Theory for the Dependence of Optical Second Harmonic Generation Intensity on Non-equilibrium Electron Temperatures at Metal Surfaces

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Abstract

We present a theory for the electron-temperature dependence $T_{el}$ of optical second harmonic generation (SHG). Such an analysis is required to study the dynamics of metallic systems with many hot electrons not at equilibrium with the lattice. Using a tight-binding theory for the nonlinear susceptibility $\chi^{(2)}(\omega, T_{el})$ and the Fresnel coefficients we present results for the SHG intensity $I^{(2)}(\omega, T_{el})$ for a Cu monolayer. In the case of linear optical response we find that the intensity will decrease monotonously for increasing $T_{el}$. In agreement with experiment we find a frequency range where $I^{(2)}(\omega, T_{el})$ may be enhanced or reduced depending on electron temperature. Note, $\chi^{(2)}(\omega, T_{el})$ rather than the Fresnel coefficients determines essentially the temperature dependence. Our theory yields also that SHG probes effects due to hot electrons more sensitively than linear optics. We also discuss the $T_{el}$-dependence of SHG for Au and Ag.

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I. INTRODUCTION

Due to its surface sensitivity, the nonlinear optical response has become a powerful probe for investigating the electronic structure of surfaces, interfaces, thin films, and multilayers. Recently, a combination of linear and nonlinear experiments [1] has been performed exploiting the time dependence of SHG. Thus, effects of hot electrons not at equilibrium with the lattice and their changes in time can be analyzed. This opens a new route to investigate the dynamics of the system during relaxation to the equilibrium state. Note, different electronic temperatures of hot electrons not at equilibrium with the lattice but among themselves result from varying the light irradiation. If intense and short laser pulses in the range of 100 fs to 1 ps are used for the SHG experiment, only the electrons will quickly thermalize (even in the approximation of Fermi liquid theory), since the slow electron-phonon coupling does not come into play [2,3]. Only later, at times of the order of several picoseconds the electrons will heat up the lattice. Thus, at short times the temperature dependence of SHG is essentially due to the varying non-equilibrium electronic temperature, which may be considerably different from the equilibrium temperature at later times, when electrons and lattice are at equilibrium.

In this paper, we present a theory for the time-resolved optical SHG response, in particular its dependence on non-equilibrium electronic temperature. We present results for the electron temperature dependence of the SHG yield at noble metal surfaces using an electronic theory for the nonlinear response. The metallic surface is modeled by a freestanding Cu monolayer. However, the model allows already to identify characteristic features of this time-dependent nonlinear optical response to be expected also for the surface of bulk Cu and for other metals like Ag and Au and to explain recent experimental results for Cu and Au [4]. Our analysis allows to identify the essential origin of the electron-temperature dependence of the nonlinear optical response. Furthermore our studies explain the different behavior of linear and nonlinear optics on non-equilibrium electronic temperatures. In general, our theory is of interest for the dynamics of nonequilibrium electronic systems.

In section II, we describe details of our theory. In section III, we present results of our calculation of the nonlinear response for several values of the electron temperature and compare with experiments. The conclusions in section IV point out possible general
features of our model calculation and explain why the important temperature dependence results from $\chi^{(2)}(\omega, T)$ and not from the Fresnel coefficients. In the appendix some details of our calculation are presented.

II. THEORY

We calculate the SHG intensity $I^{(2)}(\omega, T)$ using an electronic theory. Then the SHG yield for $p$-polarization within the electric dipole approximation is

$$I(p - SH) = |(2i\omega c)|^2 |E_0(\omega)|^4 A_p((F_c \chi^{(2)}_{xx} 2 f_c f_s + N^2 F_s (\chi^{(2)}_{zz} f_c^2 + \chi^{(2)}_{zz} f_s^2)) T_p^2 \cos^2 \varphi + N^2 F_s \chi^{(2)}_{zz} f_s^2 \sin^2 \varphi)|^2.$$  \hspace{1cm} (1)

Here, $\varphi$ denotes the angle of polarization of the incident light, $f_{c,s}$ the Fresnel coefficients and $t_{s,p}$ the linear transmission coefficients, $n = \sqrt{\epsilon(\omega)}$ and $N = \sqrt{\epsilon(2\omega)}$ the complex indices of refraction at frequencies $\omega$ and $2\omega$. Furthermore, $f_s = \sin \theta / n$ and $f_c = \sqrt{1 - f_s^2}$ for the fundamental frequency $\omega$, $F_s = \sin \Theta / N$ and $F_c = \sqrt{1 - F_s^2}$ for the doubled frequency, where $\theta$ and $\Theta$ denote the angle of incidence and the angle of reflection of the SHG light, respectively. The linear transmission coefficients are given by

$$t_p = \frac{2 \cos \theta}{n \cos \theta + f_c}, \quad t_s = \frac{2 \cos \theta}{\cos \theta + nf_c}, \quad T_p = \frac{2 \cos \Theta}{N \cos \Theta + F_c}. \hspace{1cm} (2)$$

