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Scattering of ultrashort X-ray pulses on diamonds with NV centers

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Abstract: Scattering of ultrashort X-ray pulses (USP) is an important component of the diffraction analysis of matter using modern USP sources. Usually, the specific scattering of such USPs is not taken into account to determine the structure of a substance. Taking into account the specifics of scattering on complex structures will give more accurate results when deciphering complex structures. In this work, it is shown that when X-ray USPs are scattered on diamond with NV centers, it is necessary to take into account the pulse duration. The results obtained can be very different from the widely used theory of diffraction analysis, which confirms the need to take into account the specifics of USP scattering when diagnosing complex structures. It is also shown that scattering spectra are quite sensitive to the concentration of NV centres in the diamond structure and this can be used in diffraction analysis.

Keywords: Diamond; NV centre; ultrashort pulse; scattering; scattering spectra; X-ray diffraction analysis.

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1. Introduction

X-ray diffraction analysis of matter (XRD) using ultrashort pulses (USP) has now gained great importance [1–3]. Indeed, using such USPs it is possible to investigate the structure of matter with high temporal and spatial resolution, as the technical capability exists to carry out such investigations. One of the most promising sources of USP are free-electron XFELs [4]. Investigations at such facilities are currently carried out using femtosecond pulses. At present, attosecond pulse generation is being reported by advances in X-ray free-electron lasers [5,6]. Here also a subfemtosecond barrier with a high peak power has been achieved, which allows one to study excitation in a molecular system, the motion of valence electrons with high temporal and spatial resolution, for example [7]. As powerful sources of USP are created, there is a need for new theoretical approaches that take into account the specific interaction of such USP with complex structures [8,9], including promising materials for quantum technologies. To such materials, for example, can be attributed diamond with NV centres. The NV centre (nitrogen-vacancy centre) in diamond is one of the many point defects in diamond, which appear when the carbon atom is removed from the lattice node and the resulting vacancy binds with the nitrogen atom. The defect is unique in that its individual centre electron spins are easily manipulated by light, magnetic, electric and microwave fields, allowing quantum information (qubits) to be written on the centre nucleus spin. Such manipulation is possible even at room temperature [10,11]. Of main interest for quantum technologies are the so called NV$^-$ centres (commonly denoted as NV), which have an extra electron located at the vacancy site and form a pair with spin S = 1 with one of the vacancy electrons.

Ultra-high resolution diffraction analysis of such structures is a promising trend in modern physics. Such analysis is based on scattering of X-rays by various periodic and complex structures. Usually, in the theoretical analysis of XRD scattering of X-ray ultrashort pulses are described as scattering of plane waves of infinite duration in time [3,12]. In other words, the specificity of USP scattering on such structures is not taken into account, which leads to inaccurate use of well-known approaches in XRD [3,8]. The femto- and especially attosecond time-resolved scattering processes on such structures have not been

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well studied and are being actively developed nowadays [8,13–23]. It has recently been shown that the scattering of attosecond USPs on DNA nucleotides may differ significantly from the previously known XRD theory [24,25]. Thus, the study of USP scattering on diamond with NV centres, taking into account the specificity of their scattering, is an important task.

In this paper, the specificity of USP scattering on diamond with NV centres will be investigated. The results obtained have rather simple analytical form and can be applied for calculation of scattering spectra not only with NV centres but also for other colour structures in diamond. It is shown that the scattering spectra are sensitive to the number of NV centres in the diamond. Moreover, it is shown that the consideration of the USP durations leads to a marked difference of the theory presented here to the previously known and widely used one.

Further we will use the atomic system of units: $\hbar = 1$; $|e| = 1$; $m_e = 1$, where $\hbar$ is the Dirac constant, e is the electron charge, m_e is the electron mass.

