PHYSICAL REVIEW B VOLUME 42, NUMBER 11 15 OCTOBER 1990-I

Theory for the instability of the diamond structure of Si, Ge, and C induced by a dense electron-hole plasma

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(Received 8 March 1990)

The effect of a dense electron-hole plasma on the stability of the diamond lattice of the crystalline group-IV elemental semiconductors C, Si, and Ge is examined with use of a tight-binding model. Such a plasma may result, for example, from a short, intense laser pulse. We find that the transverse-acoustic phonons of Si become soft if about 9% of the electrons are excited from the valence band into the conduction band. At higher densities of the electron-hole excitations the cubic symmetry of the diamond lattice is destroyed within less than 100 fs after the creation of the electron-hole plasma. This is much shorter than the time needed for the crystal to melt. The instability of the lattice then leads directly to a very rapid melting of the crystal structure. Our results are in agreement with recent experiments using pulsed lasers to induce disorder in crystalline Si surfaces. We obtain for C and Ge essentially the same theoretical results as for Si.

I. INTRODUCTION

A theory is presented for the instability of the diamond lattice of elemental semiconductors due to the excitation of a dense electron-hole plasma. A recent experiment[1] seems to indicate that the diamond lattice of Si distorts within 100 fs after the application of a sufficiently intense laser pulse. After this distortion, the atomic structure metals very rapidly. It will be the main goal of this study to discuss these surprisingly rapid transitions.

First, the experimental facts are described. A time-resolved experiment has been performed by Tom *et al.*[1] using an intense laser pulse of 100 fs duration to excite an electron-hole plasma below the (111) surface of Si. An incident *p*-polarized probe laser is used to examine the resulting time-dependent changes in the atomic structure. One observes that the reflected *s*-polarized second-harmonic signal, which depends directly on the $3m$ (C_{3v}) point-group symmetry of the surface and the cubic symmetry of the bulk just below the surface, has practically vanished within less than 150 fs after excitation. In contrast, the reflected *p*-polarized second-harmonic signal, which is essentially independent of the cubic symmetry, has decreased much more slowly (within about 500 fs to a remaining intensity of 63% of its value before excitation). Probably, this decrease, together with an equally slow increase in the *p*-polarized linear reflectivity, corresponds to the actual melting of the surface region. To understand these results, note that the fastest lattice vibrations of Si in the diamond structure have a period[2,3] of about 100 fs, and that melting takes at least several periods of the lattice vibration in order to obtain a thermal distribution of the vibrational energy. Thus, one may conclude that the laser-induced electron-hole excitations lead directly to the destruction of the cubic symmetry of the diamond structure of Si (as indicated by the loss of the *s*-polarized second-harmonic signal), long before the atomic lattice can melt. Since the excited electron-hole plasma extends several hundred angstroms deep into the bulk of the sample, this experiment examines the structural stability of bulk Si, and not only the stability of the structure at the surface.

These conclusions are supported by a related experiment, which has been performed by Guidotti *et al.*[4] The second-harmonic signal has been measured at a Si(111) surface, using *s*-polarized incident laser radiation. Thus, there is no second-harmonic generation from the surface (which requires incident *p* polarization), and any second-harmonic signal has to originate from the bulk. Since the unperturbed diamond structure has inversion symmetry, there should be no second-harmonic generation from its bulk. In fact, for low laser intensities no second-harmonic signal has been observed, but a second-harmonic signal has appeared at rather high irradiation intensities, which can excite a dense electron-hole plasma. This suggests that the induced electron-hole plasma has made the diamond structure unstable, thus destroying the inversion symmetry and making second-harmonic generation in the bulk possible.

In order to set up a theoretical model for describing these experimental observations, it is important to consider the results of other time-resolved experiments on crystalline semiconductors[5] and metals.[6,7] In these experiments, the time-dependent energy distribution of the electrons has been measured by the absorption of light after exciting a significant fraction of the electrons by an intense laser pulse of around 60–100 fs duration, similar to the experiment of Tom *et al.* In contrast, the fluence of the laser pulse has been an order of magnitude smaller in these experiments.[6,7] A thermalized electron distribution is already observed a short time (approximately 10 fs) after the laser excitation of the electrons. However, the resulting temperature of the electron gas (of the order of 1 eV) has been much higher than the temperature of the atomic lattice, and it did require several thousand femtoseconds to obtain thermal equilibrium between the electrons and the lattice. Note that the electron-electron interaction is much stronger than the effective screened electron-phonon interaction. Thus, the electron gas thermalizes very rapidly, whereas the heat exchange due to inelastic electron-phonon scattering between the electron gas and the lattice is, in comparison, quite slow. These conclusions should also apply if we consider the experiment of Tom *et al.*[1] The main difference is that the much stronger laser pulse induces a mechanical instability of the lattice. This results in a rapid exchange of energy between the electrons and the atomic lattice in the form of mechanical work. In comparison, the exchange of caloric heat can be neglected. This energy is then thermalized in the lattice because of the anharmonic interactions between phonons, and leads to rapid melting.

A theoretical interpretation of these experiments is of considerable interest, particularly also with respect to the possibility of annealing layers of amorphous Si using pulsed lasers.[8,9] Furthermore, regarding theory, no detailed theoretical understanding of the instability of the diamond structure of group-IV elemental semiconductors (Si, Ge, and C) resulting from the excitation of a dense electron-hole plasma has been presented so far. In the only related previous theoretical work[10] using a simple bond-charge model, it has been estimated that the diamond structure of Si should become unstable against the β-tin phase if more than roughly 16% of the electrons are excited from the valence band into the conduction band. This value is only a very rough qualitative estimate. It is the main goal of this paper to present a detailed theory explaining the important experimental facts and permitting a more accurate calculation of the lattice instability induced by the laser irradiation.

II. THEORY

In our model for the instability, we assume that an initial pump-laser pulse has excited an electron-hole plasma, which thermalizes rapidly at a temperature T_e due to the strong electron-electron interaction. Note that the experiments[5-7] indicate that the thermalization of the electron gas occurs very rapidly as compared to the movement of the atoms. Thus, the temperature T_e, as well as all other properties of the electron gas, should depend only on the actual positions of the atoms. Note that without excitation one has $T_e \simeq 0$, and the usual Born-Oppenheimer approximation can be used. However, for a dense, excited electron-hole plasma and correspondingly large electronic temperatures, $T_e \gg 0$, we have to determine how T_e evolves and how it depends on the atomic structure. As discussed, the exchange of heat (ΔQ_e) between the electron gas and the lattice can be neglected in comparison to the exchange of mechanical work during the time required for destroying the symmetry of the diamond structure.[11] Hence we assume that[12] $\Delta Q_e = T_e \Delta S_e \simeq 0$. Consequently, the electronic entropy remains constant in our model, $\Delta S_e \simeq 0$. The temperature T_e is then determined from $S_e(T_e) = \text{const}$, and an appropriate initial value for S_e, which depends on the intensity of the pump-laser excitation. This is essentially an extension of the Born-Oppenheimer approximation, since the isotherm $T_e = 0$ is equivalent to the adiabatic $S_e = 0$, as a consequence of the third law of thermodynamics.[12] It should be noted that the density of the electron-hole excitations is not a constant, but is allowed to change due to the electron-electron interaction.[13] Finally, in addition, we assume, for the discussion of the induced instability of the diamond lattice, that the volume per atom remains constant, independently of the distortion of the diamond lattice, because an effective volume expansion of large regions of the crystal requires a movement of the atoms over correspondingly large distances, and thus should be much slower than the instability.[14]

