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Transient reflectivity of gallium films induced by femtosecond laser

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Abstract

The transient reflectivity of gallium films induced by 150 fs laser pulses has been studied by the pump-probe technique at the pump intensities of 10^9 – 10^{12} W/cm². The time-resolved reflectivity rise of the femtosecond probe in the first 1–4 ps after the pump pulse excitation depends strongly on the pump pulse intensity. We demonstrate that the transient electron–phonon collision rate extracted from the reflectivity data is a strong function of the temperature, and thus the laser intensity. This collision rate is drastically different from that observed under equilibrium conditions. The scenario for the microscopic kinetics of the phase transition on the femtosecond time scale is discussed, and new experiments for observation of time-resolved optical properties are proposed.

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1. Introduction

A rapid increase in reflectivity of semiconductors and semi-metals under the excitation by a femtosecond laser pulse has attracted considerable interest in recent years [1–5]. This interest was driven by the quest for developing a microscopic theory of melting and by the opportunities to apply the observed effect in photonic devices. The observations of a significant laser pulse induced change of reflectivity from ~ 0.55 to ~ 0.8 at a gallium–glass interface [6–8] have given impetus to further detailed studies of the transient optical properties of gallium presented in this paper.

Sub-picosecond pump-probe measurements revealed that the reflectivity changes in several time stages. We demonstrate that the optical properties of matter in the transient state are different from both crystalline and liquid in the equilibrium conditions. We retrieve the electron–lattice coupling rate from the reflectivity measurements and show that it is a strong nonlinear function of the temperature. We have found that for the sub-picosecond pulses, which are shorter than all the relevant material relaxation times, the optical properties of gallium films in the transient state are strongly laser intensity (W/cm²)-dependent, while for the longer pulses (6 and 60 ps in our experiments) the optical properties depend on the energy density (fluence, J/cm²). The more detailed experimental information is needed in order to reveal the time history of the phase transition at the femtosecond time scale.

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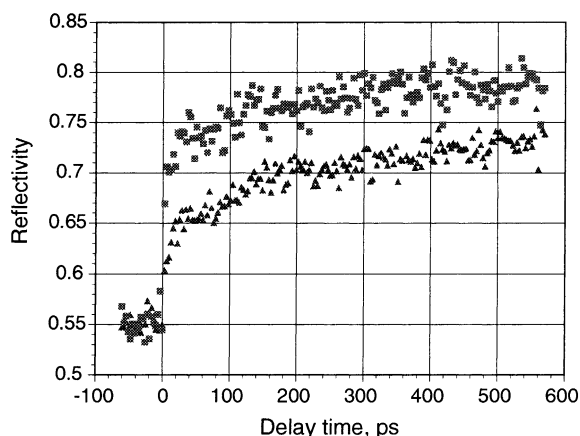


Fig. 1. Pump-probe measurements of the light-induced reflectivity in gallium films induced by a 150 fs, 800 nm laser pulse excitation at 21.5 mJ/cm² (squares) and 4.5 mJ/cm² (triangles) laser fluences. The zero point indicates the pump laser excitation; the background mirror temperature was kept at 13 °C in both experiments.

2. Experiments

The laser equipment, diagnostic techniques and method for deposition of α -gallium films were described elsewhere [8,9]. Our measurements demonstrated that, following the excitation with a pump pulse, the reflectivity of the probe beam from the