2. USP scattering on diamond with NV centres

Consider a diamond with an NV center on which the USP falls in the direction bfn_0. As a computational example, consider the system shown in Fig (1). The duration of such a pulse τ, which we will consider many times shorter than the characteristic atomic time $\tau_a \sim 1$, i.e. $\tau \ll \tau_a$. This condition will allow us to use the sudden perturbation

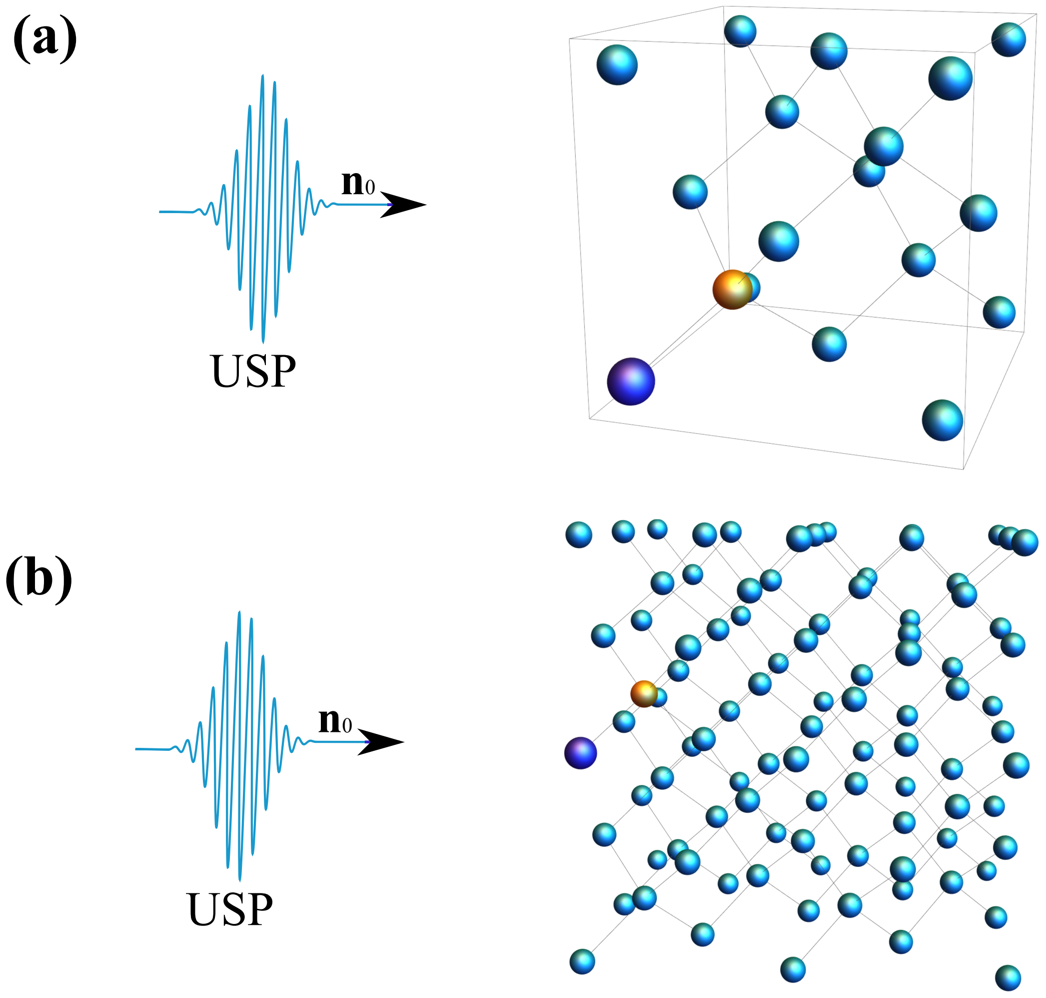

Figure 1. The USP falling on the presented system, in case (a): A diamond lattice unit cell with one NV center, where blue is carbon atoms (C), purple is a nitrogen atom (N), and yellow is a vacancy; (b): a diamond lattice with one NV center for 8 unit cells (2×2×2).

