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Explaining the x-Ray Nonlinear Susceptibility of Diamond and Silicon near absorption edges

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We report the observation and the theoretical explanation of the parametric down-conversion nonlinear susceptibility at the K absorption edge of diamond and at the L_{23} absorption edge of a silicon crystal. Using arguments similar to those invoked to successfully predict resonant inelastic x-ray spectra, we derive an expression for the renormalization term of the non-linear susceptibility at the x-ray edges, which can be evaluated by using first-principles calculations of the atomic scattering factor f_1 . Our model is shown to reproduce the observed enhancement of the parametric down-conversion at the diamond K and the Si L_{23} edges rather than the suppression previously claimed.

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I. INTRODUCTION

The advent of x-ray free electron lasers (XFELs)¹⁻³ has enabled advances in the study of x-ray nonlinear processes⁴, which are similar to nonlinear optics investigations and applications, that have followed the invention of the laser in 1960. Few x-ray nonlinear processes have been already observed with conventional x-ray sources. In particular, x-ray parametric down-conversion (PDC) is an intriguing second order nonlinear process where an x-ray pump photon of energy E_p decays spontaneously into two photons, the idler and the signal with energies E_i and E_s respectively. PDC was first discussed theoretically by Freund and Levine⁵ and was then observed experimentally by Eisenberger and McCall^{6,7} in 1971. The first observations of the PDC into the extreme ultraviolet (EUV) was reported by Danino and Freund⁸ about a decade later. This effect has been recently used to visualize the local optical response to EUV radiation with an atom scale resolution⁹. Further improvement of PDC has been recently proposed by Shwartz and collaborators¹⁰.

As illustrated in Fig. 1, x-ray PDC takes place as nonlinear diffraction in crystals with energy and momentum conservation laws given by

$$\begin{aligned} E_p &= E_i + E_s, \\ \mathbf{k}_p + \mathbf{Q} &= \mathbf{k}_i + \mathbf{k}_s, \end{aligned} \quad (1)$$

where $\mathbf{k}_s$, $\mathbf{k}_i$, and $\mathbf{k}_p$ are the wave vectors of the signal, idler, and pump photons respectively whereas $\mathbf{Q}$ is a crystal reciprocal lattice vector. The momentum conservation is also called phase-matching condition and rocking the crystal means scanning the phase-matching condition. Surprisingly, Tamasaku and Ishikawa observed asymmetric rocking curves, having not only a peak but also a distinct dip¹¹. If there were no interaction be-

tween the PDC and the Compton scattering, the rocking curve should be a Lorentzian peak on a smooth Compton background. Instead, the rocking curve is not simple, but reveals an interference with the background Compton process. The resulting lineshape is similar to the one considered by Ugo Fano^{12,13}. From the analysis of the Fano line shape, Tamasaku, Sawada and Ishikawa¹⁴ extracted the PDC non-linear susceptibility $\chi^{(2)}$. These authors noticed that a sharp peak of the non-linear susceptibility reveals a strong resonant enhancement at the K -absorption edge of diamond. This observation contradicts previous models claiming that the core resonance suppresses the nonlinear process rather than enhances it¹⁵.

We present here a renormalization factor η that captures the behavior of the non-linear susceptibility $\chi^{(2)}$ at the K -absorption edge of diamond and at the L_{23} absorption edge of Si. A similar term has been recently used to explain the enhancement of the cross section observed in the resonant inelastic x-ray scattering (RIXS)¹⁸. The factor η is derived by using the renormalization group method, that describes the variation of effective coupling constant under changes of scales¹⁹⁻²¹, and the method of dispersion relations applied to the atomic scattering factor.

The remainder of this article is organized as follows. After the introductory remarks contained in Sec. I, Sec. II introduces the model and reviews the derivation of the renormalization factor η . In Sec. III, we present the methods for the calculations of the atomic scattering factor f_1 used to obtain η and for the x-ray PDC experiments. The theoretical results are presented and compared with the experimental results in Sec. IV. Important predictions of our model and the conclusions are reported in Sec. V.

FIG. 1. Schematics explaining the x-ray PDC: (a) momentum conservation law, (b) energy conservation laws in diamond and silicon. The quantities $(E_s, \mathbf{k}_s)$, $(E_i, \mathbf{k}_i)$, and $(E_p, \mathbf{k}_p)$ are the energy-momentum of the signal, idler, and pump photons respectively.