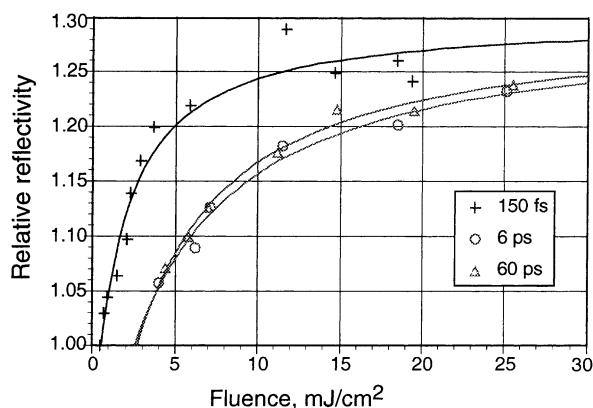


Fig. 2. Relative reflectivity ($R_{t=500\text{ps}}/R_{t=0\text{ps}}$) in gallium films on silica induced with 150 fs pulses at 800 nm (crosses) at 500 ps delay time at a sample temperature of 21 °C. For comparison, the results are presented for 6 ps (circles) and 60 ps pulses (triangles) at 1.053 μm .

gallium–silica interface increases from $R \cong 0.55$ to $\cong 0.8$ (Fig. 1) in ~ 300 –500 ps.

The reflectivity change measured 500 ps after the fs-pulse excitation for a sample at room temperature (21 °C) has a clear threshold of 0.5 mJ/cm² for 150 fs pulse (Fig. 2). Above the threshold, the reflectivity growth rate with time increases with the pump intensity increase. The growth then saturates at a level of about 20 mJ/cm². No damage of the film was detected after 10^5 – 10^6 laser pulses at the energy density up to ~ 40 –50 mJ/cm².

The increase of reflectivity is a two-stage process: a fast rise during the first 1–4 ps is followed by slower increase on the time scale of hundreds of picoseconds.

Fig. 3 shows the probe reflectivity measurements after the excitation for the pump laser fluences of 3.3–8 mJ/cm².

The reflectivity changes relate to the phase transition of gallium from the α -phase to a metal-like state. α -Gallium has semi-metal properties explained by the co-existence of molecular and metallic characters [10–12], while liquid [13] and amorphous gallium are free-electron-like. Below we concentrate on the analysis of the remarkable intensity dependence of the reflectivity changes revealed by the experiments.

3. Properties of gallium in the equilibrium conditions

The crystalline α -gallium is anisotropic [12,14]. The reflection coefficient varies from 0.56 to 0.75 ($\lambda = 800$ nm) for different crystal orientations. The crystal–liquid phase transition at 29.8 °C results in the sharp increase in the reflection coefficient: $R = 0.895$ at $T = 323$ K. Gallium possesses a variety of morphological forms [10]. The covalent and metallic features tend to coexist in the liquid state even at the temperatures up to 1000 K [15]. According to Teshev and Shebzukhov [16] and Comins [17], the effective electron–phonon collision frequency in liquid gallium in the range 323–800 K increases linearly with temperature (for $\lambda = 800$ nm):

$$\frac{\nu_{e\text{-ph}}}{\omega} = 0.42 + 0.115 \frac{T_L}{T_D} \quad (1)$$

here T_D is the Debye temperature.

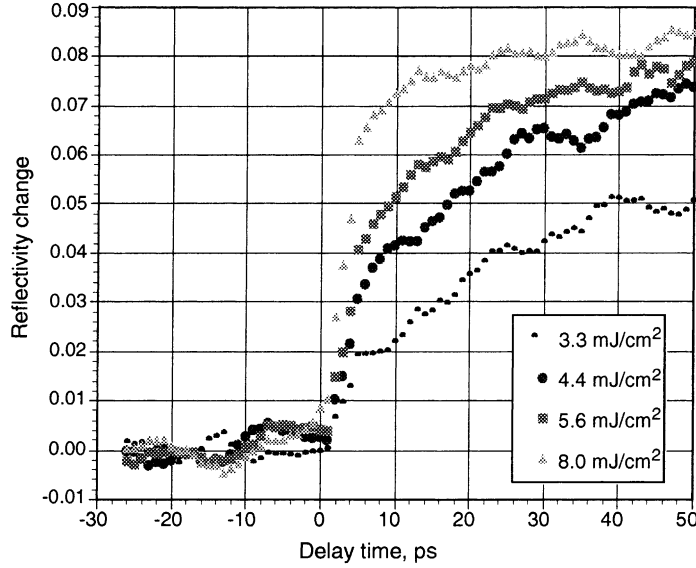


Fig. 3. Transient light-induced reflectivity increase in gallium films on silica measured with 150 fs, 800 nm pump and probe pulses at various pump energy densities. The intrinsic response of 2–4 ps of the gallium films was clearly resolved. The sample temperature was kept at 21 °C in all experiments.

