

Contribution of the decay of optical phonons into acoustic phonons to the thermal conductivity of AlN

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The thermal conductivity along two high-symmetry directions of several aluminum nitride (AlN) single crystals differing in their mass-fluctuation phonon-scattering parameter is described accurately in the full temperature range by taking into account the contribution of optical phonon decay into acoustic phonon. The accuracy of the proposed model shows the fundamental role of the optical phonon in the thermal conductivity of semiconductor materials.

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Assuming that in semiconductor materials heat is exclusively carried by acoustic phonon, the thermal conductivity (k) has taken a general qualitative behavior as function of temperature [$k(T)$]: at very low T (few kelvins), k depends on the size of the crystal and increases with T mirroring the temperature dependence of the specific heat, reaching a maximum k_m at $T_m \sim 0.05\theta_D$, where θ_D is the Debye temperature. Near this maximum, k is independent of T but sensitive to crystal imperfections. At higher T , which is comparable to the acoustic θ_D , k decreases with increasing T due to three-phonon scattering via normal and umklapp processes. The usual approach for describing $k(T)$ of a semiconductor is to use an acoustic phonon relaxation time approximation in the Boltzmann equation and then calculate the scattering cross section by perturbation techniques.^{1,2} Callaway³ introduced a model, which was modified later by Holland,⁴ which should enable fitting $k(T)$ for a large number of semiconductors with some adjustable parameters. This model, which became known as the modified Callaway theory (MCT), considers a Debye phonon spectrum and makes several assumptions as to the form of the free-phonon scattering times.

Several authors⁵⁻⁹ noticed some lack in the phonon scattering processes which prevents the description of the experimental $k(T)$ over a wide temperature range by using the MCT. They agreed on the need of an additional realistic mechanism to describe accurately $k(T)$ of semiconductors in the full T range where several mechanisms concurrently contribute.

In this work, we tackle this issue and quantitatively consider the decay of optical phonon into acoustic phonon within the MCT. We show that this model, where acoustic phonon creation partially counteracts the resistive processes, allows a rather accurate description of AlN $k(T)$ in a wide T range and for several levels of point defects density. We postulate that such mechanism is crucial to describe precisely $k(T)$ in semiconductors.

Three series of AlN polycrystalline samples differing in their oxygen content were grown by sublimation.¹⁰ However, it has been found that when the oxygen content in AlN exceeds ~ 1 at %, a change in the oxygen accommodation occurs resulting some point defects decoration.^{11,12} Therefore,

in what follows, we analyze our results as function of the mass-fluctuation phonon-scattering parameter (Γ) and not oxygen impurity concentration since Γ is related to the overall point defects density. The AlN single crystals ($\sim 2 \times 2$ mm) investigated were cut from the polycrystalline samples. The measurements were taken on single crystal facets oriented along ΓA and ΓK , as confirmed by x-ray diffraction and Raman measurements.

Data obtained from specific heat, thermal diffusivity, and bulk density measurements were used to deduce $k(T)$ along ΓA and ΓK according to the following relationship: $k^{\parallel(\perp)}(T) = \rho C_p^{\parallel(\perp)}(T) \lambda^{\parallel(\perp)}(T)$, where \parallel and \perp are related to ΓA and ΓK , respectively, ρ is the bulk density, C_p is the specific heat, and λ is the thermal diffusivity.

As it will be noticed below, the longitudinal and transverse acoustic phonon Debye temperatures $\theta_D^{L(T)}$ and velocities $v^{L(T)}$ are the most important parameters for phonon heat transport. Therefore, for reliable $k(T)$ modeling, these parameters should be known as precisely as possible. The Debye temperatures are deduced for both ΓA and ΓK directions from *ab initio* calculations of the AlN lattice dynamics.¹³ The acoustic phonon velocity $v^{L(T)}$ in both ΓA and ΓK directions were carefully deduced from Brillouin scattering measurements performed on the same AlN single crystal facets investigated in this work. These measurements are detailed in Ref. 10.

