Laser-induced thermomagnetic detection of a metastable band in bismuth

M. Sánchez Balmaseda and J. M. Guerra
Departamento de Optica, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain
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Thermal gradients were induced in bismuth films (5.5 μm thick) by $\simeq$5-nsec laser pulses of moderate intensity ($\leq 3\times 10^9$ W/m^2) under an applied magnetic field. The temporal evolution of the thermal gradient, when predicted by the heat-diffusion equation, does not correlate with the observed temporal evolution of the laser-induced thermomagnetic potential in the films. A new source term is introduced into the equation given by the electrons optically pumped to a metastable band. Agreement between experimental results and theoretical prediction is obtained. Estimations of the lifetime and the energy of the metastable band are given as well.

I. INTRODUCTION

Interest in studying the thermal gradient induced by a laser pulse in metallic films is well known. Many physical phenomena are induced by thermal gradients or by a combination of thermal gradients with electric and magnetic fields. Thus if a conductive film is irradiated with laser pulses and, simultaneously, a magnetic field is applied along the film, a transverse voltage is generated in the film. This is a typical thermomagnetic effect. Transverse voltages are also produced in certain deposited metallic films upon laser irradiation. These voltages have a thermoelectric origin. In both cases, the generated potentials should be proportional to the instantaneous thermal gradient in the material. We will designate these types of phenomena as either thermomagnetic and thermoelectric potentials to specify if they are induced with or without a magnetic field applied along the film.

The heat-diffusion equation has been often used to calculate the thermal distribution produced by laser pulses in surfaces[1] and in thin films.[2] In several works indirect evidence exists that this equation gives rise to correct predictions. Some authors point out limitations to its applicability in the case of pulses of very high intensity, $I > 10^{10}$ W/m^2.[3] In the case of ultrashort pulses (on a time scale of hundreds of picoseconds) it seems necessary to consider the electrons that are unthermalized with the lattice.[4] However, when the pulses' temporal width is in the nanosecond time scale and the radiation intensity is moderate, it has been experimentally shown that the heat-diffusion equation predicts the temporal evolution of the induced temperature in a silver surface.[5]

In other cases the predicted thermal gradient produced by laser pulses with durations of the order of tens of nanoseconds is in agreement with the observed temporal evolution of the light-induced potentials in the films. The use of the aforementioned equation in these cases is justified. Thus it has been found that laser-induced thermoelectric voltages in thin Mo films correlate extremely well with the time-dependent average normal temperature gradient as determined by computer simulation.[6] In Ref. 7 the thermomagnetic potential generated in 0.2-μm Bi films reproduces the shape of the laser pulse. This result is consistent with the predictable temporal evolution of the thermal gradient in a film with a low Fourier number F ($F<1$):

$$F=\frac{d}{(a\,\Delta t)^{1/2}}, \quad a=\frac{K_t}{\rho c_p}$$

where d is the film thickness, Δt is the temporal width of the pulse, and a is the material's thermal diffusivity, where K_t is the thermal conductivity, ρ the density, and c_p the specific heat.

Nevertheless, we have found in Bi films, with thicknesses between 0.15 and 0.35 μm, behaviors of the thermomagnetic potentials induced by 17-nsec laser pulses which did not correlate with the foreseeable temporal evolution of the thermal gradient. Those films showed a remarkable classical size effect.[8]

The aim of this work is to study the experimental and theoretical behavior of the temporal evolution of the thermal gradient induced by laser pulses in thick Bi films. This temporal evolution is studied by observing the potential generated in the films when they are irradiated under an applied magnetic field. When a thermal gradient exists in a conductor and a magnetic field is applied, an electromotive force is generated in the conductor. The field thus produced is perpendicular to both the magnetic field and the temperature gradient and it is expressed as

$$\mathbf{E}_{\mathrm{NE}}=Q_{\mathrm{NE}}\mathbf{B}\times\nabla T\ ,$$

where Q_{NE} is the known Nernst-Ettingshausen coefficient, $\mathbf{B}$ the magnetic field, and ∇T the thermal gradient induced by the laser pulse. In our setup the potential generated in the film is proportional to the field $\mathbf{E}_{\mathrm{NE}}$ and the thermal gradient is proportional to the light intensity. Since the coefficient Q_{NE} is a function of the magnetic field intensity and some parameters of the material, the temporal evolution of ∇T can be followed by studying the temporal evolution of the thermomagnetic response of the film.

