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LETTER TO THE EDITOR

**Towards the grain boundary phonon scattering problem:
evidence for a low-temperature crossover**

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Abstract. The problem of phonon scattering by grain boundaries is studied within the wedge disclination dipole (WDD) model. It is shown that a specific q -dependence of the phonon mean free path for biaxial WDD results in a low-temperature crossover of the thermal conductivity, κ . The obtained results allow us to explain the experimentally observed deviation of κ from a T^3 dependence below 0.1 K in LiF and NaCl.

The effect of low-angle grain boundaries on the thermal conductivity, κ , of LiF and NaCl over the temperature range 0.08–5 K has been investigated in [1, 2]. The main conclusions are the following: (i) the boundaries are sessile, (ii) the dominant phonon-scattering process comes from static strain fields caused by boundaries, and (iii) the experimental results are compatible with predictions of the theoretical model [3], where a grain boundary is represented as a wall of edge dislocations. In experiments, however, in addition to the expected behaviour $\kappa T^{-3} = \text{constant}$, a remarkable increase in κT^{-3} below $T^* \sim 0.1$ K was detected. A similar deviation, but beginning near 2 K, was observed in sapphire [4]. There is still no satisfactory explanation for this phenomenon. In particular, in [1] it was supposed that the measured increase can be caused by the onset of partial specular reflection from the lightly sandblasted walls. Similarly, it was suggested in [4] that ‘a frequency independent scattering mechanism should be present in these samples which becomes ineffective below 1 K’.

In 1955 Klemens [3] studied the problem of the scattering of lattice waves by grain boundaries within the Born approximation. Considering the grain boundary as an array of edge dislocations lying in the plane of the boundary, he found that the phonon mean free path is frequency independent. Hence a T^3 dependence of the thermal conductivity at low temperatures was associated with the boundary scattering. While this explains well the experimental results [1, 2, 4] above some characteristic temperature, T^* , it fails to describe the observed anomaly below T^* . It is important to note in this connection that the result [3] was obtained under the assumption that the dislocation wall is *infinitely* long. For a finite wall of well separated dislocations the problem of the phonon scattering becomes difficult and is still unresolved.

An alternative model for the description of grain boundaries has been presented in [5]. It was proposed that grain boundaries, being rotational rather than translational defects, can be described more naturally by disclinations. Moreover, what is important, the far strain fields caused by wedge disclination dipoles (WDD) were found to agree with those from *finite* walls of edge dislocations [6, 7]. For this reason, the WDD-based model allows us to study important effects due to finiteness of grain boundaries.

Notice also that additional interest to this problem was inspired by the recent consideration of disclinations and dipoles of disclinations in the context of metal glasses [8, 9], graphite films [10], and nanostructures [11]. For example, an attractive model for a metallic glass proposed in [8] results from the disordering of a Frank–Kasper disclination network. Graphite films are expected to contain a number of disclination pairs due to the presence of the five- and the seven-membered rings [10]. Disclinations and disclination dipoles are of importance in graphite nanotubes which have attracted great interest recently.

At the same time, it is known [3] that information about the nature of the principal imperfections in crystals can be extracted from a study of the thermal conductivity. In particular, the temperature dependence of the thermal conductivity arising from defects is governed by the frequency dependence of their scattering cross section for lattice waves.

In this letter, we study the problem of phonon scattering by grain boundaries in the framework of the WDD picture. These scatterers are shown to possess rather specific properties. In particular, the q -dependence of the phonon mean free path varies significantly for different types of dipoles. We show that the experimental results [1, 2] are in good agreement with the calculated thermal conductivity due to phonon scattering by *biaxial* WDD both above and below T^* .