Experimental results of the $k(T)$ measurements along ΓA and ΓK on several AlN single crystals differing in their point defects density are shown in Fig. 1 as symbols. First, the experimental data were fitted by using the full MCT and by considering the total phonon scattering rate as being the sum of the four conventional individual scattering rates,

$$(\Delta\tau^{-1})^{L(T)} = (\Delta\tau_B^{-1})^{L(T)} + (\Delta\tau_I^{-1})^{L(T)} + (\Delta\tau_N^{-1})^{L(T)} + (\Delta\tau_U^{-1})^{L(T)}. \quad (1)$$

The scattering rate from the sample borders $\Delta\tau_B^{-1}$ can be written as $(\Delta\tau_B^{-1})^{L(T)} = v^{L(T)}/d$, where d is the sample effective diameter, while that from impurities or/and point defects, $\Delta\tau_I^{-1}$ takes the form $B_I^{L(T)} x^4 T^4$, as derived in Ref. 14. Here, $B_I^{L(T)}$ is given by $B_I^{L(T)} = VK_B^4 \Gamma / 4\pi\hbar^4 (v^{L(T)})^3$, where V is the

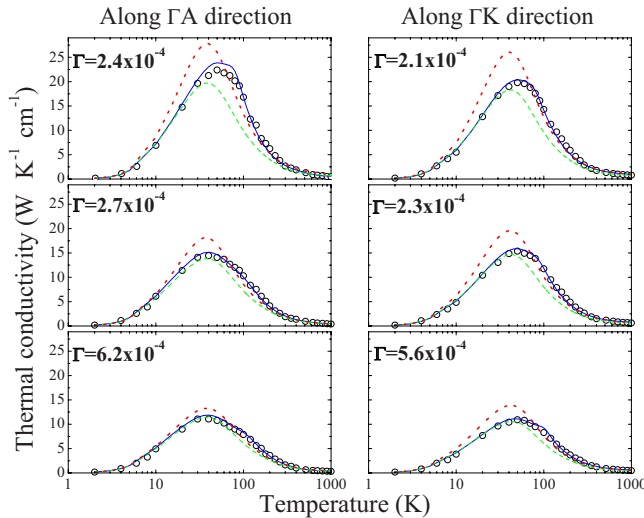


FIG. 1. (Color online) AlN thermal conductivity $k(T)$ along the ΓA and ΓK crystal directions. Symbols: measured data. Dashed lines: modeling by using Eq. (1) and values of Γ obtained from the least squares method. Dotted lines: attempt to account for more experimental points by decreasing Γ . Solid lines: modeling by using the model proposed in this work

volume per atom, K_B is the Boltzmann constant, \hbar is the reduced Planck constant, $x = \hbar\omega/K_B T$ is a dimensionless variable, and ω is the acoustic phonon frequency. The appropriate forms^{5,6} of the normal three-phonon scattering rate $\Delta\tau_U^{-1}$ for longitudinal and transversal phonon are $B_N^L x^2 T^5$ and $B_N^T x T^5$, respectively, with $B_N^L = K_B^5 (\gamma^{L(T)})^2 V / M \hbar^4 (v^{L(T)})^5$ and where M is the average atomic mass and $\gamma^{L(T)}$ the average longitudinal (transversal) Grüneisen parameter. The values for $\gamma^{L(T)}$ were deduced from *ab initio* calculations and Raman scattering studies at high pressure.¹⁵ The rate $\Delta\tau_U^{-1}$ is the three-phonon umklapp scattering rate. According to the experimental results of Slack and Galginaitis,¹⁶ the umklapp scattering rate takes the form $B_U^{L(T)} x^2 T^3 \exp(-\theta^{L(T)}/3T)$, where $B_U^{L(T)} = K_B^2 (\gamma^{L(T)})^2 / M \hbar (v^{L(T)})^2 \theta^{L(T)}$. By using the precise values of $v^{L(T)}$ and $\theta_D^{L(T)}$ deduced along the ΓA and ΓK directions in the Brillouin zone, we have fitted the measured $k(T)$ by using the four described scattering mechanisms and setting Γ as the only adjustable parameter. The best fits to the experimental data, as judged by the least squares analysis, are presented in Fig. 1 as dashed lines.