The experimental results deviate from the calculated temporal evolution of the thermal gradient using the heat-diffusion equation. This deviation can be explained

by taking into account the role played by the electrons optically pumped into a metastable band.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation and characterization

Films were grown on glass substrates by vacuum evaporation (10^{-6} Torr) of 99.9999%-pure Bi. Before evaporation the substrates underwent a standard process of ultrasound cleaning. The film thickness was controlled by a quartz-crystal monitor during evaporation and later confirmed by a surface-profile analyzer. 5.5-μm samples were evaporated at room temperature (300 K). The estimated deposition rate was 230 Å/sec. Electrical connections were made with silver paste. The films' configuration on the glass substrate, as well as the design of the support connections to extract the electrical signal, are shown in Fig. 1. The films were circular, having a diameter of 3.5 mm. The dc electrical resistance of the samples was about 1.2 Ω.

Films grown with a deposition rate between 50 and 100 Å/sec under identical conditions, having thicknesses between 0.08 and 0.09 μm, were analyzed by electron-transmission microscopy. The films had a microcrystalline structure, the trigonal axis being perpendicular to the substrate and the binary axes being randomly oriented. The grain size was of the same order of magnitude as the film thickness.

B. Measurement system

Q-switched and polarized output from a neodymium-doped yttrium-aluminum-garnet (Nd-YAG) laser was used for irradiating the films. A typical impinging laser pulse had a temporal width of $\simeq 5$ nsec and an energy of $\simeq 0.2$ mJ evenly distributed on a 15.2-mm^2 section where the sample was placed. Thus the radiation intensity was below the limit 10^{10} W/m^2.

The sample was placed between the pole pieces of an electromagnet and held by a positioner which allowed for adjustment between the laser beam and the film, and parallel adjustment between the magnetic field and the film. The light-polarization plane was perpendicular to the magnetic field (see Fig. 1).

A beam splitter was used to divide the laser beam. The first of these beams was detected by a ≤ 1-nsec-risetime photodiode to be used as a monitorizing signal. This first beam was also used to synchronize a transient programmable digitizer. The second beam fell on the surface of the film. The electrical potentials generated in the film were registered in the transient programmable digitizer, its 3-dB bandwidth being 400 MHz. After having synchronized the oscilloscope trigger, the first signal was registered with a preestablished delay on the same scan as the pulse generated in the film. The sample was directly linked with the oscilloscope through a BNC connector. All the electrical lines were impedance-matched at 50 Ω.

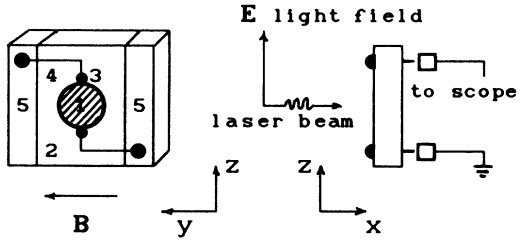

FIG. 1. 1, Bi film; 2, glass substrate; 3, Ag paste; 4, Cu electrical contact; 5, isolator.

III. RESULTS

Two films grown under identical conditions were irradiated at room temperature with an energy density of $\simeq 13$ J/m^2. For Bi, $c_p = 125.4$ J/kg K, $K_t = 8.4$ W/mK, $\rho = 9.747 \times 10^3$ kg/m^3,[9] and the absorption coefficient (at 1.06 μm) is 0.33.[10] Then, with the mentioned irradiation energy, the increase in the average film temperature is about 1 K. The applied magnetic field was varied from 0.5 to 1 T.

A typical laser pulse and the corresponding induced thermomagnetic pulse are shown in Fig. 2. As was discussed in a previous work,[11] a long fall time of the thermomagnetic pulse was foreseeable due to the high value of the Fourier number of the film ($F \simeq 30$). Identical responses were obtained with both films. The temporal profile of the thermomagnetic pulse was independent of the magnetic field intensity.