The amplitude $A_p$ in Eq. (1) is

$$A_p = \frac{2 \pi T_p}{\cos \Theta}.$$ 

Note, the nonlinear susceptibility tensor $\chi^{(2)}$ is material specific and so are the linear dielectric function $\epsilon(\omega)$ and the indices of refraction $n$ and $N$ via the electronic bandstructure.

The contributions to $I^{(2)}(\omega, T)$ due to the Fresnel factors $F_c$, $F_s$, $f_c$, and $f_s$ and the transmission coefficients $T_p$, $t_p$, and $t_s$ and $\chi^{(2)}(\omega, T)$ are all temperature dependent. In both cases the temperature dependence arises from the Fermi functions $f(E, T)$ which, due to the many hot electrons resulting from the light irradiation, have to be taken at considerably elevated electron temperatures. Note, we limit ourselves to the time regime, where the electrons have already thermalized, but electron-phonon coupling has not become really effective. By taking both temperature dependences into account it becomes possible to
decide theoretically whether $\chi^{(2)}(\omega, T)$ or the Fresnel and transmission coefficients cause the essential temperature dependence of the SHG intensities. Since it is known from theory and also experiment that the $\chi^{(2)}_{zzz}$ tensor element dominates over $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zxx}$, we restrict our calculation to this single element of the nonlinear susceptibility for the SHG yield. Then approximately

$$I(p - SH) = |(2i\omega/c)|^2 |E_0(\omega)|^4 |A_pN^2F_s\chi^{(2)}_{zzz}I_s^2t_p^2\cos^2\varphi|^2. \quad (3)$$

For the calculation of $\epsilon(\omega, T)$ and $\chi^{(2)}_{zzz}(\omega, T)$, we use eigenvalues $E_{k,l,\sigma}$ from a simple quadratic, freestanding Cu monolayer. The nearest-neighbor-distance equals $3.61/\sqrt{2}$ Å, according to the nearest-neighbor-distance of Cu bulk. The bandstructure involves five $d$-bands and four plane waves and has been obtained within the combined interpolation scheme (CIS). The $d$-bands are parameterized in terms of Fletcher-Wohlfahrt parameters, their values are given in Table 1. The parameters of the $d$-bands were evaluated by a fit to an ab initio LAPW band-structure calculation by Krakauer, Posternak, and Freeman. Furthermore, to get also the correct onset of interband transitions we shifted correspondingly the $d$ states. The energy eigenvalues were calculated for 1861 k-points in the irreducible part of the Brillouin zone (1/8 of the whole Brillouin zone). The resulting band structure shown in Fig. 5 should be thus representative for the surface layer of bulk Cu.

The calculation of the dielectric function $\epsilon(\omega, T)$ is performed by including both the intra- and interband electronic transitions. Neglecting the $q$-dependence of $\epsilon$, we take

$$\epsilon(\omega, T) = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i/\tau_{pl})} - \frac{4\pi e^2}{\Omega} \sum_{k,l,l',\sigma} M^2 \times \frac{f(E_{kl'\sigma}, T) - f(E_{kl\sigma}, T)}{E_{kl'\sigma} - E_{kl\sigma} - \hbar\omega + i\hbar\alpha_1}, \quad (4)$$

where $M$ are the dipole matrix elements, $f(E, T)$ are the Fermi functions, $\omega$ is the fundamental frequency, $\Omega$ is the unit area, $\alpha_1 = 0.1$ eV is the Lorentzian broadening, $\tau_{pl}$ the Drude relaxation time and $\omega_{pl} = 4\pi n_e e^2/m^* c$ is the plasma frequency with $n_e$ the electron density and $m^*$ the effective electron mass. Both $\omega_{pl}$ and $\tau_{pl}$ are fitted to a dielectric function using literature values at low fundamental energies, where no interband transitions occur. We use $\hbar\omega_{pl} = 9$ eV and $\tau_{pl}/\hbar = 8.5$ eV$^{-1}$.

