

Thermal conductivity and heat capacity of solid LiBr and RbF under pressure

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

1989 J. Phys.: Condens. Matter 1 3977

(<http://iopscience.iop.org/0953-8984/1/25/009>)

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

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:20

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

Thermal conductivity and heat capacity of solid LiBr and RbF under pressure

Björn Håkansson and Russell G Ross†

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

Received 1 September 1988

Abstract. The thermal conductivity λ and the heat capacity ρc_p per unit volume of solid LiBr and RbF have been measured over the temperature T range 100–400 K and at pressures p up to 2 GPa, using the transient hot-wire method. The results are compared with recent theoretical calculations. A predicted drop of $\lambda(T)$ below T^{-1} dependence is observed for LiBr.

1. Introduction

In order to understand the thermal conductivity of crystalline solids, and its variation with temperature and pressure, it is convenient to study solids with a relatively simple crystal structure. The alkali halides are suitable candidates and most of them have already been investigated experimentally (Ross *et al* 1984). However, there are no thermal conductivity data for LiBr and RbF.

LiBr is interesting because of its large mass ratio ($\sigma = 11.5$). The alkali halide with the highest mass ratio ($\sigma = 5.5$) so far investigated is NaI (Håkansson and Andersson 1986). In that case it was found that the temperature dependence of the Bridgman parameter g , defined as $g = -[\partial(\ln \lambda)/\partial(\ln V)]_T$, was much larger than for any other alkali halide investigated. Before we can attempt to attribute this behaviour of NaI to its relatively large mass ratio, further investigations of substances with even larger mass ratios, such as LiBr, are needed.

As is well known, the mass ratio affects the separation in energy between the acoustic and optic modes in a crystal of diatomic basis. This in turn should influence the relative importance of acoustic and optic phonons in the heat transport process. It has been assumed that the contribution from optic phonons can be neglected for crystals with mass ratios larger than 3. On the contrary, recent theoretical calculations (Pettersson 1987, 1988a), valid for isochoric conditions, show that optic phonons are important for the thermal conductivity for all alkali halides. The present investigation provides a test of this theory.

RbF was investigated in order to complete the data for the rubidium halides, and it is now possible to decide whether there are any systematic variations in λ and g with the mass ratio in this halide sequence.

The lithium halides have the NaCl or B1 type of crystal structure at atmospheric pressure. No phase transitions have been observed in the pressure range 0–4.5 GPa

† Permanent address: School of Physics, University of East Anglia, Norwich NR4 7TJ, UK.

(Vaidya and Kennedy 1971). The rubidium halides also have the B1 type of crystal structure at atmospheric pressure. Under a pressure of about 0.5 GPa, RbCl, RbBr and RbI transform to the CsCl or B2-type structure. The transition pressures for these alkali halides have been measured by several workers and the agreement is good, while different values of the transition pressure for RbF have been reported. The phase transition at 1.2 GPa reported by Vaidya and Kennedy (1971) has not been confirmed in the present work, or in other previous work (Darnell and McCollum 1970, Demarest *et al* 1978).

2. Experimental details

We used the transient hot-wire method to measure simultaneously both the thermal conductivity λ and the heat capacity ρc_p per unit volume, where ρ is the mass density. Details of the method have been given elsewhere (Håkansson *et al* 1988).

The hot wire was a nickel wire, 0.3 mm in diameter and with a length of 40 mm, which was installed as a circular loop between two pre-compacted plates of the specimen in a Teflon-lined pressure cell. The whole assembly was loaded into a piston-and-cylinder apparatus and the pressure was generated by a hydraulic press. The temperature was varied by either heating or cooling the whole pressure vessel and it was measured using a chromel–alumel thermocouple.

