities and mode Grüneisen parameters being obtained from acoustic measurements under pressure [12]. Since both modifications yielded adequate agreement with our results, we could not distinguish between them on the basis of our measurements. Neither modification has a firm theoretical basis.

Since we now have available data for both AgCl and AgBr, we can attempt to test theoretical formulae in more detail. In particular, we consider both $\lambda(\mathrm{AgCl})/\lambda(\mathrm{AgBr})$ and $\lambda(P)/\lambda(0)$.

We begin by considering the relative magnitude of λ for AgCl and AgBr. Comparisons of this type have been made for a number of solids by Slack [10]. The simplest procedure is to use the unmodified LS formula [17]:

$$\lambda = KMa\Theta_D^3/\gamma^2 T \tag{1}$$

where a is the lattice parameter, Θ_D is the Debye temperature, and γ is the Grüneisen parameter. K is a constant whose value is only known to about an order of magnitude, but this is unimportant in taking ratios since the constant cancels out. The LS formula strictly pertains for a crystal of monatomic basis, for which M is the mass per atom. In extending the LS formula to crystals of greater than monatomic basis, the quantity M has been assumed [10, 17, 19] to be the arithmetic mean mass. This assumption has never been justified in detail, although Slack [10] has pointed out that in the acoustic modes the atoms move together, so the arithmetic mean is appropriate. The LS formula takes only the acoustic modes into account, and we argued above that this was probably justified for both AgCl and AgBr for $T < 300$ K.

Slack [10] compared λ for various substances at their Debye temperature. Substitution of $T = \Theta_D$ then yields, in our notation,

$$\lambda \sim Ma\Theta_D^2/\gamma^2 \qquad (T = \Theta_D) \tag{2}$$

The symbols have the same meaning as above, and, in particular, M is the arithmetic mean mass. To calculate Θ_D, we used the elastic constants measured by Loje and Schuele [12] and the standard formulae relating these to Θ_D described by Alers [20]. Of the formulae Alers describes, both the power series expansion and cubic harmonics yielded $\Theta_D = 145$ K for AgCl and 136 K for AgBr. We used the high temperature values of γ calculated by Loje and Schuele [12], which were 2.03 for AgCl and 2.39 for

AgBr. Substitution in Eq. (2) then yields $\lambda(\mathrm{AgCl})/\lambda(\mathrm{AgBr}) = 1.16$, which is identical with the ratio we observed experimentally at the corresponding Debye temperatures and 0.1 GPa. Slack's analysis [10] therefore describes exactly the ratio of λ for AgCl and AgBr and supports the validity of the unmodified LS formula. In discussing the density dependence of λ, a simple procedure is to formally differentiate the LS formula (eq. 1), as is done, for example, by Slack [10], to yield

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

where $q = -(\partial \ln \gamma / \partial \ln \rho)_T$. A crucial assumption in this procedure is taking $(\partial \ln \Theta_D / \partial \ln \rho)_T = \gamma$, and we shall return later to a consideration of the validity of this assumption for AgCl and AgBr. An additional difficulty is that we do not independently know a value for q, since there are no data, but a value between 1 and 2 is probably appropriate, as quoted by Slack [10]. In fact, if we use our experimental values of g, which were given above, and the values of γ given by Loje and Schuele [12], then Eq. (3) yields $q = 1.6$ for AgCl and 1.3 for AgBr.

However, the apparent success of the immediately preceding analysis conceals a basic problem concerning γ and the density dependence of Θ_D. Loje and Schuele [12] measured sound velocities up to 0.1 GPa and quoted values for initial logarithmic derivatives, $d \ln C/dP$, where C represents an elastic constant. As in [1], we assume these derivatives to be constant, somewhat arbitrarily up to 1 GPa, on the grounds that any pressure dependence would be an effect of second order of smallness. With this assumption, we can calculate elastic constants at 1 GPa. We can then calculate Θ_D at 1 GPa, using the formulae given by Alers [20], as above. We find that, up to 1 GPa, Θ_D increases by about 2 K for AgCl and by about 5 K for AgBr. These calculations therefore imply that Θ_D changes by at most a few percent up to 1 GPa. Our calculations are supported by the results of Voronov and Grigor'ev [21], who found a similar result for polycrystalline samples of AgCl. These results in turn imply relatively small values of γ, if we assume $\gamma = (\partial \ln \Theta_D / \partial \ln \rho)_T$. Using the compressibility data of Loje and Schuele [12] at 300 K, we can estimate $\gamma = 0.6$ for AgCl and 1.5 for AgBr. These values for γ are considerably smaller than those determined by Loje and Schuele, using a more complex and probably more accurate averaging procedure.

