

Supplementary Information

Daniele Ronchetti^{1,2,3}, Andrei Benediktovitch^{1*},
Laurent Mercadier⁵, Edoardo Zavatti¹, Tobias Freund¹,
Fridtjof Kerker², Christina Bömer¹, Dietrich Krebs^{1,2},
Aliaksandr Leonau¹, Mauro Prasciolu¹, Natalia Gerasimova⁵,
Benjamin van Kuiken⁵, Giuseppe Mercurio⁵, Sergii Parchenko⁵,
Justina Schlappa⁵, Martin Teichmann⁵, Andreas Scherz⁵,
Svitozar Serkez⁵, Nikita Medvedev^{9, 10}, Michal Stransky^{5,9},
Beata Ziaja^{1,6}, Joshua J. Kas⁷, John J. Rehr⁷, Christian Laubis⁸,
Michael Kolbe⁸, Emilio Bellingeri¹¹, Saša Bajt^{1,4},
Henry N. Chapman^{1,2,4}, Nina Rohringer^{1,2,4*}

¹Center for Free-Electron Laser Science (CFEL), Deutsches
Elektronen-Synchrotron DESY, Hamburg 22607, Germany.

²Department of Physics, Universität Hamburg, Hamburg 22607, Germany.

³Max Planck School of Photonics, Friedrich-Schiller-Universität Jena,
Jena 07745, Germany.

⁴The Hamburg Center for Ultrafast Imaging, Hamburg 22761, Germany.

⁵European XFEL, Schenefeld 22869, Germany.

⁶The Henryk Niewodniczański Institute of Nuclear Physics, Polish
Academy of Sciences, Kraków 31-342, Poland.

⁷Department of Physics, University of Washington, Seattle, WA
98195-1560, United States of America.

⁸Physikalisch-Technische Bundesanstalt, Berlin 10587, Germany.

⁹Institute of Physics, Czech Academy of Sciences, Prague 8 182 00, Czech
Republic.

¹⁰Institute of Plasma Physics, Czech Academy of Sciences, Prague 8 182
00, Czech Republic.

¹¹CNR-SPIN, Genova 16152, Italy.

*Corresponding author(s). E-mail(s): andrei.benediktovitch@desy.de;
nina.rohringer@desy.de;

31	Contents	
32	1 Simulation of the reflectivity spectrum	3
33	1.1 Characterization of the multilayer	3
34	1.2 Reflectivity calculation and comparison to high-resolution measurement	4
35	2 Structural evolution of the multilayer	6
36	3 Derivation of the scattering factor of a two-level system	9
37	4 Supplementary figures mentioned in the main text	12

1 Simulation of the reflectivity spectrum

In this section we explain how the forward simulation of the low intensity (cold) Soft X-ray Reflectivity (SXR) spectrum is built and checked against measured data. Firstly, the multilayer is characterized by a Hard X-ray Reflectivity (HXR) measurement. Then, based on the referred sample parameters from the HXR result, a Parratt's approach is used to calculate the expected SXR spectrum. This result is compared to a high-resolution measurement to confirm the validity of the forward estimate of the spectrally resolved SXR reflectivity. Subsequently, we introduce the modified scattering factors to obtain the high intensity curves presented in the main text.

1.1 Characterization of the multilayer

The model structure of the multilayer mirrors is shown schematically in the article. Multilayers were characterized for their quality using a laboratory setup with Cu $K\alpha$ X-ray tube. The measured curve was fitted with the GenX software [1] to determine the thickness, density and surface roughness of every layer. Figure S1 shows an example of the fitted versus measured HXR reflectivity curve.

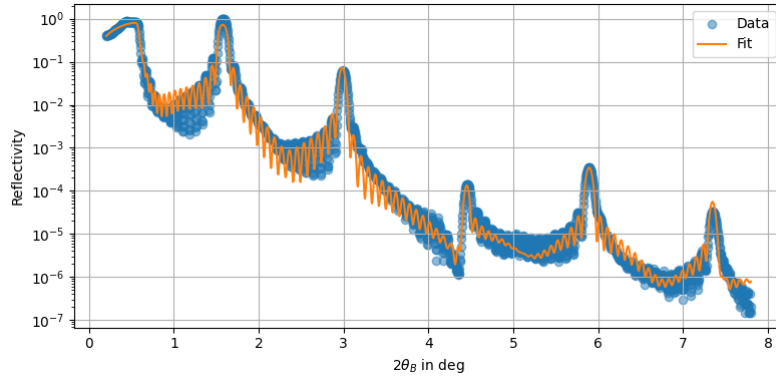


Fig. S1 Hard X-ray Reflectivity. Measurement (blue dots) and fit (orange line) of the HXR of the multilayer sample as a function of the angle between incident beam and top surface of the multilayer.

