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Effect of impurities and defect in thermal conductivity of lead sulphide

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Abstract. The phenomenon of heat conduction is important in semiconductor devices. This property is investigated on the basis of modified Callway model. The formalism was carried out using Hamiltonian, phonon Green's function and equation of motion techniques for various scattering events. It was found that every scattering mechanism is independent of each other and does not affect the others. The thermal conductivity of lead sulphide (PbS) semiconductor has been studied on the basis of this concept. The results of the present model are in good agreement with experimental results and the model shows good future scope with other semiconductors and superconductors.

Keywords. Hamiltonian; Green's function; heat conduction; scattering events.

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1. Introduction

Thermal transport in semiconductors has attracted the interest of many researchers because the properties of superconductor have wide applications in different fields. Lead sulphide (PbS) is a semiconductor with small band gap and exhibits various thermoelectric, physical and chemical properties [1–3]. PbS has fcc cubic structure with an energy band of 0.41 eV [4], and it displays outstanding optical, electrical and thermal properties. PbS belongs to lead chaleogenide family which performs a great theoretical interest to compassionate the physics of their phase transition, electric, band gap and ferroelectric-like behaviour at low temperature [5]. It is one of the oldest and most common detecting element which is used in various infrared detectors and photo-optics applications [6]. Due to its insoluble nature, it is stable in the pH of blood and so is probably one of the less toxic form of lead [7]. It is also used in friction industry for enhancing heat conduction and regulating friction coefficient. A lot of work has been done to investigate the thermal transport in lead chaleogenide family compounds. These materials show strongly anharmonic lattice dynamics which are responsible for their low lattice conductivity [8–10]. There are two processes to study the anharmonic behaviour of phonons: (1) Raman scattering, (2) scattering due to composition disorder. The first one has been used to study the optical properties of phonons: intensity, broadening of optical phonons, Raman spectra etc. [11–13]. So we shall discuss the second process to investigate the lifetime of phonons to study the thermal properties of the semiconductor specimen. In addition, noticeable thermally-induced distortion to the atomic positions has been observed experimentally [8,10,14]. Molecular dynamical simulation also is good to observe heat transport which would give rise to strong phonon scattering incidents [15]. The thermal conductivity of PbS was studied with the help of scattering processes with the involvement of umklapp process, scattering by boundaries, dislocation, imperfection and electron. These scatterings inhibit the motion of phonon inside the lattice [16]. First principle calculation was also adopted to report the thermal conductivity in PbS based on local density approximation (LDA) or generalised gradient approximation (GGA) [17]. In addition, lattice thermal conductivity was described using computationally feasible elastic properties by establishing a methodology to determine the Debye temperature and Gruneisen parameter [18]. An *ab-initio* calculation that explicitly account for strong anharmonicity and a computationally efficient stochastic phase sampling scheme to identify the origin of this low thermal conductivity as an anomalously large anharmonic interaction [19]. Further variations and modification to understand the thermal behaviour of semiconductors made a good impact on the

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application of crystal form of solid in various fields. High and low thermal conductivity exhibits different applications in a crystal. While high thermal conductivity helps to deport the energy to a heat sink, the low thermal conduction is favourable to heighten the figure of merit of alloys [20]. Thermal conductivity is one of the most important parameter of the material(s) used under variable thermal conditions. In the present work, we have reported a provisional lattice dynamics study by focussing on phonon frequency and lattice thermal conductivity. Calculations are based on anharmonicity, by including different interaction events which arise due to many-body perturbation theory. These interactions play major roles to compute the relaxation time for various scattering phenomena and predict the lattice thermal conductivity, which addresses the possibility of heat flow in all directions.

2. Methodology

The thermal conductivity of the cubic PbS under scattering processes in the linewidth approximation can be investigated using the modified Callaway expression model [21]:

$$\kappa = \left(\frac{k_\beta}{2\pi^2 v}\right)(\beta\hbar)^2 \int_0^{\omega_D} \frac{\omega^4 e^{\beta\hbar\omega}}{\tau(e^{\beta\hbar\omega}-1)^2} d\omega, \tag{1}$$

where ω_D is the Debye frequency, $t/\beta = 1/k_\beta T$ and τ is the relaxation time. This relaxation time is replaced by phonon lifetimes $\Gamma_k(\omega)$ [9,10,14].