A. Elastic constants as a function of the density of the electron-hole excitations

First, we calculate the bulk modulus B and the elastic shear constant $[c_{11} - c_{12}]$ of the elemental semiconductors for a given value of the entropy S_e of the electron gas. It is convenient to use a face-centered unit cell (with a two-atom basis), as shown in Fig. 1. Note that the diamond structure is thus represented by a fcc unit cell with equal lattice constants $a = c$, and that a shear distortion $a > c$ leads to the competing tetragonal β-tin structure.[10] The equilibrium lattice constants at $S_e = 0$ (and $T_e = 0$) are $a = c = a_0$. The cohesive energy $E_b(a,c)$ per "tetrahedral" bond (thin lines in Fig. 1) is calculated for small distortions $a \simeq a_0$ and $c \simeq a_0$, and depending on S_e using a tight-binding theory, which is discussed in detail in Appendix A. The unit cell contains 16 bonds and its volume is equal to $V_0 = a_0^3$, in the absence of distortions. Thus, we obtain that the density of the elastic energy of the distortion is

$$U(a,c) = 16[E_b(a,c) - E_b(a_0,a_0)]/V_0 \ . \quad (1)$$

We first consider uniform contractions and expansions $a = c = (1 + \delta/3)a_0$, where $\delta \simeq 0$. Without excitations ($S_e = T_e = 0$) we obtain the usual relation between U and the bulk modulus B_0,[15,16]

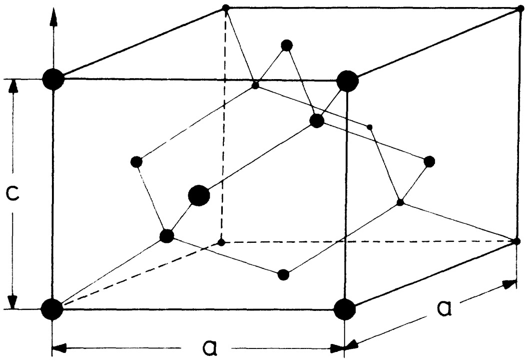

FIG. 1. Schematic picture of the face-centered tetragonal unit cell for the distorted diamond lattice ($a > c$). The black dots indicate the position of the atoms and the thin lines indicate the tetrahedral bonds.

$$U((1+\delta/3)a_0,\,(1+\delta/3)a_0)=\tfrac{1}{2}B_0\delta^2 \tag{2}$$

This is changed entirely in the presence of an excited electron-hole plasma, because the excitation of electrons from the valence band, which consists of bonding electron states, into the conduction band, of antibonding character, partially destroys the attractive bonding interaction between the atoms. On the other hand, the repulsive interaction (which for $T_e=0$ compensates the attractive bonding force at $a=c=a_0$ and determines the equilibrium bond length) remains essentially unaffected. The excited electron-hole plasma thus results in an effective repulsive force between the atoms, and the crystal is no longer in mechanical equilibrium at the lattice constant a_0. In principle, the crystal would then expand to a new equilibrium lattice constant $a(S_e)>a_0$, but we can neglect this volume expansion on the time scale (100 fs) of the instability of the diamond structure as seen in the experiment,[1] because the speed of this expansion is limited by the velocity of sound,[14] as discussed previously. Thus the elastic energy should be expanded around a_0 and includes a linear term, due to the outward directed pressure p of the electron-hole plasma. It is

$$U((1+\delta/3)a_0,\,(1+\delta/3)a_0)=\tfrac{1}{2}B(S_e)\delta^2-p(S_e)\delta\ , \tag{3}$$

where $p(S_e)=V_0^{-1}\,\Delta U/\Delta V>0$ for $S_e>0$. We obtain $B(S_e)$ and $p(S_e)$ from Eqs. (1) and (3) as the first and second derivatives of the cohesive energy E_b,

$$p(S_e)=-16a_0^{-3}\frac{\partial}{\partial\delta}E_b((1+\delta/3)a_0,\,(1+\delta/3)a_0) \tag{4}$$

and

$$B(S_e)=16a_0^{-3}\frac{\partial^2}{\partial\delta^2}E_b((1+\delta/3)a_0,\,(1+\delta/3)a_0)\ , \tag{5}$$

which have to be evaluated at $\delta=0$. To be consistent with the arguments above, we have to consider shear distortions, which keep the volume of the unit-cell constant constant, $V=a^2c=a_0^3$, in second order in the shear distortion. Thus the appropriate parametrization of the shear distortion[15–17] is $a=(1+\delta^2)(1+\delta)a_0$ and $c=(1+\delta^2)(1-2\delta)a_0$. The elastic shear constant $[c_{11}-c_{12}]$, which depends on S_e, is then defined by

$$U((1+\delta^2)(1+\delta)a_0,\,(1+\delta^2)(1-2\delta)a_0)=3[c_{11}-c_{12}]\delta^2\ . \tag{6}$$

Thus, we find that

$$[c_{11}-c_{12}](S_e)=\tfrac{8}{3}a_0^{-3}\frac{\partial^2}{\partial\delta^2}E_b((1+\delta^2)(1+\delta)a_0,\,(1+\delta^2)(1-2\delta)a_0)\ , \tag{7}$$

which is evaluated at $\delta=0$.

We now use a simple phenomenological model for the elastic energy, known as the valence-force-field model,[18] which is particularly useful for a physical interpretation of the numerical results. The tetrahedral bonds of the diamond structure are explicitly included in this model and the elastic energy per bond is determined by three phenomenological parameters. Two of these parameters are force constants, called K_0 and K_1, and the third one is a force, F. They can be directly related to the bulk modulus B, the elastic shear constant $[c_{11}-c_{12}]$, and the pressure p. The change in the energy E_{ij} of a bond between atoms i and j due to an arbitrary distortion is obtained from the corresponding changes in the bond length and in the angles between this bond and the other bonds of the atoms i and j. Thus,[19]

$$\Delta E_{ij}=\frac{K_0(S_e)}{2}(d_{ij}-d_0)^2-F(S_e)(d_{ij}-d_0)+\frac{K_1(S_e)}{4}\left[\sum_k(\cos\theta_{jik}-\cos\theta_0)^2+\sum_k(\cos\theta_{ijk}-\cos\theta_0)^2\right]\ . \tag{8}$$

Here, $d_{ij}=|\mathbf{d}_{ij}|=|\mathbf{R}_j-\mathbf{R}_i|$ is the bond length ($\mathbf{R}_i$ denotes the position of atom i) and d_0 is the equilibrium bond length. The cosine of the angle θ_{jik} between the bonds of atom i to the atoms j and k is obtained from the appropriate scalar product as $\cos\theta_{jik}=\mathbf{d}_{ij}\cdot\mathbf{d}_{ik}|d_{ij}|^{-1}|d_{ik}|^{-1}$. The equilibrium angle θ_0 between tetrahedral bonds corresponds to $\cos\theta_0=-\frac{1}{3}$. The pressure p of the excited electron-hole plasma gives rise to the additional term involving the parameter $F(S_e)$.

Next, we obtain the relation between the macroscopic elastic constants and the parameters of the phenomenological model. From Fig. 1 we can see that the tetrahedral bonds are vectors of the form $\mathbf{d}_{ij}=\mathbf{R}_j-\mathbf{R}_i=\frac{1}{4}(\pm a,\pm a,\pm c)$ and the bond length is $d=\frac{1}{4}(2a^2+c^2)^{1/2}$. Thus, the equilibrium bond length ($a=c=a_0$) is $d_0=\frac{1}{4}\sqrt{3}a_0$. Considering a uniform expansion, which only involves a change in the bond length $d=(1+\delta/3)d_0$, we find from Eqs. (4), (5), and (8) that

$$B(S_e)=\frac{1}{4\sqrt{3}d_0}K_0(S_e) \tag{9}$$

and

$$p(S_e)=\frac{\sqrt{3}}{4d_0^2}F(S_e)\ . \tag{10}$$

A shear distortion, which keeps the volume constant, results in an increase of the bond length given by $d=\frac{1}{4}(2a^2+c^2)^{-1/2}=(1+2\delta^2)d_0$. Two of the three angles θ of each bond with the three other bonds at a given atom are changed according to $\cos\theta-\cos\theta_0=4\delta/3$, and one angle becomes $\cos\theta-\cos\theta_0=-8\delta/3$. Thus, we find from Eq. (8) that the elastic energy per bond is

$$E_{ij}=(-2d_0F+\tfrac{16}{3}K_1)\delta^2\ , \tag{11}$$

and that the elastic shear constant [Eq. (7)] is

$$[c_{11}-c_{12}](S_e)=\frac{\sqrt{3}}{2d_0^3}[\tfrac{8}{3}K_1(S_e)-d_0F(S_e)] \ . \tag{12}$$

The parameters K_0, K_1, and F can be determined from a numerical calculation of the elastic constants using these relations. Alternatively, one can use a simple bond-orbital model (see Appendix B) to obtain qualitative results without needing any computer.

