

## ARTICLES

**Ultrafast electronic disorder in heat-induced structural deformations and phase transitions in metals**

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(Received 9 March 2000; revised manuscript received 26 May 2000)

Heat-induced structural deformations and phase transitions of gold and silver are studied using 1.55-eV, 120-fs ultrashort laser pulses. The dynamics of the heating process is monitored by measuring the time evolution of the dielectric constants following optical excitation. Intensity-dependent dielectric constants in silver and gold show similarities with the photon-energy-dependent dielectric constants, which is shown to indirectly map out the degree of heat-induced electronic disorder in these noble metals. This observation strongly suggests that the heat-induced structural deformations and phase transitions in metals are tied to the electronic disorder and band-structure collapse.

**I. INTRODUCTION**

Our understanding of femtosecond laser interactions with metals is largely based on the so-called two-temperature model.<sup>1</sup> An ultrashort laser pulse, with a duration less than the excited electron energy-loss lifetime, can heat electrons in a metal to a very high temperature while leaving the lattice relatively cool since the heat capacity of the electrons is much smaller than that of the lattice. Even though this two-temperature model has been shown not to be strictly valid during the first few hundred femtoseconds following laser excitation,<sup>2,3</sup> in most cases, thermalization of the hot electrons can be assumed to occur instantaneously due to the short electron-electron interaction time, and therefore the overall picture of a nonequilibrium system in metals is normally described as constituting two subequilibrium systems, the hot electrons and a cold lattice.<sup>1</sup> This transient two-temperature system will tend to reach equilibrium within a few picoseconds through electron-phonon interactions as well as electron transport out of the excited region. In the perturbative low-intensity regime, the excited region of metals will reach equilibrium with little disorder and the ultrafast dynamics of electron-electron and electron-phonon interactions in metals has been studied extensively over the past two decades.<sup>2-6</sup> In the high-intensity regime (intensity normally  $> 10^{13}$  W/cm<sup>2</sup>), on the other hand, a plasma can be created from a metal surface due to intense laser radiation and the plasma-related phenomena, such as hydrodynamic expansion, resonance absorption, etc., need to be taken into account in studying laser-plasma interactions.<sup>7-11</sup>

In this paper, we present the results of a study of laser-induced structural deformations and phase transitions in metals with intermediate laser intensity that is only high enough to elevate the final lattice temperature to the melting point without creating any significant plasma (intensity normally ranging  $10^{11} \sim 10^{12}$  W/cm<sup>2</sup>). Although the solid to liquid structural phase transition in metals is a vital problem due to

its fundamental importance as well as wide applicability in materials processing and manufacturing, the understanding of laser heat-induced melting in metals still remains at a phenomenological level. Further investigation to understand this problem at a more fundamental level is necessary.

Recently, the study of melting dynamics has been vigorously pursued in semiconductors with ultrafast optical measurements. One of the most interesting questions studied in semiconductors is so-called “plasma annealing,” a melting of diamond structure semiconductors by means of electronic excitation rather than heating.<sup>12</sup> This nonthermal melting has been experimentally demonstrated by several groups with a variety of semiconductor materials.<sup>13-18</sup> The experimental techniques in optical measurements have also evolved from studying only the change in the optical reflectivity or second-harmonic generation to directly determining the time evolution of the dielectric constant.<sup>19</sup> The study of the dielectric constant has fundamental advantages compared to studying only the change in the optical reflectivity or second-harmonic generation because the dielectric constant reveals the intrinsic optical properties of a material. The interpretation of reflectivity and second-harmonic data, in fact, often relies on an assumption of the functional form of the dielectric function such that induced changes in the dielectric function are dominated by free-carrier contributions. However, such assumptions are correct only when interband transitions can be neglected.<sup>19</sup>

More recently, we reported on a study of structural phase transitions induced by electronic excitation in metallic system.<sup>20</sup> In aluminum, the structural phase change can be induced by a resonant interband electronic excitation across a pair of parallel conduction bands. A significantly lower threshold fluence and shorter time scale for this transition compared to the traditional heat-induced melting indicate that this electronic-induced structural phase change results from a fundamentally different process. Motivated by this finding, we set out to study the traditional heat-induced melt-

ing in metals from a fundamental point of view in order to understand the electronic disorder associated with ultrafast heating.