Let us calculate a mean free path of phonons of frequency ω scattered by the potential associated with a static deformation of a lattice caused by straight WDD. Following the generally accepted approach [3, 12] we consider an effective perturbation energy due to the strain field caused by a single WDD in the form

$$U(\mathbf{r}) = \hbar\omega\gamma SpE_{AB} \quad (1)$$

where $\hbar\omega$ is the phonon energy with wavevector \mathbf{q} , $\omega = qv_s$, v_s is the sound velocity (it is assumed that three acoustic branches are equivalent), γ is the Grüneisen constant, and E_{AB} is the strain tensor due to WDD.

To simplify the problem, we assume that incident phonons are normal to disclination lines. The suitable geometry is chosen: disclination lines are directed along the z -axis, the dipole's arm is oriented along the x -axis. In this case, the strain matrix for WDD is known (see, e.g., [7]), and $U(\mathbf{r})$ takes the form:

$$U(x, y) = B \left[\frac{1}{2} \ln \frac{(x+L)^2 + y^2}{(x-L)^2 + y^2} - l_1 \frac{x+L}{(x+L)^2 + y^2} + l_2 \frac{x-L}{(x-L)^2 + y^2} \right] \quad (2)$$

where $B = \hbar q v_s \gamma \nu (1 - 2\sigma)/(1 - \sigma)$, ν is the Frank index, σ is the Poisson constant, $2L$ is the dipole separation, and parameters l_1 and l_2 specify displacements of axes of rotation from points where disclination lines pierce the xy plane. Notice that all possible types of WDD are included in (2). In general, it describes a biaxial WDD with arbitrarily arranged axes of rotation. For $l_1 - l_2 = 2L$, $l_1 = -l_2$, and $l_1 = l_2 = 0$ one obtains the uniaxial WDD, the symmetrical uniaxial WDD, and the biaxial WDD with nonskew axes of rotation, respectively.

According to (2), at chosen geometry the problem reduces to the two-dimensional case with the phonon mean free path given by

$$\Lambda_q^{-1} = n_i \int_0^{2\pi} (1 - \cos\theta) \Re(\theta) d\theta. \quad (3)$$

Here $\Re(\theta)$ is an effective differential scattering radius and n_i is the areal density of defects. Within the Born approximation $\Re(\theta)$ is determined as [12]

$$\Re(\theta) = \frac{qS^2}{2\pi\hbar^2 v_s^2} \overline{|\langle \mathbf{q} | U(\mathbf{r}) | \mathbf{q}' \rangle|^2} \quad (4)$$

where all vectors are two-dimensional, S is a projected area, the bar denotes an averaging procedure over α which defines an angle between $\mathbf{p} = \mathbf{q} - \mathbf{q}'$ and the x -axis. In other words, it means the averaging over randomly oriented dipoles in the xy plane. Evidently, the problem reduces to the estimation of the matrix element in (4) with the potential from (2). For this purpose, it is convenient to use the polar coordinates (r, ϕ)

$$U(p, \alpha) = \langle \mathbf{q} | U(\mathbf{r}) | \mathbf{q}' \rangle = \frac{1}{S} \int d^2\mathbf{r} \exp[i\mathbf{p}\mathbf{r} \cos(\phi - \alpha)] U(r, \phi). \quad (5)$$

Here $p = |\mathbf{p}| = 2q \sin(\theta/2)$. Omitting the tedious calculations (the details will be presented elsewhere) we write out the final result

$$U(p, \alpha) = B \left[-\frac{4\pi i}{p^2} \sin(pL \cos \alpha) + \frac{2\pi i \Delta_l}{p} \cos \alpha \cos(pL \cos \alpha) \right] \quad (6)$$

where $\Delta_l = l_1 - l_2$. After averaging of $|U(p, \alpha)|^2$ over α and following integration in (3) with respect to θ one obtains

$$\Lambda_q^{-1} = D^2 (vL)^2 n_i q \left\{ z^2 \left(\frac{1}{2} + J_0^2(2qL) \right) + \left(8 - \frac{z(z+8)}{2} \right) (J_0^2(2qL) + J_1^2(2qL)) - \frac{4}{qL} J_0(2qL) J_1(2qL) \right\} \quad (7)$$