The LiBr used was powder with a purity of more than 99%, obtained from Janssen Chimica, Belgium. The RbF used was also powder, obtained from two different suppliers, Ventron–Alfa, Federal Republic of Germany, and Sigma Chemical Company, USA. The purity of the powder obtained from Ventron–Alfa was claimed to be greater than 99.5% while the purity of that obtained from Sigma was unspecified. As will be discussed later, the results on λ for the two batches of RbF differed by as much as 16%, which is far outside the experimental error. In order to understand this discrepancy, we arranged that both batches were investigated by means of x-ray diffraction. Besides enabling RbF to be identified, this method makes it possible to detect the presence of impurities, although a quantitative analysis cannot be made. Two peaks not belonging to RbF were observed in the diffractograms, which were similar for both batches, but for the batch obtained from Ventron there were even more extraneous peaks. Analysis by x-ray diffraction was also carried out on LiBr, and in this case no extraneous peaks were found.

We also arranged that the weight percentages of rubidium and fluoride were measured for both batches of RbF. The rubidium content was measured by atomic absorption spectrometry and the fluoride content by the ion-selective electrode technique (by standard addition). These analyses were carried out at Boliden Metall AB, Skelleftehamn, Sweden. The ratio of the fluoride content to the rubidium content for the material obtained from Ventron-Alfa was found to be 0.260 and for the material obtained from Sigma it was 0.219. For RbF of 100% purity this ratio would be 0.222. The chemical analysis thus confirms the result of the x-ray diffraction analysis and we conclude that the RbF obtained from Sigma was the purer.

Both substances are very hygroscopic and extra care had to be taken in order to prevent water absorption from air. A powder exposed to air will become an aqueous solution in 15–30 min. The LiBr powder was dried at 180 °C and the RbF powder at 120 °C for 24 h, in each case in a vacuum oven, and then compacted in a steel die to form polycrystalline plates 39 mm in diameter and 8 mm thick. After compaction the plates

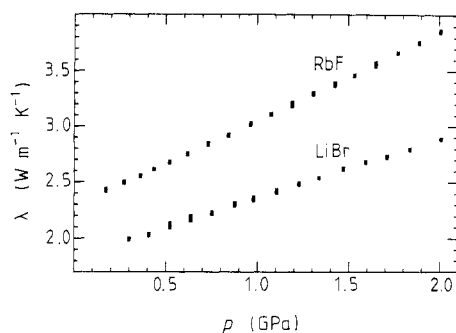


Figure 1. Isothermal pressure dependence of λ for LiBr and RbF at room temperature.

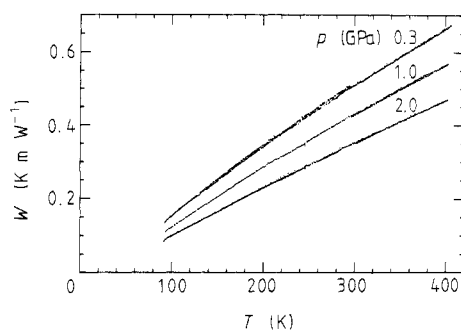


Figure 2. Isobaric temperature dependence of thermal resistivity for LiBr.

Table 1. Isothermal pressure dependence of the thermal conductivity λ of LiBr and RbF fitted to equations of the form $\lambda = A + Bp$.

Substance	A ($\text{W m}^{-1} \text{K}^{-1}$)	B ($\text{W m}^{-1} \text{K}^{-1} \text{GPa}^{-1}$)	B/A (GPa^{-1})	T (K)
LiBr	1.83	0.529	0.289	296
RbF	2.27	0.780	0.344	298

were dried by the same procedure as for the powder. The mounting of the experimental cell was performed in an argon-atmosphere glove box in the presence of P_2O_5 . In the experiments on LiBr, we used two different specimens and, in the experiments on RbF, we used two different specimens from each supplier. The water contents in one LiBr and one RbF specimen were measured after the completion of the experiments by thermogravimetry, using a Stanton Redcroft STA 785 thermal analyser. The weight loss of a small piece of a specimen was recorded during heating, at 180°C for LiBr and at 120°C for RbF, in a nitrogen atmosphere. Heating was carried out until the weight was constant with time. The weight loss was 0.8% for LiBr and 0.6% for RbF. We assume that the weight losses were due to water.