In this paper, we investigate the heat-induced structural deformations and phase transitions in both gold (Au) and silver (Ag) using 1.55-eV, 120-fs laser pulses. Since the onset of major interband transitions in both Au (2.45 eV) and Ag (4 eV) exceeds the fundamental laser photon energy used in the experiment, any laser-induced structural phase change in both metals is expected to be an ultrafast heat-induced process. The dynamics of the heating processes before and during a structural phase transition in both metals is monitored by measuring the time evolution of their dielectric constants following optical excitation. Intensity-dependent dielectric constants in Ag and Au, however, show striking similarities with the photon-energy-dependent dielectric constants, which is shown to indirectly map out the degree of the heat-induced electronic disorder in these noble metals. This observation strongly suggests that the heat-induced structural deformations and phase transitions in metals are tied to the electronic disorder and band-structure collapse.

## II. EXPERIMENTAL SETUP

The experimental setup is similar to that described in Ref. 20. The laser used in the experiment is an amplified Ti:sapphire laser system running at a 1-kHz repetition rate, producing over 800  $\mu\text{J}/\text{pulse}$  in 120-fs pulses with a central wavelength of 800 nm. The repetition rate of the laser pulses can be further reduced with a pulse selector. A pump-probe transient reflectivity technique is used to determine the time evolution of the dielectric constant at 1.55 eV following optical excitation. The laser pulse is split into an intense pump beam and a weak probe beam. The pump beam is weakly focused near normal incidence onto the sample, while the probe beam is focused to  $\sim 10$  times smaller area than the pump beam to ensure probing of a uniformly excited area. The beam spot size is measured using a scanning edge technique. In order to extract both real and imaginary parts of the dielectric constant, two independent measurements need to be made.<sup>19</sup> In our case, we further split the probe pulse into two beams with different incident angles on target. The two probe pulses are individually delayed with high precision translation stages to arrive at the sample simultaneously. The reflectance from two angles is recorded at each time delay and used to extract the dielectric constant through numerically inverting the Fresnel reflectivity formulas. A differential measurement is also made by recording the incident probe energy to minimize the effect of laser fluctuations. The pump and probe beams are cross-polarized ( $S$  polarization for pump and  $P$  polarization for probe) to minimize coherent artifacts when the pump and probe overlap temporally.<sup>21,22</sup> (In fact, no major conclusion in this paper is derived from the data points at zero time delay and therefore the possibility of coherent effects is not relevant here.) Polarizers allowing only the  $p$ -polarized light (probe) and 10-nm narrow bandpass interference filters centered at 800 nm are inserted in front of the probe detectors to minimize the effect of pump leakage and nonlinear or plasma radiation respectively since the pump beam is intense. The Au and Ag used in the experiments are polycrystalline samples prepared by high

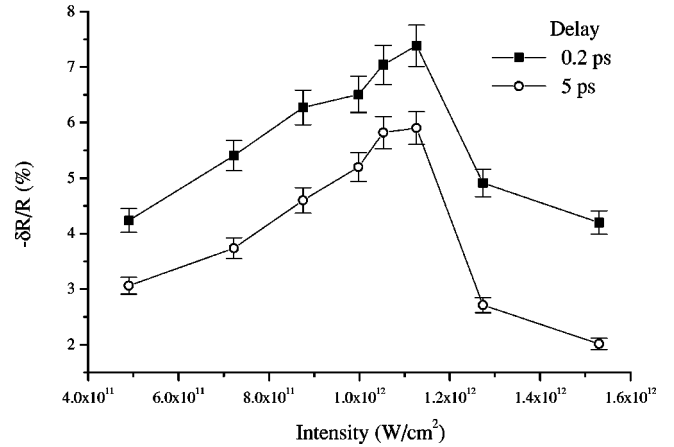


FIG. 1. Intensity-dependent reflectivity change for silver at time delays of 0.2 and 5 ps. The probe beam is incident at  $52^\circ$ . The error bars indicate a 5% uncertainty mainly due to the pump energy fluctuations.