where $D = \pi\gamma(1 - 2\sigma)/(1 - \sigma)$, $z = \Delta_l/L$, and $J_n(t)$ are the Bessel functions. It should be emphasized that (7) is the exact result which allows us to describe all types of WDD. Notice that the behaviour of Λ_q in (7) is actually governed by the only parameter $2L$ which characterizes the dipole separation. Before proceeding to important applications of (7) let us consider two limits to early solved problems. As mentioned above, a biaxial WDD (more precisely for $l_1 = l_2 = 0$) can be simulated by a finite wall of edge dislocations with Burgers vectors situated in parallel. As a consequence, with decreasing a dipole separation such dipole should be equivalent in its properties to a single edge dislocation with the Burgers vector $\mathbf{b} = 4\pi L v \mathbf{e}_y$. Indeed, for small L one can obtain from (7) that $\Lambda \sim q^{-1}$. This is the well known result for the phonon scattering by edge dislocations. In the opposite limit of large L , Λ_q for a biaxial dipole becomes constant (see details below) in agreement with the result obtained for the infinite dislocation wall [3].

In real materials, dipole separations which are of order of the grain size can lie in the broad range between 50 \AA (for nanocrystals) and 10^5 \AA (for polycrystals). As follows from (7), two specific regimes of scattering appear depending on the wavelength λ of an incident phonon in comparison with $2L$. As would be expected, the change in behaviour of Λ_q occurs at $\lambda \sim 2L$. Thus, for thermal phonons, we can estimate the typical temperature of transition

$$T^* \approx \frac{\hbar v_s}{2Lk_B} \quad (8)$$

where k_B is the Boltzmann constant.

An interesting consequence of (7) is the conclusion that despite the seemingly similar nature of scatterers, the behaviour of Λ_q differs remarkably for different types of dipoles. Let us examine two limiting cases.

1. Uniaxial dipoles, $\Delta_l = 2L$ ($z = 2$). Equation (7) takes the form

$$\Lambda_q^{-1} = 2D^2 (vL)^2 n_i q \left(1 + J_0^2(2qL) - J_1^2(2qL) - \frac{2}{qL} J_0(2qL) J_1(2qL) \right). \quad (9)$$

According to (9), for $qL \gg 1$ one obtains $\Lambda_q \sim q^{-1}$, whereas for $qL \ll 1$ $\Lambda_q \sim q^{-5}$. Thus, in the case of small wavelengths (in comparison with a dipole separation) the phonon scattering due to uniaxial WDD behaves like that for edge dislocations. In the limit $\lambda \gg L$ the scattering of phonons by uniaxial WDD is found to have a strong q -dependence, even stronger than the known Rayleigh scattering of phonons by point impurities. It should be noted that such behaviour is compatible with an overall view of uniaxial WDD as a strongly screened system [7]. It is worth mentioning that the low-angle uniaxial WDD can be simulated by a finite wall of edge dislocations complemented by two *additional* edge dislocations at both ends of the wall. The sign of these dislocations is opposite to that of dislocations in the wall and absolute values of Burgers vectors are equal to $b = 2L \tan(\pi\nu)$. Notice that just these two dislocations provide a screening. A significantly different picture arises in the case of the biaxial WDD with $l_1 = l_2$.

2. Biaxial dipoles with $\Delta_l = 0$ ($z = 0$). Equation (7) transforms to

$$\Lambda_q^{-1} = 8D^2(\nu L)^2 n_i q \left(J_0^2(2qL) + J_1^2(2qL) - \frac{1}{2qL} J_0(2qL) J_1(2qL) \right). \quad (10)$$

In this case, in the long wavelength limit one gets $\Lambda_q \sim q^{-1}$ while for $\lambda < L$ we obtain that $\Lambda_q \rightarrow \text{constant}$. It should be stressed that the appearance of the q -independent region distinguishes remarkably this scatterer from other types of WDD as well as from dislocations.

