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Non-equilibrium phonon gas in a chalcogenide semiconductor with exponential temperature dependence of conductivity

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Abstract. The distribution function for a phonon gas in the non-equilibrium case of current crowding in a chalcogenide glassy semiconductor is considered. The approximate internal energy of the gas and its heat capacity is calculated. The change in the heat capacity caused by phase changes, which according to the results of the numerical calculations, are similar to the second-order phase transition, is analyzed. The law of temperature variation with time is calculated for a homogeneous current crowding without a heat sink, taking into account the exponential dependence of the conductivity on the temperature. It is shown that the temperature dependences of the concentration and energy of phonons do not undergo significant changes and are linear. The results of this work should be useful in developing chalcogenide glass-based phase-change memory devices, where strong heating by an electric current is possible and, as a consequence, a significant effect of phonons on the current flow should occur.

Keywords: chalcogenide glasses, current filament, phonon gas

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1. Introduction

The phenomenon of current crowding (filamentation) in chalcogenide glassy semiconductors (CGSs) has been studied since the discovery of the switching effect in these materials in the 1960s [1]. With the switching effect in a CGS, the conductivity σ increases sharply, and this low-resistance state can persist for an indefinitely long time, which is the memory effect. This effect is used in the development of the new generation of memory devices based on phase-change memory (PCM) technology; these devices are expected to be faster and more durable than current ones [2-4] and can be used in photonic applications [5,6].

Current crowding in CGS has been studied both experimentally and theoretically, and, most extensively, in application to GeSbTe (GST)-related materials [7-9]. For these materials, the transition from the crystalline state into the amorphous state, which implies structural transformation in the Ge sublattice called an 'umbrella flip', means that the octahedral elementary cell transforms into a tetrahedral one [10]. Crystallization temperature for the GST family of materials varies between ~120 and ~140°C while melting points typically range from ~600 to ~620 K [11]. With recording using PCM, an initially amorphous CGS film is crystallized by exposure to external action (optical or electrical pulse) with an intensity sufficient to heat the material to a point slightly above the glass-transition temperature. Subsequent exposure to a short pulse melts the CGS so upon quenching it gets converted into the amorphous state, and a recorded bit is just an amorphized mark against the crystalline background [10].

Current filament forms at the switching effect, and not only leads to the appearance of the area with low resistivity but also allows one to describe the system using the model of negative differential conductivity. The basic, thermal model of current crowding in CGS states that the formation of the filament along the central axis of a disk-shaped semiconductor sample is due to a sharp non-uniform temperature distribution across the disk. The temperature of the filament is directly proportional to the squared temperature of the maximum temperature in the center of the filament. Indeed, in [1,12], the effect of current crowding in a CGS placed in a uniform electric field was considered in detail, and it was shown that crowding occurs due to a sharp distribution of temperature T along with the radial coordinate r. This distribution is well described by an exponential function of time t and r, and the current value in the filament appears to be inversely proportional to the value of the applied electric field F. However, current crowding in [1,12] was considered without taking into account the behavior of phonons in a semiconductor, while during switching and crowding a phase transition occurs in the system, and the amorphous state becomes crystalline [13]. An ensemble of phonons will necessarily be present in a crystalline semiconductor. In the equilibrium, they are distributed according to the Bose-Einstein law; however, with sharp heating, their distribution is not in equilibrium.

In this work, we analyze the behavior of an ensemble of phonons taking into account the time dependence of the filament temperature. The time-dependent non-equilibrium Boltzmann function for phonons and values of the internal energy of a phonon gas and its heat capacity is obtained. The results of this work can be useful in developing CGS-based PCM devices, where strong heating by an electric current is possible and, as a consequence, a significant effect of phonons on the current flow should occur.