vacuum deposition. The samples are mounted on a high-speed and high-precision motion system consisting of a rotation stage on top of a translation stage, which allows translation of the sample to a fresh spot between laser shots. The dielectric constants of both metals at 1.55 eV are measured with this two-angle technique first without laser excitation, and the result shows excellent agreement with the published values.<sup>23</sup>

## III. EXPERIMENTAL RESULTS AND DISCUSSION

By varying the pump laser intensity with a high quality variable optical attenuator, time-resolved reflectivity measurements are made at different pump intensities. The intensity-dependent reflectivity change for Ag at time delays of 0.2 and 5 ps are plotted in Fig. 1. The magnitude of the reflectivity change increases with incident laser intensity to a threshold value of about  $1.13 \times 10^{12} \text{ W/cm}^2$  for Ag. When the pump intensity is further increased, the change of the probe reflectivity drops rapidly. Examination of the sample under an optical microscope reveals that irreversible damage appears when the laser intensity is just above this threshold value. Similar behavior is also observed in the intensity-dependent reflectivity change for Au. Therefore the sudden change of the reflectivity indicates structural phase transitions in Au and Ag in our experiments.

The dynamic processes due to laser excitation in Au and Ag are studied by monitoring the time evolution of their dielectric constants at 1.55 eV through the two-angle probe measurement. Both real and imaginary parts of the dielectric constants of Ag and Au versus pump intensity at time delays of 0.2 and 5 ps are plotted in Figs. 2 and 3. The error bars correspond to a 5% uncertainty in the reflectivity measurements. Despite the relatively simple dependence of reflectivity on intensity as shown in Fig. 1, these dielectric constants exhibit a complicated dependence on intensity at the delay time of 5 ps (especially Ag). The  $\text{Re}(\epsilon)$  of Ag at time delay of 5 ps, in Fig. 2 for example, increases with intensity from  $-22$  to over zero, then drops drastically to around  $-10$  at an intensity of  $1.13 \times 10^{12} \text{ W/cm}^2$ , and increases slowly again with pump laser intensity. The  $\text{Im}(\epsilon)$  of Ag, on the other

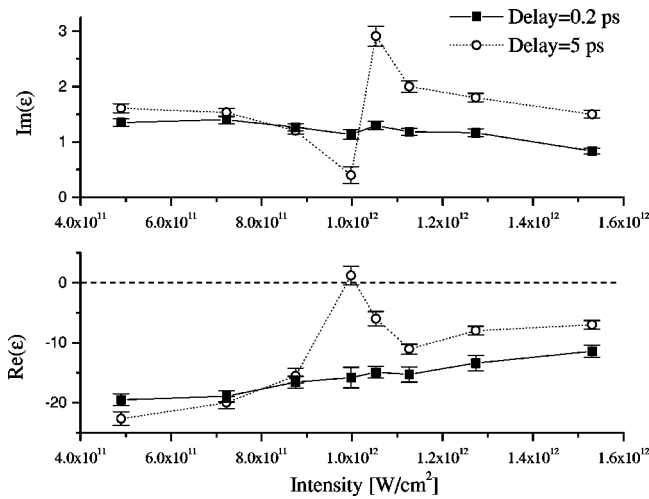


FIG. 2. Dielectric constant of silver versus laser intensity at time delays of 0.2 and 5 ps.

hand, shows a corresponding change on a different scale. Note that the large changes in dielectric function occur below the threshold intensity ( $1.13 \times 10^{12}$  W/cm<sup>2</sup> shown in Fig. 1) indicating that such changes occur prior to the melting.

For Ag, this rapid change of dielectric constant versus pump intensity before melt is similar to the dielectric constant change versus excitation photon energy around the resonant absorption energy of 4 eV, as shown in Fig. 4 (the plotted dielectric constants of Ag versus photon energy in Fig. 4 is reproduced from Ref. 23). The dielectric constant for a metal can be decomposed into free and bound electron contributions  $\epsilon^f$  and  $\epsilon^b$ . The free electron contribution  $\epsilon^f$  will follow the Drude model over the whole photon energy range, while the bound electron contribution  $\epsilon^b$  will reflect the resonant absorption. The values of  $\text{Re}(\epsilon)^f$  and  $\text{Re}(\epsilon)^b$  of real part of the dielectric constant are negative and positive, respectively. The  $\text{Re}(\epsilon)^b$  for Ag at 4 eV in fact is large enough to overcome the small negative  $\text{Re}(\epsilon)^f$  driving the total  $\text{Re}(\epsilon)$  across zero to positive values, as shown in Fig. 4 and discussed in detail in Ref. 24. The overall dependence of dielectric constant on photon energy (Fig. 4) shows surprising similarity to our experimental results for the transient