The measurements of λ and ρc_p were carried out either as isobaric runs at various pressures in the temperature range 100–400 K or as isothermal runs up to about 2 GPa. To ensure good thermal contact between the hot wire and the specimen, a minimum pressure of at least 0.3 GPa was used. The inaccuracies in λ and ρc_p were estimated as $\pm 2\%$ and $\pm 5\%$, respectively, but the standard deviation of the measurements was as low as 0.2% for λ and 1% for ρc_p .

3. Results

3.1. Thermal conductivity

Figure 1 shows the results for $\lambda(p)$ for LiBr and RbF at room temperature. As already mentioned, the results on λ for RbF for the materials obtained by the two different manufacturers differed by 16%. The material obtained from Ventron–Alfa gave the lower value. This is consistent with the results of x-ray diffraction and chemical analysis,

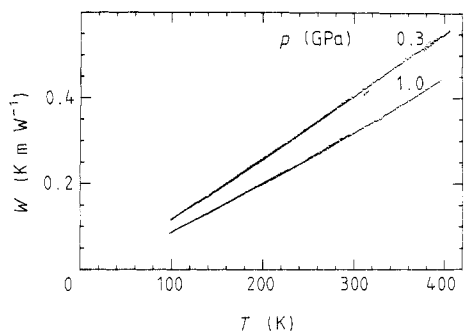


Figure 3. Isobaric temperature dependence of thermal resistivity for RbF.

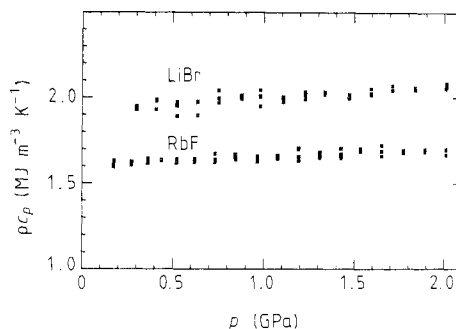


Figure 4. Isothermal pressure dependence of heat capacity per unit volume for LiBr and RbF at room temperature.

since impurities are expected to decrease the thermal conductivity. We therefore present in figure 1 only the results on RbF obtained from Sigma. The results agree within 2% for different specimens from the same supplier.

The results for the isothermal runs can be represented by straight lines of the form $\lambda = A + Bp$. The values of the quantities A and B together with that of B/A are given in table 1. The results for the isobaric runs are conveniently presented in terms of the thermal resistivity $W (=1/\lambda)$. Figures 2 and 3 show our results for $W(T)$.

The data given in table 1 provide the value of λ at $p = 0$ and the pressure derivative for the particular isotherms stated. In order to obtain similar data over the whole range of temperatures, we compared the measured values of λ along the isobars at pressures of 0.3, 1.0 and 2.0 GPa for LiBr and 0.3 and 1.0 GPa for RbF. We assumed that λ varied linearly with p at all temperatures as was the case for room temperature. The resulting values of A and B as functions of temperature are given in table 2.

A phase transition from the B1 to the B2 type of structure causes a relatively large drop in the thermal conductivity in the relevant alkali halides previously investigated (Andersson 1985). As can be seen in figure 1, there is no evidence for a phase transition in RbF in the pressure range 0–2 GPa according to our results. Demarest *et al* (1978) suggest that the reason why Vaidya and Kennedy (1971) found a phase transition at 1 GPa is that their specimen was contaminated with water. As already mentioned, the water content in our RbF specimens was about 0.6%.