Figure 1 shows Λ_q for three types of WDD at $2q_D L = 6 \times 10^3$ (or $L \approx 2 \times 10^3 \text{ \AA}$). One can clearly see the characteristic points where crossover occurs. In accordance with our estimation in (8), crossover takes place at $q/q_D \sim (1/6) \times 10^{-3}$ or, respectively, at $T^* \sim \Theta/6000$ where Θ is the Debye temperature. In the general case of arbitrarily arranged axes of rotation, $0 < \Delta < 2L$, the mean free path interpolates between two limiting curves. The constant in (7) is chosen to be $D^2(\nu L)^2 n_i q_D = 10^6 \text{ cm}^{-1}$.

Let us discuss briefly the applicability of the Born approximation to the considered problem. Notice that, as in the case of dislocations, the far field of the potential in (2)

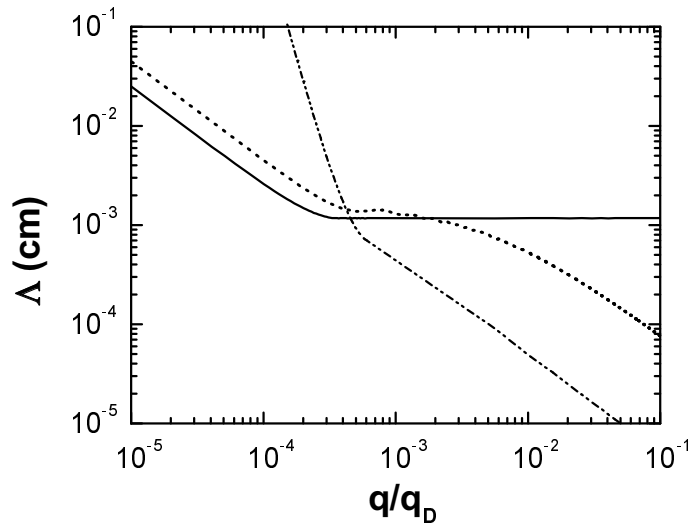


Figure 1. Phonon mean free path Λ_q as a function of scaled frequency q/q_D at $2q_D L = 6 \times 10^3$ for $\Delta_l = 0$ (solid line), $\Delta_l = 2L$ (dashed line), and $\Delta_l = 0.5L$ (dotted line). The parameter set used is: $L = 1.35 \times 10^{-5} \text{ cm}$, $\nu = 0.023$, $D = 2.6$, $n_i = 1.8 \times 10^7 \text{ cm}^{-2}$, and $\nu_s = 4.8 \times 10^5 \text{ cm s}^{-1}$.

behaves like $1/r$. Thus, all arguments in support of the validity of the Born approximation for the problem of phonon scattering by dislocations (see, e.g., [12, 13]) are also appropriate here. Nevertheless, it is useful to perform a rough estimation. In our case, by analogy with the unscreened Coulomb potential [14], we obtain $2qL \ll (1 - 2\sigma)/[(1 - \sigma)v\gamma]$. Thus, one can conclude that the Born approximation should be valid for the description of low-angle WDD and/or small dipole separation $2L$. Otherwise, one has to restrict the region of admissible q . One can expect, however, that the qualitative behaviour of Λ_q will remain unchanged even beyond the applicability of the Born approximation. Notice also that when axes of WDD are orientated randomly, one has to perform an additional averaging. However, the known result for dislocations [3, 12] indicates that such averaging should lead only to a modification of the numerical factor in (7).

