Aust. J. Phys., 1976, **29**, 19–24

Analysis of the Effect of Resonant Phonon Scattering on the Thermal Conductivity of CaF_2

P. R. W. Hudson and E. E. Gibbs

Department of Physics, Monash University, Clayton, Vic. 3168.

Abstract

An analysis is presented of the various phonon contributions to the thermal conductivity of CaF_2 doped with 1·0% and 0·1% of yttrium or thulium. The broad phonon resonant scattering term is found to reduce the low frequency phonon conduction significantly. This is responsible for the relatively stronger suppression of the conductivity at low temperatures in the phonon boundary scattering region. Thus broad quasilocalized phonon resonant scattering mechanisms have a similar effect to phonon precipitate scattering. It also follows that, in the case of a broad resonant scattering mechanism, a dip will not necessarily be seen in the conductivity.

Introduction

Localized phonon modes have been known to exist in impure dielectric crystals since 1962 (Pohl 1962). If the mode frequency, which is a characteristic of the interaction between the impurity and host lattice, lies outside the host lattice phonon frequency spectrum, the mode has a spatial exponential decay around the impurity site and is truly localized. In this case the impurity will have a similar effect on the thermal conductivity of the material as will any other small imperfection. If on the other hand the mode is not localized and its frequency lies within the phonon spectrum, it may be excited by phonons of the appropriate frequency and a unique resonant phonon scattering mechanism will exist. The purpose of the present work was to investigate in detail the effect such scattering mechanisms have on the thermal conductivity of the material. Doped CaF_2 was used as a model for the investigation.

Previous Work

Pohl (1962) was the first to observe the effect of phonon resonant behaviour on thermal conductivity. The resonant frequency of NO_2^- ions in KCl crystals lay within the phonon frequency spectrum, such modes often being termed quasilocalized. Schwartz and Walker (1966) observed resonant behaviour due to lattice vacancies in KCl. Baumann and Pohl (1967) and Schwartz and Walker (1967) observed resonant behaviour due to monatomic impurities in alkali halides. True localized vibrations have also been observed: Elliott *et al.* (1965) discussed the absorption spectra of H^- and D^- ions in CaF_2, SrF_2 and BaF_2. The theoretical estimates of the resonant frequencies based on the concept that the light ion was positioned on fluorine sites agreed well with experiment.

The resonant phonon scattering discussed here is that arising from point defects which introduce impurity phonon modes into the crystal phonon spectrum due to the

different force constants which bind the impurity atom. Two other mechanisms are known to exist which can scatter phonons in a resonant fashion: one is the presence of molecular impurities and the other is the more complicated case of point defects which lie in off-centre positions so that tunnelling may occur between similar positions.

The resonant frequencies, due to the different force constants, do not follow a simple formula (Caldwell and Klein 1967). A great deal of work has been carried out with alkali halides as the host material, and the effect on the thermal conductivity has been found to be quite dramatic (Baumann and Pohl 1967). Harrington and Walker (1970) chose to investigate doped XF_2 (where X = Ca, Sr, and Ba) for resonant phonon scattering, as Moore and Klein (1969) had been unsuccessful with doped CdS using impurity concentrations of up to 500 p.p.m. Harrington and Walker measured the thermal conductivity of CaF_2 doped with either 10^{25} atoms m^{-3} of Sm^{2+} or U^{3+}, or 10^{26} atoms m^{-3} of H^-. In all cases no resonant behaviour was apparently observed, although the low temperature crystal-dependent conductivity was considerably lower than that of pure CaF_2, which they ascribed to precipitates.

Hayes *et al.* (1973) investigated impure CaF_2 with larger dopant concentrations of $2{\cdot}65\times10^{25}$ atoms m^{-3} of Y or Tm and $2{\cdot}65\times10^{26}$ atoms m^{-3} (1 at. %) of Y. A broad infrared absorption was found at ~ 80 cm^{-1} and the thermal conductivities were considerably lower than those measured by Harrington and Walker (1970). In particular, an anomalous dip was found in the thermal conductivity at about 30 K in the case of 1 at. % of Y.