approximation. In this approximation the eigen Hamiltonian of the system can be neglected, since the electron in the atom does not have time to evolve under the action of the USP field because the momentum interaction with the electron in the [26] atom is too fast. It should be added that the condition $\tau \ll \tau_a$ to use our approximation is not strict. In the case of X-ray USPs, as was shown in [18,26], it is sufficient to assume that $\omega_0 \tau_a \gg 1$, where ω_0 is the carrier frequency of the incident USPs. This condition is already satisfied for X-ray USPs. We choose the electromagnetic field strength of the USP in the general form $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 h(t - \mathbf{n}_0 \mathbf{r}/c)$, i.e. we will consider spatially inhomogeneous, where $\mathbf{E}_0$ is the field amplitude, and $h(t - \mathbf{n}_0 \mathbf{r}/c)$ is an arbitrary function defining the shape of the USP, c is the speed of light (in a.u. $c \approx 137$). We will consider the USP fields not so strong as to account for the magnetic field of the USP, i.e., we will assume that $\mathrm{E}_0/c^2 \ll 1$ or in intensity units $\mathrm{I} \ll 10^{25} \mathrm{W/sm}^2$. In this case, as was shown in [24,25], the scattering spectra (scattered energy USP to a unit solid angle in a unit frequency interval) can be represented as

$$\frac{d^2\varepsilon}{d\Omega_{\mathbf{k}} d\omega} = \frac{[\mathbf{E}_0 \mathbf{n}]^2}{(2\pi)^2} \frac{|\tilde{h}(\omega)|^2}{c^3} \left[\sum_{i=1}^{s} N_{e,i} N_{A,i} (1 - |F_i|^2) + \sum_{i,j=1}^{s} \delta_{i,j} N_{e,i} N_{e,j} F_i F_j^* \right], \tag{1}$$

where $\tilde{h}(\omega) = \int\limits_{-\infty}^{+\infty} h(\eta) e^{i\omega\eta} d\eta$, and $\mathbf{p} = \frac{\omega}{c}(\mathbf{n} - \mathbf{n}_0)$ has the meaning of recoil momentum when a USP is scattered on a bound electron; $N_{e,i}$ is the number of electrons in the atom i variety; $N_{A,i}$ is the number of atoms i variety; $F_i = \frac{1}{N_{e,i}} \int \rho_{e,i}(\mathbf{r}) e^{-i\mathbf{p}\mathbf{r}} d^3\mathbf{r}$ is the form factor of the i atom of the variety with electron density $\rho_{e,i}(\mathbf{r})$. The factor $\delta_{i,j} = \sum_{Ai,A'j} e^{-i\mathbf{p}(\mathbf{R_{Ai}} - \mathbf{R_{A'j}})}$ depends only on the coordinates of atoms i of the variety (with number Ai) whose position is determined by the radius vector $\mathbf{R}_{Ai}$. Of greatest interest for XRD is the $\tau\omega_0 \gg 1$ case (τ is the pulse duration, ω_0 is the USP carrier frequency). If we assume that $\tau \to \infty$, i.e. the radiation source is continuous, we get the well-known XRD theory. It is this theory that is used in XRD even in the case of ultrashort pulses, without taking into account the specifics of USP scattering.

Using Eq. (1) we can obtain a physically measurable value (scattering energy to a unit solid angle)

$$\begin{aligned} \frac{d\varepsilon}{d\Omega_{\mathbf{k}}} = \frac{[\mathbf{E}_0 \mathbf{n}]^2}{(2\pi)^2 c^3} \tau \int_{-\infty}^{\infty} |\tilde{f}(x)|^2 dx \Bigg[\sum_{i=1}^{s} N_{e,i} N_{A,i} (1 - |F_i(\mathbf{p}_0)|^2) + \\ \sum_{i,j=1}^{s} \gamma_{i,j}(\mathbf{p}_0, \mathbf{p}_\tau) N_{e,i} N_{e,j} F_i(\mathbf{p}_0) F_j^*(\mathbf{p}_0) \Bigg], \\ \gamma_{i,j}(\mathbf{p}_0, \mathbf{p}_\tau) = \sum_{Ai,A'j} e^{-i\mathbf{p}(\mathbf{R_{Ai}} - \mathbf{R_{A'j}})} \frac{\int_{-\infty}^{\infty} |\tilde{f}(x)|^2 e^{-ix\mathbf{p}_\tau(\mathbf{R}_{Ai} - \mathbf{R}_{A'j})} dx}{\int_{-\infty}^{\infty} |\tilde{f}(x)|^2 dx}. \end{aligned} \tag{2}$$