Let us estimate a contribution to the thermal conductivity caused by the phonon scattering due to WDD. For this purpose, one can use the known kinetic formula written in the dimensionless form

$$\kappa = \frac{k_B^4 T^3}{2\pi^2 \hbar^3 v_s^2} \int_0^{\Theta/T} x^4 e^x (e^x - 1)^{-2} \Lambda(x) dx \tag{11}$$

where $x = \hbar\omega/k_B T$, and the specific heat capacity is chosen in the standard Debye form. We have restricted ourselves to the thermal phonons with $T < \Theta$. Then, for uniaxial WDD one obtains that $\kappa \sim T^{-2}$ at low temperatures while $\kappa \sim T^{-1}$ for $T \rightarrow \Theta$.

Let us examine (11) in detail for biaxial WDD with Λ_q from (10). In accordance with the above analysis, the thermal conductivity should exhibit a crossover from $\kappa \sim T^2$ to $\kappa \sim T^3$ with increasing T . Although the crossover temperature T_0 differs from T^* , it is still determined by the value of $2L$. Figure 2 shows the reduced thermal conductivity calculated theoretically according to (11). We would like to stress that, within our scenario, an increase in κT^{-3} below T^* arises from the phonon scattering by biaxial WDD with $l_1 = l_2$ and is quite universal. It should be observed in polycrystals with appropriate sizes of grains.

We have considered the experimental results for LiF [1, 2], NaCl [2] and sapphire [4].

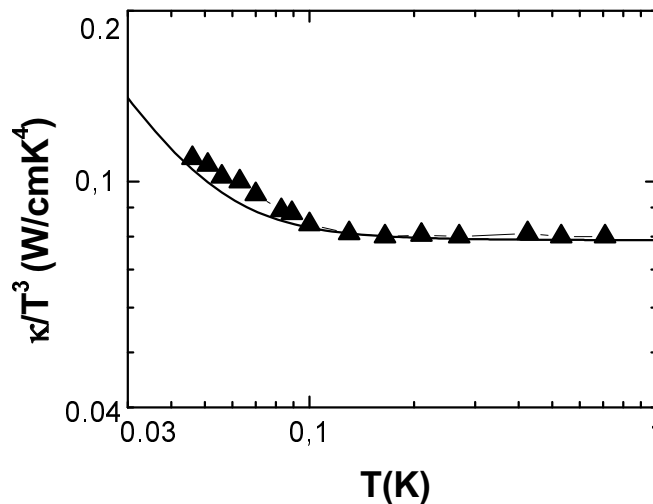


Figure 2. Reduced thermal conductivity due to WDD scattering, $\kappa \times T^{-3}$ versus temperature T , calculated according to (11) with the same parameter set as in figure 1. Measured points for the boundary-limited thermal conductivity in LiF (from [1]) are indicated by triangles.

Experimental data due to boundary-induced phonon scattering in LiF from [1] are shown in figure 2. As is seen, the data are in a good agreement with our results for an appropriate choice of model parameters. Notice that for a qualitative comparison we need the only parameter which is a size of the grain. For NaCl the thermal conductivity was found to have similar behaviour but with larger magnitude [2]. In sapphire, the measured crossover temperature is essentially higher. This can be explained by smaller grain sizes. It is interesting to note in this connection that small L can take place in glasses where the crossover temperature $T_0 \sim 1$ K and even higher. Thus, the dependence $\kappa \sim T^2$ can be extended up to these temperatures. A detailed study of physics of dielectric glasses on the basis of biaxial WDD will be presented in a separate paper.

To conclude, the grain-boundary-induced phonon scattering has been studied within the WDD-based model. The proposed model is shown to take into account the finiteness of the boundary which is important for thermal phonon scattering. The phonon mean free path due to scattering by static wedge disclination dipoles has been exactly calculated. We have shown that the thermal conductivity exhibits a crossover from $\kappa \sim T^2$ to $\kappa \sim T^3$ with T increasing. Thus, the biaxial WDD is a good candidate for the specific scatterer proposed in [4]. The results obtained allow us to explain the deviation of the thermal conductivity from a T^3 -dependence below 0.1 K observed in LiF and NaCl. We expect that this crossover has a universal character and should be observed in various materials with the pronounced granular structure.

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