Each value obtained for Γ is near the respective spectrum. It is very clear that the MCT using only the described scattering rates underestimates the experimental data near k_m . This underestimation increases with decreasing point defects density (or decreasing Γ). Several attempts have been made to improve the fit. We have tried to decrease Γ and bring the theoretical curve closer to the experimental points at temperatures slightly above T_m . As shown in Fig. 1 by the dotted lines, this leads to a large discrepancy at T_m and below. Also, we have considered longitudinal and transversal normal scattering rates having the general form $(\hbar \gamma^2 V^{(a+b-2)/3} / M V^{(a+b)}) (K_B / \hbar)^b \omega^a T^b$ and tuned a between 1.0 and 2.0 for each value of b between 2.0 and 4.0. Despite using several forms including all the commonly reported forms for the normal three-phonon process,^{5,6,17-20} we did

not find any combination of a and b , which could further improve the agreement between the theoretical and the experimental results. Other forms of the umklapp three-phonon scattering rate cannot give better theoretical results near k_m since its effect on the phonon mean free path is noticeable at much higher temperatures. It should be noted that this difficulty to describe $k(T)$ near k_m by using the MCT has been also observed for Ge,⁵ Si,⁶ and III-nitride semiconductors.^{7,8} This systematic discrepancy near k_m between the MCT and the experimental results strongly suggests that additional phonon process should be considered within the MCT to accurately describe $k(T)$ in semiconductors in the full temperature range. The consideration of a resistive phonon process would further underestimate $k(T)$.

Due to the anharmonicity of the lattice forces, an optical phonon can interchange energy with other phonons and in this way maintains thermal equilibrium energy. Therefore, optical phonon annihilation is balanced by a creation of acoustic phonon. This generation mechanism, which is never considered before in phonon heat transport, partially counteracts the resistive processes. The anharmonic terms in the potential energy give rise to higher-order terms in the Hamiltonian describing the total potential energy of a lattice.

In the case of AlN, due to the small energy band gap between the acoustic and optical phonon branches,¹³ the optical phonon preferentially decays into two acoustic phonons. Therefore, here we only consider the cubic anharmonicity. This cubic term describing the interaction between one optical phonon of wave vector Q_0 and two acoustic phonons of wavevectors Q and Q' is of the form,

$$H'_{(3)} = \sum_{Q_0, Q, Q', x} e^{i(Q_0 - Q - Q')x} V(Q_0, Q, Q') a(Q_0) a^+(Q) a^+(Q'), \quad (2)$$

where $V(Q_0, Q, Q')$ is a coefficient related to the cubic anharmonicity, and a and a^+ are the annihilation and creation operators, respectively. From standard perturbation theory, the rate of change of the optical phonon occupation number can be obtained in terms of $V(Q_0, Q, Q')$ and becomes

$$t \frac{d}{dt} (\delta n_0) = 2 \frac{V^2 \hbar^3}{M^3 \omega_0 \omega \omega'} \frac{1 - \cos \Delta \omega t}{\hbar^2 \Delta \omega} [(\delta n_0 + n_0 + 1) n n' - (\delta n_0 + n_0)(n + 1)(n' + 1)], \quad (3)$$

where ω_0 , ω , and ω' are the frequencies of the decayed optical phonon and the two generated acoustic phonons, respectively, $\Delta \omega = \omega_0 - \omega - \omega'$, δn_0 is the deviation of the optical phonon occupation number from its thermal equilibrium value, and n_0 and n and n' are the occupation numbers of the acoustic phonons. Summing over all modes Q_0 and using the equilibrium condition $[n_0(n+1)(n'+1) - (n_0+1)nn'] = 0$, Eq. (3) can be rewritten in the following form:

$$t \frac{d}{dt} (\delta n_0) = 2 \sum_{Q_0} \frac{V^2 \hbar^3}{M^3 \omega_0 \omega \omega'} \frac{1 - \cos \Delta \omega t}{\hbar^2 \Delta \omega^2} (1 + n + n'). \quad (4)$$

We consider here that the summation over all wave vectors Q_0 includes also the phonon polarizations, and among the various possible decay channels, the optical phonon sym-