3.2. Heat capacity

Figure 4 shows the results for $\rho c_p(p)$ at room temperature for LiBr and for RbF obtained from Sigma. Using density and compressibility data (Vaidya and Kennedy 1971), $c_p(p)$ for LiBr was calculated and found to be essentially constant with a value of $554 \text{ J kg}^{-1} \text{ K}^{-1}$. This value is 3.5% lower than the value of $574 \text{ J kg}^{-1} \text{ K}^{-1}$ reported by Paukov *et al* (1974); so agreement is good.

To obtain the value of c_p for RbF was more complicated since there is some confusion in the literature about the density. Vaidya and Kennedy (1971) give the value of 3.8665 g cm^{-3} for RbF but the value given in *Gmelins Handbuch* (1937) is 3.557 g cm^{-3} . This is also the value given by the suppliers. However, the density can be calculated using the formula

$$\rho = \bar{M}/N_A \delta^3 \quad (1)$$

where \bar{M} is the average atomic weight, N_A is Avogadro's number and δ is the cube root

Table 2. Temperature dependence of the quantities A and B in the equation $\lambda = A + Bp$, for LiBr and RbF.

T (K)	LiBr		RbF	
	A (W m ⁻¹ K ⁻¹)	B (W m ⁻¹ K ⁻¹ GPa ⁻¹)	A (W m ⁻¹ K ⁻¹)	B (W m ⁻¹ K ⁻¹ GPa ⁻¹)
100	6.04	2.04	7.55	3.29
120	4.71	1.63	6.12	2.64
140	3.91	1.35	5.22	2.18
160	3.39	1.12	4.45	1.88
180	2.98	0.962	3.88	1.65
200	2.68	0.843	3.46	1.43
220	2.44	0.760	3.13	1.24
240	2.23	0.684	2.84	1.13
260	2.06	0.672	2.62	0.987
280	1.92	0.572	2.41	0.888
300	1.80	0.526	2.26	0.775
320	1.70	0.490	2.10	0.703
340	1.61	0.452	1.96	0.660
360	1.53	0.422	1.84	0.602
380	1.46	0.394		
400	1.40	0.370		

of the average volume per atom. The nearest-neighbour distance d_0 is equal to δ and, using the value for d_0 given by Roberts and Smith (1970), we obtained the value of 3.843 g cm⁻³ for the density of RbF which is within 0.6% of the value given by Vaidya and Kennedy (1971). This density value and compressibility data also obtained from Roberts and Smith (1970) were used to calculate $c_p(p)$ for RbF. It was found that c_p is essentially constant with pressure. The value of c_p at room temperature for RbF obtained from Sigma is 419 J kg⁻¹ K⁻¹ which is 14% lower than the value of 485 J kg⁻¹ K⁻¹ given by Roberts and Smith (1970). On the contrary, the value of c_p for the less pure RbF obtained from Ventron-Alfa is 471 J kg⁻¹ K⁻¹, which is closer to the value obtained by Roberts and Smith (1970). These discrepancies are probably a consequence of the difficulties involved in manufacturing pure RbF and avoiding absorption of water during sample preparation and experiments. The confusion about the density also shows that RbF is difficult to handle. Our best estimate for c_p of RbF at room temperature is 419 J kg⁻¹ K⁻¹.

4. Discussion

4.1. Density, temperature and mass ratio effects

The density dependence of the thermal conductivity is usually discussed in terms of the Bridgman parameter, which can be expressed as

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

where B_T is the isothermal bulk modulus. The pressure dependence of $g(p)$ was evaluated using the room-temperature data for $\lambda(p)$ given in table 1 and data for $B_T(p)$. For LiBr, $B_T(p)$ from two different papers was used in order to make a comparison (Ching

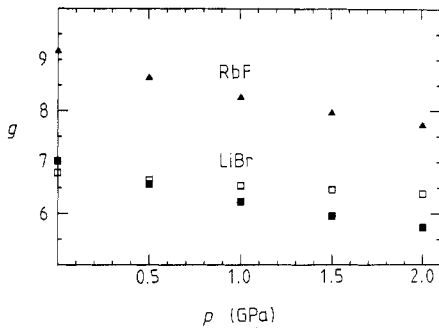


Figure 5. Values of the Bridgman parameter g as a function of pressure at room temperature: \square , $B_T(p)$ from Ching *et al* (1972); \blacksquare , $B_T(p)$ from Vaidya and Kennedy (1971); \blacktriangle , $B_T(p)$ from Roberts and Smith (1970).