To simplify our calculation, we assume constant matrix elements $M$, which fit to the dielectric function $\epsilon(\omega, T = 0K)$ at low fundamental energies, where no interband transitions occur. This approximation is reasonable because the $k$-dependence of the matrix elements is expected to become less important in two dimensions.
due to the shrinking of the $d$-band width for the reduced coordination number and also due to the occurrence of additional allowed optical transitions. Additionally, as will be shown later, the main contribution of the SHG intensity has its origin in $d \rightarrow d \rightarrow s$ transitions, so the matrix elements give a simple prefactor to the sum and cancel, when only intensity differences are considered. Once $\epsilon(\omega, T)$ is calculated, it is straightforward to get the Fresnel factors and transmission factors from Eq. (2).

For evaluating the second-order susceptibility, we employ the microscopic theory developed in Ref. [16]. Thus, the tensor element $\chi^{(2)}_{zzz}$ is given by

$$\chi^{(2)}_{zzz}(\omega, T) = \frac{e^3}{\Omega} \sum_{k,l,l',l''} (M_z)^3 \left\{ \frac{f(E_{k,l''}, \alpha) - f(E_{k,l''}, \alpha)}{E_{k,l''} - E_{kl} - \hbar \omega + i \hbar \alpha_1} - \frac{f(E_{k,l'}, \alpha) - f(E_{k,l'}, \alpha)}{E_{k,l'} - E_{kl} - \hbar \omega + i \hbar \alpha_1} \right\}. \quad (5)$$

Note, for experiments not detecting absolute intensities (as is usually the case), the prefactor in this formula is of no further importance for comparison with experimental data. As in the calculation of $\epsilon(\omega)$, we neglect the $k$-dependence of the matrix elements, taking the values for $M_z$ from the $\epsilon(\omega)$-fit. We only take into account the dominant $\chi^{(2)}_{zzz}$-tensor element and neglect the contributions of the other tensor elements, as pointed out earlier. This completes then the theory for the determination of the SHG intensity $I^{(2)}(\omega, T)$ with the two essential inputs $\epsilon(\omega, T)$ and $\chi^{(2)}(\omega, T)$.

### III. RESULTS

The most important results of our calculations are presented in Figs. 1-4. For these results we used an electronic structure which is shown in Fig. 5 and which was obtained using inputs discussed in section II. In Fig. 1 we present results for the change

$$\Delta I^{(2)}(\omega) = \frac{I^{(2)}(\omega, T_{el}) - I^{(2)}(\omega, 300K)}{I^{(2)}(\omega, 300K)}$$

of the SHG yield as a function of frequency for different non-equilibrium electronic temperatures $T_{el}$. In particular, in the inset of Fig. 1 we show for the frequency range from 0.4 to 1.5 eV, that $I^{(2)}(\omega)$ may be reduced or enhanced due to increasing non-equilibrium temperature for the electrons. In order to demonstrate what causes essentially the dependence on the electronic temperature, namely $\chi^{(2)}(\omega, T)$ or the Fresnel coefficients, we present in Fig. 2 results for
and in Fig. 3 results for the difference

\[
\Delta \frac{I(2)}{|\chi(2)|^2} = \frac{I(2)(\omega, T_{el})/|\chi(2)(\omega, T_{el})|^2 - I(2)(\omega, 300K)/|\chi(2)(\omega, 300K)|^2}{I(2)(\omega, 300K)/|\chi(2)(\omega, 300K)|^2}.
\]

Note, in Fig. 3 we present results for \(I(2)(\omega, T)\) using a frequency and temperature independent susceptibility \(\chi(2)\). The comparison of the results in Figs. 2 and 3 show clearly that \(I(2)(\omega, T)\) results essentially from \(\chi(2)(\omega, T)\). Furthermore, from comparing the results in Figs. 1 and 3 together with those in 2 and 3, we note that the crossover behavior with respect to the temperature dependence is only present in the case of the nonlinear response \(I(2)(\omega, T)\), but not in the Fresnel and transmission coefficients.

In Fig. 4 we present results for \(I(2)(\omega, T = 2000K)\) as a function of frequency. The different curves (b), (c), (d), and (e) refer to cases where we artificially excluded certain optical transitions from contributing to \(\chi(2)(\omega, T)\). Thus, we are able to demonstrate which transitions are of particular significance for the temperature dependence of \(I(2)(\omega, T)\). While curve (a) still includes all transitions, in the case of curve (b) we excluded contributions to \(\chi(2)(\omega, T)\), where the initial electronic state is not in the \(d\)-band. In the case of curve (c) we excluded contributions to \(\chi(2)(\omega, T)\), where the initial state is not in the \(d\)-band or the intermediate state is in the \(d\)-band. Curve (d) results when the initial and the intermediate states are in the \(d\)-band, and in curve (e) we excluded transitions, where the initial state is in the \(d\)-band or the intermediate state is not in the \(d\)-band. Similar results are obtained for 300 K and 6000 K.