2. Results and discussion

As mentioned above, the temperature distribution involves not only radial coordinate r but also time t. This distribution was studied, e.g., in [12]. The layout of a sample with current flow and radial temperature distribution is shown in Fig. 1. The contacts are considered to be smaller than the semiconductor sample and the current filament is smaller than the contacts (Fig. 1a). The dependence of the conductivity on the reciprocal temperature leads to strongly pronounced current re-distribution along with r. We consider a disk-shaped sample of CGS with a thickness L of the order of 1 µm, where the temperature is exponentially distributed along with r during the current crowding (Fig. 1*b*). For this sample, the expression $\sigma = \sigma_0 \exp(-\Delta E/k_B T)$ is used for the dependence of σ on T. Here, σ_0 is the initial conductivity, ΔE is the activation energy of conductivity, and k_B is the Boltzmann constant. To take into account the contribution of the phonon gas to the redistribution of heat in the sample, it is necessary to describe its behavior by introducing a stationary non-equilibrium function $f(r,v) = f_0(r,v) + \Delta f$, where v is the velocity, $f_0(r,v) = 1/(\exp(\hbar\omega/k_B T) - 1)$, $f_0(r,v) = 1/(\exp(\hbar\omega) - 1)$, Δf is a correction (ħ is the Planck constant, ω is the frequency).

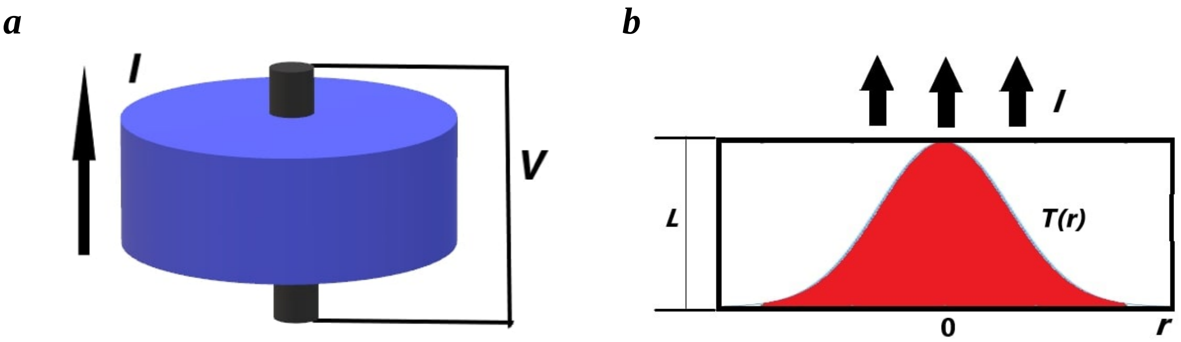

Fig. 1. A model of a CGS disk with the current flow at the center (*a*); the maximum temperature is at the center. The heterogeneous temperature distribution *T*(*r*) in the disk (side view) (*b*)

To find a non-equilibrium kinetic distribution function, we should solve the Boltzmann kinetic equation:

$$\frac{\partial f}{\partial t}+v\frac{\partial f}{\partial r}+\frac{F}{m}\frac{\partial f}{\partial v}=-\frac{f-f_0}{\tau_0}. \tag{1}$$

Using the simplest way to obtain a new function, we assume that heating in a certain region of the CGS is uniform, and then (1) is transformed into the expression $\frac{\partial f}{\partial t}=-\frac{f-f_0}{\tau_0}$, where τ_0 is the relaxation time.

In the case of uniform and fast quasi-adiabatic heating, the thermal conductivity equation takes the form $\mathrm{d}y/\mathrm{d}u=\beta\exp(-1/y)$, where $y=k_B\,Tu/\Delta E$, $u=\alpha t/L^2$ is the dimensionless time, α is thermal diffusivity, $\beta=F^2/F_s^2\exp(F/F_0)$, $F_s^2=2\,\lambda\Delta E/\sigma_0\,Lk_B$, λ is the coefficient of heat removal, $F_0\approx10^{-6}$ V/m [9]. The heating here is considered to be more intensive than heat removal. We will solve the equation in the first approximation assuming that thermal diffusivity does not change with time. Let us expand the formula in the exponent near a certain high-temperature value y_m: $\frac{\partial y}{\partial u}=\beta\exp\left(\frac{y-2y_m}{y_m^2}\right)$. The solution to this differential equation is the function:

$$y(u)=2y_m^2\ln(t_m)-y_m^2\ln\left(y_m^2\exp\left(\frac{-y_0}{y_m^2}\right)\right)-y_m^2\ln\left(1-\frac{u}{u_d}\right)\approx y_0+y_m^2\frac{u}{u_d}, \tag{2}$$

where $u_d=\frac{y_m^2\exp\left(\frac{-y_0}{y_m^2}\right)}{\beta\exp\left(\frac{-1}{y_m}\right)}$ defines the time when the temperature of the heated area turns to infinity.