where $F_i(\mathbf{p}_0), \delta_{i,j}(\mathbf{p}_0)$; $\mathbf{p}_0 = \frac{\omega_0}{c}(\mathbf{n} - \mathbf{n}_0)$ and $\mathbf{p}_\tau = \frac{1}{c\tau}(\mathbf{n} - \mathbf{n}_0)$; $h = e^{-i(\omega_0 t - \mathbf{k}_0 \mathbf{r})} f((t - \mathbf{n}_0 \mathbf{r})/\tau)$, where the f function defines the USP profile, then we get$\tilde{f}((\omega - \omega_0)\tau) = \int_{-\infty}^{\infty} e^{-i(\omega - \omega_0)\tau\eta} f(\eta) d\eta$ is the Fourier transform of the function $f(\eta)$. The electron density of such atoms $\rho_{e,i}(\mathbf{r}) = \frac{N_{e,i}}{4\pi r} \sum_{k=1}^{3} A_{k,i} \alpha_{k,i}^2 e^{-\alpha_{k,i} r}$, where $A_{k,i}, \alpha_{k,i}$ are constant coefficients (for all varieties of atoms with number i) defined in [27]. The result is a simple expression for $F_i = \sum_{k=1}^{3} \frac{A_{k,i} \alpha_{k,i}^2}{p^2 + \alpha_{k,i}^2}$. Next, we need to determine the form of the incident USP, which we choose as a Gaussian form $h(t) = e^{-i(\omega_0 t - \mathbf{k}_0 \mathbf{r})} e^{-\alpha^2 (t - \mathbf{n}_0 \mathbf{r}/c)^2}$, where $\alpha = 1/\tau$, $\mathbf{k}_0 = \mathbf{n}_0 \omega_0 / c$. The Gaussian USP is chosen as one of the best known for describing USP. For example, in [28] an exact description of the subcyclic pulse beam (SCPB) was found, where in the case considered in this paper ($\omega_0/\alpha \gg 1$) the solution has the form of a Gaussian impulse. In the chosen USP case, we obtain $\tilde{h}(\omega) = \frac{\sqrt{\pi}}{\alpha}e^{-(\omega-\omega_0)^2/4\alpha^2}$. Consider the case of multi-cycle momentum, i.e., when $\omega_0/\alpha \gg 1$, which is mainly used in diffraction analysis of matter. Using the Eq. (2) we obtain

$$\frac{d\varepsilon}{d\Omega_{\mathbf{k}}} = \frac{[\mathbf{E}_0\mathbf{n}]^2}{4c^3\alpha\sqrt{2\pi}}\left[\sum_{i=1}^{s} N_{e,i}N_{A,i}(1-|F_i(\mathbf{p}_0)|^2) + \sum_{i,j=1}^{s}\gamma_{i,j}(\mathbf{p}_0,\mathbf{p}_\tau)N_{e,i}N_{e,j}F_i(\mathbf{p}_0)F_j^*(\mathbf{p}_0)\right],$$

$$\gamma_{i,j}(\mathbf{p}_0,\mathbf{p}_\tau) = \sum_{Ai,A'j} e^{-i\mathbf{p}(\mathbf{R}_{Ai}-\mathbf{R}_{A'_j}))}e^{-\frac{1}{2}(\mathbf{p}_\tau(\mathbf{R}_{Ai}-\mathbf{R}_{A'_j}))^2}. \quad (3)$$

