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Evaporation of Atoms from Femtosecond Laser-Heated Gallium Arsenide

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Abstract. The surface temperature of a GaAs crystal irradiated with 150 fs laser pulses is determined from the Maxwell velocity distribution of the evaporated atoms. The crystal is strongly superheated, and melting is observed to occur at a temperature 600–1000 K above the equilibrium melting point.

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Interaction of short laser pulses with surfaces is a topic of great current interest, both from an applications and a fundamental-physics point of view. It has been established that the action of picosecond visible and infrared pulses on absorbing metals and semiconductors can be very well described in classical thermodynamic terms [1] as a rapid heating process. The very short time scale in picosecond laser heating may lead to interesting phenomena such as very large degrees of superheating and supercooling [2]. In fact, superheating of a GaAs crystal by as much as 540 K has recently been measured [3]. However, the simple thermal picture is expected to break down with the use of yet shorter pulses, say, pulses of the order of 10^{-13} s, which is comparable to the vibrational cycle of atoms in a solid.

In recent laser heating experiments with pulses less than 100 fs in duration it has been shown [4] that the lattice symmetry of a silicon crystal disappears in about 500 fs, and that the system is transformed into an isotropic, highly reflective phase, very much like ordinary metallic molten silicon. However, these experiments did not provide any information on the temperature of the system, and on thermal or possibly non-thermal aspects of the phase transition.

Theory and Experiment

This report describes some preliminary results of a study which addresses this issue. In our experiments we measure the velocity distribution of atoms [5] emitted from the laser-irradiated surface of a GaAs crystal. If the atomic emission is a simple thermal evaporation process the velocity distribution of the atoms is expected to be a Maxwellian distribution characterized by some temperature T, which is equal to the surface temperature. In pulsed-laser heating experiments the measured velocity distribution would in fact represent the temporal and spatial average of the actual temperature distribution, but the average temperature derived from the velocity distribution of the emitted atoms is expected to be close to the maximum temperature because the atomic current increases exponentially with temperature, and as a result the high temperatures dominate in the averaging process. Thus, if for laser-heating with femtosecond pulses a thermal description is still valid the velocity distributions of the emitted atoms should be Maxwellian reflecting the maximum temperature of the surface. Determination of the surface temperature from measurements of the velocity distributions has worked

successfully in previous nanosecond and picosecond laser heating experiments [3] of GaAs, which have demonstrated normal melting at 1511 K and melting under highly superheated conditions for nanosecond and picosecond laser-heating pulses, respectively.

The present femtosecond experiments are performed under ultra-high-vacuum conditions with GaAs crystals of (100) surface orientation being irradiated at an angle of about 45°. The samples are raster-scanned to provide a fresh area for each laser pulse. The velocity of individual atoms is measured by recording the time-of-flight from the sample surface to a quadrupol mass spectrometer (QMS) situated at a known distance in the direction of the surface normal of the sample.

The laser heating pulses are obtained from a passively mode-locked rhodamine 6 G dye laser operating in the colliding-pulse mode, followed by a four-stage pulse - amplifier system which is pumped at a rate of 10 Hz by the second harmonic of a Q-switched Nd : YAG laser. The output pulses of the amplifier are passed through a dispersive delay line consisting of a pair of gratings to make up for the pulse spreading suffered during amplification. Using the background-free second-harmonic autocorrelation method the duration of the final pulses was measured to be 150 fs. The system provided pulses at 625 nm of several hundred microjoules of energy.

An example of a measured time-of-flight distribution of gallium atoms is shown by the solid curve in Fig. 1, which represents the result of 31 individual measurements. The important point to be noted is that the measured distribution can be very well described by a Maxwellian. The dotted curve corresponds to a Maxwellian velocity distribution characteristic of a temperature of 2200 K.

Comparison of different experimental runs indicates that in some cases the velocity distributions are broadened and cannot be represented by Maxwellians. However, careful studies of the laser-induced changes of the surface morphology of the GaAs crystal suggest that this observation is not an indication of a non-thermal character of the laser-surface interaction. Rather, we believe that the broadening of the velocity distributions is related to distortions of the spatial profile of the laser beam. It turned out that the spatial energy distribution of the femtosecond pulses over the sample surface could not be reproduced sufficiently well from one experimental run to the next. Sometimes non-uniform distributions were obtained, e.g., taking the form of two separate lobes with different areas and different laser fluences. In these cases velocity distributions with two distinct peaks were seen. Careful realignment of the laser system was necessary to avoid this problem. The data discussed here represent experimental runs in which the energy distribution of the laser beam was reasonably uniform, as judged from post-irradiation inspection of the laser-generated spots on the sample surface using an optical microscope.