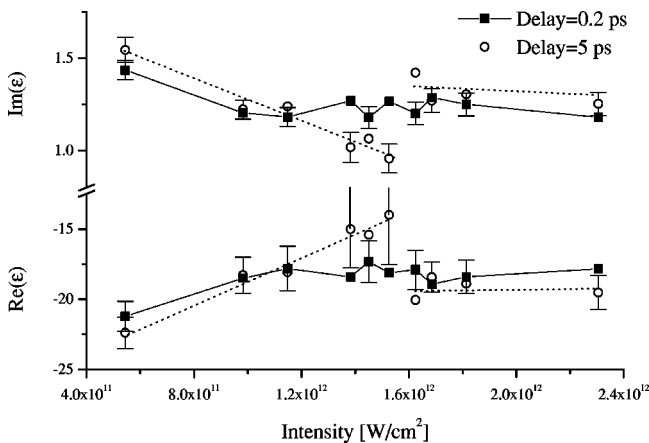


FIG. 3. Dielectric constant of gold versus laser intensity at time delays of 0.2 and 5 ps.

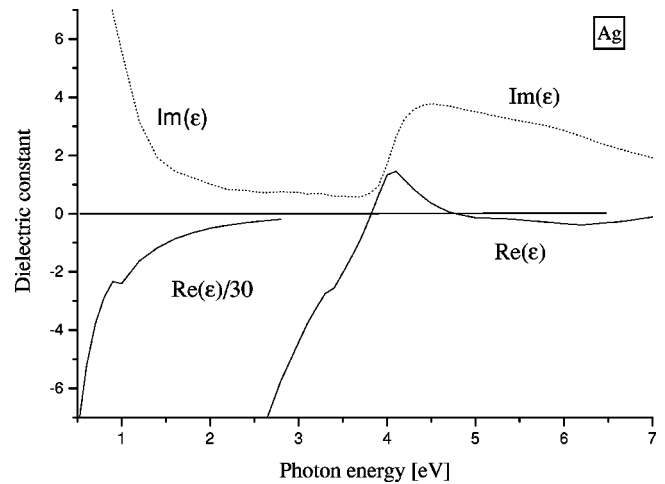


FIG. 4. Dielectric constant for silver as a function of photon energy. The data are reproduced from Ref. 23.

dielectric constant versus laser intensity (Fig. 2), as well as the similarity for the values of the maximum  $\text{Re}(\epsilon)$  in Figs. 2 and 4, although the dependent variables in the two figures are totally different physical quantities, photon energy and laser intensity.

Electron screening can occur when a large number of mobile free electrons are created from bound states or a significant change in the conduction electron distribution. These photoexcited electrons can partially screen the ionic potential and change the electronic band structure in materials such as semiconductors.<sup>25</sup> The strength of electronic screening varies with the free-electron density and the degree of redistribution, and the effects due to screening should be a maximum right after the pump excitation since the subsequent recombination, diffusion, and relaxation processes will reduce the free-carrier density and the total change of the conduction electron distribution.<sup>19</sup> Unlike semiconductors, however, the electron screening normally does not play a significant role in metals since many excitations (e.g., intraband transitions) in metals do not increase the number of free electrons significantly. Even assuming that many free electrons are created from bound states through multiphoton excitation (since the photon energy here is smaller than the onset interband transition energies for both Au and Ag) and that the conduction electron distribution is strongly modified by laser excitation, our experimental results show that the changes of dielectric constant grow with time delay and the resonancelike structures become clear several picoseconds after laser excitation (Figs. 2 and 3). Such a delay would not be observed from the electron screening since the effect should be maximum immediately after the excitation. Therefore electron screening does not seem to play an important role in influencing the intensity dependence of the transient dielectric constants in Ag and Au.

