

A THEORETICAL APPROACH TO THE THERMAL CONDUCTIVITY OF BORON CARBIDES

V. M. KENKRE and X. FAN

Department of Physics and Astronomy

University of New Mexico, Albuquerque, NM 87131

ABSTRACT

The thermal conductivity of boron carbides at high temperatures presents a fundamental challenge to theory. One of the striking features is that, while in B_4C it displays "normal" behaviour in that it decreases with increasing temperature, in B_3C it is nearly temperature-independent. We address this feature through a model calculation which assumes the heat current to be due to carrier phonons whose frequency is modulated by lower-frequency phonons which "dress" the carrier phonons through strong interaction. Preliminary calculations show satisfactory but partial agreement with experiment for reasonable parameters and delineate areas for further investigation of the vibrational properties of boron carbides.

INTRODUCTION

The problem presented to the theorist by recent experimental results[1] on the thermal conductivity of boron carbides in the high temperature region (300 K to 1700 K) is two-fold. The temperature behaviour of the thermal conductivity observed in B_3C is in itself intriguing in that it is largely independent of temperature (or rises slightly with increasing temperature). In addition, a transition from this unusual behaviour to the traditional one involving an increasing thermal conductivity with decreasing temperature is observed as one passes from B_3C to B_4C . Of these two parts of the problem, it is the first one that we are primarily interested in in this paper. In other words, our main goal here is to develop a hopping theory of thermal conductivity which is applicable in the region wherein the mean free path of the heat carriers is short enough to be comparable to the lattice constant and which is capable of addressing a non-increasing thermal conductivity. Standard momentum space theories of heat transport are obviously useless for boron carbides in this region.

The basic model we employ is one wherein the heat carriers are high frequency (optical) phonons which are strongly coupled with lower frequency (acoustic) phonons. The coupling is strong enough to require a nonperturbative treatment. Thus, we assume the simple picture of the carriers being scattered from momentum states to momentum states through their interaction with the acoustic phonons to be inapplicable. Instead, the acoustic phonons are assumed to "dress" the carrier phonons by modulating their frequency. The behaviour of the thermal conductivity is therefore "polaronic" [2-4] in nature. We calculate the relevant correlation functions explicitly and obtain from them expressions for the thermal conductivity. We find that reasonable fits can be obtained to the B_3C data.

We also find that, while we can use the same theory to fit the B_4C data, the parameter values that emerge indicate a lowering of the effective velocity of the carriers in going from B_3C to B_4C . This appears to be counterintuitive in the light of the reasonable assumption [1] that increased disorder should make the effective carrier velocity smaller (not larger) in B_3C relative to B_4C . Our tentative conclusions from these preliminary investigations are that it is possible to construct a reasonable theory to explain the data on B_3C involving the weakly temperature-dependent thermal conductivity in terms of strong interactions between carrier phonons and dressing phonons, but that the transition from B_3C to B_4C requires a theoretical development capable of treating disorder at a more sophisticated level.

THEORY

The familiar expression for the thermal conductivity κ which states its proportionality to the specific heat c and to the product of the carrier velocity v and the carrier mean free path Λ , equivalently the product of the square of v and the mean collision time τ , viz.,

$$\kappa = (1/3) c v \Lambda = (1/3) c v^2 \tau, \quad (1)$$

can be shown [5,6] to be a simple case of a more general expression which involves an integral over all time of an appropriate correlation function. At high temperatures, as is the case for the observations of interest [1] in boron carbides, that correlation function may be taken to separate into a product of the temperature-independent specific heat c and the velocity autocorrelation function $\langle v(t)v \rangle$:

$$\kappa = (1/3) c \int_0^{\infty} dt \langle v(t)v \rangle \quad (2)$$

The equivalence of (1) and (2) is obvious under the identification of τ with the standard expression $\int_0^{\infty} dt \langle v(t)v \rangle / \langle v^2 \rangle$. Our analysis takes (2) as its point of departure and proceeds to calculate the velocity autocorrelation function $\langle v(t)v \rangle$ of the carrier phonons. Our model for the interaction between carrier phonons and dressing phonons is one wherein the latter modulate the frequency of the former. For simplicity we will retain only the linear term in a Taylor expansion of the frequency of the carrier phonons in orders of the acoustic displacements, and use the notation that b_m^+ creates a carrier phonon (vibration) of frequency Ω_m at site m , c_q^+ creates a dressing (acoustic) phonon of frequency ω_q and wavevector q , V_{mn} describes the intersite interaction which moves the carrier phonon from site n to site m , and g_q is the dimensionless coupling constant which