B. Determination of the phonon frequency

We now determine the dependence of the frequency of the transverse-acoustic phonon at the boundary of the Brillouin zone on the density of the electron-hole plasma. We use the valence-force-field model and proceed similarly as Harrison.[8] The wave vector $\mathbf{k}$ of the phonon at the X point is parallel to the (1,1,1) direction, and the transverse displacements of the atoms are described by the unit vectors $\mathbf{e}_1=2^{-1/2}(1,-1,0)$ and $\mathbf{e}_2=6^{-1/2}(1,1,-2)$, which are perpendicular to $\mathbf{k}$. We can use the inversion symmetry of the diamond structure around the bond centers (see Fig. 1), and we find that two atoms move in opposite directions if they are connected by a bond parallel to $\mathbf{k}$. On the other hand, two atoms move parallel to each other if they are connected by a bond that is oblique to $\mathbf{k}$ and provides a much larger rigidity against relative displacements. To calculate the elastic energy of the phonon, we assume that the displacement $\mathbf{x}(t)$ of the atom in position $(a_0/4, a_0/4, a_0/4)$ is given by $\mathbf{x}(t)=\mathbf{e}_1 a \exp(-i\omega t)$ ($\mathbf{e}_1$ might also be replaced by $\mathbf{e}_2$, giving the same final result) and consider the bonds of this atom. As discussed above, the displacement of the atoms at $(a_0/2, 0, 0)$, $(0, a_0/2, 0)$ and $(0, 0, a_0/2)$ are the same, and the corresponding bonds remain unchanged. In contrast, the displacement of the atom at (0,0,0) is opposite to the displacement of the atom at $(a_0/4, a_0/4, a_0/4)$ and equal to $-\mathbf{x}(t)$. Thus the length of this bond increases to $d=(d_0^2+4|\mathbf{x}|^2)^{-1/2}$, giving $d-d_0\simeq 2\alpha^2/d_0$. Note that this results in an important negative contribution in the elastic energy for $F(S_e)>0$, which significantly softens the phonon. In addition, the orientation of this bond changes, resulting in a distortion of the bond angles with the other three bonds and a corresponding positive energy, which determines the phonon frequency at $S_e=0$. The elastic energy ΔE_a per atom is found to be 2 times the change in the average energy ΔE_b of these four bonds; using Eq. (8) we obtain

$$\Delta E_a=\tfrac{1}{2}\kappa|\mathbf{x}(t)|^2 \ , \tag{13}$$

where the effective atomic force constant κ for the transverse-acoustic phonon at the X point is $\kappa=2(\frac{8}{3}K_1 d_0^{-2}-Fd_0^{-1})$, which is simply [Eq. (12)]

$$\kappa=\frac{4}{\sqrt{3}}d_0[c_{11}-c_{12}](S_e) \ . \tag{14}$$

The frequency of the transverse-acoustic phonon at the X point is then given by

$$\omega_{\mathrm{TA}(X)}^2\simeq\frac{\kappa}{M}=\frac{4}{\sqrt{3}}d_0M^{-1}[c_{11}-c_{12}](S_e) \ , \tag{15}$$

if M is the mass of the atom. It is crucial that the force $F(S_e)$ enters into the force constant κ in the same way as into the elastic shear constant.

III. RESULTS

The details of our numerical calculation and the values of parameters, which are independent of the particular element, are presented in Appendix A. The values of those parameters, which are different for each element, are given in Table I. Note that the calculation of the elastic energies is done for constant entropies S_e of the electron gas and that, accordingly, the relative density ξ of electron-hole excitations varies if the structure is distorted. However, it is inconvenient to present the results in terms of the entropy S_e, since S_e is difficult to interpret and cannot be measured. Thus, instead of S_e, we use the relative density $\xi_0(S_e)$ of electron-hole excitations, which is obtained for the undistorted diamond structure $(a=c=a_0)$ from Eq. (A8), to characterize the dependence of the elastic constants and phonon frequencies on the strength of the excitation of the electron gas. Note that ξ_0 is a unique function of S_e and corresponds to the density of the thermalized electron-hole plasma at the instant before any distortion of the lattice has occurred. Thus, it is appropriate to use ξ_0 in the discussion below.

The numerical result for the dependence of the bulk modulus B and the elastic shear constant $[c_{11}-c_{12}]$ of Si on the density ξ_0 of a laser-induced electron-hole plasma is shown together with the result for the pressure p of the plasma in Fig. 2. Note that the volume per atom is kept constant in the calculation of the shear constant. The values of the parameters A_1 and A_2 of the repulsive interaction between atoms [see Eq. (A7)] are chosen in such a way that $p=0$ at the experimental equilibrium bond length (see Table I) and that B agrees with the experimental bulk modulus (Table I) in the absence of excitations ($\xi_0=0$ or, equivalently, $T_e=0$). However, these two parameters have no influence on the dependence of p, B, and $[c_{11}-c_{12}]$ on ξ_0, which is entirely given by the electronic band structure. Our theoretical result for $[c_{11}-c_{12}]$ at $\xi_0=0$ is 1.07×10^{12} ergs cm^{-3}, which is in good agreement with the experimental value[20] of 1.02×10^{12} ergs cm^{-3} and with the result of a similar calculation by Chadi and Martin.[21] Note that this result is independent of the parameters A_1 and A_2.

We obtain an approximately linear increase of $B(\xi_0)$ and $p(\xi_0)$ for increasing values of $\xi_0>0$, whereas the shear constant $[c_{11}-c_{12}](\xi)$ decreases (see Fig. 2). This decrease is more rapid for small ξ_0 than for large ξ_0, since

TABLE I. Various parameters of the tight-binding model.

	C	Si	Ge
d_0 (Å)	1.55	2.35	2.45
ε_s^0 (eV)	-17.52	-13.55	-14.38
ε_p^0 (eV)	-8.97	-6.52	-6.36
B_0 (10^{12} ergs cm^{-3})	5.45	0.99	0.77

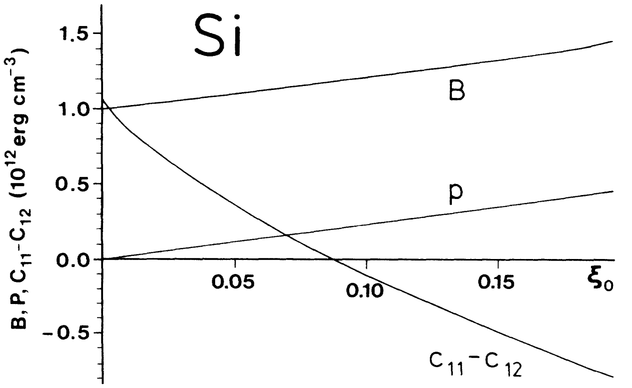

FIG. 2. Numerical results for the dependence of the bulk modulus B, the elastic shear constant $[c_{11}-c_{12}]$, and the internal pressure p of Si on the relative density ξ_0 of a laser-induced electron-hole plasma. Note that elastic distortions around the $T=0$ equilibrium diamond structure are considered.

the temperature T_e of the electron-hole plasma has to increase for an increasing density ξ_0. Note that the first derivative $(\partial/\partial\xi)[c_{11}-c_{12}]$ has a logarithmic singularity for $\xi_0 \rightarrow 0$, as discussed qualitatively in Appendix B; see Eq. (B20). Thus the shape of the curve for $[c_{11}-c_{12}](\xi_0)$ in Fig. 2 is not very accurate for small $\xi_0<0.01$, because of numerical difficulties due to this singularity. However, the results shown in Fig. 2 should be reliable for larger $\xi>0.01$, which are of primary interest. The shear constant vanishes and becomes negative at $\xi_0 \simeq 0.09$, which corresponds to an absolute density of excited electrons of around 1.4×10^{22} cm^{-3}, a value which might well have been reached and exceeded in the experiments.[1,4]

Obviously, the crystal structure cannot develop very rapidly a uniform shear distortion.[22] Instead, one has to consider the instability of phonons. Only the transverse-acoustic phonons, which are related to the elastic shear constant, become unstable in the presence of an electron-hole plasma. The strongest instability results from the phonons with a large wave vector, such as, for example, the transverse-acoustic phonon at the X point. From the valence-force-field theory [Eq. (15)] and from the theoretical result for the elastic shear constant (Fig. 2), we find that the frequency of this phonon is $\omega_{\mathrm{TA}(X)}=3.5\times10^{13}$ sec^{-1} in Si and in the absence of excitation ($\xi_0=0$), using the fact that $M=28.1$ amu. Note that a reasonable quantitative agreement[23] is achieved with the experimental value[3] $\omega_{\mathrm{expt}} \simeq 2.8\times10^{13}$ sec^{-1}. We further obtain from Eq. (15) that the frequency of the phonon decreases for an increasing density ξ_0 of the electron-hole plasma, being roughly proportional to the square root of the elastic shear constant. This results in a considerable softening of the phonon already for small values of ξ_0, as can be seen from the results presented in Table II. The phonon becomes soft around $\xi_0 \simeq 0.09$ and becomes unstable for larger densities of the electron-hole plasma; see Table III.