In our case s can be considered equal to 2, since the presented system can be represented by two independent atoms: carbon (C) and nitrogen (N). It should be taken into account that the place where there is a vacancy is empty, i.e. there are no atoms there. Eq. (3) takes into account the specificity of USP scattering on the system under study. Indeed, in this expression there are characteristics responsible for the duration τ of the USP. If in this expression we take into account only the coherent USP scattering term (the second sum in Eq.(3)) and we take $\tau \to \infty$ away, we obtain the well-known expression for the scattering of long duration (monochromatic) X-rays [25]. Indeed, at $\tau \to \infty$ the expressions for $\mathbf{p}_\tau = \frac{1}{c\tau}(\mathbf{n}-\mathbf{n}_0) \to 0$ and Eq. (3) becomes proportional to τ (Fermi's golden rule). Thus, the main difference between the Eq. (3) from the previously known theory is determined by the factor $\gamma_{i,j}(\mathbf{p}_0,\mathbf{p}_\tau)$, analysis of which determines the difference of our theory from the previously known one. It turns out that this difference is mainly observed when using attosecond and shorter pulses. Indeed, at such pulses when $\tau \lesssim 1$ the factor $e^{-\frac{1}{2}(\mathbf{p}_\tau(\mathbf{R}_{Ai}-\mathbf{R}_{A'_j}))^2}$ is close to unity at quite small $\mathbf{R}_{Ai}-\mathbf{R}_{A'_j}$ (groups of units, tens and hundreds of atoms). In this case on such atoms, where $\mathbf{R}_{Ai}-\mathbf{R}_{A'_j}$ is small enough, the scattering is coherent, otherwise the factor $\gamma_{i,j}(\mathbf{p}_0,\mathbf{p}_\tau)$ quickly tends to zero and the scattering goes in more complicated way. In the case of continuous radiation (when $\tau \to \infty$) the coherent radiation comes from all atoms. Qualitatively, this can be explained quite simply. The portion of the atoms in the matter that falls within the spatial region of size of the USP ($\sim c\tau$) emits coherently. This is a very important specification, because if some region with NV centers does not fall into such a size ($\sim c\tau$), the results of our theory and the previously known one will be very different. This, in turn, will lead to incorrect use of the previously known theory of diffraction analysis (XRD) of matter. As an example, let's take the USP scattering calculations on the systems presented in Fig.1. Calculation of scattering spectra using Eq. (3) are shown in Fig.2 and Fig.3. The pulse falls as shown in Fig.1 with photon energy $\hbar\omega_0 = 7.46\ keV$, pulse duration $\tau = 10$(as). The results in Fig.3 are presented in relative units normalized to the maximum value of the spectrum. Let us show that using USP scattering is sensitive to finding NV centers in the diamond, even at low concentrations. To do this, let us show the difference δ (normalized to the maximum value of the spectrum, i.e. $\delta = \left(\left[\frac{d\varepsilon}{d\Omega_{\mathbf{k}}}\right]_{NV} - \frac{d\varepsilon}{d\Omega_{\mathbf{k}}}\right)/\left[\frac{d\varepsilon}{d\Omega_{\mathbf{k}}}\right]_{max}$) between scattering spectra of diamond lattice with NV center and diamond lattice. The results of the calculations are shown in Fig. 4 From Figs. 2-4 one can see that the scattering spectra are quite sensitive to the NV centers in the diamond structure, i.e., sensitive to the concentration of NV centers in the diamond. Indeed, comparing the graphs in Figs. 3 and 4 one can see that for case (a) the spectral values do not differ by more than an order of magnitude, and in case (b) by more than 2 orders of magnitude.

3. Discussion and Conclusion

Thus, using Eq. (3) we obtained two important results. The first result is responsible for the necessity to use the theory of USP scattering on complex multi-atomic systems developed in this work and in [24,25] in the case of using attosecond pulses. We have shown that when using attosecond pulses, the previously well known XRD theory can carry significant errors and it is necessary to use the theory developed here. The theory