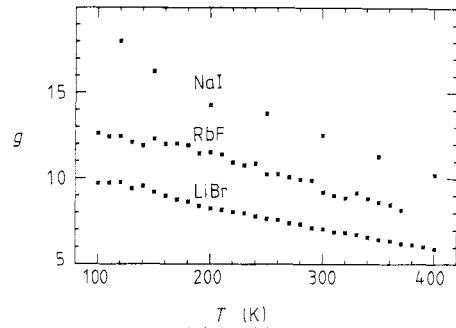


Figure 6. Values of the Bridgman parameter g as a function of temperature at zero pressure for NaI, LiBr and RbF. The values for NaI are obtained from Håkansson and Andersson (1986).

et al 1972, Vaidya and Kennedy 1971). For RbF, $B_T(p)$ was obtained from Roberts and Smith (1970). Figure 5 shows the resulting values of g as a function of pressure. As can be seen, g decreases with increasing pressure. The agreement between values of g for LiBr corresponding to the two sets of data for $B_T(p)$ is good at zero pressure but becomes worse as the pressure increases. The error in g is estimated as 10–15%.

The pressure dependence of the thermal conductivity of the alkali halides has recently been investigated theoretically (Pettersson 1989). For LiBr, the theoretical value of g at low pressures is 14% lower than the experimental value and, for RbF, it is 12% higher.

The temperature dependence of g can be evaluated using the data given in table 2 and information about $B_T(T)$. The pressure and temperature dependence of the elastic constants for LiBr in the temperature range 220–340 K have been measured by Ching *et al* (1972). They also give values of B_T and $(\partial B_T/\partial p)_T$ in that interval. Since B_T and $(\partial B_T/\partial p)_T$ vary linearly with temperature, values for these quantities could be evaluated in the temperature range 100–400 K by extrapolation. No experimental data for $B_T(T)$ for RbF could be found in the literature. However, the adiabatic bulk modulus $B_S(T)$ as a function of temperature, can be evaluated using elastic constant data (Cleavelin *et al* 1972). The temperature dependence of B_T can then be obtained from the identity

$$B_T = B_S/(1 + \beta\gamma T) \quad (3)$$

where β is the thermal expansivity and γ the Grüneisen parameter. We obtained the room-temperature value of $0.86 \times 10^{-4} \text{ K}^{-1}$ for β using thermal expansion data (Trost 1963). The temperature dependence of β for RbF was estimated from theoretical calculations (Pautamo 1963). The room-temperature value for γ was obtained from Roberts and Smith (1970). For the sodium halides and the lithium halides, γ is approximately constant in the temperature range 100–400 K (White and Collins 1973, Ruppini 1972). We therefore assumed that the temperature variation in γ for RbF could be neglected. The resulting values of $g(T)$ are shown in figure 6. Also included in the figure are values of $g(T)$ for NaI. It can be seen that g for NaI is always larger than for LiBr and RbF and also has the strongest temperature dependence. The decrease in g from 100 to 400 K is 44% for NaI and 40% for LiBr and RbF.

In figure 7, we have plotted values of λ and g at room temperature and zero pressure as a function of mass ratio for the rubidium halides. As can be seen, neither of these quantities is strongly dependent on mass ratio σ although $dg/d\sigma$ is detectably positive.