TABLE II. Dependence of the frequency $\omega_{\mathrm{TA}(X)}$ of the transverse-acoustic phonon at the X point at the boundary of the Brillouin zone and of the time-averaged displacement $\bar{\alpha}$ of the atoms, due to lattice vibrations, on the density ξ_0 of the electron-hole plasma. Note that these results are only valid during a very short time after the excitation of the plasma (see text). The atomic lattice is assumed to be at room temperature ($T_l=300$ K$\equiv$0.03 eV).

ξ_0	$\omega_{\mathrm{TA}(X)}$ (10^{13} s^{-1})	$\bar{\alpha}$ (Å)
0.00	3.5	0.122
0.02	2.8	0.153
0.04	2.3	0.186
0.06	1.7	0.252
0.08	0.9	0.475

Essentially, all transverse-acoustic phonons will become soft or unstable in the same way, and it is interesting to examine the displacement of the atoms around their equilibrium position due to these phonons. We use some simplifying approximations, which have already been introduced in phenomenological theories of melting.[24] Note that there is just one transverse-acoustic phonon mode per atom because only one-third of all phonons are transverse acoustic. The average frequency $\bar{\omega}_{\mathrm{TA}}$ of the transverse-acoustic phonons is estimated[25] to be $\bar{\omega}_{\mathrm{TA}} \simeq \frac{3}{4}\omega_{\mathrm{TA}(X)}$. At ξ_0, this corresponds to a phonon energy of $\hbar\omega_{\mathrm{TA}} \simeq 0.017$ eV. Thus, assuming that the lattice is at room temperature, $k_b T_l \simeq 0.03$ eV, we can use the equipartition theorem[12] to estimate the average displacement $\bar{\alpha}$ of the atoms due to the lattice vibrations at thermal equilibrium. From the average force constant $\bar{\kappa}=M\bar{\omega}^2_{\mathrm{TA}}$ and $\frac{1}{2}\bar{\kappa}\bar{\alpha}^2 \simeq \frac{1}{2}k_B T_l$, we obtain

$$\bar{\alpha}(\xi_0) \simeq \left[\frac{k_B T_l}{M}\right]^{1/2} \left[\tfrac{3}{4}\omega_{\mathrm{TA}(X)}(\xi_0)\right]^{-1} . \tag{16}$$

Without excitation ($\xi_0=0$) we find that $\bar{\alpha}(\xi_0) \simeq 0.122$ Å, which is reasonably small compared to the bond length of 2.35 Å in Si. For an increasing density ξ_0, we obtain a significant increase in the average displacement; see Table II. Note that $\bar{\alpha}(\xi_0) \propto [\omega_{\mathrm{TA}}(\xi_0)]^{-1}$ diverges as the phonons become soft. The frequency of the transverse-

TABLE III. Dependence of the phonon frequency $\omega_{\mathrm{TA}(X)}$ (see caption of Table II) on the density ξ_0. Note that the phonon becomes unstable for these large values of ξ_0 and that the frequency is thus imaginary. $\bar{\alpha}(t_1)$ is an estimate for the average displacement of the atoms at $t_1=100$ fs after the generation of the electron-hole plasma, and t_m is approximate lower limit for the time when the crystal begins to melt.

ξ_0	$\omega_{\mathrm{TA}(X)}$ (10^{13} s^{-1})	$\bar{\alpha}(t_1)$ (Å)	t_m (fs)
0.10	1.1i	0.278	330
0.12	1.8i	0.471	204
0.14	2.2i	0.635	167
0.16	2.5i	0.796	145
0.18	2.8i	0.996	130

acoustic phonons becomes imaginary if the density of the electron-hole plasma is further increased [for $\xi_0 > 0.09$, it is $\omega_{\mathrm{TA}}^2(\xi_0) \propto [c_{11} - c_{12}](\xi_0) < 0$], and the displacement $\mathbf{x}(t)$ of the atoms thus increases exponentially in time, instead of doing the usual oscillation. Neglecting anharmonic forces, we find that the average displacement $\bar{\alpha}(t)$ at a time t after the excitation of the plasma is

$$\bar{\alpha}(t) \simeq \bar{\alpha}_0 \exp(-i\bar{\omega}_{\mathrm{TA}} t) \simeq \bar{\alpha}_0 \exp(\tfrac{3}{4}|\omega_{\mathrm{TA}(X)}|t) , \tag{17}$$

where $\bar{\alpha}_0 \simeq 0.122$ Å is the average displacement before the excitation (at $\xi_0 = 0$). Based on this exponential growth, we now estimate the minimum time required for melting. The distance between the atoms in the planes perpendicularly to the tetrahedral bonds (see Fig. 1) is $D = a_0/\sqrt{2} = 2(\frac{2}{3})^{1/2} d_0$. The network structure of the bonds[18] is destroyed if the average displacement becomes too large in comparison to this distance, $\bar{\alpha}(t) > D/2$. Thus the crystal could only begin to melt a certain time t_m after the excitation of the plasma. From the condition $\bar{\alpha}(t_m) = D/2$ and Eq. (17), we obtain the estimate

$$t_m \simeq \tfrac{4}{3} \omega_{\mathrm{TA}(X)}^{-1} \ln(D/2\alpha_0) . \tag{18}$$

Results for the average displacement $\bar{\alpha}(t_1)$ at $t_1 = 100$ fs after the excitation of the electron-hole plasma and for the time t_m are shown in Table III. Note that $\bar{\alpha}$ is expected to be slightly too large and t_m to be somewhat too small because anharmonic forces, which would moderate the exponential growth, are neglected in Eqs. (17) and (18). However, we conclude that the displacement $\bar{\alpha}(t_1)$ becomes a significant fraction of the lattice constant, such that the symmetries of the diamond lattice are destroyed within 100 fs after the excitation of a sufficiently dense plasma. Further, our results for t_m indicate that the crystal should begin to melt in the presence of the plasma within a time of around 200–300 fs. Thus, these results are in good agreement with the experiment[1] on laser-induced disorder in crystalline Si surfaces.