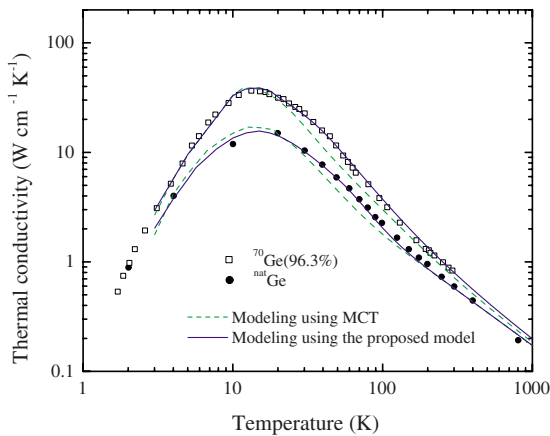


FIG. 2. (Color online) Ge thermal conductivity. Symbols: experimental data obtained from Refs. 5 and 6. Dashed lines: Fitting to the experimental data by using the MCT. Solid lines: Fitting to the experimental data using the proposed model.

metrically decays into two acoustic phonons of equal energy, i.e., $\omega = \omega' = \omega_0/2$, with $Q_0 = Q + Q'$ (Klemens model, Ref. 21). Following the mathematical method of Klemens,²¹ the rate of the anharmonic optical phonon decay into two acoustic phonons can be deduced as

$$(\Delta\tau_{anh}^{-1})^{L,T} = \frac{1}{\delta n_0} \frac{d}{dt}(\delta n_0) = \frac{5a^3 K_B^5 \gamma_{L,T}^2}{8\pi M \hbar^4 v_O^5} x^5 T^5 \coth\left(\frac{x}{4}\right), \quad (5)$$

where v_O is the average optical phonon velocity. Note that Eq. (5) only describes the case of anharmonic decay of optical phonon into two acoustic phonons. However, the optical phonon decay into other phonons of lower energies is due to the combined effects of anharmonic decay together with scattering of optical phonon by point defects. In the case of Ge, the isotopic disorder allowed a quantitative experimental study of this effect.²² The decay of the longitudinal optical phonon at the zone center was found by using high resolution Raman experiment to vary linearly with Γ as $\Gamma(\pi\omega^2/12)N(d)$, where $N(d)$ is the density of states, which contains the anharmonic effect. The convolution of anharmonic effect with defect scattering²³ allowed the overall optical phonon decay to be obtained. By analogy, the AlN optical phonon decay rate, which here is considered as acoustic phonon generation rate, can be written as

$$(\Delta\tau_G^{-1})^{L,T} = B^{L,T}(\Delta\tau_{anh}^{-1})^{1/2}(xT)^{1/2}\Gamma, \quad (6)$$

where $B^{L,T}$ are the fitting parameters.

The total acoustic scattering rate, which takes into account the decay of optical phonon into acoustic phonon, can now be written as

$$\begin{aligned} (\Delta\tau^{-1})^{L(T)} &= (\Delta\tau_B^{-1})^{L(T)} + (\Delta\tau_I^{-1})^{L(T)} + (\Delta\tau_N^{-1})^{L(T)} \\ &\quad + (\Delta\tau_U^{-1})^{L(T)} - (\Delta\tau_G^{-1})^{L(T)}. \end{aligned} \quad (7)$$

However, the optical phonon must decay in such a way the total energy and momentum are conserved. Thus, Eq. (7) should be applied only in a specific frequency range. The examination of AlN phonon dispersion curves¹³ suggests that this frequency range should be between 120 cm^{-1} and the