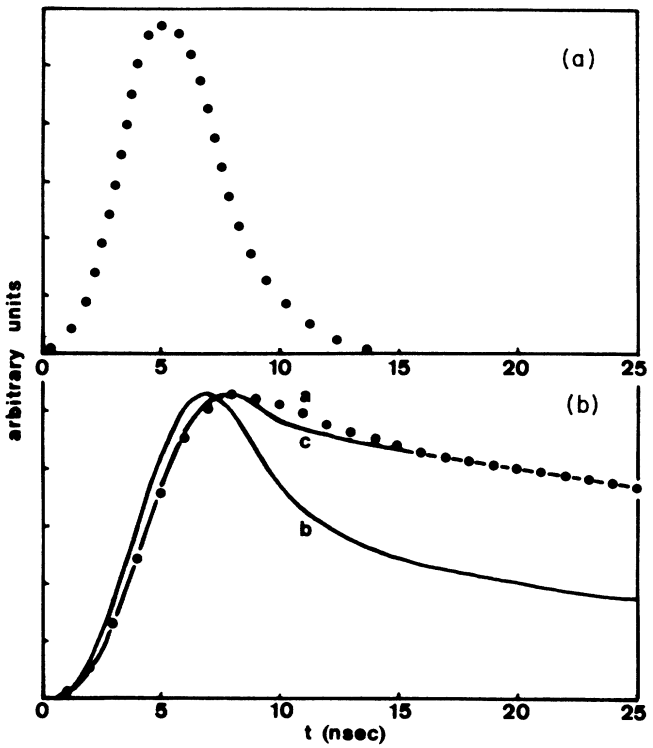

FIG. 2. (a) Experimental laser pulse. (b) Curve a, experimental thermomagnetic film response, the magnetic intensity being 1 T; curve b, theoretical result using Eq. (1); curve c, theoretical result using Eq. (6).

IV. THEORETICAL INTERPRETATION

The average thermal gradient can be calculated with the heat-diffusion equation and the boundary conditions used by Katrich and Kuz'michev.[7] With these conditions the substrate conductivity is neglected since it is much lower than the Bi conductivity.

The thermal power per unit of volume entering the film is the source term in the heat-diffusion equation and it can be written

$$\phi_s=\phi_0 e^{-\delta(x/d)} f(\tau) , \tag{1}$$

$$\phi_0=\frac{AW_r}{\Delta t \int_0^d e^{-\delta(x/d)}dx \int_0^\infty f(\tau)d\tau} , \tag{2}$$

where $\delta=d/x_L$ and $\tau=t/\Delta t$; x_L is the attenuation distance of the laser radiation in the material, $f(\tau)$ is the temporal profile of the laser pulse, A is the absorption coefficient, and W_r is the ratio E_r/s, where E_r is the laser-pulse energy and s the beam cross section. Thus the heat-diffusion equation becomes

$$\rho c_p \frac{\partial T}{\partial t}=\phi_s+K_t\frac{\partial^2 T}{\partial x^2} . \tag{3}$$

Averaging across the thickness, the thermal gradient obtained when solving (3) is

$$\overline{\text{grad}T}=\frac{2d\phi_0}{K_t F^2\delta}\sum_{n=1}^{\infty}\frac{[(-1)^n-1][1-(-1)^n e^{-\delta}]}{(1+\chi_n^2)\gamma_n^2}\left[f(\tau)-e^{-\gamma_n^2\tau}\left[f(0)+\int_0^\tau e^{\gamma_n^2\lambda}\frac{df}{d\lambda}d\lambda\right]\right] , \tag{4}$$

where $\gamma_n=n\pi/F$ and $\chi_n=n\pi/\delta$. The temporal profile of the excitation pulse is approximated by the function

$$f(\tau)=\begin{cases}0, & \tau<0\\ 1-\cos(\pi\tau), & 0\le\tau\le 2\\ 0, & \tau>2 .\end{cases} \tag{5}$$

If we now substitute the experimental parameters of the registered laser pulse [Fig. 2(a)]—$W_r=14$ J/m^2 and $\Delta t=5.5$ nsec—and the following values for Bi—$F=28.3$ and $x_L=192$ Å (Ref. 10)—we have the solution drawn in Fig. 2(b). The solution thus obtained has a fall time much shorter than that of the corresponding registered thermomagnetic pulse. In Fig. 2(b), theoretical curves have been normalized to the maximum of the experimental curve.

