Initial stages of the melting of a GaAs surface by femtosecond laser pulses: Study by second-harmonic-generation method

S. V. Govorkov and I. L. Shumaĭ
M. V. Lomonosov Moscow State University

W. Rudolph and T. Schröder
Friedrich-Schiller University, Jena, GDR

(Submitted 15 June 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **52**, No. 2, 755–758 (25 July 1990)

A substantial difference has been found experimentally between the time scales for the loss of short-range order and long-range order in a GaAs lattice during the application of intense laser pulses with a length of 100 fs.

1. The development of lasers which emit pulses less than 100 fs long has made possible a real-time study of fundamental electron-electron and electron-photon relaxation processes in photoexcited semiconductors.[1] Structure-sensitive nonlinear-optics methods, e.g., reflection second-harmonic generation, are extremely important for the diagnostics of laser-induced phase transitions. Shank *et al.*[2,3] have found experimentally that the crystalline order disappears from a surface layer of Si less than 1 ps after excitation by intense laser pulses with a length of 90 fs. Kash *et al.*[4] have found, by a method of time-resolved spontaneous Raman scattering, that the total duration of the energy transfer from excited carriers to the lattice in GaAs is about 2 ps. Tom *et al.*[5] subsequently carried out a study of the dynamics of the melting of a Si surface by the method of second-harmonic generation. They found that the crystal lattice loses its long-range order in ~ 150 fs. This result has started a discussion of the possibility of a "cold" melting of a lattice.[6]

2. In this letter we are reporting a study of the initial stage of the melting of a GaAs surface by laser pulses 100 fs long. We studied the melting by the methods of second-harmonic generation and linear reflection. The efficiency of second-harmonic generation differs from that of linear reflection in that it depends on the lattice symmetry in the surface layer; according to the selection rules, this efficiency should fall off as GaAs loses its long-range order. We have observed that the decay of the second-harmonic intensity occurs over a time scale of about 100 fs, while the linear reflection coefficient increases to the value characteristic of molten GaAs much more slowly, with a time constant 1 ps. These results suggest that the long-range order of the crystal structure is lost over a time while the lattice is still relatively cold.

3. We used a laser system which generates spectrally limited pulses 100 fs long at half-maximum with an energy up to 0.1 mJ at a wavelength of 620 nm. The laser system consisted of a ring dye laser with passive mode locking and a four-stage dye laser amplifier pumped by a XeCl laser.[7] The level of the spontaneous emission from the amplifier did not exceed 1% of the energy of the pulses. The light beam *1* was split

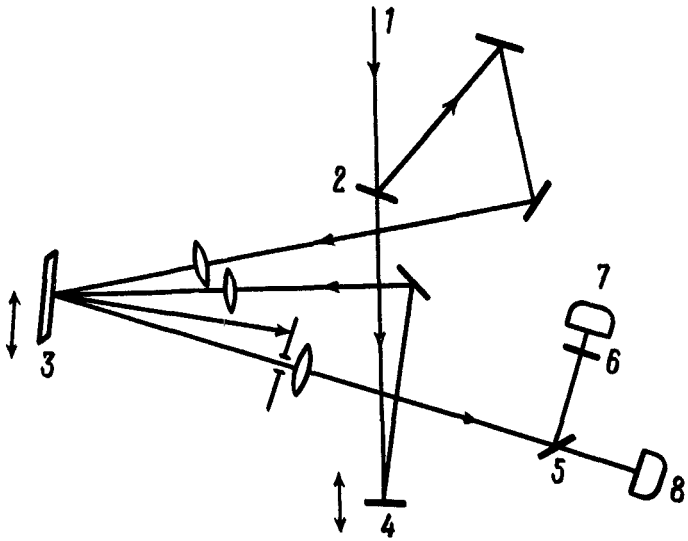

FIG. 1. The laser beams in the experiments.

into two beams (with an energy ratio 10:1) by a dielectric mirror *2* (Fig. 1). The stronger exciting beam was directed to the surface of the GaAs(110) single crystal *3* at an angle of 10° from the normal and was focused into a spot 150 μm in diameter. After a delay *4*, the weaker probe pulse was focused to a spot at the center of the pump beam; this spot was half the diameter of the pump-beam spot. The total radiant energy density at the surface was about 0.15 J/cm^2, which is about three times the threshold for the conversion of the surface layer to an amorphous structure. The second harmonic of the probe pulse was singled out by a diaphragm, a dielectric mirror *5*, and filters *6*. This second harmonic was detected by a photomultiplier *7*. Part of the energy of the reflected probe beam was sent to a photodiode *8* for measurements of the linear reflection coefficient. After each laser flash (at a repetition frequency of 1 Hz), the sample was moved in the direction parallel to the plane of the surface, to avoid buildup effects.