It is of interest to discuss whether our theory could also shed some light on laser-induced annealing of amorphous Si layers. Pulsed lasers have been used in these earlier experiments[8] to anneal layers of amorphous Si on a single-crystal substrate. A conversion of the amorphous layer to coarse-grained polycrystalline Si has already been obtained at rather low laser fluences, which could not have fully melted the amorphous layer. Thus it is not possible that the crystalline-Si layer has grown epitaxially from the liquid Si on the crystalline support. Instead, the usual explanation[8] assumes that the laser has melted only a narrow surface region, being a small fraction of the amorphous layer, and that crystalline Si then resolidifies from the molten surface region. Note that amorphous Si melts at temperatures much lower than the melting point of crystalline Si. Thus it is expected that a melt front propagates inwards through the entire layer of amorphous Si, leaving behind a fully crystalline Si layer. In contrast to this interpretation, Van Vechten *et al.*[9] have argued that the surface region might not have melted and recrystallized during this annealing process. They have suggested that the rather dense electron-hole plasma, which is excited by the absorbed laser light, might decrease the rigidity of small crystalline regions, existing within the amorphous phase, with respect to shear distortions. Thus, these microcrystals become soft (or plastic), without losing the tetrahedral bonding network of the diamond structure. A spontaneous nonthermal reconstruction of the amorphous regions in between the microcrystals might then become possible, since the energy barrier against annealing, due to the rigidity of the microcrystals, is eliminated. We can conclude from our theoretical results that the rigidity of the diamond lattice against shear distortions is indeed reduced in the presence of an electron-hole plasma. This might have an important effect on the solidification of liquid Si to crystalline Si following the melt-front propagation.[8] On the other hand, Van Vechten's alternative model[9] requires that crystalline Si has a plastic phase for high densities, ξ, of the electron-hole plasma (e.g., $[c_{11} - c_{12}](\xi) \to 0$ for increasing ξ), in order to make a nonthermal annealing effective. However, assuming that the crystal does not expand significantly, we do not obtain such a plastic phase. Instead, the diamond structure becomes unstable ($[c_{11} - c_{12}](\xi) \ll 0$) if ξ exceeds a critical value, and rapid melting is expected, as discussed previously. Thus, there should be strong competition between nonthermal annealing processes and melting in amorphous Si after the excitation of an electron-hole plasma. Clearly, though, more theoretical work is necessary, particularly with respect to the time-dependent changes in the atomic structure.

The dependence of the parameters K_0, K_1, and F of the valence-force-field model on the density ξ_0 of the plasma is obtained from the numerical results (Fig. 2) using Eqs. (9), (10), and (12). The results are shown in Fig. 3 using dimensionless atomic units, which are convenient for a theoretical discussion. It is interesting to make a comparison with the analytical results of the simple theory presented in Appendix B, which depend only on the bond length of Si ($d_0 = 4.43$ a.u.). In Appendix B we

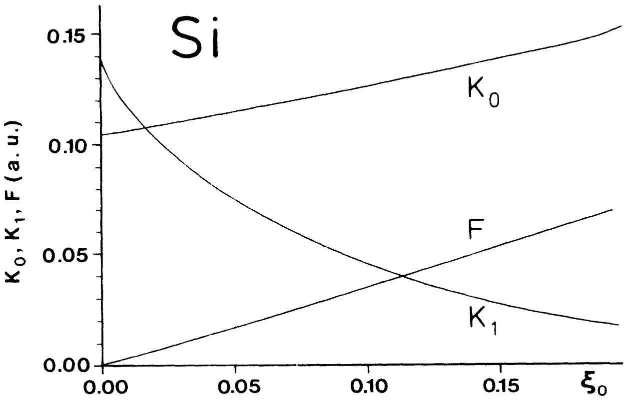

FIG. 3. Phenomenological parameters K_0, K_1, and F of the valence-force-field model [see Eq. (8)], derived from the numerical results presented in Fig. 2. Note that these results are given in a.u. and that 1 a.u. corresponds to the following physical units: 96.8 eV Å^{-2} for K_0, 27.2 eV for K_1, and 51.3 eV Å^{-1} for F.

find that K_0 and F should increase roughly linearly with ξ_0 with a coefficient between 0.21 and 0.24 [using Eqs. (B22) and (B14)] for K_0 and between 0.31 and 0.36 [Eqs. (B23) and (B15)] for F. This is in good quantitative agreement with the results of Fig. 3, which also show a nearly linear increase with a coefficient, which is approximately 0.23 for K_0 and 0.35 for F. For $\xi_0=0$ we find from Appendix B that $K_0=0.146$ [Eq. (B7)], which agrees rather well with the numerical value of $K_0=0.138$ (Fig. 3). The dependence of K_1 on ξ_0 is qualitatively well reproduced, but the decrease of $K_1(\xi_0)$ for small ξ_0 [Eq. (B19)] is overestimated by a factor of about 3 (see discussion in Appendix B). It is important to note that the force constant K_1 remains positive throughout the region, where the elastic shear constant becomes negative and where the diamond structure becomes unstable. Thus the rigidity of the lattice against bond-angle distortions is effectively only reduced, but not lost in the presence of the electron-hole plasma. The diamond lattice thus only becomes instable because of the pressure p of the excited plasma and because the crystal cannot expand rapidly enough to a new equilibrium lattice constant.[26,27]

The numerical results for the elastic constants of C (see Fig. 4) and Ge are very similar to the results for Si (see Fig. 2). The theoretical results for the elastic shear constant $[c_{11}-c_{12}]$ at $\xi_0=0$ (or $T=0$) are 9.37×10^{12} ergs cm^{-3} for C and 0.80×10^{12} ergs cm^{-3} for Ge. Both are in good agreement with the experimental values of 9.51×10^{12} ergs cm^{-3} for C (Ref. 28) and 0.81×10^{12} ergs cm^{-3} for Ge.[20] The dependence of the shear constant of C and of Ge on ξ_0 is then almost the same as for Si, if the shear constant is scaled by an appropriate constant factor. Most important, the shear constant vanishes for $\xi_0 \simeq 9\%$ for all three elements. Note that this is in agreement with the main result of Appendix B [Eq. (B25)], which indicates that the dependence of the shear constant on the bond length and the density of an electron-hole plasma should be roughly the same for C, Si, and Ge.

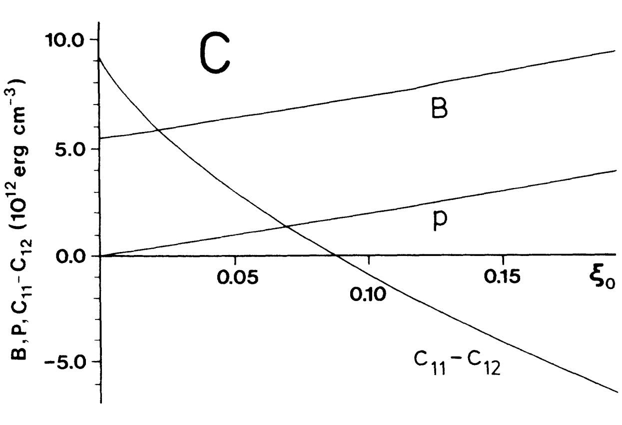

FIG. 4. Numerical results for the bulk modulus B, the elastic shear constant $[c_{11}-c_{12}]$, and the internal pressure p of carbon in the diamond structure, depending on the relative density ξ_0 of a laser-induced electron-hole plasma.

In summary, a simple tight-binding model has been used to examine the instability of the diamond lattice resulting from a laser-induced dense electron-hole plasma. We find that the transverse-acoustic phonons of the diamond lattice of Si, Ge, and C become unstable if more than about 9% of the valence electrons are excited into the conduction band. Thus, the symmetries of the diamond structure are very rapidly destroyed, leading afterwards to a similarly rapid melting of the crystal. The crystal does not become unstable for smaller densities of the electron-hole plasma, but a significant softening of the transverse-acoustic phonons is expected. This explains the main experimental facts[1] referred to in the Introduction.

APPENDIX A

We use a tight-binding model to calculate the cohesive energy per bond, as well as the electronic entropy and the density of the electron-hole excitations for finite temperatures of the electron gas. First, the total cohesive energy per tetrahedral bond is given by[18,29,30]

$$E_b=E_c+E_r\ , \tag{A1}$$

where E_c is an attractive energy due to occupation of bonding electronic orbitals and E_r is a repulsive energy between the atoms, which determines the bond length. E_c is determined from the electronic density of states $\rho(\varepsilon)$ of the semiconductor, which we obtain from a tight-binding Hamiltonian H.[18] Note that we suppress the spin indices because we consider a nonmagnetic system and that we use atomic units ($\hbar=e=m_e=1$) in our calculation. Thus,

$$H=\sum_{i,\alpha}\varepsilon_\alpha^0 c_{i\alpha}^+ c_{i\alpha}+\sum_{i,\alpha,j,\beta} t_{i\alpha,j\beta}c_{i\alpha}^+ c_{j\beta}\ , \tag{A2}$$