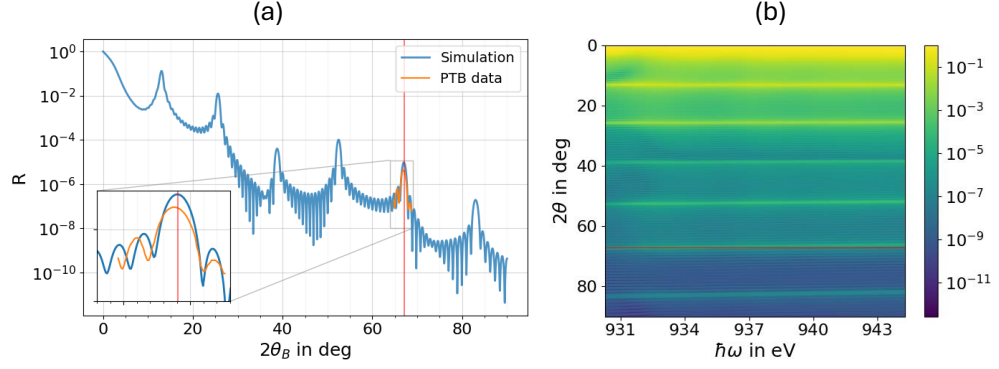


Fig. S2 Soft X-ray Reflectivity curve and 2D map. (a) Simulation of the SXR curve for a wavelength of 932.2 eV (1.33 nm) based on Parratt’s formalism. The simulation (blue) is compared to the measurements done at the PTB (orange). (b) Two dimensional map of the SXR. In both panels the red line corresponds to the maximum of the fifth super-lattice peak.

1.2 Reflectivity calculation and comparison to high-resolution measurement

Based on the parameters obtained from the HXR fit we employ a Parratt’s recursive formalism [2, 3] to simulate the SXR reflectivity curve. We decided to develop an in-house code for the Parratt simulation, such that we can grant the required flexibility of modifying the atomic scattering factor of the Cu atoms.

The SXR measurement was done at the Physikalisch-Technische Bundesanstalt (PTB) soft X-ray beamline of the BESSY II synchrotron using a high-resolution reflectivity setup in a two step procedure. Firstly, the sample is rocked to find the maximum of the relevant peak. This measurement is done using a constant photon energy of 932.2 eV (1.33 nm). Once the maximum is found, the sample angle is fixed and the reflectivity spectrum is measured by scanning the incoming wavelength.

Similarly, we first simulate the SXR curve for the same fixed wavelength as used in the experiment and select the angle where the fifth order peak is maximum, see panel (a) of figure S2. We then re-run the code for a number of energies and select the slice corresponding to the angle previously found, as shown in panel (b) of the same figure. The final result of this procedure is the SXR spectrum presented in figure S3, together

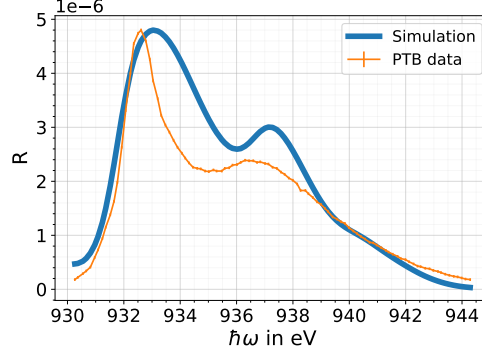


Fig. S3 Soft X-ray Reflectivity spectrum. Simulation (blue) and measurement (orange) of the SXR spectrum. A scaling factor of 0.41 has been applied to the simulated curves.