4. The difference between the intensity of the reflected second harmonic, ΔI_{2H}, and that of the linearly reflected probe beam ΔI_R, was measured during the application of the exciting beam and also without the exciting beam, at various values of the delay τ of the probe pulse with respect to the exciting pulse. The results are shown in Fig. 2. It can be seen that even during the pump pulse there is a sharp (70%) decay in the intensity of the second harmonic. The intensity of the linearly reflected light increases more slowly, and at large values of the delay time (above 10 ps) it reaches the value characteristic of molten GaAs. On the $\Delta I_R(\tau)$ curve we see a sharp peak at $\tau = 0$, which essentially coincides in time with the cross-correlation function of the pump and probe pulses. The reason for the appearance of this peak is apparently a coherent interaction of the pulses, which leads to an additional scattering of the pump pulse in the direction of the reflected probe beam. Furthermore, one cannot rule out

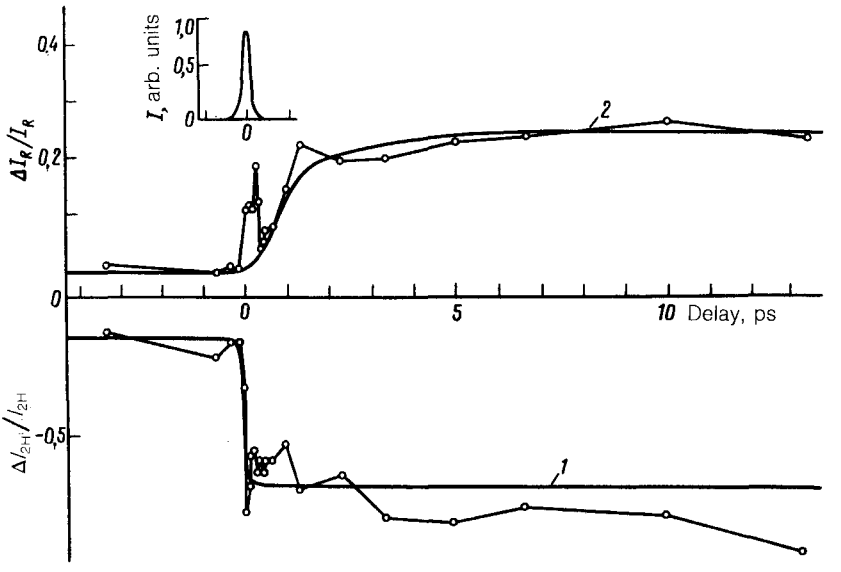

FIG. 2. Changes in (1) the intensity of the second harmonic and (2) the intensity of the linearly reflected probe beam versus the delay of the probe pulse with respect to the exciting pulse. The magnitudes of these changes have been normalized by division by the intensity in the absence of the exciting pulse. Points—Experimental; smooth curves—theoretical with $\tau_R = 1$ ps and $\tau_{2H} = 100$ fs. The inset shows the temporal cross-correlation function of the probe and exciting pulses.

the possibility of a "filling-of-states" effect in the conduction and valence bands with an energy difference close to the energy of the laser photon.[8] The relaxation time of the filled states is no longer than 100 fs, so this effect is manifested only during the intense pulse. This circumstance apparently explains the negative peak on the $\Delta I_{2H}(\tau)$ curve, with a length of about 200 fs.