where α and β denote the atomic orbitals (s,p_x,p_y,p_z), and the ε_α^0 are the energies of these orbitals for the free atoms (see Table I). It is convenient to use a face-centered tetragonal lattice containing eight atoms and 16 tetrahedral bonds (see Fig. 1). Only hopping between nearest-neighbor atoms i and j (corresponding to the tetrahedral bonds) is included in H, and we use Harrison's universal parametrization for the hopping elements t. If $\mathbf{n}=\mathbf{d}_{ij}/d$ is the unit vector in the bond direction $\mathbf{d}_{ij}=\mathbf{R}_j-\mathbf{R}_i$, we obtain

$$\begin{aligned} t_{isjs}&=\eta_{ss\sigma}d^{-2}\ ,\\ t_{ip_\mu js}&=n_\mu\eta_{sp\sigma}d^{-2}=-t_{isjp_\mu}\ ,\\ t_{ip_\mu jp_\nu}&=[n_\mu n_\nu(\eta_{pp\sigma}-\eta_{pp\pi})+\delta_{\mu\nu}\eta_{pp\pi}]d^{-2}\ , \end{aligned} \tag{A3}$$

where μ and $\nu=1,2,3$. We use $\eta_{ss\sigma}=-1.4$, $\eta_{sp\sigma}=1.84$, $\eta_{pp\sigma}=3.24$, and $\eta_{pp\pi}=-0.81$. These values have been obtained by Harrison from a fitting to the band structures of C, Si, and Ge. This Hamiltonian results in a band structure with a valence band and a direct gap which are in good agreement with the band structures of these semiconductors. The conduction band is only roughly approximated and one does not obtain an indirect gap below the direct gap. However, the overall density of states of the conduction band is reasonably well reproduced, and fairly good results are obtained for the dielectric constant that is related to the structural stability.[2,18] Note, that the d^{-2} dependence of the hopping elements relates rather well the different band structures[18] of C, Si, and Ge to the different bond lengths d. An increase in d results in a decreasing bandwidth and a decreasing gap. Similarly, the changes in the band structure of one element due to a small change in the bond length (e.g., in the case of elastic distortions) is well reproduced.

The electronic density of states per bond $\rho(\varepsilon)$ is obtained by diagonalizing the Hamiltonian H, using the periodicity of the lattice and normalizing $\rho(\varepsilon)$ to four effective tight-binding electron states per bond $\int_{-\infty}^{+\infty}d\varepsilon\,\rho(\varepsilon)=4$, which corresponds to the basis of eight different electronic orbitals (if spin is included) per atom. For finite temperatures, $\beta_e=(k_BT_e)^{-1}$, of the electron gas, one gets

$$E_c=\left[\int_{-\infty}^{+\infty}d\varepsilon\,\varepsilon f(\varepsilon)\rho(\varepsilon)\right]-(\varepsilon_s^0+\varepsilon_p^0)\ , \tag{A4}$$

where $f(\varepsilon)=\{1+\exp[\beta_e(\varepsilon-\mu)]\}^{-1}$ is the Fermi-Dirac distribution. The chemical potential μ depends on T_e and it has to be determined to give the correct number of two electrons per bond,

$$\int_{-\infty}^{+\infty}d\varepsilon\,f(\varepsilon)\rho(\varepsilon)=2\ . \tag{A5}$$

The electronic entropy S_e results from the fractional occupation $f(\varepsilon)$ of the electronic states and is given by[12]

$$S_e=-k_B\int d\varepsilon\,\rho(\varepsilon)\{f(\varepsilon)\ln f(\varepsilon)+[1-f(\varepsilon)]\times\ln[1-f(\varepsilon)]\}\ . \tag{A6}$$

In our numerical work we replace the integration by an appropriate sum over special points in the first Brillouin zone for the face-centered tetragonal lattice. A sum using 16 inequivalent points has given almost the same results as a sum based on 54 points, with a relative error of less than 1%. The convergence of the sum is very rapid because of the high electronic temperatures and the presence of a gap around the chemical potential μ. The results presented in this article are based on the sum using 16 points, which is thus accurate enough. It should be noted that these 16 points correspond to 64 inequivalent points in the first Brillouin zone of the diamond lattice.

The repulsive energy per bond, E_r, is mainly due to an increase in the kinetic energy of the electrons upon compression of the bond, and accounts for the effects due to the nonorthogonality of the atomic orbitals.[29-31] This energy should be nearly temperature independent because it depends essentially only on the total number of electrons, which is temperature independent. We use a simple Born-Meyer form,

$$E_r(d)=A_1\exp[-A_2(d-d_0)]\ , \tag{A7}$$

where $d_0=\frac{1}{4}\sqrt{3}a_0$ and parameters A_1 and A_2. Without excitation ($\xi=T_e=0$), the total energy per bond has to give a mechanical equilibrium at $a=c=a_0$ and the correct bulk modulus B_0. Thus, the values of A_1 and A_2 are determined using Eqs. (4) and (5) together with the conditions $p(0)=0$ and $B(0)=B_0$, respectively.

The relative density ξ of the electron-hole excitations in comparison to the total density of valence electrons is obtained from the number of holes in the valence band. Thus,

$$\xi=\frac{1}{2}\int_{-\infty}^{\varepsilon_F}d\varepsilon[1-f(\varepsilon)]\rho(\varepsilon)\ , \tag{A8}$$

where ε_F lies in the gap and corresponds to the Fermi energy at $T_e=0$. The factor $\frac{1}{2}$ arises because there are two electrons per bond and $\int_{-\infty}^{\varepsilon_F}d\varepsilon\,\rho(\varepsilon)=2$. The absolute density of the electron-hole excitations is then given by $32a_0^{-3}\xi$.

APPENDIX B

The tight-binding Hamiltonian H yields rather complex valence and conduction bands. However, a simple discussion of the stability of the diamond structure not requiring extensive numerical work is possible if one uses the bond-orbital approximation.[18] Four different hybridized sp^3 orbitals are formed at each atom, pointing in the directions of its four tetrahedral bonds. Due to the tetragonal symmetry of the distorted diamond lattice, all bonds are equivalent to each other, and it is sufficient to consider just one bond (see Fig. 1). We consider the bond between the atom at the position (0,0,0) and the atom at $(a/4, a/4, c/4)$. The sp^3-hybrid orbitals pointing from these atoms in the direction of their mutual bond are represented by $|h_1\rangle=(|1,s\rangle+|1,p_x\rangle+|1,p_y\rangle+|1,p_z\rangle)/2$ for the first atom, and $|h_2\rangle=(|2,s\rangle-|2,p_x\rangle-|2,p_y\rangle-|2,p_z\rangle)/2$ for the second atom, where $|i,\alpha\rangle$ denotes the atomic orbital α of atom i. We can now form a bonding orbital $|b\rangle=2^{-1/2}(|h_1\rangle+|h_2\rangle)$, which roughly represents the valence band, and an antibonding orbital $|a\rangle=2^{-1/2}(|h_1\rangle-|h_2\rangle)$ representing the conduction band. The energy of the bonding orbital is [using Eqs. (A2) and (A3) for H]

$$\varepsilon_b=\langle b|H|b\rangle=\varepsilon_h+d^{-2}\eta_h\ , \tag{B1}$$

and that of the antibonding orbital is

$$\varepsilon_a=\langle a|H|a\rangle=\varepsilon_h-d^{-2}\eta_h\ , \tag{B2}$$

where

$$\varepsilon_h=\tfrac{1}{4}(\varepsilon_s^0+3\varepsilon_p^0) \tag{B3}$$

and

$$\eta_h=\tfrac{1}{4}[\eta_{ss\sigma}-3\eta_{pp\pi}-2(n_1+n_2+n_3)\eta_{sp\sigma}-(n_1+n_2+n_3)^2(\eta_{pp\sigma}-\eta_{pp\pi})]\ . \tag{B4}$$

The values for the parameters η are given in Appendix A, and $n_1=n_2=\frac{1}{4}a/d$ and $n_3=\frac{1}{4}c/d$ in the case of the tetragonal symmetry of Fig. 1. If there is no shear distortion ($a=c$), we find that $n_1=n_2=n_3=1/\sqrt{3}$, and thus

$$\eta_h\equiv\eta_0=\tfrac{1}{4}[\eta_{ss\sigma}-(3+2\sqrt{3})\eta_{sp\sigma}]=-3.32\ . \tag{B5}$$