We will look for a non-equilibrium distribution function at high temperatures that are larger than Debye temperatures T_D, which for various materials typically fall into the range 90 K (lead) to 1860 K (diamond):

$$f_0=\frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}\approx\frac{\Delta Ey}{\hbar\omega}. \tag{3}$$

Taking into account Eqs. (2) and (3), the solution of the simplified Eq. (1) is the function:

$$f_1(t)=\frac{\Delta Ey_0}{\hbar\omega}+\frac{y_m^2\Delta Eu}{u_d\hbar\omega}+\frac{\Delta Ey_m^2\tau}{\hbar\omega u_d}\left(\exp\left(\frac{-u}{\tau}\right)-1\right). \tag{4}$$

In what follows, the dimensionless time $\tau=\alpha\tau_0/L^2$ will be used as the relaxation time. For the calculations, the authors took the CGS parameters used in [12], which are characteristic of GST CGSs.

Let us consider our crystal to be volumetric ('bulk') for the analytical calculation of the thermodynamic parameters of the phonon gas. In a bulk crystal, the internal energy of a phonon gas $U=\int_0^{\omega_d}\hbar\omega f_1(\omega)g(\omega)d\omega$, where $g(\omega)$ is the density of phonon states,

$$\omega_d = v\left(\frac{6\pi^2}{V}N\right)^{1/3}.$$

Here N is the number of unit cells in the crystal, and V is its volume.

The density of phonon states can be determined using the formula $g(\omega) = \frac{3V\omega^2}{2\pi^2 v^3} = \frac{9N\omega^2}{\omega_d}$. Substituting the expressions for $g(\omega)$ and $f_1(T)$ into the integral for U, we obtain:

$$U = 3Nk_B\left[T + \frac{k_B T_m^2 \tau}{\Delta E u_d}\left(\exp\left(\frac{-(T-T_0)u_d\Delta E}{k_B T_m^2 \tau}\right) - 1\right)\right], \qquad (5)$$

where T_m is the maximum temperature of the filament. With an increase in temperature, the internal energy increases, this process can be described as isochoric heating, since the phonon gas does not increase its volume during the temperature increase. For an ideal gas of molecules, the isochoric heat capacity is a constant value. The heat capacity of a phonon gas is calculated as $C=dU/dT$, that is:

$$C = 3Nk_B\left[1 - \exp\left(\frac{-(T-T_0)u_d\Delta E}{k_B T_m^2 \tau}\right)\right]. \qquad (6)$$

Figure 2a shows the results of the calculations. Hereinafter, in the calculations, we assumed $L = 10^{-5}$ m, $\Delta E = 0.5$ eV, $\sigma_0 = 10^6$ Ω·m, thermal conductivity $\kappa = 20$ W/K, $n = N/V = 1.25\times10^{29}$ m^{-3}, $\alpha = 10^6$ m^2/s, $T_0 = 300$ K, $T_m = 700$ K, $T_D = 500$ K. It is seen how fast C increases with time ($\tau \sim 10^{-6}$ s here is assumed to be a constant value of $3Nk_B$). A similar sharp jump in the heat capacity can be observed during a second-order phase transition. The temperature rise with time in the analytical case is described by a polynomial of the first order.

The pressure in the isochoric process can be estimated using the expression $p = 2U/3V$. From Fig. 2b it follows that under the given conditions it is of the order of 10^9 Pa. Pressure and internal energy have an extremum at $T = T_0$. The heat capacity at this temperature is zero, which is typical for an adiabatic process. However, as has already been shown, the process almost instantly becomes isochoric.