describes the (strong) interaction between the carrier and the dressing phonons. The Hamiltonian of the carrier is then

$$H = \sum_m \Omega_m b_m^\dagger b_m + \sum_{mn} V_{mn} b_m^\dagger b_n + \sum_q \omega_q c_q^\dagger c_q \\ + \sum_{mq} g_q e^{iqm} \omega_q (c_{-q}^\dagger + c_q) b_m^\dagger b_m \quad (3)$$

The calculation of the velocity autocorrelation function from (3) can be carried out through one of several available methods. We employ the method of generalized master equations [7] which has been explained in detail elsewhere in the context of exciton transport. The result is

$$\langle v(t)v \rangle = 2\tilde{V}^2 [\exp(-\alpha^2 t^2)] [1 + f(t)] \quad (4)$$

$$f(t) = \exp[\sum_q 4(\sin^2 \frac{1}{2}q)(|g_q|^2 \text{csch } \frac{1}{2}\beta\omega_q)(\cos \omega_q t)] - 1 \quad (5)$$

where $\tilde{V} = V \exp[-2(\sin^2 \frac{1}{2}q)(|g_q|^2 \coth \frac{1}{2}\beta\omega_q)]$, α measures the fluctuation (assumed to follow a Gaussian distribution) in the site frequencies Ω_m brought about by static disorder, and $1/\beta$ is the product of the Boltzmann constant and the temperature. The correlation function in (4) consists of two terms and, on being integrated, yields the thermal conductivity as a sum of two terms. The second term is essentially identical to the Holstein [2] expression for the polaronic mobility in the strong coupling regime if the frequency fluctuation parameter α is neglected. The first term represents a contribution to the conductivity which decreases with an increase in temperature not because of an increase in the collision time but because of a decrease in the effective velocity of the carrier. This decrease arises from the strong coupling reduction of the bandwidth of the carrier.

COMPARISON OF THEORY WITH EXPERIMENT

Figs. 1 and 2 show the results of fitting (2),(4) to the high temperature data in boron carbides from fig. 1. Dashed lines represent the experimental observations (different curves represent different samples - see ref. 1 for details) and solid lines represent the best fit from our theoretical expressions. The maximum effective frequency ω_D of the dressing phonons is taken to lie between 700 and 1000 K, in keeping with the estimated Debye temperature in boron carbides. The data on B_4C and B_9C is fitted separately in Fig. 1 whereas, in fig. 2, the parameters obtained from the fit to the B_9C data are used to fit the B_4C data.

The fits are found to be sensitive to the choice of ω_D and can be thrown way out of kilter by choosing an unrealistic value of ω_D such as 50 K. While they are quite reasonable in fig. 1 and therefore appear to indicate that (2),(4) can be used for both B_4C and B_9C , fig. 2 shows that it is not possible to achieve even passable fits which employ the same parameter values for both substances. Indeed, the fits in fig. 1 require values of the carrier velocity for the B_4C fits which are smaller than those for the B_9C ones by a