70 with the high-resolution measurement. The simulated reflectivity is overestimated by
 71 the idealized model. We applied a scaling factor of 0.41 to the simulation to re-scale it's
 72 absolute value to match the experimental curve. Uncertainties of the model stem from
 73 the limited SNR of the HXR data that can lead to errors in the fit of the multilayer
 74 parameters, especially towards the more critical larger angles. Furthermore, a period
 75 of a few months elapsed between the HXR and the SXR measurement, during this time
 76 the sample might have acquired an oxidation capping layer which is responsible for
 77 the lower signal. A lower reflectivity also arises from unavoidable sample imperfections
 78 such as interface roughness and layer interdiffusion, which are not accounted for in
 79 the simple model. Importantly, the spectral position and width of the overall feature
 80 is well reproduced by the model, meaning that all wavelength dependent physical
 81 properties, such as the atomic scattering factors, are treated accurately. We should
 82 point out here that the modification of the scattering factor is calculated only for
 83 copper atoms. This is justified by the fact that all other elements in the multilayer
 84 (Si, C and B) are much lighter than Cu and their absorption edges and emission lines
 85 are not resonant with the used wavelength. Thus, there is no transient modification
 86 of their scattering properties beside a small reduction of the scattering signal due
 87 to the photo-ionization. Furthermore, we assume that the lattice structure of the
 88 multilayer remains fixed. This is justified by considering that the radiation damage

89 evolves on a much longer time scale (ps) as compared to the pulse duration of 15 fs.
90 This assumption is corroborated by the theoretical modeling reported in section 2.
91 Considering all these arguments we can confirm that the forward model reproduces
92 the spectral shape of the reflectivity reasonably well.

93 Differently than the measurement at PTB, where the spectral signature of the
94 reflectivity curve has been measurement via a monochromatic wavelength scan of
95 the incoming beam, the X-ray Free Electron Laser (XFEL) measurements are done
96 with broad-band, fluctuating Self Amplified Spontaneous Emission (SASE) pulses
97 which are spectrally not characterized on a shot-by-shot basis. The predictions of the
98 ensemble averaged spectral reflectivity curve of the XFEL measurements assumes a
99 spectral gaussian profile and the introduction of the modified scattering factors for
100 the pumped case (as described in the main text). The description of the transient
101 electronic state, which is reported in the main text, gives us the modified values of
102 the scattering factors to be included in the model. Combining all this components we
103 are able to reliably simulate the transiently modified reflectivity spectrum.

104 2 Structural evolution of the multilayer

105 To confirm the assumption that the multilayer structure remains unchanged dur-
106 ing the pulse, we have performed simulations with a hybrid code XTANT-3 that
107 combines Monte Carlo method for modeling photon-induced electron kinetics, the
108 Boltzmann equation for low-energy electrons populating the valence and conduction
109 bands, transferable tight binding method to calculate the transient electronic struc-
110 ture and interatomic forces, and molecular dynamics for tracing atomic motion [4].
111 The Density-Functional based Tight-Binding (DFTB) parameterization matsci-0-3 is
112 used to model Cu and Si atoms [5]. As a model that would provide realistic insights
113 but is computationally tractable, we have employed a system consisting of a crystalline
114 Cu layer (144 atoms in the fcc structure, 1.4 nm thick) and an amorphous Si layer (144

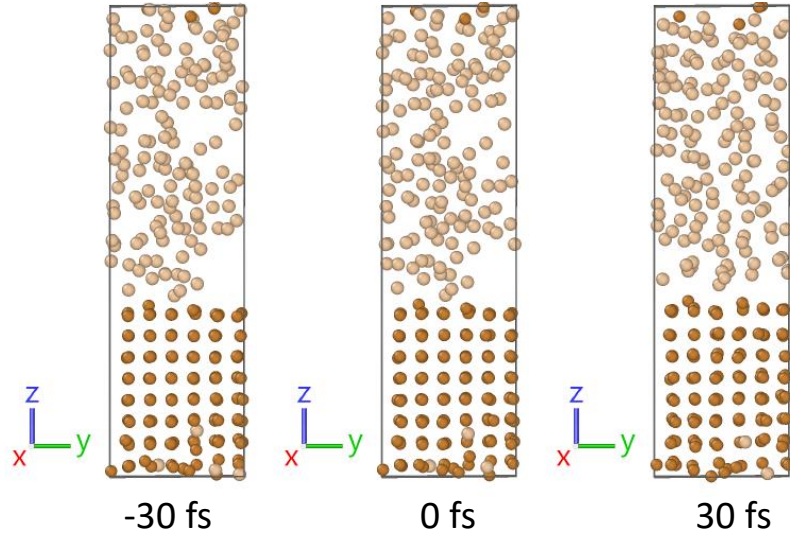


Fig. S4 Multilayer structure simulated with XTANT-3 code. Snapshots of the evolution for the case of irradiation with an FEL pulse with 950 eV photon energy, 15 fs FWHM, absorbed dose 40 eV atom⁻¹. Dark brown atoms are copper, light brown are silicon.