The difference in strength of resonant phonon scattering between CaF_2 and the alkali halides is most interesting. A concentration of 1·0% Y in CaF_2 was necessary to produce an anomalous thermal conductivity dip, while Baumann and Pohl (1967) found dips for ~0·02% Tl in KCl. The purpose of the present paper is to analyse the thermal conductivity of the doped CaF_2 in order to suggest a reason for such differences.

Theory

The method used to compute the thermal conductivities was that based on a phonon relaxation rate τ_i^{-1} for the various scattering processes i which were assumed to be independent. Normal processes were ignored due to the large amount of phonon resistive scattering in doped CaF_2. The thermal conductivity K is given by a sum of phonon heat currents over all phonon frequencies. The reader is referred to Callaway (1959) and Holland (1963) for theoretical details. Four phonon scattering mechanisms were considered relevant to this problem: boundary, point defect, Umklapp, and resonant scattering. Only the latter is discussed here in detail, and for details of the others the reader is referred to Klemens (1955), Berman and Brock (1965) and Klein (1966).

Resonant phonon impurity scattering

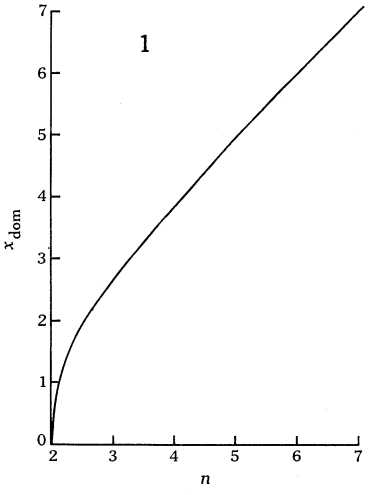
Baumann and Pohl (1967) have discussed the relative difficulty found in fitting experimental data by resonant scatter relaxation rates. Many forms have been used which are theoretically justifiable (Schwartz and Walker 1967). Pohl (1962) originally used

$$\tau_{\text{res}}^{-1} = \beta\omega^2/\{(\omega_0^2-\omega^2)^2+\delta\omega^2\}, \qquad (1)$$

where β and δ are constants, ω is the phonon angular frequency and ω_0 is the resonant frequency. One of us (P.R.W.H.) obtained a reasonable fit to the experimental data of CaF_2 doped with 0·1% and 1·0% Y and 0·1% Tm using a total resistive relaxation rate given by Hayes *et al.* (1973). The form of the resonant phonon relaxation rate was important. The value of δ was taken to be zero in equation (1), as it made little impact on the result. Other relaxation rates were used, including

$$\tau_{\text{res}}^{-1} = \eta\omega^4/\{(\omega_0^2-\omega^2)^2+\rho\omega^6\}, \tag{2}$$

where η and ρ are constants, but a good fit could not be obtained with these resonant relaxation rates. The exact contributions of the various processes are presented in the following section.



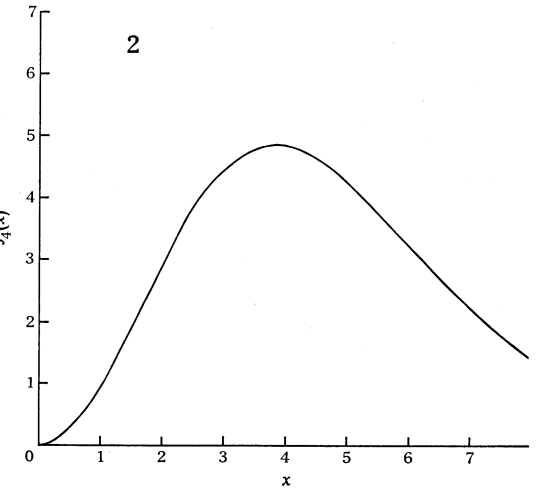


Fig. 1. Dominant phonon scattering parameter x_{dom} as a function of the scattering power n.
Fig. 2. Phonon heat conduction distribution $J_4(x)$ in the boundary scattering region.