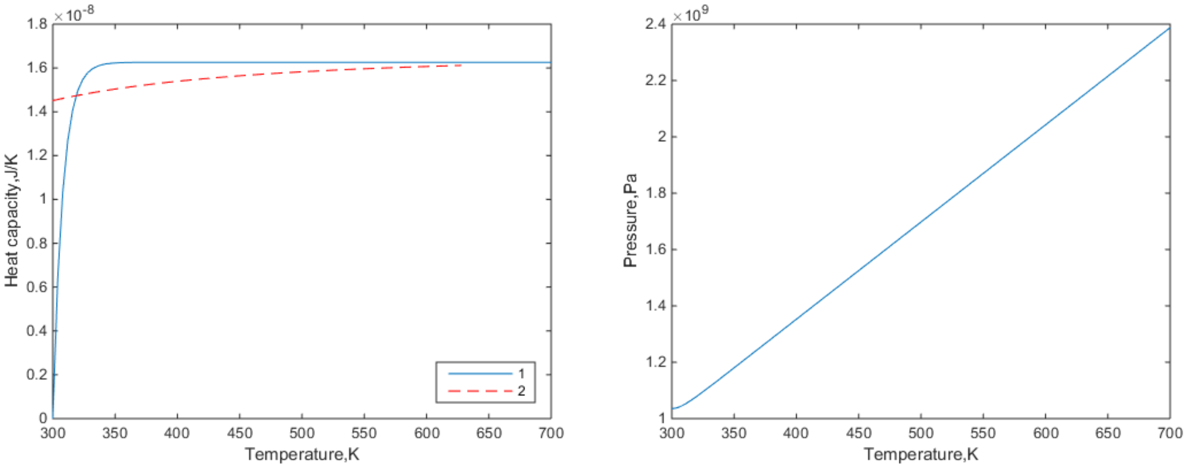

Fig. 2. Analytically (*1*) and numerically (*2*) calculated dependences of heat capacity of the phonon gas C on the temperature (a) and analytically obtained pressure dependence of the gas on the temperature (b)

The phonon concentration can be calculated as ($\gamma = \alpha/u_d$):

$$n_{\text{ph}} = \frac{9N}{V\omega_d^3}\int_0^{\omega_d}\omega^2 f_1(\omega)d\omega = \frac{9Nk_B}{2V\hbar\omega_d}\left[T + \frac{k_B T_m^2 \gamma \tau_0}{\Delta E L^2}\left(\exp\left(\frac{-(T-T_0)\Delta E}{k_B T_m^2 \tau}\right) - 1\right)\right]. \qquad (7)$$

Let us turn to the results of the numerical calculations of thermodynamic coefficients. The calculations were completed using MATLAB. From Eq. (6), the zero value of the heat capacity at the initial moment of time is derived; it indicates the adiabatic nature of the process of changing the internal energy of the phonon gas near the zero time coordinate. In [12], the heat removal near the zero coordinate was neglected. Figure 3 shows a graph of the temperature obtained when heating according to the law $\frac{dT}{dt} = \eta\exp(-\frac{\Delta E}{k_B T})$, where $\eta = \sigma_0 F^2 \alpha/\kappa$.

Heating in films with a thickness of the order of micrometers occurs in a few milliseconds. The non-equilibrium distribution function in general form, taking into account the above expressions for *df*/*dt* and *dT*/*dt*, will take the form:

$$f_1(\omega) = f_0(\omega) - \tau\eta\exp(\frac{\Delta E}{k_B T})\frac{df}{dT}. \quad (8)$$

Taking into account that the selected value of τ is small compared to the heating time $\frac{\alpha}{L^2}u_d$ up to the temperatures $T \gg T_0$, we can assume that the non-equilibrium distribution function does not differ much from the equilibrium function f_0, and $\frac{df}{dT} = \frac{df_0}{dT}$. Then,

$$f_1 = f_0 - \frac{\tau\eta\hbar\omega exp\frac{\hbar\omega-\Delta E}{k_B T}}{k_B T^2(\exp\left(\frac{\hbar\omega}{k_B T}\right)-1)^2}. \quad (9)$$

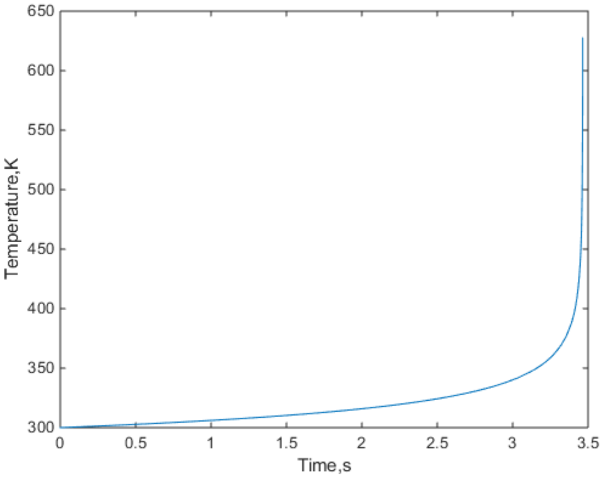

Fig. 3. Numerically calculated heating time dependence of the semiconductor temperature