For a detailed analysis of the results presented in Figs. 1 - 4 we like to make the following remarks. Investigating the relative changes of SHG intensity with temperature and its contributions due to the Fresnel factors and the nonlinear susceptibility \(\chi(2)(\omega, T)\), we observe in Figs. 1, 2, and 3, that the shape of the dependence on the fundamental frequency is given by the second-order susceptibility \(\chi(2)(\omega, T)\) for fundamental energies below 3 eV. In the range between 1.2 eV and 3 eV, the SHG intensity decreases with increasing temperature. Most important is the result that indeed an energy window at a fundamental energy of 1.1 eV exists, where a small temperature increase (300 K to 2000 K) results in a SHG intensity increase, but a stronger temperature increase (300 K to
6000 K) results in a rapid SHG intensity decrease. From Figs. 2 and 3 we conclude that \( \chi^{(2)}(\omega, T) \) is responsible for this. This clarifies then the physical origin of the temperature dependence of \( I^{(2)}(\omega, T) \) observed on Cu polycrystalline surfaces \(^4\), where in 2 eV photon energy pump–probe SHG experiments on Cu surfaces for weak pump pulses an increase of the SHG intensity has been observed, but a decrease when the pump pulse becomes stronger and thus the electron temperature higher.

Note, it is remarkable that our model bandstructure yields already such a fair agreement with the experimental results. This is so, since the temperature dependence of \( \chi^{(2)}(\omega, T) \) and \( I^{(2)}(\omega, T) \) is strongly governed by the correct position of the upper \( d \) band edge and also because the important features of the bandstructure are already simulated correctly by our model. Furthermore, SHG probes the surface layer only, so our bandstructure is a fair approximation for the experimental situation. In view of this, we may also use with proper changes the model in Fig. 5 to describe the SHG response of Au and Ag. For this we change the onset of \( d \)-band transitions \( \Delta \) to \( \Delta = 3.95 \) eV in the case of Ag and to \( \Delta = 2.3 \) eV in the case of Au, since this is expected to cause the most important differences, s. Fig. 5. The other energy levels shift accordingly.

Since the “mismatch” between \( (E_d - E_F) \) and the photon energy \( \hbar \omega \) in Au is by 230 meV larger than in Cu (Cu bulk: \( E_d - E_F = 2.15 \) eV), one may simulate in our calculation the Au surface by using approximately the SHG spectrum of the Cu monolayer, but considering a photon energy which is 230 meV below the respective energy value for the Cu monolayer. While for Cu we found the crossover behavior at 1.1 eV, we have to take for Au a fundamental photon energy of 0.87 eV. Then our results presented in Fig. 1 yield an increase of SHG for all temperatures. The increase for 6000 K is higher than that for 2000 K. These results seem in reasonable agreement with experiments for a Au polycrystalline surface, where a monotonic increase of the SHG yield for both temperatures has been observed \(^4\). Thus, our electronic theory is able to explain the ultrafast electronic relaxation process on both Cu and Au surfaces. From our direct calculation of the dielectric functions (see Fig. 6) we find that the temperature dependence of \( I^{(2)} \) is mainly caused by \( \chi^{(2)}(\omega, T) \). At a frequency \( \hbar \omega = 0.9 \) eV we find that the \( \chi^{(2)}(\omega, T) \)-dependence on the electron temperature begins to saturate for higher temperature, as is observed in the experiment \(^4\). Note, the SHG
response of Ag may be modeled similarly as has been described for Au. Further remarks on this are given later.

Regarding the origin of the temperature dependence of the SHG contribution (on transitions), it is necessary to investigate the contribution of the \(d\)-band electrons to \(\chi^{(2)}_{zzz}(\omega, T)\) and its influence on the SHG yield in some detail. Results of this analysis are shown in Fig. 4. To interpret the results, one has to be careful not to neglect the interferences between the various terms in Eq. (5). Therefore, calculating \(\chi^{(2)}_{zzz}(\omega, T)\) and the SHG intensity for just a few transitions, neglecting all others, is of little value, since then the interferences between the various complex quantities are almost completely neglected. Thus, we calculated the SHG intensity with a \(\chi^{(2)}_{zzz}(\omega, T)\), Authors: T. A. Luce, W. Hübner, and K. H. Bennemann