The increasing changes of the dependence of dielectric constant on intensity over picoseconds time scale for Ag suggests that the change involves phonon processes, e.g., increasing lattice vibration and deformation. The electronic band structure of a noble metal is illustrated in Fig. 5, which consists of a free-electron band and a localized  $d$  band. A 1.55-eV photon will not excite electrons from the filled  $d$  band to the conduction band above Fermi level through one-

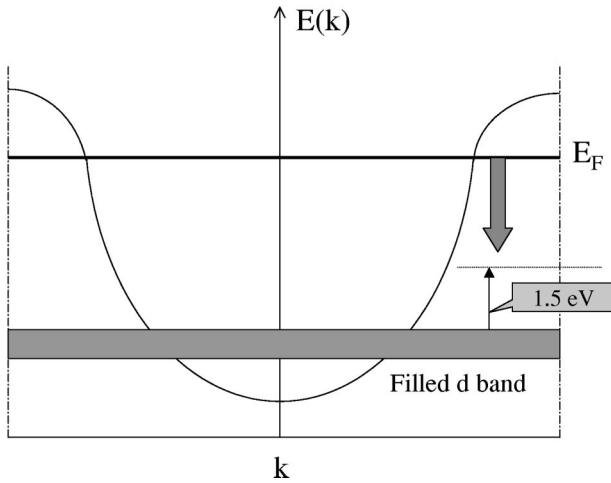


FIG. 5. Structural change decreases the energy separation between Fermi level and  $d$  band in a noble metal.

photon excitation. However, the structure of a noble metal will start to deform when exposed to intense laser heating, and such a process becomes irreversible above the threshold intensity for damage. This structural change will induce a change in electronic band structure since the internuclear distance of the metal atoms changes. To illustrate this point, the Fermi energy using a free electron model can be expressed as follows:<sup>26</sup>

$$\epsilon_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}, \quad (1)$$

where  $r_s$  is the radius of a sphere whose volume is equal to the volume per conduction electron and  $a_0$  is the Bohr radius. When the lattice constant or  $r_s$ , in the nearly free-electron noble metal Ag, increases due to intense laser heating, the simple expression in Eq. (1) indicates that the Fermi energy will drop. The energy change of the  $d$  band will be smaller since the  $d$ -band electrons are relatively localized (non-free-electron like). Now we can understand the striking similarity of the dielectric constant for Ag between its photon energy dependence and pump intensity dependence. The effect of the electronic-level shift due to the structure change will be lowering the Fermi level towards the filled  $d$  band in a noble metal, as illustrated in Fig. 5. As the metal is illuminated with increasing intensity, the decreased energy separation between the Fermi level and  $d$  band scales as increasing photon energy while fixing electronic band structure. Therefore the effects of increasing the pump intensity are in a sense equivalent to increasing photon energy while fixing the electronic band structure. Thus we observe the similar dependence of the dielectric constant for Ag on pump intensity as on photon energy below the threshold intensity of irreversible structure change, and the resonance feature observed in dielectric constant indicates that the decreased energy separation sweeps through the 1.55-eV photon resonance. The deviation between the dependence of the dielectric constant on intensity and photon energy above the damage threshold is expected and reflects the liquid values.<sup>29</sup> This observation suggests that the heat-induced structural deformation and phase transition in Ag are actually tied to electronic band-structure collapse. Laser-induced electronic dis-

order associated with structural changes has also been studied in semiconductors.<sup>19</sup> It needs to be pointed out that the free-electron-model-based Eq. (1) may not be able to quantitatively predict the electronic-level shift in real metallic system due to its simplicity. The expression, however, gives the correct direction of energy shift as do the full band-structure calculations in noble and transition metals.<sup>27,28</sup> Further theoretical investigation possibly using large-scale simulations is necessary to fully understand the highly dynamic process of electron disorder in structural deformations and phase transitions.