II. THEORETICAL MODEL

As explained by Freund and Levine⁵, the origin of the PDC nonlinearity is the Doppler shift, where the induced valence charge at the idler frequency scatters x-rays at a different frequency. An effective theory for this process is therefore equivalent to an inelastic x-ray scattering by valence electrons oscillating in the idler field. In the proximity of an absorption threshold, the idler photon generates a set of virtual intermediate states involving a core hole and a corresponding electron excited in a virtual state which can be described by an effective dielectric function ϵ experienced by the valence electrons. Therefore, the effective coupling constant can be modified through the dielectric response if the idler photon energy is tuned near to the binding energy of a core electron level in certain materials.

In general, the dimensionless interaction of quantum electrodynamics (QED) is not constant but varies with the energy scales. In fact, the vacuum of QED can be considered as some kind of polarizable medium, where virtual pairs of fermions and anti-fermions screen the electric charge. For instance, in the standard model of particle physics, the coupling varies because of the crossing of particles production thresholds as illustrated by Jegerlehner²². Similarly, in materials such as FeTe or TiSe₂¹⁸, photons with energies at the proximity of the L_3 absorption threshold generate a set of virtual intermediate states involving a $2p$ core hole and a corresponding electron excited in a $3d$ state, which can be described by an effective dielectric function experienced by the valence electrons. Therefore, we can reduce the dimensionless interaction strength g in a material by introducing photons with energies just below the threshold of x-ray edges, thereby increasing dielectric screening. Consequently, the x-ray scattering cross section σ can be significantly enhanced due to an increased background polarizability. The connection between the effective coupling g and the length scale $\ell = \sqrt{\sigma}$ can be described by a renormaliza-

tion group equation

$$\beta(g) = \frac{dg}{d\ln(\ell)}, \quad (2)$$

where the function $\beta(g) = -3g^2$ was derived from a thermodynamic argument²³ involving a pressure needed to set the scale of ℓ for a given coupling g . The solution of Eq. 2 implies that the x-ray scattering cross section σ is renormalized by the factor

$$\eta = \exp\left[\frac{2}{3\alpha}(\epsilon_1/\epsilon_0 - 1)\right], \quad (3)$$

where ϵ_0 is the dielectric constant in vacuum, α is the fine structure constant (i.e. the effective coupling g when $\epsilon = \epsilon_0$) and ϵ_1 is the real part of an effective dielectric function ϵ . Near absorption edges, there are anomalous dispersions that allow x-ray PDC to be enhanced within a narrow energy range, since ϵ_1/ϵ_0 can be larger from unity in this energy domain. As already mentioned above, the Compton scattering mixes with the PDC and both processes experience the same renormalization factor η because they involve the same valence electrons embedded in the effective medium described by ϵ . Zambianchi²⁴ noticed that $|\chi^{(2)}|^2$ is proportional to the cross section. Hence, the renormalization of the cross section also yields a renormalization for $|\chi^{(2)}|^2$ given by

$$|\chi^{(2)}|^2 = \eta |\chi_{NR}^{(2)}|^2, \quad (4)$$

where $|\chi_{NR}^{(2)}|^2$ represents the non-resonant part of the non-linear susceptibility. The real part of the dielectric function ϵ_1/ϵ_0 contained in the exponent of η depends on the atomic scattering factor f_1 through the equation

$$\frac{\epsilon_1}{\epsilon_0} = 1 - \frac{4\pi r_0 \rho}{k_i^2} f_1, \quad (5)$$

where k_i is the norm of the idler wave-vector, r_0 is the classical electron radius and ρ is the number of C or Si atoms per unit volume. The factor f_1 can be written using the Kramers-Kronig transform¹⁶ as

$$f_1(E) = Z^* + \frac{2}{\pi} \int_0^\infty \frac{\omega f_2(\omega)}{E^2 - \omega^2} d\omega, \quad (6)$$

where Z^* is the effective atomic charge and f_2 is the imaginary part of the complex scattering factor. Thus, f_1 becomes negative when the number of anomalous electron near the absorption edge (given by the second term in the right side of Eq. 6) is greater the number of electrons. Moreover, both f_1 and ϵ_1 contain the Lorentz oscillator for the core electrons appearing also in the treatment of RIXS and in a fit of $|\chi^{(2)}|$ proposed by Tamasaaku, Sawada, and Ishikawa¹⁴. Nevertheless, one should notice that in resonant PDC, ϵ_1 depends of the idler energy while in RIXS, ϵ_1 is a function of the incident energy of the photons¹⁵.