4. Electron and lattice temperatures in the skin layer

The approximate relationship between the electron–phonon momentum–quasi-momentum exchange rate v_{e-ph} , and the electron-to-phonon energy transfer rate v_{en} [21,22] is as follows [19]:

$$v_{en} \approx v_{e-ph} \frac{3}{4} \left(\frac{m^*}{M} \right)^{1/2} \quad (2)$$

where m^* is the effective electron mass [18]. The heat conduction coefficient κ and coefficient of diffusion D for gallium at $T_L > T_D$ are as follows [25]:

$$\kappa_e = C_e(T_e) n_e \frac{l_e v_F}{3}, \quad D_e = \frac{l_e v_F}{3} \cong \frac{v_F^2}{3v_{e-ph}(T_L)}, \quad (3)$$

$$l_e \cong \frac{v_F}{v_{e-ph}(T_L)}$$

For liquid gallium, the Fermi velocity equals to $v_F = 1.91 \times 10^8$ cm/s. The cooling time for gallium skin layer of $l_s \sim 30$ nm estimates $t_{cool} \sim l_s^2/D \sim 1$ ps.

The electron heating and the energy transfer to the lattice (at $T_D < T_L \ll T_e < \varepsilon_F$) are calculated in $2T$ -approximation [23,24] assuming that the electron and

lattice are characterized by time-dependent $T_e(t)$ and $T_L(t)$:

$$C_e n_e \frac{\partial T_e}{\partial t} = - \frac{\partial Q}{\partial x} - v_{en}(T_L) n_e k_B (T_e - T_L) + \frac{\partial}{\partial x} \kappa_e(T_e; T_L) \frac{\partial T_e}{\partial x},$$

$$3k_B n_a \frac{\partial T_L}{\partial t} = v_{en}(T_L) n_e k_B (T_e - T_L) \quad (4)$$

The electron–lattice coupling and the heat conduction are temperature-dependent. The electron heat capacity at $T_D \ll T_e < \varepsilon_F$ expresses as [18]

$$C_e(T_e) = \frac{\pi^2 k_B^2 T_e}{2 \varepsilon_F} \quad (5)$$

The flux of the energy absorbed in the normal skin-effect regime reads

$$- \frac{\partial Q}{\partial x} = - \frac{\partial}{\partial x} A \frac{cE_0^2}{8\pi} \exp\left\{ - \frac{2x}{l_s} \right\} \equiv \frac{2AI_1(t)}{l_s} \exp\left\{ - \frac{2x}{l_s} \right\} \quad (6)$$

Here A is the absorption coefficient, $l_s = c/\omega k$ the skin depth, $I_1(t) = cE^2/8\pi$ the laser intensity in W/cm^2 .

It is shown [26] that $A/l_s \sim 2\omega/c$. As it follows from [16,17], $A/l_s \sim 1.05 \times 10^5 \text{ cm}^{-1}$ (α -Ga) and $A/l_s \sim 0.7 \times 10^5 \text{ cm}^{-1}$ for liquid gallium.

During the period of the electron–lattice equilibration $0 < t < t_{e=L}$, Eq. (5) was solved numerically with the heat conduction neglected due to $t_{\text{heat}} \gg t_{e=L}$. At $t > t_{e=L}$ $T(t)$ was found from the analytical solutions of the nonlinear heat conduction equation (at $x = 0$) as $T \sim (t_{\text{char}}/t_{\text{ps}})^{1/3}$ (see Appendix). The characteristic cooling time explicitly depends on the laser intensity $t_{\text{char}} \sim I^{-1}$. The calculated electron and lattice temperatures are presented in Fig. 4 for the laser fluence of 4.5 mJ/cm^2 ($I_1 = 3 \times 10^{10} \text{ W/cm}^2$) and for the electron-to-lattice energy exchange time of 0.15 and 0.9 ps.