A possible interpretation of this result could be that the thermophysical properties of the film are different from the bulk properties for which the values used in this work apply. In order to fit the theoretical thermal response to that experimentally observed, the parameter K_t should be 0.013 W/mK. The size and interfacial effects influencing K_t and c_p have been studied in Bi. These studies have been carried out on films with thicknesses of several thousands of Å, where these kinds of effects are relevant.[12–14] The lower experimental value found in Bi for K_t is 2.5 W/mK (at 300 K and for a 280-Å film),[13] i.e., 2 orders of magnitude higher than the value needed to fit the experimental results. Since k_t and c_p influence the temporal evolution through the ratio $(K_t/c_p)^{1/2}$, the same arguments apply for the parameter c_p. In fact, it can be assumed that the behavior of Bi films that are so thick is very similar to that of bulk material.[15,16]

Another possible interpretation could be that the thermal gradient does not follow the behavior predicted by Eqs. (1) and (3).

As we have previously pointed out, we think that laser radiation can greatly alter the population density of an upper state by optical pumping through a direct transition from the valence band to an excited band. The increase of population in this excited band was estimated to be $\Delta n\simeq 4\times 10^{24}$ m^{-3} with the same irradiation energy.[11] This increase is even larger than the carrier density in the conduction band of Bi.[17]

Bearing in mind all these points, it is reasonable to think that the thermal gradient does not follow the temporal evolution predicted by the model used. This model assumes the thermalization of electrons in the conduction band on a subnanosecond time scale. In Bi there is some evidence of the existence of a band with the absorption edge for optical transitions located at about 0.3 eV (Ref. 18 and 19) and the absorption maximum at 0.6 eV (Ref. 20) both above the Fermi level.

Since the energy of 1.064-μm photons is about 1 eV, the radiation pulse can excite electrons from the valence band to the mentioned band via direct optical transitions. These excited electrons will transmit a part of their energy to the lattice in a quick nonradiative relaxation process, occupying afterwards the levels which are closest to the band edge. The rest of the energy will be liberated in a recombination process which would presumably take a time on the order of nanoseconds. If this recombination is carried out through nonradiative channels, the thermal energy will be liberated during the time needed for the process to occur. This could explain the maintenance of the thermal gradient for a much longer time than that predicted by the heat-diffusion equation with the source term given by expression (1). Besides, it is necessary that, during the recombination time, the valence-band holes do not spread excessively. In this way the thermal energy during recombinations would enter basically with the same spatial distribution of the incident radiation. Since Bi holes have very low mobility, the condition mentioned last can be assumed.

With this model (see the Appendix), the source term in Eq. (3) would be

$$\phi_s(\tau)=\phi_0 e^{-\delta(x/d)}\left[\left[1-\frac{E_m}{h\nu_L}\right]f(\tau)+\frac{E_m}{h\nu_L}S_m\,\Delta t\int_0^{\tau}f(\tau')e^{-S_m\,\Delta t(\tau-\tau')}d\tau'\right], \tag{6}$$

where $h\nu_L$ is the photon energy, S_m the recombination probability per unit of time, and E_m the average recombination energy.

The best fit to several experimental registers were obtained with values for E_m between 0.56 and 0.62 eV and for S_m^{-1} between 11 and 14 nsec. In Fig. 2(b), curve *c*, the fit to the experimental register [Fig. 2(b), curve *a*] was obtained with the parameters $E_m=0.62$ eV and $S_m^{-1}=14$ nsec. The tail of the theoretical pulse immediately after the maximum lies below the experimental data. We attribute this misfit to the fact that the experimental fall time of the laser pulse is $\frac{5}{3}$ of the rise time, and the function $f(\tau)$ is symmetric. The energy E_m thus obtained agrees with the value given by Lenham *et al.*[20]

The peak of the average thermal gradient calculated with Eq. (6) is 1.6×10^3 K/mm. This result is almost half of the value calculated with the source term given in Eq. (1).