Results and Discussion

The thermal conductivity may be written

$$K = GT^3 \int_0^{\theta/T} \tau J_4(x)\,\mathrm{d}x, \tag{3}$$

where G is a constant, $x = \hbar\omega/kT$, with T the absolute temperature, θ is the Debye temperature, τ is the total phonon relaxation time, and $J_4(x)$ is the phonon heat distribution function for scattering power $n = 4$, which is given more generally for arbitrary n by

$$J_n(x) = x^n \exp(x)/\{\exp(x)-1\}^2. \tag{4}$$

If, at a given temperature, one particular phonon scattering mechanism is dominant then τ would be proportional to a power of x, and the thermal conductivity would be given by

$$K \propto T^m \int_0^{\theta/T} J_n(x)\,\mathrm{d}x. \tag{5}$$

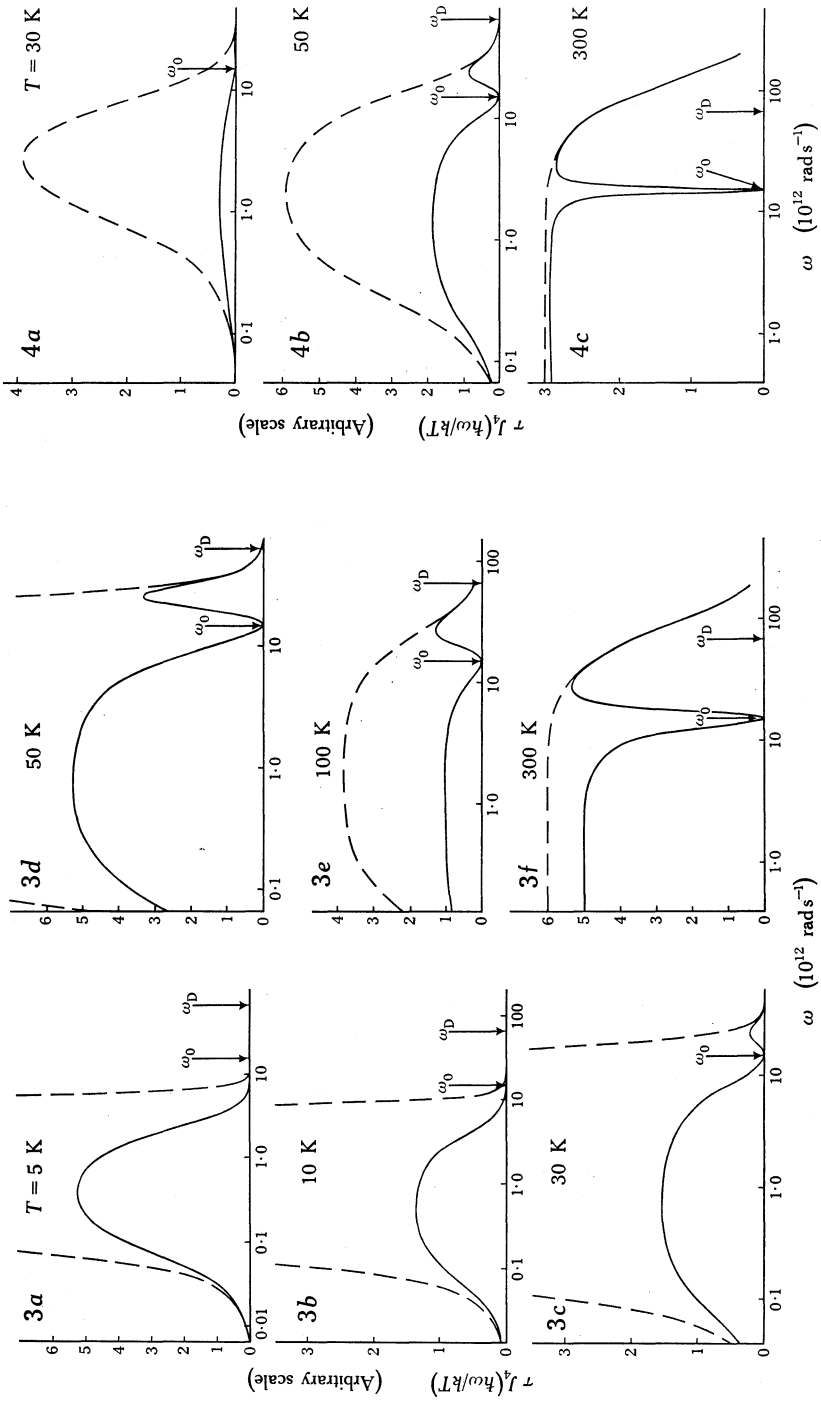
To determine the effect of resonant phonon scattering on the crystal thermal conductivity, a first approximation would be to consider dominant phonons only. One would expect that, when the dominant phonons have a frequency about the resonant frequency, the thermal conductivity would be reduced most. This effect would be influenced by the bandwidths of the phonon heat distribution function $J_n(x)$ and of the resonant scattering mechanism. To this end the various phonon heat current distributions $J_n(x)$ were constructed as functions of x (and therefore ω for a given T) and the dominant phonon x values, x_{dom}, were determined as functions of n. The result is shown in Fig. 1. No account was taken of the various bandwidths which affect the validity of the dominant phonon concept. The phonon current distribution for $n = 4$, which corresponds to the low temperature boundary scattering case, is illustrated in Fig. 2. The area under the curve is related to the thermal conductivity. If a low-frequency sharp resonant mode existed in a material then the maximum effect on the conductivity would occur at a temperature $T_0 = 0{\cdot}26\hbar\omega_0/k$, subject to the condition that the conductivity was dominated by boundary scattering at this temperature. If the mode has a large bandwidth, the effect would be spread around temperatures $\sim T_0$, and it would be possible to confuse the behaviour with precipitate scattering.