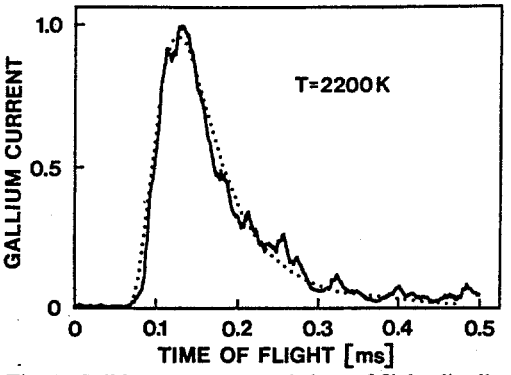

Fig. 1. Solid curve: measured time of flight distribution of the gallium atoms from 31 individual measurements. Dotted curve: Maxwell velocity distribution for a temperature of 2200 K

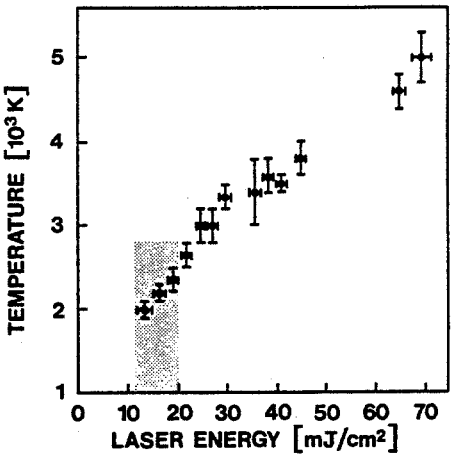

Fig. 2. Temperature as a function of laser energy. Dotted area: Threshold energy for melting of the surface

The main result of our measurement can be seen in Fig. 2, where we plot the temperature determined from the measured Maxwellian velocity distribution of the gallium atoms as a function of the laser energy. There are three distinct energy regimes with the following principal features.

(i) A low laser energy the temperature (T) rises monotonically from about 2000 K at 10 mJ/cm^2 up to 3300 K at 30 mJ/cm^2.

(ii) From 30 to 40 mJ/cm^2 the temperature stagnates around 3400 K.

(iii) For energies greater than 40 mJ/cm^2 T rises again reaching a maximum value of 5000 K at 70 mJ/cm^2, the highest energy used in our experiments.

We note that in previous measurements of laser evaporation of GaAs both with nanosecond and picosecond excitation similar plateaus have been observed at approximately the same T (3300–3500 K) [3].

The interpretation of these plateaus is not clear as yet. Here, we shall focus our attention on the temperature evolution below the plateau regime.

In these preliminary femtosecond experiments reported here it was difficult to detect the onset of surface melting in the usual way by monitoring the change of the optical reflectivity accompanying the phase transition. Therefore, the threshold energy for the onset of melting was obtained as follows. We measure the diameter of the laser-generated spots on the surface of the sample as a function of the pulse energy and extrapolate to zero spot diameter. The dotted area in Fig. 2 around $15\,mJ/cm^2$ indicates the threshold energy of the phase transition, as determined by this method. There is some uncertainty in the determination of the threshold energy – indicated by the width of the shaded area – due to the rather faint appearance of the surface changes under the optical microscope. The absolute value of the threshold energy of $15\,mJ/cm^2$ is subject to an experimental uncertainty of about a factor of two.

Having established the threshold energy of surface melting, it follows from the data of Fig. 2 that the transition temperature falls between 2000 and 2500 K. This value is to be compared with the normal melting temperature of GaAs, $T_m = 1511\,K$. Using the same experimental apparatus and the same type of GaAs samples we have recently established that with 10 ns laser heating pulses the solid-to-liquid transition does indeed occur at a surface temperature $T = T_m$. With this reasuring observation in mind we believe it can be safely concluded from the present data that with femtosecond laser heating the GaAs crystal is strongly superheated. The observed superheating at the melting threshold lies between 500 and 1000 K, i.e., it appears to be greater than the superheating of 540 K that has been measured with laser pulses of 25 ps duration.

There is an interesting basic distinction between the liquid-solid phase transition effected by femtosecond pulses and laser pulses of much longer duration. It has been demonstrated that for laser pulses with tens of picoseconds or longer duration melting occurs *during* the pulse [7, 8]. On the other hand, for excitation with pulses of 100 fs or less the entire energy of the pulse is deposited in the material well *before* the phase transition has a chance to develop. It follows immediately that the material is superheated if a sufficiently energetic femtosecond pulse is used, and that the actual amount of superheating is primarily a function of the total absorbed energy. However, if an element of volume is to be completely transformed to a liquid, the stored thermal energy of the superheated state must exceed the latent heat of fusion. This consideration suggests a rough estimate of the expected superheating at the melting threshold, $(T - T_m)_{th} = L/C$, where L and C are, respectively, the latent heat and the heat capacity at $T = T_m$. For GaAs we obtain $(T - T_m)_{th} = 1350\,K$, which is greater than the actually observed threshold superheating, but still in reasonable agreement regarding the crude nature of the estimate and the uncertainty of the threshold energy.

Conclusion

In conclusion the following points should be emphasized. We have measured the velocity of atoms emitted from the surface of a GaAs crystal irradiated with femtosecond laser pulses. The velocity distributions are found to be Maxwell distributions, suggesting that the laser energy is thermalized prior to the emission of the atoms. The surface temperature derived from the measured velocity distributions signifies strong superheating of the GaAs crystal. According to the present data the surface temperature at the onset of melting exceeds the equilibrium melting point by 500–1000 K, but the threshold energy is subject to some uncertainty.

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