III. COMPUTATIONAL AND EXPERIMENTAL METHODS

Henke *et al.*¹⁶ have provided a complete tabulation of values for the atomic scattering factor f_1 calculated for all the elements $Z = 1$ to 92 in the energy range from 50 eV to 30 keV. However, their atomic-like assumption is clearly insufficient in the vicinity of absorption edges because of condensed matter effects¹⁷. For this reason, we have calculated the atomic scattering factor from the program FDMNES (standing for finite difference method near-edge structure)²⁵, which is a first-principles, free and open source code. The program directly calculates the complex scattering factor $f = f_1 + if_2$ without using the Kramers-Kronig transform given by Eq. 6. FDMNES is a real-space program, that does not involve Bloch states and Brillouin zone samplings. Therefore, whether, one considers a molecule or a periodic system, FDMNES builds a cluster around the absorbing atom. The clusters radius is chosen large enough in order to achieve convergence with respect to the accuracy of the calculation of the final states. The program performs DFT self-consistent calculations in the ground and the excited state. The excited state calculation at a given edge involves the presence of the corresponding core hole. The computed wave functions provide the matrix elements for the direct calculation of the complex scattering factors. We have used the default exchange-correlation potential of FDMNES, which is within the local density approximation (LDA). In fact, the gradient correction to LDA does not give a notable difference for C and Si. The core level energy is adjusted to the experiment. Many-body corrections have been implemented via a time dependent DFT (TDDFT) kernel²⁶ containing the Hartree term (which gives the main effects) and an exchange-correlation LDA term. We will check that the present TDDFT procedure in Si is validated by a very good agreement with reflectivity experiments. The lattice constants used in the present calculations were 3.56 Å and 5.43 Å for diamond and Si respectively. For diamond, $\rho = 1.77 \times 10^{23} \text{ cm}^{-3}$ while for Si, $\rho = 0.50 \times 10^{23} \text{ cm}^{-3}$. After obtaining the self-consistent electronic structure, f_1 was computed at the C K edge and at the Si L_{23} edge.

To reveal the resonance effect around the absorption edge, we measured $|\chi^{(2)}|$ of silicon near the L_{23} edge in addition to the previous report on the diamond for the K edge¹⁴ with $\mathbf{Q} = (2, 2, 0)$. The experiments were performed at the 27-m undulator beamline BL19LXU at SPring-8 described by Yabashi and coworkers²⁷. The pump photon energy was set to 9.67 keV, which is just above the K edge of Zn. A (111) silicon plate with a thickness of 1.0 mm was used as the nonlinear crystal. The nonlinear diffraction was measured with $\mathbf{Q} = (1, 1, 1)$. The scattering plane was taken in the horizontal plane, and the polarization of the pump x-rays is also horizontal. The signal photon energies were selected around the silicon L edge by a bent crystal analyzer with the Ge 220 reflection. The photon energy resolution of the

FIG. 2. (Color online) K edge of diamond: In the top frame the solid curve represents the model for f_1 as a function of the idler energy. The label " f_1 solid" emphasizes that the factor f_1 for the solid is different from the one calculated for free atoms. A dashed horizontal line at 0 highlights the f_1 changes of sign. In the bottom frame the black circles and the solid curve are the $|\chi^{(2)}|^2$ in units of $|\chi_{NR}^{(2)}|^2$ and the model for the renormalization factor η respectively, plotted against the idler energy. The experimental data are reproduced from the experiment by Tamasaku, Sawada, and Ishikawa¹⁴.

analyzer was measured to be 2.7 eV. In order to separate the signal from the pump beam, a 25- μm -thick Zn foil was inserted before the analyzer. The signal photon was monitored by a NaI scintillation counter, while the idler photon was deduced by the energy conservation given in Eq. 2.