Doped CaF_2

The data which were used to fit the experimental conductivity of CaF_2 doped with Y and Tm were analysed to determine the phonon contribution per unit frequency as a function of temperature. All results are plotted in Figs 3 and 4. The ordinate is the integrand $\tau J_4(x)$ in equation (3) and is related to the phonon heat current per unit temperature gradient per unit phonon frequency interval, or to the phonon contribution to the thermal conductivity per unit frequency interval. In each part of Figs 3 and 4, the dashed curve represents the 'pure' CaF_2 while the continuous curve represents the doped CaF_2.

Doping with 1·0% Yttrium

Fig. 3 illustrates the 1·0% Y case for temperatures of 5, 10, 30, 50, 100 and 300 K. As was indicated for the thermal conductivity, it can be seen that the resonant scattering is responsible for an enormous reduction in the integrand over all phonon frequencies. Only at the higher temperatures does resonance scattering start to be negligible and, even then, this is only the case for phonon frequencies just below the Debye frequency. The effect of the broad resonance term can be seen most clearly in Fig. 3*f*. In this case (300 K) the resonant scattering is comparatively weak and the effect on the integrand $\tau J_4(x)$ is relatively small. However, phonons of $\omega < \omega_0$ are scattered more strongly than those of $\omega > \omega_0$. In practice this must be the case, since for $T < 30$ K the phonon contribution from frequencies $\omega \gtrsim \omega_0$ is negligible although the reduction in thermal conductivity due to the impurities is quite enormous (Hayes *et al.* 1973). In fact it can be seen that the dip in the conductivity, which occurs at $\sim$30 K is associated with the enormous low frequency ($\omega < \omega_0$) reduction in heat flow rather than with scattering of phonons of frequencies $\sim\omega_0$. A clear dip in the integrand only occurs at $T \geqslant 50$ K. It is thus the scattering of the low frequency phonons rather than 'resonant' phonons which is responsible for the reduced conductivity. This explains the low-temperature conductivity data of Harrington and Walker (1970) and indicates that precipitates were probably not