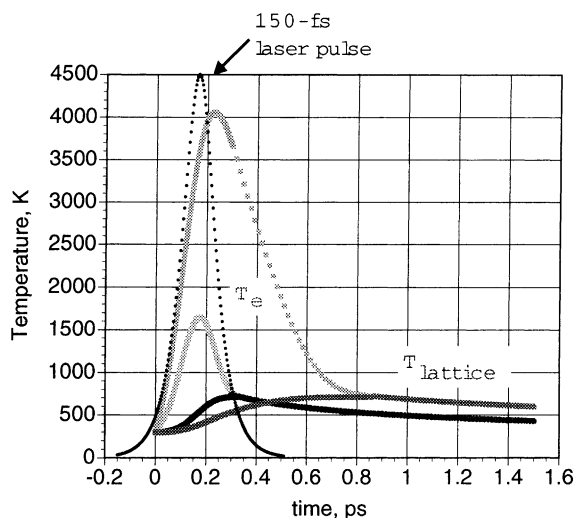


Fig. 4. Electron and lattice temperatures calculated in the conditions of temperature-dependent heat conduction and electron–phonon energy exchange rate.

5. Transient reflectivity of the gallium–silica interface

We consider the dielectric function of gallium in the Drude-like form $\epsilon(\omega_p^2/\omega^2; \nu_{\text{eff}}/\omega)$. This approximation reproduces well the experimentally observed optical properties for both crystalline [12,14] and

liquid metal-like gallium [16,17] in the equilibrium conditions.

We suggest, in accordance to Refs. [15,16,20], that ω_p^2/ω^2 and ν_{eff}/ω are changing stepwise during the

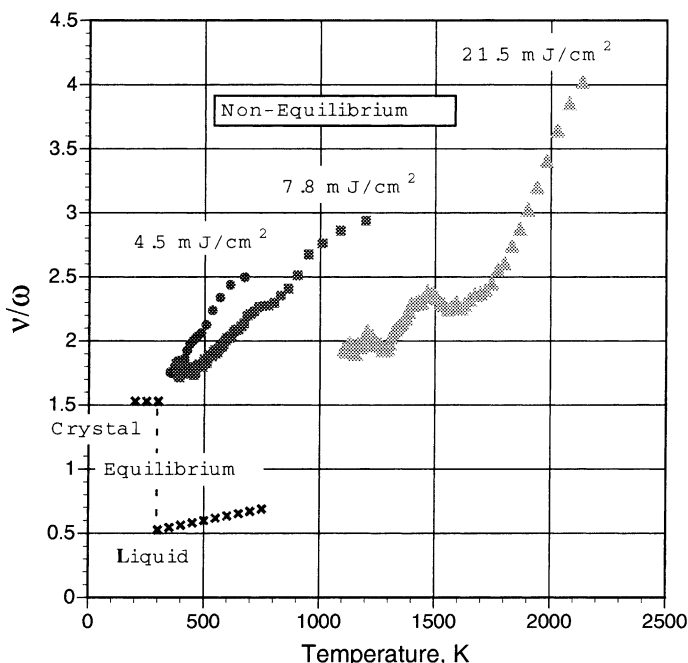


Fig. 5. Temperature dependence of the non-equilibrium effective collision frequency recovered from the reflectivity measurements. The equilibrium data for crystalline and liquid phases are also shown.