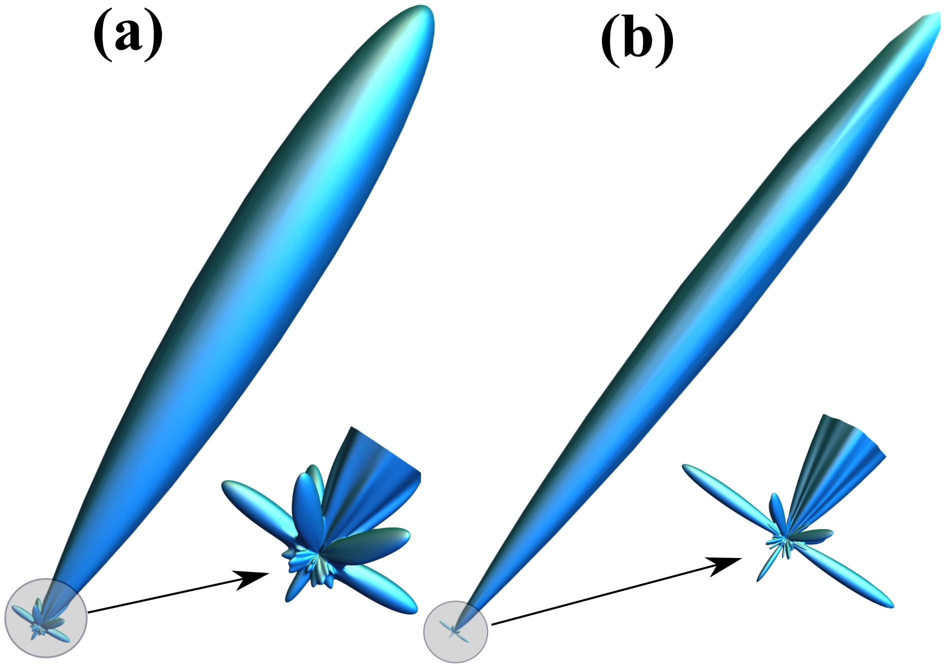

Figure 2. The figures show 3D USP scattering spectra: (a) a diamond unit cell with an NV center (see Fig. 1 (a)) and on the diamond structure presented in Fig. 1 (b).

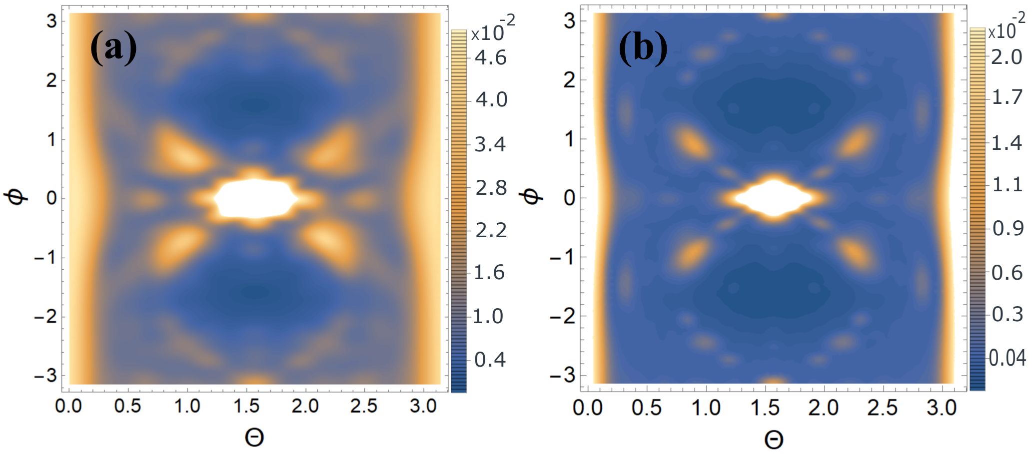

Figure 3. The figures show 2D USP scattering spectra presented as contour plots: (a) a diamond unit cell with an NV center (see Fig. 1 (a)) and (b) this on the diamond structure presented in Fig. 1 (b).

developed here should be used in the case of USP scattering on a diamond structure with NV centers when the parameter $\gamma_{i,j}(\mathbf{p}_0, \mathbf{p}_\tau)$ differs from unity. The reason why the parameter $\gamma_{i,j}(\mathbf{p}_0, \mathbf{p}_\tau)$ may differ from unity arises when the spatial pulse duration ($\sim c\tau$) is comparable or smaller than the size of the NV centers being studied in the diamond structure. This can be when the NV centers are concentrated in some region in the diamond. It should be added that nowadays more and more attention is paid to single NV centers and their relatively small groups, as well as their orientation in the diamond structure. In order to study such NV centers in the diamond structure using attosecond pulses, the theory developed here should be used. The second important conclusion is that the USP scattering spectra are quite sensitive to the concentration of NV centers in the diamond structure. This leads to the fact that USP scattering can be used to determine the concentration of NV centers. It should be added that determining the concentration of NV centers in a diamond structure is a rather difficult task, which is relevant at present.