where just some transitions with a specific combination of the three states necessary for a nonlinear transition were neglected. States were identified as \(d\)-states if their energy eigenvalue was between -5.25 and -1.45 eV below \(E_F\). Note, here we neglected the symmetry of the states. Apparently, we find that the initial state is almost always a \(d\) state, since both intensities nearly coincide. The SHG intensity \(I^{(2)}(\omega, T)\) from transitions \(d \rightarrow (s, p) \rightarrow (d, s, p)\), where the initial state is in the \(d\)-band and the intermediate state is not (curve (c)), nearly vanishes. The ratio of the maximum values of the SHG intensity and the total SHG intensity \(I^{(2)}(d \rightarrow (s, p) \rightarrow (d, s, p))/I^{(2)}(total)\) is equal to 1/90. Of course, both intensities are taken at the same frequency. This shows that most transitions contributing to the SHG intensity have the initial and intermediate state in the \(d\)-band. This is confirmed by the respective dotted curve (d). Due to interference of the various interband transitions in \(\chi^{(2)}_{zzz}(\omega, T)\), this curve and the total SHG intensity yield differ at the maximum by a factor of 3. Comparing this ratio \(I^{(2)}(d \rightarrow d \rightarrow (d, s, p))/I^{(2)}(total) = 3\) with the ratio \(I^{(2)}(d \rightarrow (s, p) \rightarrow (d, s, p))/I^{(2)}(total)\), it is reasonable to assume that only the transitions with the initial and the intermediate state in the \(d\)-band contribute significantly to the SHG yield.

From curve (e) in Fig. 4 it can be seen that considerable SHG intensity is created by \((s, p) \rightarrow d \rightarrow (s, p, d)\) transitions. This is readily understood if one notes that all terms in the sum of \(\chi^{(2)}_{zzz}(\omega, T)\), Eq. (5), consist of differences

\[
\frac{1}{E_3 - E_1 - 2\hbar\omega + 2i\hbar\alpha_1} \left\{ \frac{f(E_3, T) - f(E_2, T)}{E_3 - E_2 - \hbar\omega + i\hbar\alpha_1} - \frac{f(E_2, T) - f(E_1, T)}{E_2 - E_1 - \hbar\omega + i\hbar\alpha_1} \right\}. \tag{6}
\]
Here, $E_1$, $E_2$ and $E_3$ denote the initial, intermediate, and final state in the considered transition, respectively. This difference will give a contribution even if one of the terms in curly brackets is zero, so the intensity $I^{(2)}(s,p \rightarrow d \rightarrow s, p, d)$ mainly results from the first term.

Compared with these transitions, all other combinations of states contribute only a small amount to the SHG. Even at low energies ($\hbar \omega \sim 1$ eV), the probability that all three states of a nonlinear transition are $d$-states is rather small. Since the main contribution to the SHG intensity results from transitions with the two lower states in the $d$-band, nearly all contributing terms have the corresponding dipole matrix element product $\langle d|z|d\rangle \langle d|z|(s,p)\rangle \langle (s,p)|z|d\rangle$. This can be handled as a prefactor. In view of this result, our simplification of using one value for all dipole matrix elements is justified.

In order to avoid confusion, one should note that our calculation of $I^{(2)}(\omega, T)$ demonstrates that the mismatch energy $\delta = E_F - E_d - \hbar \omega$ is crucial for the $T$-dependence of the SHG yield and gives for a fixed photon energy $\hbar \omega$ the following results: First, if $\delta < \delta_{Cu}$, where $\delta_{Cu}$ refers to the value where the reflectivity of Cu saturates, the temperature dependence of the Fresnel factors and transmission coefficients is sufficient to describe $I^{(2)}(\omega, T)$. In the range $\delta_{Cu} < \delta < \delta_{Au}$, $I^{(2)}(\omega, T)$ is essentially due to $\chi^{(2)}(\omega, T)$, and for $\delta > \delta_{Au}$, $I^{(2)}(\omega, T)$ results from $\chi^{(2)}(\omega, T)$ for both Cu and Au. This is consistent with experimental observations regarding the dependence of the reflectivity on $\delta$.

In summary, our results for $I^{(2)}(\omega, T)$ suggest that the temperature dependence is essentially due to $\chi^{(2)}(\omega, T)$. In particular, $\chi^{(2)}(\omega, T)$ is responsible for the nonmonotonous temperature dependence $I^{(2)}(\omega, T)$.