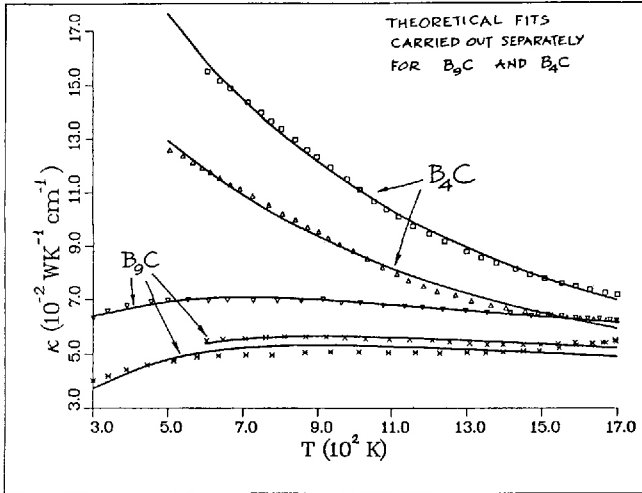


Fig. 1: Theoretical fits carried out separately for B_9C and B_4C

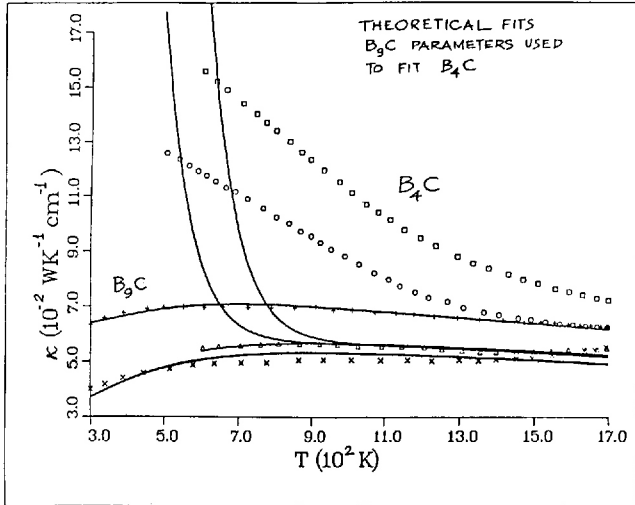


Fig. 2: Theoretical fits: B_9C parameters used to fit B_4C

factor of about 2. This tendency appears to be unexpected and probably unphysical. Following the ideas of Wood, Emin and Gray [1], it is reasonable to suppose that the passage from B_4C to B_3C involves a lowering of the effective velocity brought on by disorder in the site frequencies of the icosahedral links. One would be hard put to explain in those terms an increase in the velocity as one passes from B_4C to B_3C .

In all our B_3C fits, the value of the dimensionless coupling constant, i.e. the square root of the ratio of the polaronic lowering of the carrier frequency to ω_D , is quite reasonable at least from the point of view of internal consistency. It lies between 1 and 2. Values less than 1 would invalidate a strong-coupling (dressing) theory as we have used since then the acoustic phonons would merely scatter the carrier phonons rather than dressing them. Values which are very large would not be compatible with the observed weak temperature dependence of κ . Also, in all the cases fitted, the value of the fluctuation of the site frequency of the carrier phonons giving rise to static disorder is at most about $(0.2)\omega_D$. Since by using a dressing theory we have assumed ω_D to be much smaller than the site frequency of the carrier phonon, the fluctuation enters the theory only as a small perturbation. Finally, the dispersion of the carrier frequency, which is directly related to the carrier velocity, is found to be about 100 K. This value is consistent with our use of a hopping rather than a momentum theory of heat transport. The failure of the traditional theoretical approach involving long-wavelength acoustic phonons as the heat carriers, made particularly clear by experiments on α -boron, has been detailed by Emin, Howard, Green and Beckel elsewhere in this volume.

CONCLUSIONS

While our investigations reported here are preliminary, they tend to support several suggestions and to delineate further avenues of investigation. Thus, a dressing theory is found to be compatible with the weak temperature independence of κ observed in B_3C . The parameters that emerge from an application of the theory to the data appear reasonable and are internally consistent. The theory is also found to be compatible with the data on B_4C if applied separately. Fig. 1 shows both these. However, if the disorder parameter α is the only one allowed to change in going from B_3C to B_4C , the theory is found to fail unambiguously. Fig. 2 makes this clear. Our conclusion is, therefore, that it is quite likely that dressing ideas as put forth here address the correct physics of the thermal conductivity in boron carbides but that the effect of disorder [1] brought about by changing the relative B-C content requires a more detailed and more sophisticated theoretical framework than the one presented here.

Among the further questions and avenues of research that this study suggests, we mention the following as deserving immediate attention in our opinion. If we are to consider our explanation of the B_3C fits to be reasonable, what precise modes of the solid can we consider to be the carrier phonons? What are the modes that provide the dressing phonons and why? What is the precise nature of the coupling between carrier phonons and the dressing phonons? Is the inverted molecular crystal idea of Emin [8], which provides a conceptually clear and practically useful model of boron carbides, valid quite generally or are modifications of that idea

necessary? How can one develop a proper theory of disorder [1] which would explain the transition from D_4C to D_8C ? We hope that these and related questions will be answered by theoretical studies in the near future.

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