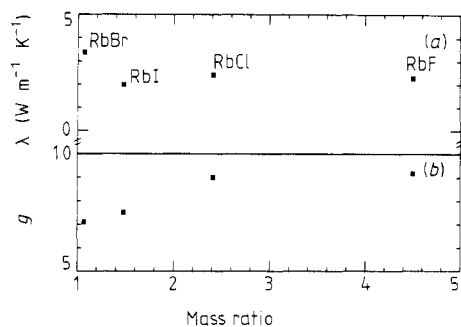


Figure 7. Values of (a) the thermal conductivity λ and (b) the Bridgman parameter g at room temperature and zero pressure as functions of the mass ratio for the rubidium halides. The values for RbCl, RbBr and RbI are obtained from Andersson (1985).

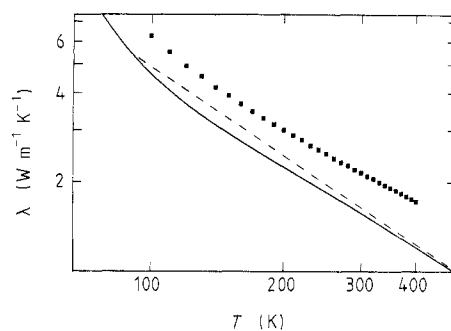


Figure 8. Isochoric temperature dependence of thermal conductivity λ for LiBr: —, theory (Pettersson 1988b); ■, experimental values reduced to the volume pertaining to zero temperature and pressure; ---, guide to the eye, showing T^{-1} dependence.

4.2. Isochoric temperature dependence of λ

4.2.1. Reduction to constant volume. Theoretical calculations of the temperature dependence of λ are made for isochoric conditions. In order to make a comparison with theory, the experimental isobaric values must be reduced so that they correspond to constant-volume conditions. If g is approximately constant, we can use the formula

$$\lambda(V_0) = \lambda(V)(V_0/V)^{-g} \quad (4)$$

where V_0 is the volume to which we wish to reduce our data. However, as can be seen in figure 6, g varies relatively strongly with temperature for LiBr and RbF. Therefore the following procedure was used instead. The data were reduced to the volume pertaining to zero temperature and pressure. The isobaric temperature dependence of λ at zero pressure has already been given in table 2; what remains to be done is to correct for thermal expansion. The difference between the zero-temperature volume and the volume corresponding to some other temperature can be calculated using thermal expansivity data. If $V(p, T)$ is known, the pressure required to retrieve the zero-temperature volume can be calculated. The reduced value of λ is then obtained by inserting this pressure value in the equation $\lambda = A + Bp$, with appropriate values of A and B .

Thermal expansivity data for LiBr were obtained from Touloukian (1977). Given B_T and $(\partial B_T/\partial p)_T$ (Ching *et al* 1972), we can calculate the pressure needed to cause a certain reduction in volume using the Murnaghan equation of state

$$p = B_T/B'_T[(V/V_0)^{-B'_T} - 1] \quad (5)$$

where B'_T is $(\partial B_T/\partial p)_T$.

It is more difficult to reduce the RbF data to constant volume owing to incomplete equation-of-state data. The temperature dependence of the volume for RbF was estimated from data given by Trost (1963). Since the pressure dependence of B_T is available only at room temperature, $B_T(T)$ at zero pressure was used in the calculations. In order to estimate the error in this approximation, the reduced value at room temperature was also calculated taking account of the pressure dependence, and the difference was found to be only 1%.

4.2.2. *Comparison with theory.* The thermal conductivities of 17 alkali halides with the B1 type of structure have recently been calculated with a variational method (Pettersson 1987, 1988a). A deformation dipole model was used to obtain the dispersion relations throughout the whole first Brillouin zone. It was found that optic phonons are important both for the heat current and also for the three-phonon scattering processes in all the alkali halides. This was especially notable in connection with LiI for which it was found that the contribution to λ from the optic phonons was about 60% of the total at temperatures above the Debye temperature θ_D . Furthermore, as a result of the very high group velocities of the optic phonons obtained using the deformation dipole model, λ for LiI was predicted to drop below the extension of the high-temperature T^{-1} dependence in the temperature range 70–150 K. There are no experimental data for λ of LiI.