**IV. CONCLUSIONS**

We calculated the dependence of the SHG yield on electron temperatures for electrons not at equilibrium with the lattice, caused by light irradiation for a Cu surface and for a Ag and a Au surface. We find that for energies below 3.2 eV the temperature effects result mainly from $\chi^{(2)}(\omega, T)$ and not from the Fresnel coefficients. In particular, our calculation yield that in the frequency range between 0.8 and 1.1 eV, the SHG intensity even may increase with increasing electron temperature. This is the case for Cu at low light intensities and for Au for
all light intensities that cause no damage. Note, for Au we use the same bandstructure and smaller light frequencies in order to study the same electronic transitions as for Cu. Clearly, $I^{(2)}(\omega, T)$ depends on the position of the $d$-band with respect to the Fermi-energy. The interesting effect that mainly $\chi^{(2)}(\omega, T)$ causes the temperature dependence comes about due to extra two photon absorption processes making use of the high $d$-band density of states and occurring only at elevated electronic temperatures. Note, however, that only due to the interference of these transitions with others a considerable temperature dependence comes about. The situation is illustrated in Fig. 7. Note, without the effects due to the indicated transitions, the nonmonotonic temperature dependence would be absent. The figure illustrates also the difference between the temperature dependence in nonlinear and linear response, where for the latter only $d$-states as initial states are possible.

As already remarked the essential features of our results should be valid independent of our model calculations. This is supported by the fact that we already find such a fair agreement with the experiments by Hohlfeld, Conrad and Matthias [4]. Our theory shows clearly how $I^{(2)}(\omega, T)$ depends on the electronic structure and thus what can be expected for other noble metals and transition metals. For example, for Ag ($E_F - E_d = 3.98$ eV for bulk Ag) we would expect, using the previously discussed argument, a similar behavior for the linear and nonlinear response in the frequency range from 0.8 to 1.1 eV in view of Fig. 7, while in the frequency range 4 eV a decrease of the SHG yield due to the very small negative mismatch is expected. For Ag and for this mismatch the SHG intensity $I^{(2)}(\omega, T)$ should always decrease as a function of $T$. Also for Fe, in addition to the changes due to the electronic structure (position of the $d$-band) we expect interesting non-equilibrium temperature effects due to the additional dependence of the magnetization $M$ on $T_{el}$, since $I^{(2)}$ depends on $T_{el}$ and $M(T_{el})$.

Regarding the time dependence of our results, for larger times the electron-phonon coupling will become more effective and cause the decrease of the electronic temperature via an energy transfer from the hot electrons to the lattice. The resulting equilibrium temperature will be only a few hundred degrees higher than before the light irradiation. Then, $I^{(2)}(\omega, T)$ will be similar to $I^{(2)}(\omega, 300K)$, which is given in the appendix. Such temperature dependences should be compared with those obtained for systems due to usual equilibrium
thermodynamical effects. It is straightforward to extend our calculation to thicker films consisting of several atomic layers. Such calculations are in progress [19].

As a resumé, our studies show that SHG can be used to study the dynamics of excited hot electrons in crystals. Note, in this paper we considered the time window where the electrons are far from equilibrium and have their own temperature different from the lattice temperature. Obviously, using SHG for studying the time evolution of the electronic system far from equilibrium offers new perspectives, in particular for studying magnetism.

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APPENDIX

In this appendix we present some details of our calculations. In Fig. 5 we show results for our band-structure calculation, evaluated with the parameters fitted to the ab initio bandstructure. Our CIS calculation is in good agreement with the ab initio calculations. The resulting density of states (DOS) in the inset of Fig. 6 gives a d-band edge approximately 1.45 eV below the Fermi-energy \( E_f \). The total d-band width is 3.05 eV. d-band transitions with lowest energy are possible at energies around 2.1 eV (near the \( \bar{X} \)-point). The constant values of the matrix elements are \( M_z = 5.4 \times 10^{-10} \) m. The numerical value was obtained by fitting the maximum values of the dielectric function to literature values [15]. From atomic orbitals, one would expect values about \( 0.01 \times 10^{-10} \) m for the \( \langle p|z|d \rangle \) matrix elements [16]. This shows that the atomic orbitals give the correct symmetry of the wave functions, but the absolute values differ considerably due to the periodicity of the monolayer wave functions which delocalizes the d-electrons.

The real and imaginary parts of the dielectric function for the Cu monolayer as a function of the incident photon energy are plotted in Fig. 6 for three different electronic temperatures (300 K, 2000 K, and 6000 K). These temperatures are chosen as realistic estimates of the electron temperature caused by experimental pump–probe pulses.