5. The time constants of the variation in $\Delta I_{2H}(\tau)$ and $\Delta I_R(\tau)$ were found by fitting the formulas

$$\Delta I_{2H}(\tau) \propto \int_{-\infty}^{\infty} I^2(t-\tau)\chi^{(2)}(t)dt, \tag{1}$$

$$\Delta I_R(\tau) \propto \int_{-\infty}^{\infty} I(t-\tau)R(t)dt, \tag{2}$$

to the experimental data. Here $I(t)$ is the intensity of the probe pulse (which was assumed to have a Gaussian temporal profile). The time evolution of the second-order nonlinear susceptibility, $\Delta\chi^{(2)}$, and that of the linear reflection coefficient, ΔR, was assumed to be

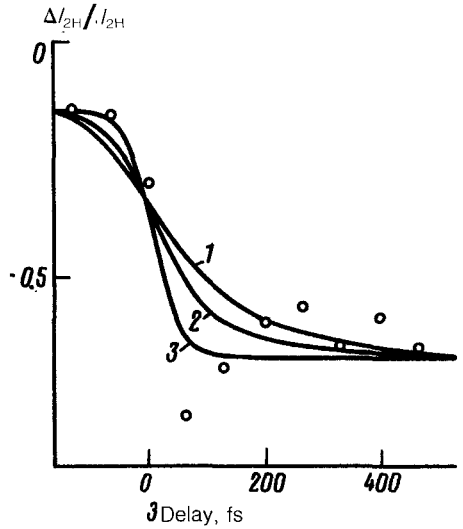

FIG. 3. Decay of the second-harmonic intensity near $\tau = 0$. Points—Experimental; smooth curves—theoretical with $\tau_{2H} = 150$ fs (curve *1*), $\tau_{2H} = 100$ fs (curve *2*), and $\tau_{2H} = 25$ fs (curve *3*).

$$\Delta\chi^{(2)}(t) = \begin{cases} 0, & \text{at } t \leqslant t_0 \cdot \\ \Delta\chi_0^{(2)}(\exp(-(t-t_0)/\tau_{\text{вг}}) - 1), & \text{at } t > t_0, \end{cases} \tag{3}$$

$$\Delta R(t) = \begin{cases} 0, & \text{at } t \leqslant t_0 \\ \Delta R(-\exp(-(t-t_0)/\tau_R) + 1), & \text{at } t > t_0, \end{cases} \tag{4}$$

where t_0 is the time at which the phase transition begins, and τ_{2H} and τ_R are the time scales of the variation in I_{2H} and I_R. It can be seen from Fig. 2 that a satisfactory agreement with experiment is reached with the values $\tau_R = 1$ ps and $\tau_{2H} = 100$ fs. Figure 3 shows, in a larger time scale, the decay of the second-harmonic intensity during the pump pulse, along with theoretical predictions for $\tau_{2H} = 25$ fs, 100 fs, and 150 fs. We see that the value $\tau_{2H} = 100$ fs is an upper estimate of the time scale of the disordering of the crystal lattice. The deviation of the pump and probe beams from a perfectly collinear configuration had only a slight effect on the time resolution, because the angle between these two beams was small.

6. These experimental results thus show that the loss of long-range order in the lattice, which is manifested in a decay of the second-harmonic intensity, occurs considerably more rapidly than the change in the linear optical properties of GaAs, which reflect the state of the short-range order. The time scale $\tau_{2H} = 100$ fs turns out to be shorter than the time scale for the transfer of energy from the electron subsystem to the lattice,[4] while the time scale for the increase in R is close in order of magnitude to the latter value and thus agrees with the suggestion of a thermal melting. These results

support the suggestion that a short-lived intermediate nonequilibrium phase of the crystal, with a disrupted long-range order, precedes the melting and exists in a relatively "cold" lattice.[5]

[1]J. L. Birman, H. Z. Cummins, and A. A. Kaplyanskii (editors), *Laser Optics of Condensed Matter*, Plenum Press, New York, 1988.
[2]C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983).
[3]C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **51**, 900 (1983).
[4]J. A. Kash, J. C. Tsang, and J. M. Hvam, Phys. Rev. Lett. **54**, 2151 (1985).
[5]H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz, Phys. Rev. Lett. **60**, 1438 (1988).
[6]I. Van Vechten, J. Phys. (Paris) **44**, Suppl. No. 10, C5, 11 (1983).
[7]W. Dietel *et al.*, Appl. Phys. B **B46**, 183 (1988).
[8]J. L. Oudar *et al.*, Phys. Rev. Lett. **55**, 2074 (1985).

Translated by D. Parsons