The electron disorder in Ag due to the lattice deformation and phase change is studied here with intensities around or below the melting point and much lower than intensities involving significant plasma effects, as discussed in the introduction. Especially, the intensity corresponding to the interesting structure appearing in the dielectric constants that is maximum around  $1 \times 10^{12} \text{ W/cm}^2$  is even below the melting threshold to form a liquid (thus far from forming a significant plasma). Therefore the structural deformation we describe here is different from high-intensity plasma phenomena, such as hydrodynamic expansion (normally with intensity  $> 10^{13} \text{ W/cm}^2$ ).<sup>10</sup> Furthermore, plasma-related effects normally become more significant with increasing intensity, which cannot account for the resonantlike structure in the dielectric constants around a certain intensity ( $\sim 1 \times 10^{12} \text{ W/cm}^2$ ) in our observations. Therefore high intensity plasma effects do not play any significant role in our measurements.

The bound electron excitation contributes to the dielectric constant in Au at 2.45 eV, where the free-electron component  $\epsilon^f$  is still relatively large. Thus the bound electron component  $\epsilon^b$  does not modify the dielectric constant in Au as drastically as in Ag, e.g., there is no clear resonance structure in the dielectric constant in Au and the total  $\text{Re}(\epsilon)$  in Au, unlike in Ag, is not driven across zero to positive values.<sup>23</sup> We can see from Fig. 3 that the dielectric constant versus pump intensity for Au does not show as clear a resonance structure as seen in Ag below the melting intensity of  $1.53 \times 10^{12} \text{ W/cm}^2$ . The overall dependence of the dielectric constant on intensity in Au below the melting threshold again agrees reasonably well with the dielectric constant change versus photon energy reported previously.<sup>23,30</sup> Such agreement reinforces our argument that increasing the pump intensity has the same effect as increasing the photon energy with fixed electronic band structure and therefore the electronic structure is distorted with the pump excitation in Au as well, even before the structural phase transition occurs. The sudden jump of the dielectric constant in Au at  $1.53 \times 10^{12} \text{ W/cm}^2$  occurs at the melting threshold, in agreement with the change of dielectric constants from solid to liquid values.<sup>29</sup>

#### IV. CONCLUSION

In summary, we describe the ultrafast heat-induced structural deformations and phase transitions in both Au and Ag using 1.55-eV, 120-fs ultrashort laser pulses. The dynamics of the ultrafast heating process is monitored by measuring the time evolution of the dielectric constants following optical excitation. Unlike the simple dependence of reflectivity

on intensity, the intensity-dependent dielectric constants in Ag, as well as in Au, show striking similarities with the photon-energy-dependent dielectric constants, which are shown to indirectly map out the degree of the heat-induced electronic disorder in noble metals. These results indicate that the heat-induced structural deformations and phase transitions in metals are tied to electronic disorder and band-structure collapse. Further theoretical studies are necessary to fully understand the dynamics of electron disorder in the structural deformations and phase transitions. The experimental observation presented in this paper demonstrates pronounced electronic effects in the thermal melting in metals.

This result should provide direction for future theoretical investigation that may lead to a more complete understanding of the melting mechanism in metals.

#### ACKNOWLEDGMENTS

We would like to acknowledge the technical assistance of J. P. Roberts, G. Rodriguez, A. I. Lobad, and C. Mombourquette. This research was supported through the Los Alamos Directed Research and Development Program by the U.S. Department of Energy.