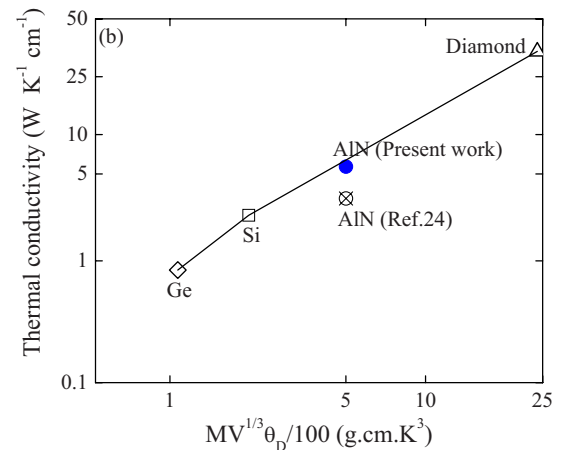
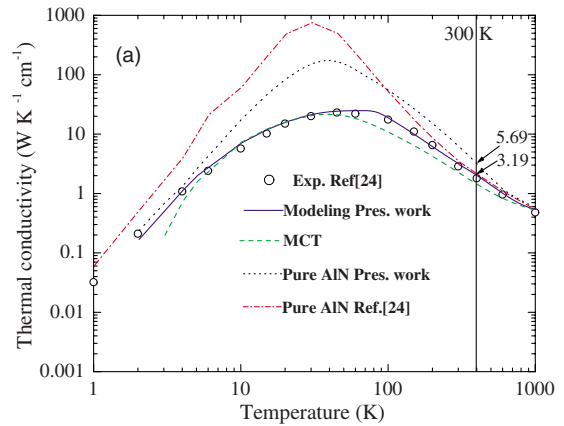


FIG. 3. (Color online) (a) Symbols: Experimental $k(T)$ data reported by Slack *et al.* (Ref. 24). Dashed line: fitting to the experimental data using Eq. (1). Solid line: fitting to the experimental data by using the proposed model. Dot-dashed line: estimation of $k(T)$ for pure AlN by using the model in Ref. 24. Dotted line: estimation of $k(T)$ for pure AlN by using the proposed model. (b) k at RT for pure AlN, predicted from this work and Ref. 24, compared to a plot of k for several adamantine structure crystals vs the LS parameter.

Debye frequency in ΓA direction and between 170 cm^{-1} and the Debye frequency in ΓK direction.

The best fit to the experimental results obtained by using the proposed model is shown as solid lines in Fig. 1. As can be noted, the consideration of the optical phonon decay as a mechanism of acoustic phonon generation, as described, provides a rather accurate description of $k(T)$ in a wide T range. This is verified along two different high-symmetry directions and for several point defect densities.

In the case of Ge, due to the isotopic composition, it can be assumed a phonon scattering by “perfect” point defects, and Γ can be analytically calculated.⁶ This allows setting $B^{L,T}$ as the only adjustable parameters. In Fig. 2, we plot experimental data on Ge obtained from Refs. 5 and 6 together with calculations using the MCT model and the proposed model. The improved agreement between the theory and the experimental results on Ge when the proposed model is used adds strong support to the hypothesis that the optical phonon decay into acoustic phonon is a crucial process for conducting heat in a semiconductor.

Finally, let us apply the proposed model to previously

reported experimental AlN $k(T)$ data and evaluate the effect of the optical phonon decay on $k(T)$ in a pure (no oxygen contamination) AlN single crystal. The symbols in Fig. 3(a) present the experimental AlN $k(T)$ along ΓA reported by Slack *et al.*²⁴ The dashed line presents the best fit to these experimental data by using Eq. (1) while the solid line presents the result obtained when using the model proposed here. Again, the optical phonon decay into acoustic phonon proves to have an essential contribution to $k(T)$.

The dotted line in Fig. 3(a) presents the modeling of $k(T)$ for pure AlN single crystal by using the proposed model. In order to compare our results for pure material to those of Slack *et al.*, which are plotted in the same figure by the dot-dashed line, we have considered also a heat flow propagating along the c axis in AlN single crystal having a 0.54 cm diameter and $\Gamma=0.35 \times 10^{-6}$ estimated from the natural abundances of Al and N. The inclusion of the optical phonon decay contribution leads to k at RT higher than that predicted by Slack *et al.* A value of $5.69 \text{ W K}^{-1} \text{ cm}^{-1}$ is estimated for pure AlN single crystal, while Slack predicted a value of $3.19 \text{ W K}^{-1} \text{ cm}^{-1}$.

Slack *et al.*²⁴ also compared the results for $k(\text{RT})$ on pure AlN with a plot of data on several pure adamantine structure crystals as a function of the Leibfried–Schlömman (LS) pa-

rameter $MV^{1/3}\theta_D$. However, since 1987, several purer semiconductors have been grown, and more precise data became available in the literature regarding the thermal conductivities and the values of θ_D .^{5,6,25} Therefore, k at RT as function of LS scaling parameter should be reanalyzed considering the new data.