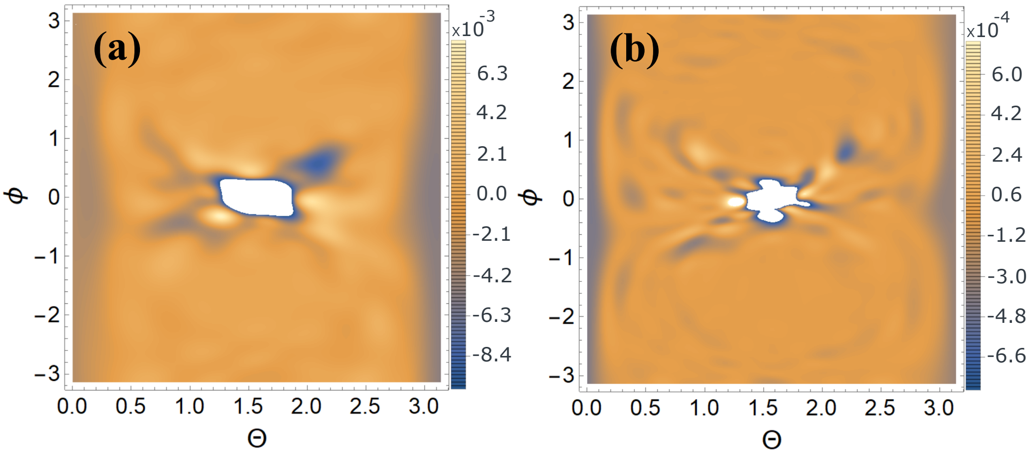

Figure 4. The figures show the contribution to the scattering spectra of a diamond lattice with a single NV center (presenting the calculation of the δ parameter) as 2D contour plots: (a) a diamond unit cell with an NV center (see Fig. 1 (a)) and (b) this on the diamond structure presented in Fig. 1 (b).

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References

1. Jones, N. Crystallography: Atomic secrets. *Nature* **2018**, *505*, 602–603.
2. Benediktovich, A.; Feranchuk, I.; Ulyanenkov, A. *Theoretical Concepts of X-Ray Nanoscale Analysis*; Springer-Verlag Berlin Heidelberg, 2014.
3. Eseev, M.K.; Matveev, V.I.; Makarov, D.N. Diagnostics of Nanosystems with the Use of Ultrashort X-Ray Pulses: Theory and Experiment (Brief Review). *JETP Lett.* **2021**, *114*, 387–405.
4. Schoenlein, R.; Elsaesser, T.; Holldack, K.; Huang, Z.; Kapteyn, H.; Murnane, M.; Woerner, M. Recent advances in ultrafast X-ray sources. *Philos. Trans. R. Soc. A* **2019**, *377*, 20180384.
5. Duris, J.; Li, S.; Driver, T.; Champenois, E.G.; et al. Tunable isolated attosecond X-ray pulses with gigawatt peak power from a free-electron laser. *Nature Photonics* **2020**, *14*, 30–36.
6. Maroju, P.K.; Cesare Grazioli, M. Di, F.; et al. Attosecond pulse shaping using a seeded free-electron laser. *Nature* **2020**, *578*, 386–391.
7. Mukamel, S.; Healion, D.; Zhang, Y.; Biggs, J.D. Multidimensional attosecond resonant X-ray spectroscopy of molecules: lessons from the optical regime. *Annu. Rev. Phys. Chem.* **2013**, *64*, 101–127.
8. Dixit, G.; Vendrell, O.; Santra, R. Imaging electronic quantum motion with light. *PNAS* **2012**, *109*, 11636–11640.
9. Leone, S.R.; McCurdy, C.W.; Burgdörfer, J.; et al.. What will it take to observe processes in "real time"? *Nature Photonics* **2014**, *8*, 162–166.
10. Balasubramanian, G.; I.Y.Chan.; Kolesov, R.; Al-Hmoud, M.; Tisler, J.; et al. Nanoscale imaging magnetometry with diamond spins under ambient conditions. *Nature* **2008**, *455*, 648–651.
11. Doherty, M.W.; Manson, N.B.; Delaney, P.; Jelezko, F.; Wrachtrup, J.; Hollenberg, L.C. The nitrogen-vacancy colour centre in diamond. *Physics Reports* **2013**, *528*, 1–45.
12. James, R.W. *The Optical Principles of the Diffraction of X-rays (Ox Bow)*; Woodbridge, Conn.: Ox Bow Press, 1982.
13. Henriksen, N.E.; Moller, K.B. On the Theory of Time-Resolved X-ray Diffraction. *J. Phys. Chem. B* **2008**, *112*, 558–567.
14. Astapenko, V.A.; Sakhno, E.V. Excitation of a quantum oscillator by short laser pulses. *Applied Physics B* **2020**, *126*, 23.