A similar theoretical analysis can be made for LiBr (Pettersson 1988b) and the results are shown in figure 8. It can be seen that also for LiBr the theoretical values lie below the extension of the line showing T^{-1} dependence, in the region where the measurements were made. Also plotted in figure 8 are our experimental data, reduced to constant volume. At 300 K, the theoretical value of λ is 27% lower than the experimental value. For most other alkali halides the agreement between theory and experiment is 10–20%; so the agreement is reasonable in this case also. What is more interesting is the qualitative agreement between theory and experiment on the temperature dependence. The experimental results thus indicate that the role of the optic phonons in the thermal conductivity of LiBr is adequately described by the theoretical model.

The theoretical value of λ for RbF is 52% lower than the experimental at 300 K. Both theoretical and experimental values follow T^{-1} dependence in the region 100–400 K. The largest uncertainty in the theoretical calculations is the third-order derivative of the potential energy between a pair of nearest neighbours (Pettersson 1987). This may be one explanation of the difference between the absolute theoretical value of λ and the absolute experimental value.

Acknowledgments

This work was supported financially by the Swedish Natural Science Research Council and the Swedish Board for Technical Development. We are grateful for the assistance provided by our friend and colleague Dr Per Andersson in the early stages of the present investigation. The authors thank Professor G Bäckström for discussions during the course of this work. We wish to thank Dr Sune Pettersson for many helpful and valuable discussions and for providing us with theoretical calculations for LiBr. We would also like to express our gratitude to Ann-Marie Nenner at the Department of Inorganic Chemistry of the University of Umeå, who carried out the x-ray diffraction analyses, and to Åsa and Christer Albano at the Peat Research Project, Röbäcksdalen, Umeå, who did the thermogravimetry analyses.

References

- Andersson P 1985 *J. Phys. C: Solid State Phys.* **18** 3943
- Ching L S, Day J P and Ruoff A L 1972 *J. Appl. Phys.* **44** 1017
- Cleavelin C R, Pederson D O and Marshall B J 1972 *Phys. Rev. B* **5** 3193

- Darnell A J and McCollum W A 1970 *J. Phys. Chem. Solids* **31** 805
- Demarest H H, Cassell C R and Jamieson J C 1978 *J. Phys. Chem. Solids* **39** 1211
- Gmelin's Handbuch der Anorganischen Chemie* 1937 vol 24 (Berlin: Chemie)
- Håkansson B and Andersson P 1986 *J. Phys. Chem. Solids* **47** 355
- Håkansson B, Andersson P and Bäckström G 1988 *Rev. Sci. Instrum.* at press
- Paukov I E, Anisimov M P and Luk'yanova I G 1974 *Russ. J. Phys. Chem.* **48** 946
- Pautamo Y 1963 *Ann. Acad. Sci. Fenn. A* **6** 129
- Petersson S 1987 *J. Phys. C: Solid State Phys.* **20** 1047
- 1988a *J. Phys. C: Solid State Phys.* **21** 1727
- 1988b private communication
- 1989 *J. Phys.: Condens. Matter* **1** 347
- Roberts R W and Smith C S 1970 *J. Phys. Chem. Solids* **31** 2397
- Ross R G, Andersson P, Sundqvist B and Bäckström G 1984 *Rep. Prog. Phys.* **47** 1347
- Ruppin R 1972 *J. Phys. Chem. Solids* **33** 945
- Touloukian Y S, Kirby R K, Taylor R E and Lee T V R 1977 *Thermophysical Properties of Matter* vol 13 (New York: Plenum) p 836
- Trost K F 1963 *Z. Naturf. b* **18** 662
- Vaidya S N and Kennedy G C 1971 *J. Phys. Chem. Solids* **32** 951
- White G K and Collins J G 1973 *Proc. R. Soc. A* **333** 237