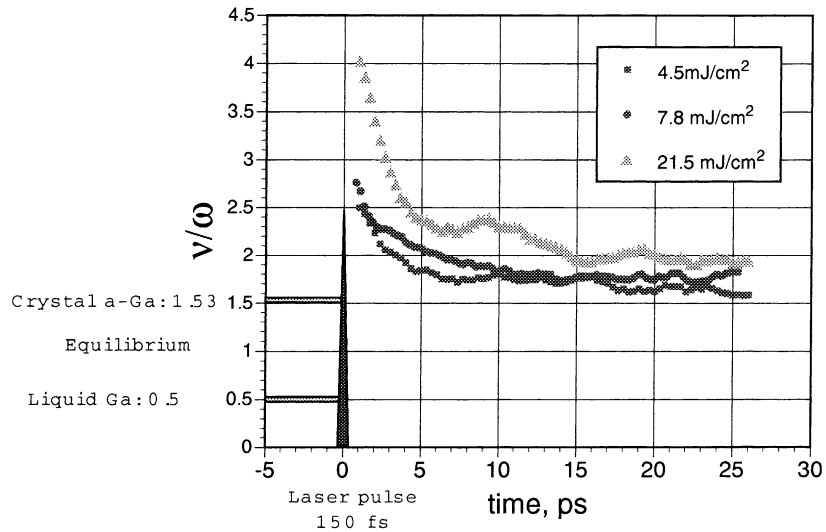


Fig. 6. Time dependence of the non-equilibrium effective collision frequency recovered from the reflectivity measurements. The equilibrium data for crystalline and liquid phases are also shown.

laser pulse. After the pulse termination, the reflectivity change occurs mainly due to the decrease in the electron–lattice frequency (v_{eff}/ω), while the variations in ω_p^2/ω^2 are slow. Then, the reflectivity is the function of the electron–phonon exchange rate only, and vice versa. This allows us to calculate the dependence of electron–phonon exchange rate on the temperature (and time) after the electron–lattice temperature equilibration by using the calculated time-dependent temperature and the measured reflectivity. The results are presented in Figs. 5 and 6.

For the low intensity case $I_1 = 3 \times 10^{10} \text{ W/cm}^2$, the electron–phonon exchange rate is proportional to the temperature but larger than in the equilibrium melt. At the high intensity ($F_1 = 21.5 \text{ mJ/cm}^2$; $I_1 = 1.4 \times 10^{11} \text{ W/cm}^2$), the electron–phonon exchange rate reproduces the experimentally observed fast rise in reflectivity at $1 \text{ ps} < t < t_{e=L}$. It is a strong nonlinear function of the temperature: $v_{\text{eff}}/\omega \sim (T/T_D)^3$.

6. The kinetics of the α -gallium-to-liquid phase transition

The experimentally established threshold fluence It_p , for the reflectivity changes equals to $5 \times 10^{-4} \text{ J/cm}^2$ that corresponds to the energy density of 100 J/cm^3 . This is about five times less than the

equilibrium enthalpy of gallium melting, which is 470.79 J/cm^3 .

We suggest that the swift rise in the electron temperature induces strong anharmonic vibrations of a lattice affecting the electron–lattice coupling that leads to the reflectivity changes. The lattice reconstruction near the threshold is minimal due to lack of time and energy.

At the high laser intensity, the electron and lattice temperatures reach thousands of Kelvins within the equilibration time $\sim 1 \text{ ps}$. The anharmonism of the lattice vibrations increases with increase of temperature, finally resulting in instabilities and reconstruction of the lattice to a new state. The key features explaining the observed transient reflectivity are nonlinear electron-to-lattice coupling rate and relevant nonlinear heat conduction responsible for the fast cooling.

At $t \gg t_{e=L}$, the atomic and electronic structures change slowly in comparison to the electron–phonon collision frequency that decreases linearly with temperature.