The influence of the plasma frequency \( \omega_{pl} \) at low frequencies leads to a strong drop (increase) of the real (imaginary) part of \( \epsilon(\omega) \) upon lowering the frequency \( \omega \). A variation of
the Drude relaxation time $\tau_{pl}$ causes only minor changes \[17\]. If $\omega_{pl}$ is reduced, the minimum of $\text{Im} \{\epsilon\}$ increases in value and moves to lower energies. The increase of $\text{Im} \{\epsilon\}$ at 2 eV is caused by transitions from the $d$-band to unoccupied states at $E_f$ at this energy. Due to the Lorentzian broadening introduced by the calculation, the increase of $\text{Im} \{\epsilon\}$ is not as steep as expected from optical measurements. Rising the electron temperature results in a flattening of the curves for $\text{Re} \{\epsilon\}$ and $\text{Im} \{\epsilon\}$. The minimum of $\text{Im} \{\epsilon\}$ becomes less pronounced for higher temperatures. Since there are more vacant states below $E_f$ at higher temperatures, interband transitions occur at lower energies, thus weakening the rise of $\text{Im} \{\epsilon\}$ at 2 eV. It is to be expected that the main temperature effects are observable at photon energies $\omega$ with either $\hbar \omega \approx E_f - E_d$ or $2\hbar \omega \approx E_f - E_d$, depending on the influence of the Fresnel factors or the nonlinear susceptibility on the temperature dependence. Then the transitions are strongly influenced by the effects which a temperature increase induces on the occupation of states at $E_f$.

In order to trace back the origin of this effect we separately calculate the contribution of the Fresnel factors and nonlinear contributions to the SHG yield. To obtain the contributions of the Fresnel factors we calculate the SHG intensity $I(2\omega)$ from Eq. (3) with $\chi^{(2)}_{zzz}$ set to unity, thus including the interaction of the incident light and the frequency-doubled light with the monolayer. For the nonlinear contributions we compute $\chi^{(2)}_{zzz}(\omega, T)$. Inserting the dielectric function from Eq. (4) and $\chi^{(2)}_{zzz}(\omega, T)$ from Eq. (5) in Eq. (3), in Fig. 8 we show the calculated SHG intensity $I^{(2)}(\omega, T)$ for the three different electronic temperatures (300 K, 2000 K, 6000 K). The SHG intensity rises strongly at photon energies around 2 eV and peaks at approximately 2.8 eV. Then it drops without exhibiting further peaks. For increasing temperature, the intensity maximum decreases and moves to slightly higher photon energies. From Fig. 9 we find a similar shape of the $\chi^{(2)}_{zzz}(\omega, T)$-plots, with maxima shifted to photon energies around 1.9 eV. From Eq. (5) it becomes clear that even at low energies in the range of 1 eV contributions to $\chi^{(2)}_{zzz}(\omega, T)$ are to be expected due to $2\hbar \omega$-resonances of the form

$$\frac{1}{E_{k+2q} - E_{kl} + 2\hbar \omega + i2\hbar \alpha_1}.$$  

The maximum decreases with rising temperature, but its position remains at 1.9 eV. Fig. 10 displays the contributions of the Fresnel- and transmission factors to the SHG intensity. We
find a strong increase at energies larger than 2 eV, due to the interband transition threshold in this energy range. Decreasing the plasma frequency increases the SHG intensity and shifts the maximum to lower frequencies (e.g. for $\omega_{pl} = 2.2$ eV we find a maximum at 1.1 eV, the intensity amplitude there is about 1000 times larger). The plasma frequency influences both Fresnel factors $f(\omega)$ and $F(2\omega)$. However since it is necessary that both $F(2\omega)$ and $f(\omega)$ are nonvanishing to make SHG possible, in the Fresnel factor contributions of the SHG yield mainly the effect of $f(\omega)$ is visible, because $F(2\omega) \neq 0$ for photon energies greater than energies where $f(\omega)$ is nonvanishing.

Analyzing the contributions of the linear and the nonlinear response to the SHG intensity, we find that the overall shape of the intensity is dominated by the $\chi^{(2)}_{zzz}(\omega, T)$ - contribution, if compared with the corresponding $\chi^{(2)}_{zzz}(\omega, T)$ -plots in Fig. 9. The apparent shift of the $\chi^{(2)}_{zzz}(\omega, T)$ -plot to higher photon energy results from the strong increase of the Fresnel factor contribution to the SHG in this energy range, as can be seen from Fig. 10.
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TABLE I. Fletcher - Wohlfahrt parameters fitted to *ab initio* calculations for the Cu monolayer. ($E_0$: On-site energy, $A_i$: Overlap integrals of the $d$-orbitals)

| parameter | value [eV] |
|-----------|------------|
| $E_0$     | $-2.904$   |
| $A_1$     | 0.106      |
| $A_2$     | 0.088      |
| $A_3$     | 0.147      |
| $A_4$     | 0.220      |
| $A_5$     | 0.170      |
| $A_6$     | 0.200      |
FIGURES

FIG. 1. Change of the SHG intensity $\Delta I^{(2)}(\omega) = \frac{I^{(2)}(\omega,T_{el}) - I^{(2)}(\omega,300K)}{I^{(2)}(\omega,300K)}$ due to a rise of electron temperature as a function of the incident photon energy $\hbar \omega$ in percent for $T_{el} = 2000K$ and $T_{el} = 6000K$. The inset shows the energy range between 0.4 and 1.5 eV at an enlarged abscissa scale.