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- <sup>1</sup>M. I. Kaganov, I. M. Lifshitz, and L. V. Tanatarov, *Zh. Éksp. Teor. Fiz.* **31**, 232 (1956) [*Sov. Phys. JETP* **4**, 173 (1957)].
- <sup>2</sup>W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, *Phys. Rev. Lett.* **68**, 2834 (1992); *Phys. Rev. B* **46**, 13 592 (1992).
- <sup>3</sup>C.-K. Sun, F. Vallee, L. Acioli, E. P. Ippen, and J. G. Fujimoto, *Phys. Rev. B* **48**, 12 365 (1993); **50**, 15 337 (1994).
- <sup>4</sup>G. L. Eesley, *Phys. Rev. Lett.* **51**, 2140 (1983).
- <sup>5</sup>J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen, *Phys. Rev. Lett.* **53**, 1837 (1984).
- <sup>6</sup>H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou, *Phys. Rev. Lett.* **58**, 1212 (1987).
- <sup>7</sup>W. L. Kruer, *The Physics of Laser Plasma Interactions* (Addison-Wesley, Reading, MA, 1988).
- <sup>8</sup>H. M. Milchberg, R. R. Freeman, S. C. Davey, and R. M. More, *Phys. Rev. Lett.* **61**, 2364 (1988).
- <sup>9</sup>R. Fedosejevs, R. Ottmann, R. Sigel, G. Kuhnle, S. Szatmari, and F. P. Schafer, *Phys. Rev. Lett.* **64**, 1250 (1990).
- <sup>10</sup>X. Y. Wang and M. C. Downer, *Opt. Lett.* **17**, 1450 (1992).
- <sup>11</sup>A. Ng, P. Celliers, A. Forsman, R. M. More, Y. T. Lee, F. Perrot, M. W. C. Dharmawardana, and G. A. Rinker, *Phys. Rev. Lett.* **72**, 3351 (1994).
- <sup>12</sup>J. A. Van Vechten, R. Tsu, and F. W. Saris, *Phys. Lett.* **74A**, 422 (1979).
- <sup>13</sup>C. V. Shank, R. Yen, and C. Hirlimann, *Phys. Rev. Lett.* **50**, 454 (1983); **51**, 900 (1983).
- <sup>14</sup>H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz, *Phys. Rev. Lett.* **60**, 1438 (1988).
- <sup>15</sup>P. Saeta, J. K. Wang, Y. Siegal, N. Bloembergen, and E. Mazur, *Phys. Rev. Lett.* **67**, 1023 (1991); L. Huang, J. P. Callan, E. N. Glezer, and E. Mazur, *ibid.* **80**, 185 (1998).
- <sup>16</sup>D. H. Reitze, H. Ahn, and M. C. Downer, *Phys. Rev. B* **45**, 2677 (1992).
- <sup>17</sup>K. Sokolowski-Tinten, J. Bialkowski, M. Boing, A. Cavalleri, and D. von der Linde, *Phys. Rev. B* **58**, R11 805 (1998); K. Sokolowski-Tinten, J. Solis, J. Bialkowski, J. Siegel, C. N. Afonso, and D. von der Linde, *Phys. Rev. Lett.* **81**, 3679 (1998).
- <sup>18</sup>C. W. Siders, A. Cavalleri, K. Sokolowski-Tinten, Cs. Tóth, T. Guo, M. Kammler, M. Horn von Hoegen, K. R. Wilson, D. von der Linde, and C. P. J. Barty, *Science* **286**, 1340 (1999).
- <sup>19</sup>E. N. Glezer, Y. Siegal, L. Huang, and E. Mazur, *Phys. Rev. B* **51**, 6959 (1995).
- <sup>20</sup>C. Guo, G. Rodriguez, A. Lobad, and A. J. Taylor, *Phys. Rev. Lett.* **84**, 4493 (2000).
- <sup>21</sup>J. L. Oudar, D. Helin, A. Migus, A. Antonetti, and F. Alexander, *Phys. Rev. Lett.* **55**, 2074 (1985).
- <sup>22</sup>S. V. Govorkov, I. L. Shumai, W. Rudolph, and T. Schroder, *Pis'ma Zh. Éksp. Teor. Fiz.* **52**, 755 (1990) [*JETP Lett.* **52**, 117 (1990)].
- <sup>23</sup>E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, New York, 1985).
- <sup>24</sup>H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).
- <sup>25</sup>D. H. Kim, H. Ehrenreich, and E. Runge, *Solid State Commun.* **89**, 119 (1994).
- <sup>26</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College Pub., Philadelphia, 1976), Chap. 2.
- <sup>27</sup>R. C. Albers, A. K. McMahan, and J. E. Muller, *Phys. Rev. B* **31**, 3435 (1985).
- <sup>28</sup>A. K. McMahan and R. C. Albers, *Phys. Rev. Lett.* **49**, 1198 (1982).
- <sup>29</sup>J. C. Miller, *Philos. Mag.* **20**, 1115 (1969).
- <sup>30</sup>D. E. Aspnes, E. Kinsbron, and D. D. Bacon, *Phys. Rev. B* **21**, 3290 (1980).