Taking account of quantum dynamics to analyse the scattering events, we consider the second quantised form of Hamiltonian as [22–25]

$$H = H_0 + H_D + H_A. \tag{2}$$

In the above expression, H_0 is the unperturbed Hamiltonian, H_D and H_A are the defect and anharmonic parts of Hamiltonian respectively. Various components of these Hamiltonian are given as

$$H_0 = \frac{\hbar}{4}(A_k A_k^* + B_k B_k^*) \tag{3}$$

$$H_D = -\hbar \sum_{k_1,k_2} [C(k_1,k_2) B_{k_1} B_{k_2} - D(k_1,k_2) A_{k_1} A_{k_2}] \tag{4}$$

$$H_A = \sum_{s\geqslant 3} \sum_{k_1 \ldots k_s} \hbar V_s(k_1,k_2,\ldots k_s) A_{k_1} A_{k_2} \ldots A_{k_s}. \tag{5}$$

The parameters, $C(k_1,k_2)$ and $D(k_1,k_2)$, act in place of change in mass and force constant respectively. These changes are due to the defects inside the crystal because of deformation, dislocation etc. $V_s(k_1,k_2,\ldots k_s)A_{k_1}A_{k_2}\ldots A_{k_s}$ is expressed as Fourier transform of the anharmonic force constant of the lattice. For a many-particle system, the double time temperature-dependent phonon Green's function can be written as

$$G_{kk'} = -i\theta(t-t')\langle A_k(t), A_{k'}(t')\rangle. \tag{6}$$

Green's function is evaluated with the help of Hamiltonian given above by using the equation of motion techniques of Zubarev [27]. Following the technique of successive approximation [25] and complex algebra, the Green's function can be evaluated as

$$G_{kk'}(\omega) = \frac{\omega_k \eta_{kk'}}{\pi[\omega^2 - \tilde{\omega}_k^2 - 2i\omega_k \tilde{P}(k,k',\omega)]}, \tag{7}$$

where ω_k is the renormalised phonon frequency and $\tilde{P}(k,k',\omega)$ is the self-energy operator or response function which can be explained as

$$\tilde{P}(k,k',\omega) = \lim_{\epsilon\to 0^+} \Delta_k(\omega) - i\Gamma_k(\omega). \tag{8}$$

In the above expression, the real part is shifted in the phonon frequency whereas, linewidth of the phonon frequency at half of its frequency peak is represented by the imaginary part. The relaxation time as per Callaway model is given by $\tau^{-1} = \sum_i \tau_i^{-1}$ for i type of scattering mechanism. Scattering is independent of each other, which is not possible in any real system. So this assumption is contrary to the Matthiessen rule. So to overcome this problem, we use dispersion relation with the addition of relation time and this can be resolved by taking the approach of renormalised and perturbed mode frequencies and $\tau^{-1} = \Gamma_k(\omega)$ as

$$\Gamma_k(\omega) = \tau_{CB}^{-1} + \Gamma_k^D + \Gamma_k^A + \Gamma_k^{AD}. \tag{9}$$

Callaway model faced many objections despite the fact that it has wide acceptability to analyse thermal conductivity by using the theory of relaxation time with dependency on frequency, temperature and other distribution function and scattering processes.

3. Scattering affairs

To investigate the thermal transport in a semiconductor, using quantum dynamical approach, we looked up to different types of scatterings, which are important to study the motion of phonons to transport heat in any crystal structure. The descriptions of the scattering events are given in the following sections.