atoms, 2.4 nm thick) with periodic boundary conditions. The system was relaxed to the ground state and thermalized, and then irradiated with the pulse of 15 fs FWHM, 950 eV photon energy, and absorbed doses of 2 and 40 eV atom⁻¹ – that for our case would correspond to a pump pulse intensity of 2.5×10^{13} W cm⁻² or 5.0×10^{14} W cm⁻² respectively. A few snapshots of the structure evolution are shown in figure S4.

Figure S5 (a) shows the absolute mean displacement of the atoms within the bulk of the layer, figure S5 (b) demonstrates the projections of the Mean Square Displacement (MSD). The projection on the Z axis allows to identify the motion of the interfacial layer. The displacements of Cu atoms are small, even though the interfacial layer is moving as a whole (MSD of Cu atoms along Z is larger than along other axes). Displacements of the Si atoms along all the axes, including the direction normal to the interface, are larger, as Si behaves more like a liquid. However, both the mean and mean square displacements within ± 30 fs – corresponding to the time when FEL

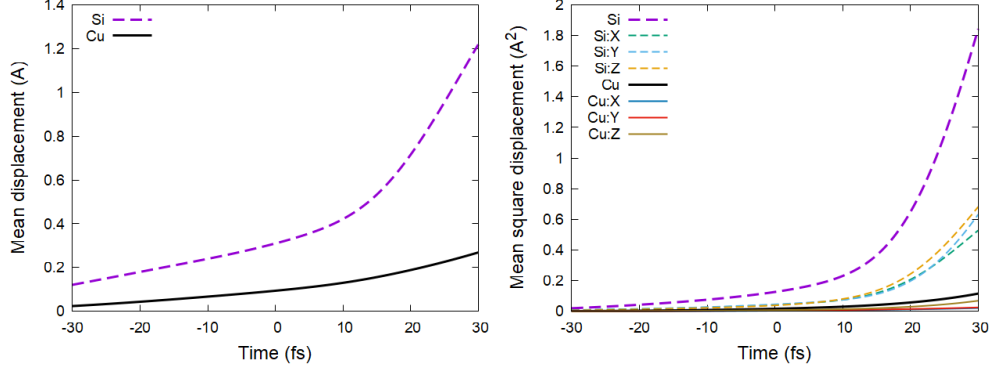


Fig. S5 Atomic displacements in Cu/Si multilayer. Atomic displacement in the Cu/Si multilayer when excited by an Free Electron Laser (FEL) pulse with 950 eV photon energy, absorbed dose 40 eV atom⁻¹. (a) Mean atomic displacements within the whole volume for Cu and Si subsystems. (b) Total and projected mean square displacements. Directions x,y,z correspond to the axes displayed in figure S4

128 pulse interacts with the system – for Si atoms are only ≈ 1 Å, whereas for Cu atoms
 129 they are < 0.3 Å.

130 To estimate the behavior of Cu/B₄C system, we assume the following approxima-
 131 tion: we use the same tight binding parameters and the structure as above for Cu/Si,
 132 but artificially change the mass of Si atoms to be equal to the mass of boron. This way,
 133 we can accelerate the dynamics (for lighter “boron” atoms vs. silicon ones), and mimic
 134 a response of B₄C to irradiation. Then, we simulate the irradiation of this multilayer
 135 target with the same laser pulse as above. Lighter atoms of “boron” move faster upon
 136 irradiation; however, the interlayer surface does not seem to be very different from
 137 the previous case. We may conclude that the interface roughness is mainly defined
 138 by the behavior of the heaviest component, copper. As the copper atoms’ movement
 139 during the FEL pulse (at the studied absorbed doses up to 40 eV atom⁻¹) is below
 140 1 Å, we conclude that changes in the interface roughness of a multilayer system may
 141 be neglected.