Without electron-hole excitations ($\xi=0$ and thus $T_e=0$), the valence band is filled and we can approximate the electronic band-structure energy per bond (containing two electrons) as $E_c \simeq 2\varepsilon_b$. The repulsive energy E_r is adjusted such that the correct equilibrium bond length and bulk modulus is obtained. The dependence of the total energy on the bond length is thus, using Eqs. (8) and (9),

$$E_b(0) \simeq 2\varepsilon_b + E_r = 2\sqrt{3} d_0 B_0 (d-d_0)^2 + \text{const} \tag{B6}$$

for uniform contractions ($a=c$). To obtain an estimate for K_1 at $\xi=0$, we have to consider the change of η_h upon a shear distortion (characterized by the parameter δ), due to the change in bond angles. It is $n_1=n_2=(1-\delta^2)(1+\delta)/\sqrt{3}$ and $n_3=(1-\delta^2)(1-2\delta)/\sqrt{3}$; thus $n_1+n_2+n_3=\sqrt{3}(1-\delta^2)$ and it follows from Eq. (B4) that

$$\eta_h(\delta)=\eta_0+\sqrt{3}/2[\eta_{sp\sigma}+\sqrt{3}(\eta_{pp\sigma}-\eta_{pp\pi})]\delta^2 \;.$$

The repulsive energy E_r depends only on the bond length and is independent of the angle between bonds. Thus we obtain, from Eqs. (11), (A1), and (B1),

$$K_1(0)=\frac{3}{32}\frac{\partial^2}{\partial\delta^2}E_c \simeq \tfrac{3}{16} d_0^{-2} \frac{\partial^2}{\partial\delta^2}\eta_h \;,$$

which results in

$$K_1(0) \simeq \frac{3\sqrt{3}}{16 d_0^2}[\eta_{sp\sigma}+\sqrt{3}(\eta_{pp\sigma}-\eta_{pp\pi})]=2.87 d_0^{-2} \;. \tag{B7}$$

Note that this result for the angular force constant of semiconductors in their ground state has already been obtained by Harrison using a different geometry.[18]

A finite density ξ of the electron-hole excitations results in a corresponding change in the total energy and thus in the force constants. These changes are obtained from the average excitation energy, which depends on the electronic density of states and the temperature T_e of the electron gas. For the rather qualitative arguments of this appendix, we assume that ξ remains constant. Actually, our numerical results indicate that ξ depends only weakly on small distortions of the diamond lattice and that the small changes in ξ have only a minor influence on the elastic constants.

For small ξ and correspondingly low T_e, the electron-hole excitations are located around the gap. Thus the important hole states are at the top of the valence band. They can be roughly represented by the states at the Λ point ($\mathbf{k}=\mathbf{0}$), which have pure p-like character. Their energy is given by the p-p hopping elements and the fourfold coordination of the atoms. Thus the energies for the p_x- and p_y-like states are [Eqs. (A2) and (A3)]

$$\varepsilon_{p_x}=\varepsilon_{p_y}=\varepsilon_p^0-4d^{-2}[n_1^2(\eta_{pp\sigma}-\eta_{pp\pi})+\eta_{pp\pi}] \;, \tag{B8}$$

and, for the p_z-like state,

$$\varepsilon_{p_z}=\varepsilon_p^0-4d^{-2}[n_3^2(\eta_{pp\sigma}-\eta_{pp\pi})+\eta_{pp\pi}] \;. \tag{B9}$$

Similarly, the relevant electron states at the bottom of the conduction band have mainly s-like character. They are represented by the corresponding state at the Λ point, which has pure s-like symmetry. Its energy is

$$\varepsilon_s=\varepsilon_s^0-4d^{-2}\eta_{ss\sigma} \;. \tag{B10}$$

The energies of the electron-hole excitations around the direct gap are then approximated as $\varepsilon_s-\varepsilon_{p_\mu}$. The dependence on small shear distortions in first order in $\delta \simeq 0$ is

$$\varepsilon_s-\varepsilon_{p_x}=\varepsilon_s-\varepsilon_{p_y} \simeq \varepsilon_s-\bar{\varepsilon}_p+\tfrac{8}{3}d^{-2}(\eta_{pp\sigma}-\eta_{pp\pi})\delta \tag{B11}$$

and

$$\varepsilon_s-\varepsilon_{p_z} \simeq \varepsilon_s-\bar{\varepsilon}_p-\tfrac{16}{3}d^{-2}(\eta_{pp\sigma}-\eta_{pp\pi})\delta \;, \tag{B12}$$

where

$$\begin{aligned}\varepsilon_s-\bar{\varepsilon}_p &= \varepsilon_s^0-\varepsilon_p^0+\tfrac{4}{3}d^{-2}(\eta_{pp\sigma}+2\eta_{pp\pi}-3\eta_{ss\sigma}) \\ &= \varepsilon_s^0-\varepsilon_p^0+7.76d^{-2}\end{aligned} \tag{B13}$$

is the average energy of the electron-hole excitations, which depends only on the bond length. The total number of electron-hole excitations per bond is 2ξ. Thus, the change in the total energy per bond due to uniform changes in the bond length is given by $E_b(\xi) \simeq E_b(0)+2\xi(\varepsilon_s-\bar{\varepsilon}_p)$. Expanding $d^{-2} \simeq d_0^{-2}-2d_0^{-3}(d-d_0)+3d_0^{-4}(d-d_0)^2$, we obtain, from Eq. (8) (using the numerical values derived above),

$$F(\xi) \simeq 31.04 d_0^{-3}\xi \;, \tag{B14}$$

and, together with Eq. (2),

$$K_0(\xi)=4\sqrt{3}d_0 B_0+93.1 d_0^{-4}\xi \;, \tag{B15}$$

for small ξ. It can thus be clearly seen that the presence of an electron-hole plasma results in a large pressure, $p(\xi) \propto d_0^{-2}F(\xi) \propto d_0^{-5}\xi$, at the ground-state equilibrium bond length. Considering shear distortions, we observe that the energy of an electron-hole excitation with a p_x- or p_y-like hole state increases for an increasing distortion parameter δ, whereas the energy of the excitation with a p_z-like hole state decreases at the same time. At finite temperatures T_e, the number of excitations with decreasing energy increases and the number of excitations with increasing energy decreases. Thus the average energy of the electron-hole plasma decreases upon a shear distortion, resulting in a decrease (or softening) of the effective shear constant. The thermal average of the excitation energy is

$$E_x \simeq \sum_{\mu=1}^{3}(\varepsilon_s-\varepsilon_{p_\mu})[1-f(\varepsilon_{p_\mu})] \Big/ \sum_{\mu=1}^{3}[1-f(\varepsilon_{p_\mu})] \;, \tag{B16}$$

where $1-f(\varepsilon_{p_\mu})$ is the number of holes. For small $\varepsilon_{p_\mu}-\bar{\varepsilon}_p \propto \delta$, we obtain that $1-f(\varepsilon_{p_\mu}) \simeq 1-f(\bar{\varepsilon}_p)+f(\bar{\varepsilon}_p)[1-f(\bar{\varepsilon}_p)]\beta_e(\varepsilon_{p_\mu}-\bar{\varepsilon}_p)$. Thus the sum of Eq. (B16) can be easily evaluated as

$$E_x(\xi) \simeq (\varepsilon_s-\bar{\varepsilon}_p)-\frac{\beta_e f(\bar{\varepsilon}_p)}{3}\sum_{\mu=1}^{3}\varepsilon_{p_\mu}^2 \;,$$

which results in

$$E_x(\xi)\simeq(\varepsilon_s-\bar{\varepsilon}_p)-\tfrac{128}{9}\beta_e f(\bar{\varepsilon}_p)(\eta_{pp\sigma}-\eta_{pp\pi})^2 d^{-4}\delta^2 \,, \tag{B17}$$

where we have been using Eqs. (B11) and (B12). For small $\xi\simeq 0$ it is $f(\bar{\varepsilon}_p)\simeq 1-\xi\simeq 1$. The temperature required to give a finite ξ can qualitatively be estimated from the difference between the energies of the bonding and antibonding orbitals (representing the valence and conduction bands, respectively). The chemical potential is approximately in the middle of the gap; thus $\mu\simeq(\varepsilon_b+\varepsilon_a)/2$ and $\xi\simeq\exp[-\beta_e(\varepsilon_a-\varepsilon_b)/2)]$. It follows [Eqs. (B2)–(B5)] that $\beta_e\simeq d_0^2\eta_0^{-1}|\ln\xi|$ and we obtain, from Eq. (B17), to second order in δ,

$$E_x\simeq(\varepsilon_s-\bar{\varepsilon}_p)-d_0^{-2}\frac{128}{9\eta_0}(\eta_{pp\sigma}-\eta_{pp\pi})^2\delta^2|\ln\xi| \,. \tag{B18}$$