Figure 3(b) shows the trend of k at RT observed for several pure adamantine crystals, together with the results for AlN obtained by Slack *et al.* and the value deduced here. Clearly, the value we obtain for pure AlN agrees much better with the observed trend than the previous result. This agreement adds further support to the accuracy of the proposed model outlined in this work.

In summary, we have demonstrated that, in contrast to the commonly accepted view, the optical phonon has an indirect, yet fundamental role, in thermal conductivity in semiconductors. We have illustrated our model with reference to set of AlN single crystals with different point defects densities and an excellent agreement with our experimental results, as well as with previously reported data, could be obtained. The proposed model can be readily extended to accurately model the thermal conductivity in any semiconductor material.

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- ¹P. G. Klemens, Proc. R. Soc. London, Ser. A **208**, 108 (1951).
- ²P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).
- ³Joseph Callaway, Phys. Rev. **113**, 1046 (1959).
- ⁴M. G. Holland, Phys. Rev. **132**, 2461 (1963).
- ⁵M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A. P. Zhernov, A. V. Inyushkin, A. Taldenkov, V. I. Ozhogin, K. M. Itoh, and E. E. Haller, Phys. Rev. B **56**, 9431 (1997).
- ⁶D. T. Morelli, J. P. Heremans, and G. A. Slack, Phys. Rev. B **66**, 195304 (2002).
- ⁷Weili Liu and Alexander A. Balandin, J. Appl. Phys. **97**, 073710 (2005).
- ⁸M. D. Kamatagi, N. S. Sankeshwar, and B. G. Mulimani, Diamond Relat. Mater. **16**, 98 (2007).
- ⁹D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, Appl. Phys. Lett. **91**, 231922 (2007).
- ¹⁰M. Kazan, B. Rufflé, Ch. Zgheib, and P. Masri, Diamond Relat. Mater. **15**, 1525 (2006).
- ¹¹L. E. McNeil, M. Grimsditch, and R. H. French, J. Am. Ceram. Soc. **76**, 1132 (1993).
- ¹²M. Kazan, B. Rufflé, Ch. Zgheib, and P. Masri, J. Appl. Phys. **98**, 103529 (2005).
- ¹³V. Yu. Davydov, Y. E. Kitaev, I. N. Goncharuk, A. N. Smirnov, J. Graul, O. Semchinova, D. Uffmann, M. B. Smirnov, A. P. Mirgorodsky, and R. A. Evarestov, Phys. Rev. B **58**, 12899 (1998).
- ¹⁴P. G. Klemens, Proc. Phys. Soc., London, Sect. A **68**, 1113 (1955).
- ¹⁵Piotr Perlin, Alain Polian, and Tadeusz Suski, Phys. Rev. B **47**, 2874 (1993).
- ¹⁶G. A. Slack and S. Galginaitis, Phys. Rev. **133**, A253 (1964).
- ¹⁷N. V. Novikov, A. P. Podoba, S. V. Shmegara, A. Witek, A. M. Zaitsev, A. B. Denisenko, W. R. Fahrner, and M. Werner, Diamond Relat. Mater. **8**, 1602 (1999).
- ¹⁸R. Berman and J. C. F. Brock, Proc. R. Soc. London, Ser. A **289**, 66 (1965).
- ¹⁹R. M. Kimber and S. J. Rogers, J. Phys. C **6**, 2279 (1973).
- ²⁰C. Mion, J. F. Muth, E. A. Preble, and D. Hanser, Appl. Phys. Lett. **89**, 092123 (2006).
- ²¹P. G. Klemens, Phys. Rev. **148**, 845 (1966).
- ²²J. M. Zhang, M. Giehler, A. Göbel, T. Ruf, M. Cardona, E. E. Haller, and K. Itoh, Phys. Rev. B **57**, 1348 (1998).
- ²³P. G. Klemens, Physica B **316**, 413 (2002).
- ²⁴Glen A. Slack, R. A. Tanzilli, R. O. Pohl, and J. W. Vandersande, J. Phys. Chem. Solids **48**, 641 (1987).
- ²⁵A. Witek, Diamond Relat. Mater. **7**, 962 (1998).