FIG. 2. Change of the second order susceptibility $\Delta \chi^{(2)}(\omega, T) = \frac{\chi^{(2)}(\omega,T_{el}) - \chi^{(2)}(\omega,300K)}{\chi^{(2)}(\omega,300K)}$ due to a rise of electron temperature as a function of the incident photon energy $\hbar \omega$ in percent. $\chi^{(2)}_{zzz}$ is very similar to the SHG yield for energies below 3.2 eV, indicating that the temperature effects for these fundamental energies on the SHG intensity are caused by $\chi^{(2)}_{zzz}$. The inset displays this similarity for incident energies between 0.4 and 1.5 eV.

FIG. 3. Results for the relative change of the SHG yield $\Delta \frac{I^{(2)}}{|\chi^{(2)}|^2} = \frac{I^{(2)}(\omega,T_{el})/|\chi^{(2)}(\omega,T_{el})|^2 - I^{(2)}(\omega,300K)/|\chi^{(2)}(\omega,300K)|^2}{I^{(2)}(\omega,300K)/|\chi^{(2)}(\omega,300K)|^2}$ for $T_{el} = 2000K$ and $T_{el} = 6000K$. In contrast to the results shown in Fig. 1, the frequency and temperature dependence of $\chi^{(2)}(\omega, T)$ is neglected. The inset shows at an enlarged abscissa scale the energy range between 0.4 and 1.5 eV. These results demonstrate the importance of the temperature dependence of $\chi^{(2)}(\omega, T)$.

FIG. 4. Contributions of the different electronic transition combinations to the SHG intensity as function of the incident photon energy $\hbar \omega$ (arbitrary units). Note, the contributions due to transitions with the incident state a $d$-band (curve (b)) nearly coincides with the total SHG intensity.

FIG. 5. Calculated bandstructure of a Cu monolayer using the Combined Interpolation Scheme. The $d$ band edge is 1.45 eV below $E_F$. $\Delta$ is the interband transition onset energy. The symmetry of the bands is indicated by the $s$ and $d$ labels.

FIG. 6. Real and imaginary parts of the dielectric function as a function of the incident photon energy $\hbar \omega$ for three nonequilibrium electronic temperatures (300 K, 2000 K, 6000 K), calculated from Eq. (4). The inset shows the DOS of the Cu monolayer bandstructure.
FIG. 7. Illustration of important electronic transitions generating SH from noble metals. Note, both initial and intermediate state belong to the $d$-band. Actually, by neglecting such transitions in our calculation, we find a drastically reduced $I^{(2)}(\omega, T)$. Since in the case of the linear optical response, at best only the initial state can be a $d$ state, nonequilibrium temperature effects are drastically reduced and less interesting with regards to probing the electronic structure.

FIG. 8. Calculated total SHG intensity of a Cu monolayer for three different electronic temperatures (300 K, 2000 K, 6000 K) as a function of the incident photon energy $\hbar\omega$ (arbitrary units). This quantity has been used for the calculation of the intensity changes.

FIG. 9. Calculated total susceptibility $\chi^{(2)}_{zzz}$ for three different temperatures (300 K, 2000 K, 6000 K) as a function of the incident photon energy $\hbar\omega$ (arbitrary units). These results have been used for the calculation of the susceptibility changes given in Fig. 2.

FIG. 10. Temperature dependence of the SHG intensity resulting from the temperature dependence of the Fresnel factors and putting $\chi^{(2)}_{zzz}(\omega, T)$ equal to unity in Eq. (3). These results have been used to calculate the differences in Fig. 3.
\[ \Delta \left\{ \frac{I^{(2)}(\omega)}{|\chi^{(2)}_{zzz}(\omega)|^2} \right\} (\%) \]
$T = 2000\ \text{K}$

energy (eV)

$I^2(\omega)$ (a.u.)

energy $h\omega$ (eV)

$5 \times 10^6$

$3 \times 10^6$

$10^6$

$10^5$
Energy (eV)

$\Delta = 2.1 \text{ eV}$
\[ \chi^{(2)}_{zzz}(\omega) \text{ (a.u.)} \]

Energy \( \hbar \omega \) (eV)

- 300 K
- 2000 K
- 6000 K

The graph shows the second-order susceptibility \( \chi^{(2)}_{zzz} \) as a function of energy \( \hbar \omega \) for different temperatures: 300 K, 2000 K, and 6000 K.