The formula for the heat capacity *C* takes the form

$$C = \frac{9N}{\omega_d^3}\int_0^{\omega^d}\frac{df_1}{dT}\hbar\omega^3 d\omega.$$

The temperature dependences for internal energy *U* are shown in Fig. 4a. Internal energies are of the same order of magnitude, and their dependence on the temperature resembles those of an ideal gas. In Fig. 4b, it is seen that the phonon concentration exceeds the concentration of unit cells and increases linearly with time, which corresponds to the behavior of phonons at high temperatures ($T > T_d$).

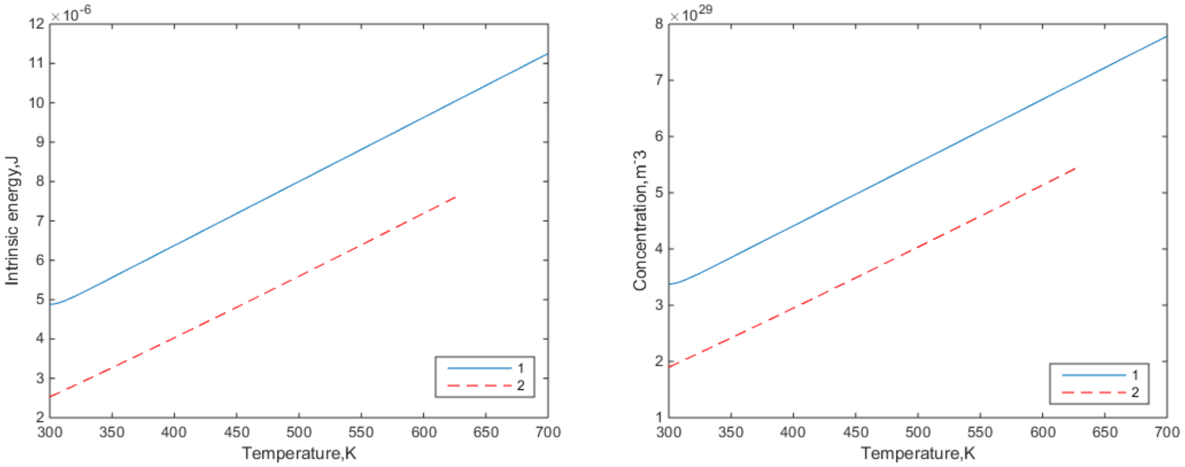

Fig. 4. Analytically (*1*) and numerically (*2*) calculated dependences of the internal energy of the phonon gas U on the semiconductor temperature (*a*) and the temperature dependence of the phonon concentration (*b*)

3. Discussion

From Figure 2a, it follows that the numerically calculated heat capacity does not experience such a sharp jump as its analytical counterpart. As the former grows, it tends to the limiting value of $3Nk_B$. However, a sharp change, similar to an increase in the analytically calculated heat capacity, does not occur, although at high temperatures both values tend to be the same value. The temperature of the sample, calculated numerically (Fig. 3) and analytically (not shown, but basically represented by Eq. (2)), differed greatly in the nature of their time dependence. We believe the data for the numerically calculated heat capacity are more credible, since they approximately reproduce the nature of the dependence for the derivative dU/dT, and both dependences become similar at $T > T_0$. The analytical dependence indicates a rapid increase in the temperature at the initial moment of time, while in the numerical dependence, a rapid increase in temperature occurs after some time $t >> t_d$, where t_d is the characteristic time of the increase.

4. Conclusion

For the conditions of current crowding in a CGS, we have calculated the thermodynamic parameters of the phonon gas. It is shown that the numerically calculated heat capacity of the gas increases sharply upon heating a CGS with a conductivity that exponentially depends on the temperature, which can be interpreted as a manifestation of a second-order phase transition. The solution was obtained for a region with a uniform heating temperature. Due to its high conductivity, this region corresponds to the current filament. The temperature dependences of the concentration and energy of phonons do not undergo significant changes and are linear. The disadvantage of the obtained analytical solution is its applicability only in a limited temperature range.

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