In the case of thin films, the diffusion length covered by holes during the recombination time could be larger than the film thickness. Therefore, in these films, the recombinations would be carried out uniformly and they will not affect the temporal evolution of the thermal gradient appreciably. This fact thermomagnetic potentials follow the temporal evolution of the radiation intensity in thin films. On the other hand, in the case of thick films the light temporal evolution will be also reproduced by the thermomagnetic potential if the film's Fourier number is less than unity and the temporal width of light pulses is larger than S_m^{-1}.[21]

V. CONCLUSIONS

We have found some discrepancies between the temporal evolution of the thermal gradient predicted by the heat-diffusion equation and the temporal evolution of the thermomagnetic potential generated in Bi films by such a gradient. This disagreement, bearing in mind our conditions of light intensity and laser-pulse temporal width, was not expected to appear. However, the heat-diffusion equation can always be applied, provided the additional source term given by the electrons optically pumped to metastable states in Bi is taken into account. The maximum of the thermal gradient thus calculated is quite lower than that obtained without this additional source term.

Moreover, with this interpretation we confirm the existence of a metastable band in Bi. The energy found for this band is in good agreement with that deduced from dispersion measurements by other authors and it lies between 0.56 and 0.62 eV. The recombination time for this band is found to be between 11 and 14 nsec.

As far as we know, this is the first time that a metastable state has been detected through the dynamic thermal response of the solid. This, in principle, would represent the introduction of a new technique for detection and measurement of metastable states that decay nonradiatively in solids.

APPENDIX

In the case of optical pumping of electrons by laser radiation, the power entering the film, Eq. (1), is employed in generating holes in the valence band with a spatial distribution proportional to $e^{-\delta(x/d)}$. This is done by exciting electrons to short-lived levels located at an energy $h\nu_L$ above the Fermi level. Electrons will decay nonradiatively from these levels to a long-lived (metastable) band without sufficient time to spread appreciably (see Fig. 3). During this process, electrons will dissipate a thermal energy per unit of volume which will be spatially distributed as $e^{-\delta(x/d)}$ and which can be expressed by the source term

$$\phi_t=\left[1-\frac{E_m}{h\nu_L}\right]\phi_s\ , \tag{A1}$$

where E_m is the energy of the metastable states above the Fermi level in the valence band.

The number of electrons decaying to the metastable band per unit of volume and per unit of time will equal $\phi_s/h\nu_L$. Due to the low mobility of holes in Bi, the spatial distribution of the valence-band holes will not change appreciably during the recombination time of the electrons stored in the metastable band. Then the rate equation for the metastable band population n_m will be

$$\frac{dn_m}{dt}=\frac{\phi_s}{h\nu_L}-S_m n_m \tag{A2}$$

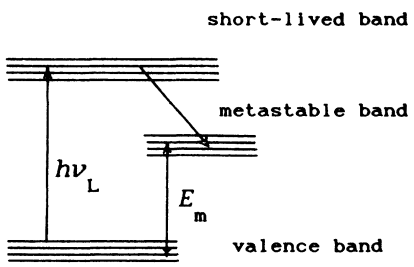

FIG. 3. Energy-level diagram showing the optical pumping of electrons and the subsequent transitions.

where S_m is the nonradiative-transition probability or recombination rate of the metastable band electrons. Then the population n_m may be expressed as

$$n_m(t)=\int_0^t \frac{\phi_s}{h\nu_L} e^{-(t-t')S_m}\,dt' \,. \tag{A3}$$

The thermal power per unit of volume produced during this recombination process is a second source term and it is given by

$$\phi_m = S_m n_m E_m = S_m \frac{E_m}{h\nu_L} \int_0^t \phi_s e^{-(t-t')S_m}\,dt' \,, \tag{A4}$$

so that the new source term to be included in the heat-diffusion equation is

$$\begin{aligned}\phi_s=\phi_t+\phi_m &= \left[1-\frac{E_m}{h\nu_L}\right]\phi_s + S_m \frac{E_m}{h\nu_L}\int_0^t \phi_s e^{-(t-t')S_m}\,dt' \\ &= \phi_0 e^{-\delta(x/d)}\left[\left[1-\frac{E_m}{h\nu_L}\right] f(\tau)+\frac{E_m}{h\nu_L} S_m \Delta t \int_0^\tau f(\tau') e^{-S_m \Delta t(\tau-\tau')}\,d\tau'\right] \,.\end{aligned} \tag{A5}$$

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