It seems that there is a basic flaw in the procedure of using the formulae for Θ_D described by Alers [20] together with the definition $\gamma = (\partial \ln \Theta_D / \partial \ln \rho)_T$. Furthermore, the agreement of Eq. (3) with experiment, for reasonable values of q, is probably fortuitous. This is made more

Table III. Calculated Values of Thermal Conductivity Ratio $\lambda(1\ \mathrm{GPa})/\lambda(0)$ at 300 K Compared with Experiment[a]

Substance	A	B	C_1	C_2	C_3	Experiment
AgCl	1.03	1.21	1.20	1.18	1.18	1.22[b]
AgBr	1.10	1.28	1.07	1.13	1.21	1.25

[a] Calculational procedures A, B, and C are described in the text. Results C_1, C_2, and C_3 correspond to phonon velocities in directions [100], [110], and [111], respectively.
[b] From ref. [1].

explicit if we try to predict $\lambda(1\ \mathrm{GPa})/\lambda(0)$ using the unmodified LS formula (eq. 1) from which Eq. (3) was derived by formal differentiation. We used values of Θ_D at 0 and 1 GPa, calculated as described in the preceding paragraph. We assumed γ was independent of pressure. This manner of calculation is referred to hereafter as procedure A, and the results are shown in Table III. There is evidently poor agreement with experiment. The situation is therefore that the LS formula can describe the ratio $\lambda(\mathrm{AgCl})/\lambda(\mathrm{AgBr})$, but not the ratio $\lambda(1\ \mathrm{GPa})/\lambda(0)$ for either substance. We suspect, but cannot prove, that the difficulty lies with the definition $\gamma = (\partial \ln \Theta_D/\partial \ln \rho)_T$, or perhaps more fundamentally with attempting to characterize the whole complex vibrational spectrum by means of a single parameter Θ_D. We conclude that the LS formula cannot adequately describe the density dependence of λ and that use of its formally differentiated form (Eq. 3) is of doubtful validity. We can, however, attempt to modify the LS formula, as was done in [1], and we tried two different modifications.

In procedure B, the LS formula (Eq. 1) was multiplied by the empirical factor [1, 18] $(c_{11}(P)/c_{44}(P))^{0.6}$. In procedure C, we used the expression [1]

$$\lambda \sim Ma^{-2} \sum_i v_i^3/\gamma_i^2 T \tag{4}$$

where, for the ith mode, v_i is the mode phonon velocity and γ_i is the mode Grüneisen parameter. $\sum_i$ indicates summation over the modes. Using Eq. (4), values of $\lambda(1\ \mathrm{GPa})/\lambda(0)$ were calculated corresponding to phonon (sound) velocities in the [100], [110], and [111] directions.

Results obtained using these three procedures are presented and compared with experiment in Table III. It can be seen that only procedure B yields adequate agreement with experiment for both AgCl and AgBr. However, procedure B lacks a firm theoretical basis and, moreover, provides a poor prediction of the ratio $\lambda(\mathrm{AgCl})/\lambda(\mathrm{AgBr})$. This is shown in Table IV, where we used the arithmetic mean masses.

Table IV. Calculated Values of Thermal Conductivity Ratio λ(AgCl)/λ(AgBr) at 300 K and Zero Pressure Compared with Experiment[a]

A	B	C_1	C_2	C_3	Experiment
1.26	1.43	0.54	0.87	1.26	1.23

[a] Calculational procedures A, B, and C, are described in the text. Results C_1, C_2, and C_3 correspond to phonon velocities in directions [100], [110], and [111], respectively.

[a] See ref. [1] for AgCl.

5. CONCLUSIONS

AgCl and AgBr were found to be similar in their thermal properties. Only the acoustic modes needed to be taken into account in connection with the conduction of heat at temperatures up to 300 K. At somewhat higher temperatures, we conclude that optic phonons were effective in carrying heat. This effect was much less pronounced for AgBr than for AgCl.

The Leibfried-Schlömann (LS) formula could adequately describe the ratio λ(AgCl)/λ(AgBr), using arithmetic mean masses, but not the ratio λ(1 GPa)/λ(0). An empirical modification, which lacks a firm theoretical basis, could describe the latter ratios but not the former. Since no single formula can describe both the ratio of λ for these substances, and also their density dependences, we conclude that renewed theoretical attention is required before we shall achieve adequate understanding of the density dependence of λ for even such relatively simple substances as AgCl and AgBr.

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