3.1 *Boundary scattering*

The concept of this phenomenon comes from the fact that at low temperature, the high-frequency phonons could not get enough energy to be excited. So phonons

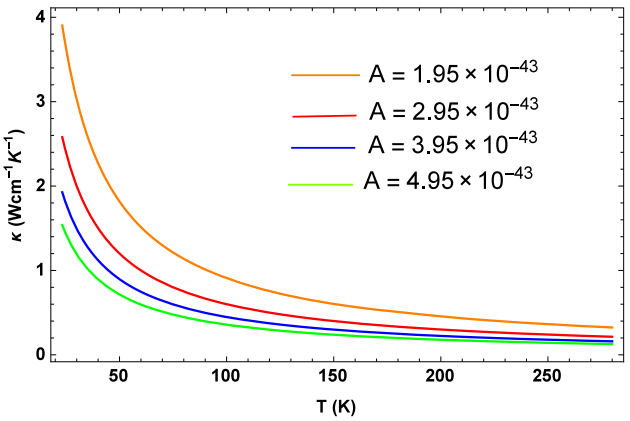

Figure 1. Effect of mass change parameter on the thermal conductivity of the PbS semiconductor.

of low frequency moves and scatters from the crystal boundaries with relaxation time [27–30]

$$\tau_{CB}^{-1} = \frac{v}{L}, \tag{10}$$

where L is the Casimir length [22] and $L = 1.12(l_1 l_2)^{1/2}$. l_1 and l_2 are the cross-section area of the semiconductor sample. v represents the velocity of phonons. Figure 1 shows that with rising temperature, more phonons scatter from the boundary and the thermal conductivity due to boundary scattering increases with rising temperature.

3.2 *Defect scattering*

As the temperature increases the defect will form in the crystal. It can be due to impurities, doping, disorder, dislocation or break of miniboundaries inside the crystal. Therefore, the phonon with higher frequency begins to scatter. These phonons gather around the impurity sites and interact with impurities which offer much thermal resistance. By developing many-body quantum mechanical theory, the lifetime, for this phenomenon can be obtained in the following form [28–32,34]:

$$\Gamma_k^D(\omega) = 8\pi\varepsilon(\omega)\sum_{k_1} R(k,k_1)R^*(k,k_1)\omega_{k_1}\delta(\omega^2-\tilde{\omega}_k^2). \tag{11}$$

After some algebraic simplification the above expression can be expressed as follows:

$$\Gamma_k^D(\omega) = A_1\omega^2 + A_2\omega^4. \tag{12}$$

In the above expression the first term is similar to Klemens [35] expression, while the second term arises due to the defects present in the crystal. This relaxation time gives the simplest meaning to describe the problem in semiconductor materials. Figure 1 shows that with increasing temperature the thermal conductivity due to defect anharmonic decreases continuously due to the interaction of phonons with defects and enhancement of thermal resistance. As we decrease the amount of defects, the thermal conductivity also increases because there is less scattering between defects and phonons and when the scattering rate is less, the thermal conductivity decreases. This behaviour is shown in figure 2.

3.3 *Multiphonon scattering*

With the elevation of temperature, phonons with larger frequencies begin to excite and start colliding with cubic and quartic phonon fields. This interaction with each other produces three or four phonon process, which is an umklapp process and momentum is not conserved in this incidence. So the field becomes anharmonic and gives rise to multiphonon scattering. The lifetime of this scattering shows a dependence on frequency and temperature. This was undertaken with quantum dynamical study [24,36] and the simplified expression is

$$\begin{aligned}\Gamma_k^{3A}(\omega) = 18\pi\varepsilon(\omega)\sum_{k_1,k_2}|V_3(k_1,k_2,-k)|^2\eta_1 \\ \times[s_{+\alpha}\omega_{+\alpha}\delta(\omega^2-\omega_{+\alpha}^2) \\ -s_{-\alpha}\omega_{-\alpha}\delta(\omega^2-\omega_{-\alpha}^2)].\end{aligned} \tag{13}$$

The details of parameters used in the above expression is given in refs [34,35]. The simplified form of eq. (13) can be written as

$$\Gamma_k^{3A}(\omega) = B\omega^2 T. \tag{14}$$

4. Analysis of thermal conductivity

Distinctive scattering mechanism was considered for investigating the thermal conductivity of the cubic PbS. The lattice thermal conductivity was considered with the concept of relaxation time which is calculated from scattering phenomenon. The experimental data of temperature-dependent thermal conductivity of PbS was taken from [20]. In ref. [20], PbS was crystallised under normal pressure in a cubic structure with space group FM-3M. There are two atoms in the unit cell: the lead atom at the centre and the sulphide atom at the vertex site. The Pb(5d 6s 6p) and S(3s 3p) were treated as valence sites. The geometry for all the systems is optimised and the lattice parameters are taken as $a = b = c = 0.586$ nm.