IV. RESULTS

Figure 2 illustrates the resonant behavior of the non-linear susceptibility of diamond as the function of the idler energy E_i . The $|\chi_{NR}^{(2)}|$ value fitted with our model is $1.4 \times 10^{-16} \text{ cm}^2/\text{StC}$ which is consistent with perturbation theory²⁸. The corresponding atomic scattering factor f_1 calculated within FDMNES is shown in the top frame of Fig. 2. Near the K absorption edge, one can notice the negative excursion of f_1 reaching about -11 that allows ϵ_1/ϵ_0 to be larger from unity near the absorption edge. The peak value of the calculated $\epsilon_1/\epsilon_0 - 1$ is 0.033. A similar dielectric function behavior can also be seen in the optical data from interstellar dust grains of graphite provided by Draine²⁹. However, the peak for graphite is smaller than the one for diamond since the higher density of diamond leads $\epsilon_1/\epsilon_0 - 1$ to be larger by approximately the density ratio. In the bottom frame of Fig. 2, the resonant part of the non-linear susceptibility obtained by Tamasaku, Sawada, and Ishikawa¹⁴ is compared to the model. The overall agreement between

FIG. 3. (Color online) Rocking curves of the 111 nonlinear diffraction of a Si crystal. Symbols represent the measurements and full lines are fits to the data with the Fano formula used by Tamasaku, Sawada, and Ishikawa¹⁴

the experimental data and η is good below the threshold energy. Some discrepancies above the absorption threshold can be explained by the fact that the present theory neglects some resonant fluorescent effects due to the core electrons¹⁸. Interestingly, tuning the idler photon energy above 295 eV makes ϵ_1/ϵ_0 to be smaller from unity in a certain energy window. Thus, $|\chi^{(2)}|^2$ becomes smaller than $|\chi_{NR}^{(2)}|^2$ in this region.

The measured Si rocking curves corresponding to the 111 nonlinear diffraction³⁰ are shown in Fig 3. The horizontal axis indicates the deviation angle $\Delta\theta$ from the phase-matching condition at each E_i . When E_i approaches the L_{23} threshold from below the line shape is asymmetric while when E_i is well above threshold a dip characterizes the spectrum. The data has been fitted with the Fano formula by Tamasaku, Sawada, and Ishikawa¹⁴ to extract the ratio $|\chi^{(2)}/\chi_{NR}^{(2)}|^2$ shown in the bottom of Fig. 4. The top of Fig. 4 shows that the FDMNES result for f_1 near the L_{23} edge predicts an amplitude of about -4 after an energy of $E_i = 100$ eV. This result is in good agreement with x-ray reflectivity measurements by Tripathi *et al.*³¹ and validates the TDDFT kernel used in FDMNES. In fact, the peak value of the experimental $\epsilon_1/\epsilon_0 - 1$ is 0.024 while our calculated value gives 0.025. Clearly, the calculated negative excursion of

FIG. 4. (Color online) Same as Fig. 2 for the Si L_{23} edge.

f_1 leads to a good overall agreement with the experimental ratio $|\chi^{(2)}/\chi_{NR}^{(2)}|^2$. Thus, the resonant fluorescent effects neglected by the theory seem to be small at the L_{23} edge of Si. We did not measure the pump intensity in the case of Si, therefore it was not possible to obtain the non linear susceptibility in unit of cm^2/StC .

Interestingly, the enhancement of $|\chi^{(2)}|$ is not observed at the Si L_1 absorption edge around 150 eV since f_1 does not present any negative excursion in the L_1 edge energy region¹⁷. Therefore, the sign change in f_1 is a crucial condition for the resonant enhancement of $|\chi^{(2)}|^2$ at a given absorption edge.

V. CONCLUSIONS

We have refuted the claim that the major effect of resonance is a decrease in the strength of PDC. Moreover, we have explained the factor determining the renormalization of the nonlinear susceptibility $\chi^{(2)}$ at some absorption edges. In our model, the square of the nonlinear susceptibility $|\chi^{(2)}|^2$ has been connected to an effective scattering cross section, whose resonant enhancement is a function of the scattering factor f_1 , which is strongly modulated when the idler energy is varied across resonant absorption edges. An important prediction of our scheme is that the resonant enhancement of $|\chi^{(2)}|^2$ for the carbon K -edge and the Si L_{23} edge occurs only when f_1 becomes negative otherwise a de-enhancement is obtained. This condition for f_1 explains why the resonant enhancement is not observed at the L_1 edge of Si. Our first principles calculations of f_1 based on the FDMNES are able to faithfully reproduce the dispersion at the edges needed for the reliability of the model since they account for bonding and condensed matter effects. Finally, a related cross section enhancement effect has also been observed in RIXS experiments¹⁸. Therefore, very accurate RIXS

and PDC experiments by XFELs³² can lead to more fundamental theoretical insights.

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