Figs 3a–3f. Phonon conduction spectra for CaF_2 doped with 1·0% Y at the indicated temperatures. Dashed curves are for 'pure' CaF_2.
Figs 4a–4c. Phonon conduction spectra for CaF_2 doped with 0·1% Y or Tm at the indicated temperatures. Dashed curves are for 'pure' CaF_2.

present in their crystals. It is deduced that the effect of a dip in the thermal conductivity was fortuitous and not a necessary consequence of resonant scattering, if the scattering has a large bandwidth. Certainly one could not predict that the resonant frequency would be related to the temperature at which the dip was found by the approximation $T_{\text{dip}} \approx \alpha\hbar\omega_0/k$, where in this case $\alpha \approx 0{\cdot}3$. The same conclusions apply to the $0{\cdot}1\%$ impurity level.

Doping with $0{\cdot}1\%$ Yttrium or Thulium

The results for $0{\cdot}1\%$ doping are illustrated in Fig. 4. The resonant phonon scattering can be seen to reduce the phonon contribution considerably at all frequencies. Despite this strong resonant scatter and the dip in the integrand $\tau J_4(x)$ at ω_0, no dip was seen in the thermal conductivity at this level of impurity. Once again the low temperature integrands suffer a more drastic reduction than the high temperature ones.

Conclusions

It has been shown by analysing the individual phonon contributions to the thermal conductivity of CaF_2 doped with Y and Tm that a broad high-frequency resonance phonon-scattering mode can produce a marked effect at low frequencies. This prominent low frequency phonon scattering produces a considerable reduction in the thermal conductivity at low temperatures, similar to that observed in phonon precipitate scattering. The lack of a conductivity dip for moderate ($\sim 0{\cdot}1\%$) impurity concentration is shown not to be evidence for the absence of resonant scattering. On the contrary, resonant scattering is extremely strong but diverse in this case.

References

Baumann, F. C., and Pohl, R. O. (1967). *Phys. Rev.* **163**, 843–50.
Berman, R., and Brock, J. C. F. (1965). *Proc. R. Soc. London* A **289**, 46–65.
Caldwell, R. F., and Klein, M. V. (1967). *Phys. Rev.* **158**, 851–75.
Callaway, J. (1959). *Phys. Rev.* **113**, 1046–51.
Elliott, R. J., Hayes, W., Jones, G. D., MacDonald, H. F., and Sennett, T. (1965). *Proc. R. Soc. London* A **289**, 1–33.
Harrington, J. A., and Walker, C. T. (1970). *Phys. Rev.* B **1**, 882–90.
Hayes, W., Wiltshire, M. C. K., Berman, R., and Hudson, P. R. W. (1973). *J. Phys.* C **6**, 1157–65.
Holland, M. G. (1963). *Phys. Rev.* **132**, 2461–71.
Klein, M. V. (1966). *Phys. Rev.* **141**, 716–23.
Klemens, P. G. (1955). *Proc. Phys. Soc. London* A **68**, 1113–28.
Moore, G. E., and Klein, M. V. (1969). *Phys. Rev.* **179**, 722–30.
Pohl, R. O. (1962). *Phys. Rev. Lett.* **8**, 481–3.
Schwartz, J. W., and Walker, C. T. (1966). *Phys. Rev. Lett.* **16**, 97–8.
Schwartz, J. W., and Walker, C. T. (1967). *Phys. Rev.* **155**, 959–79.

Manuscript received 20 August 1975