15. Rosmej, F.B.; Astapenko, V.A.; Lisitsa, V.S.; Li, X.D.; Khramov, E.S. Scattering of ultrashort laser pulses on "ion-sphere" in dense plasmas. *Contrib. Plasma Phys.* **2019**, *59*, 189–196.
16. Makarov, D.N. Quantum theory of scattering of ultrashort electromagnetic field pulses by polyatomic structures. *Optics Express* **2019**, *27*, 31989–32008.
17. Eseev, M.K.; Goshev, A.A.; Makarov, D.N. Scattering of Ultrashort X-ray Pulses by Various Nanosystems. *Nanomaterials* **2020**, *10*, 1355.
18. Eseev, M.K.; Goshev, A.A.; Makarova, K.A.; Makarov, D.N. X-ray diffraction analysis of matter taking into account the second harmonic in the scattering of powerful ultrashort pulses of an electromagnetic field. *Scientific Reports* **2021**, *11*, 3571.
19. Moller, K.B.; Henriksen, N.E. Time-resolved x-ray diffraction: The dynamics of the chemical bond. *Struc. Bond.* **2012**, *142*, 185.
20. Tanaka, S.; Chernyak, V.; Mukamel, S. Time-resolved x-ray spectroscopies: Nonlinear response functions and liouville-space pathways. *Phys. Rev. A* **2001**, *63*, 63405–63419.
21. Dixit, G.; Slowik, J.; Santra, R. Proposed Imaging of the Ultrafast Electronic Motion in Samples using X-Ray Phase Contrast. *Phys. Rev. Lett.* **2013**, *110*, 137403.
22. Kraus, P.M.; Zürch, M.; Cushing, S.K.; Neumark, D.M.; Leone, S.R. The ultrafast X-ray spectroscopic revolution in chemical dynamics. *Nature Reviews Chemistry* **2018**, *2*, 82–94.
23. Peng, P.; Marceau, C.; Villeneuve, D.M. Attosecond imaging of molecules using high harmonic spectroscopy. *Nature Reviews Physics* **2019**, *1*, 144–155.
24. Makarov, D.; Kharlamova, A. Scattering of X-ray Ultrashort Pulses by Complex Polyatomic Structures. *Int. J. Mol. Sci.* **2022**, *23*, 163.
25. Makarov, D.N.; Makarova, K.A.; Kharlamova, A.A. Specificity of scattering of ultrashort laser pulses by molecules with polyatomic structure. *Scientific Reports* **2022**, *12*, 1–9.
26. Makarov, D.N.; Eseev, M.K.; Makarova, K.A. Analytical wave function of an atomic electron under the action of a powerful ultrashort electromagnetic field pulse. *Optics Letters* **2019**, *44*, 3042–3045.
27. Salvat, F.; Martnez, J.D.; Mayol, R.; Parellada, J. Analytical Dirac-Hartree-Fock-Slater screening function for atoms (Z = 1-92). *Phys. Rev. A* **1987**, *36*, 467–474.
28. Lin, Q.; Zheng, J.; Becker, W. Subcycle pulsed focused vector beams. *Phys. Rev. Lett.* **2006**, *97*, 253902.