The total energy per bond is $E_b(\xi)\simeq E_b(0)+2\xi E_x$ and the angular force constant K_1 [see Eq. (11)] is given by $K_1(\xi)=\frac{3}{32}[(\partial^2/\partial\delta^2)E_b(\xi)+4d_0F(\xi)]$, where the second term eliminates the effect of the bond-length expansion ($\propto\delta^2$). Thus,

$$\begin{aligned} K_1(\xi)&\simeq K_1(0)-d^{-2}\tfrac{16}{3}\eta_0^{-1}(\eta_{pp\sigma}-\eta_{pp\pi})^2\xi/|\ln\xi| \\ &\simeq d_0^{-2}(2.87-26.3\xi|\ln\xi|) \end{aligned} \tag{B19}$$

for small ξ. Note that the first derivative of $K_1(\xi)$ with respect to ξ has a logarithmic singularity at $\xi=0$, because the temperature $T_e\rightarrow 0$ for $\xi\rightarrow 0$. The dependence of the shear constant on ξ is then

$$[c_{11}-c_{12}](\xi)\simeq d_0^{-5}(6.62-11.5\xi-60.6\xi|\ln\xi|) \,. \tag{B20}$$

The shear constant decreases for increasing ξ, but not linearly, in contrast to the roughly linear dependence of K_0 and F on ξ. We expect that Eq. (B20) overestimates the effect of the holes on the shear constant, because the majority of the electron-hole excitations depends less on a shear distortion of the lattice than the electron-hole excitations at the top of the valence band (note that, e.g., the bottom of the valence band is of pure s-like symmetry, and the energy of this hole state does not depend on a shear distortion).

Considering large densities, $\xi\rightarrow 0.5$ (which require high temperatures T_e), we observe that the electron-hole excitations have to be distributed on the whole valence and conduction bands. A rough estimate of the average energy of the electron-hole excitations is the obtained from the difference between energies of the bonding and antibonding orbitals; thus $E_x\simeq\varepsilon_a-\varepsilon_b$ and the total energy per bond becomes

$$E_b(\xi)=E_b(0)+4d^{-2}\eta_h\xi=-2d^{-2}\eta_h(1-2\xi)+E_r \,. \tag{B21}$$

As before, we expand in a Taylor series around $d=d_0$ and obtain

$$F(\xi)\simeq-8\eta_0 d_0^{-3}\xi=26.6d_0^{-3}>0 \tag{B22}$$

and

$$K_0(\xi)\simeq(4\sqrt{3})d_0B_0-24\eta_0 d_0^{-4}\xi \tag{B23}$$

for $\xi\rightarrow 0.5$. In comparison with the results for small ξ [Eqs. (B14) and (B15)], we see that a linear increase of $f(\xi)$ and $K_0(\xi)$ with ξ is predicted in both cases with nearly the same coefficient (the relative deviation is less than 20%). Thus we expect that a linear behavior approximately holds for all ξ, including intermediate values. Note that the dependence of the angular force constant $K_1(\xi)$ on ξ is of a rather different nature. From Eq. (B11) one would find that $K_1(\xi)\simeq(1-2\xi)K_1(0)$ for $\xi\rightarrow 0.5$. This is in strong contrast to the decrease of K_1 obtained for small ξ from Eq. (B20), which is several times as large. Thus one would expect that $K_1(\xi)$ first decreases rather rapidly, and then levels off, approaching zero slowly for large ξ. Thus, the shear constant becomes [Eq. (12)]

$$[c_{11}-c_{12}](\xi)\rightarrow-22.7d_0^{-5}\xi<0 \,, \tag{B24}$$

due to $K_1(\xi)\simeq 0$ and the presence of a positive F. Note that the shear constant becomes negative only because of the force F (acting along the bond direction) due to the presence of an electron-hole plasma.

We observe that the shear constant is, for a given value of ξ, always directly proportional to d_0^{-5} in Eqs. (B20) and (B24), and we thus expect that the shear constant could be described by the universal form

$$[c_{11}-c_{12}](\xi)\simeq 6.62d_0^{-5}g(\xi) \,, \tag{B25}$$

where $g(\xi)$ is approximately the same function [with $g(0)\simeq 1$ and $g(0.09)\simeq 0$] for all three group-IV elements C, Si, and Ge.

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[11] Heat exchange between an electron gas and a lattice occurs on a time scale of 10^4 fs (Ref. 6), and thus only about 1% of the energy of the electron-hole plasma could have been lost as heat to the lattice during the occurrence of the instability of the diamond structure.

[12] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980), Pt. 1.

[13] Note that an electron and a hole can recombine, the excess energy being absorbed by an additional electron; the inverse process is also possible. This is especially important for large distortions of the diamond structure, when the valence and conduction bands begin to overlap. Without a gap at the Fermi level, only the entropy and the temperature of the electron gas are well-defined quantities.

[14] Note that the velocity of longitudinal sound in Si is on the order of $c_l \simeq 10\,000 \text{ m s}^{-1}$ (as estimated from the dispersion of longitudinal-acoustic waves; see Ref. 2), and the typical size of the excited regions is $L > 1000$ Å; thus the typical time required for volume expansion is $t \simeq L/c_l > 10\,000$ fs.

[15] C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1953).

[16] C. Kittel, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Oliver and Boyd, London, 1966).

[17] Note that the usual way of writing the shear distortion would be $a = (1+\delta)a_0$ and $c = (1-2\delta)a_0$; see Refs. 15 and 16. This would result in an artificial contraction of the volume by $V(\delta) \simeq (1-3\delta^2)V(0)$ and an additional energy density (due to the artificial compression) of $3p(S_e)\delta^2$. Thus one would obtain a value for the shear constant which, wrongly, would be too high by $p(S_e)$.

[18] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[19] Note that our definition of K_1 is slightly different from the definition used by Harrison. Our definition is more convenient for the calculation of elastic properties.

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[22] Note that the speed of such a uniform distortion is limited by the velocity of sound, as is similar for a uniform expansion (Ref. 14).

[23] The theoretical result for the phonon frequency is somewhat higher, because the simple valence-force-field model [Eq. (8)] results in a force constant κ [Eq. (14)], which is systematically too high. Note that covalent bonding gives rise to effective forces of long range (Ref. 18) that are not included in Eq. (10).

[24] A. R. Ubbelohde, *The Molten State of Matter* (Wiley, New York, 1978).

[25] In a very simple approximation, see Refs. 18 and 23, we assume a linear dispersion $\omega_{\mathrm{TA}}(\mathbf{k}) \simeq c|k|$ for the transverse-acoustic phonons and a spherical Brillouin zone. Calculating the average of $\omega_{\mathrm{TA}}(\mathbf{k})$ in the $\mathbf{k}$-space region with $|\mathbf{k}| < k_{\max} \simeq c/\omega_{\mathrm{TA}(X)}$, we obtain $\bar{\omega}_{\mathrm{TA}} \simeq \frac{3}{4}\omega_{\mathrm{TA}(X)}$.

[26] Note the similarity to the phase transition of Si from the diamond structure to a β-tin structure at high applied pressures, which arises as a reaction to the isotropic compression of the lattice. The new equilibrium bond length of the diamond structure after the excitation of an electron-hole plasma is, in principle, given as $d(p) \simeq d_0 + p/B$, but note that the inertial mass of the Si atoms does not allow a rapid volume expansion (Ref. 14), resulting in a large effective pressure for short time scales.

[27] Using Eq. (12) and observing that $F=0$ at the expanded bond length $d > d_0$, we find that the elastic shear constant remains positive because $[c_{11} - c_{12}] \simeq 2.31 d^{-3} K_1 > 0$.

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