To study the thermal conductivity of the PbS semiconductor cubic structure, the derivation has been carried out analytically to express the linewidth term for different scattering mechanisms. Due to the non-availability

Table 1. Parameters used to analyse the thermal conductivity of PbS.

Sample	L (cm)	V (cm/s) $\times 10^5$	A (s^3) $\times 10^{-43}$	A_1 (s) $\times 10^{-44}$	B (s/K) $\times 10^{-22}$
PbS	0.687	7.08	4.95	4.00	0.07

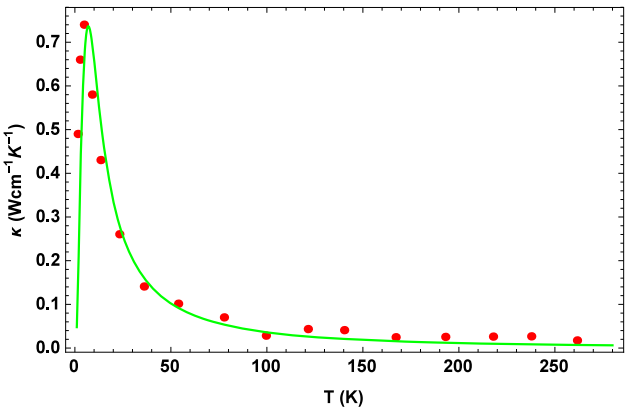

Figure 2. Thermal conductivity of the PbS semiconductor. The dots represent the experimental data and the thick line depicts theoretical results.

of all parametric information about the crystal, the fitting of parameter has been admitted. And the graphical representation has been done by *Mathematica* software. The values of fitting parameters are provided in table 1. However, these quantities can be exactly evaluated after gathering the data about effective anharmonic forces and impurity scheme, which is not applicable in the present study and may be attempted in future.

It was observed that at very low temperature, the main donation comes from the combined boundary scattering because of the involvement of long-range order wavelength phonons. These phonons move inside the crystal and collide with the boundaries. As the temperature starts to increase, the microscale boundaries begin to deviate from their original positions, resulting in defects in crystals, which give rise to defect scattering. The amount of defects determines the maximum value of thermal conductivity. If the defects are less, the thermal conductivity of the semiconductors increases. The defects can be created by impurity, doping, imperfection or dislocations. After the temperature reaches a point, where conductivity is maximum, the curve shows a sharp decay due to the inclusion of multiphonon scattering because of the rise in temperature. Here three-phonon process plays a role and due to phonon–phonon collision, thermal resistance increases which decreases the thermal conductivity. At elevated temperature, or at higher temperature, the phonon started to collide with the phonons in the anharmonic fields, resulting in a decrease of heat transport. Due to these collisions, the thermal resistance becomes comparatively high and curve of conductivity comes down as depicted in figure 2. The curve in figure 2 shows that the behaviour of thermal conductivity is the same as the experimental curve. At low temperature the conductivity increases initially but with further increase in temperature, the phonons collide with impurities and the thermal resistance increases due to which we obtain a sharp decay of conductivity at higher temperature.

5. Conclusion and future scope

In the present work, the thermal transport with the help of various scattering mechanism was studied. The linewidth was explored by taking into account the Hamiltonian and double time temperature-dependent retarded Green's function. Later, the thermal conductivity was probed with Callaway model. The result shows that the boundary scattering plays a major role at low temperature and at higher temperature, other scatterings show their influence. We get decay at higher temperature because of elevation of thermal resistance. Our model gives good compliance with the experimental data. This approach can be used for other semiconductors and superconductors too.

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