7. Discussion and conclusions

Let us summarize the main results of this paper. First, the experimentally established energy density threshold for the reflectivity changes induced by femtosecond

pulses comprises the value almost five times lower than the equilibrium enthalpy of gallium melting. The lifetime of the melting phase at the laser energy just above the threshold comprises several picoseconds. The reflectivity rise, as well as electron–phonon exchange rate, is a strong function of intensity and a power function of temperature, $\nu \sim T^n$ ($n > 1$). The latter is a result of a strong (increasing with temperature) anharmonism of the lattice vibrations.

Second, the threshold for the reflectivity changes induced by 6 and 60 ps pulses coincides with the equilibrium enthalpy of melting and does not depend on intensity.

We argue that at the electron and lattice temperatures in excess of 10^3 K, the disordering of the initial lattice and the shift of the atoms from the crystalline positions proceeds very fast, on the femtosecond time scale.

The presented experimental results are questioning fundamental issues. First, the description of the lattice vibrations in harmonic (phonon) approximation on the time scale of a hundreds of femtoseconds at $T_L \gg T_D$ appears to be invalid. The experimentally observed transient reflectivity can be understood under assumption that the electron–lattice coupling rate ν_{opt} is a power function of the lattice temperature. The transient non-equilibrium description of lattice vibrations is needed.

The measurement of the transient reflectivity with one pump beam and two simultaneous identical femtosecond probe beams at different angles will allow us to retrieve both the real and imaginary parts of the dielectric function. Therefore, the time dependence of both parameters ν_{opt}/ω and ω_p^2/ω^2 for the given frequency of the probe can be recovered. These experiments are underway now.

We anticipate that a tuning of the laser and target parameters to the optimum combination would allow the re-crystallization time to be reduced. As a result, a new all-optical switching devices in ps-range time scale could be designed utilizing the nonlinear temperature-dependent dielectric properties of the non-equilibrium solid-state plasma.

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Appendix

At $t > t_{e=L}$ ($T_e \sim T_L$), the specific heat is dominated by lattice while the heat conduction dominates by electrons. With, $\nu_{e-ph} = n_0 T^n$ and $\kappa_e = c T^{1-n}$ (at $T \geq T_D$), the heat conduction equation takes the form

$$C_L n_a \frac{\partial T}{\partial t} = - \frac{\partial}{\partial x} c T^{1-n} \frac{\partial T}{\partial x}, \quad \nu = \nu_0 \left(\frac{T}{T_D} \right)^n, \\ \kappa_e = \left(\frac{\nu_F^2}{6\nu_0} \frac{\pi^2 n_e T_D^n}{\varepsilon_F} \right) T^{1-n} \equiv c T^{1-n} \quad (\text{A.1})$$

The energy conservation law for one-dimensional case reads

$$Q = \int C_L n_a T dx = A I t_p = \text{const} \quad (\text{A.2})$$

The problem now reduces to that as in Ref. [27]:

$$W = C_L n_a T = \left(\frac{Q^2}{bt} \right)^{1/(3-n)} f(\xi), \\ \xi = \frac{x}{(Q^{1-n} bt)^{1/(3-n)}}, \quad b = \frac{\nu_F^2 W_D^n}{3\nu_0 W_F}, \\ W_F = \left(\frac{2\varepsilon_F C_L^2 n_a^2}{\pi^2 n_e} \right), \quad W_D = C_L n_a T_D \quad (\text{A.3})$$

Here W-F is the energy density characteristic for the degenerated Fermi gas. Depending on n , the function $f(\xi)$ takes different forms [28]. At $n = 0$, and taking l_s as a skin length at $t = t_p$, one obtains

$$T(x=0, t) = \frac{A I t_p}{C_L n_a l_s} \left(\frac{W_F l_s^3}{A I t_p D_e} \right)^{1/3} \quad (\text{A.4})$$

At high intensity, the effective collision frequency expresses as $\nu \sim T^n$ with $n \sim 2.6$. It follows from the above solution that the temperature decreases as fast as $T \sim t^{-2.5}$. This fast temperature decrease corresponds to the experimentally observed fast reflectivity rise.

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