142 3 Derivation of the scattering factor of a two-level 143 system

144 Let us consider an ensemble of atoms with concentration n . Each atom is described
145 as a two-level system with ground state $|g\rangle$ and excited state $|e\rangle$. The system has one
146 resonant frequency ω_0 , a total decay rate γ_2 , and a spontaneous decay rate Γ_{sp} . If
147 we consider the interaction with an external field of frequency ω – and corresponding
148 wavelength λ – defined in terms of its Rabi frequency Ω_s , the evolution of the system
149 is described by the optical Bloch equations [6]. In particular, the coherence element
150 (ρ_{eg}) of the density matrix of a single atom evolves as

$$\frac{\partial \rho_{eg}(\tau)}{\partial \tau} = -i\omega_0 \rho_{eg}(\tau) - i\Omega_s(\tau)(\rho_{ee} - \rho_{gg}) - \frac{\gamma_2}{2} \rho_{eg}(\tau). \quad (1)$$

151 We assume that the population of the ground (ρ_{gg}) and excited state (ρ_{ee}) are
152 stationary. We can then Fourier transform equation 1 to obtain:

$$-i\omega \hat{\rho}_{eg}(\omega) = -i\omega_0 \hat{\rho}_{eg}(\omega) - i\hat{\Omega}_s(\omega)(\rho_{ee} - \rho_{gg}) - \frac{\gamma_2}{2} \hat{\rho}_{eg}(\omega). \quad (2)$$

153 By simple algebra and defining the detuning parameter between the incoming field
154 frequency and the resonant frequency of the two-level system $\Delta\omega = \omega - \omega_0$, one can
155 obtain the expression for the coherence element:

$$\hat{\rho}_{eg}(\omega) = \frac{i(\rho_{ee} - \rho_{gg})}{i\Delta\omega - \frac{\gamma_2}{2}} \hat{\Omega}_s(\omega). \quad (3)$$

156 On the other hand, the field propagates through the ensemble of atom and evolves
 157 following Maxwell's equation in the paraxial approximation:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) \right] \hat{\Omega}_s(\omega) = \left(i \frac{3}{8\pi} \lambda^2 \Gamma_{sp} n \right) \hat{\rho}_{eg}(\omega) \quad (4)$$

158 where $k_0 = 2\pi/\lambda$ is the wave vector of the field and χ the susceptibility of the material.
 159 We can now substitute $\hat{\rho}_{eg}$ in equation 4 with equation 3, obtaining:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) \right] \hat{\Omega}_s(\omega) = - \frac{3}{8\pi} \lambda^2 \Gamma_{sp} n \frac{\rho_{ee} - \rho_{gg}}{i\Delta\omega - \frac{\gamma_2}{2}} \hat{\Omega}_s(\omega). \quad (5)$$

160 The right side of equation 5 is an extra source of radiation, thus can be expressed in
 161 terms of a new susceptibility term (χ_T). With this definition equation 5 becomes:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) - i \frac{k_0}{2} \chi_T(\omega) \right] \hat{\Omega}_s(\omega) = 0, \quad (6)$$

162 with:

$$\chi_T(\omega) = \frac{3}{8\pi^2} \lambda^3 n \Gamma_{sp} \frac{-i(\rho_{ee} - \rho_{gg})}{i\Delta\omega - \frac{\gamma_2}{2}}. \quad (7)$$

163 This last equation is the transient contribution to the susceptibility of every atom due
 164 to the interaction with the external field.

165 The atomic scattering factor (f) is intrinsically related to the susceptibility:

$$\chi = \frac{n r_e \lambda^2 f}{\pi}. \quad (8)$$

166 Therefore, we can find the transient contribution to the atomic scattering factor (f_T)
 167 by substituting χ_T (equation 7) in equation 8, leading to:

$$f_T(\omega) = - \frac{3}{8\pi} \frac{\lambda}{r_e} \Gamma_{sp} (\rho_{ee} - \rho_{gg}) \frac{\Delta\omega - i\gamma_2/2}{\Delta\omega^2 + (\gamma_2/2)^2}. \quad (9)$$

168 This last equation is the atomic scattering factor of an unbalanced two-level system,
169 which we used in our simulation codes as mentioned in the main text.

4 Supplementary figures mentioned in the main text

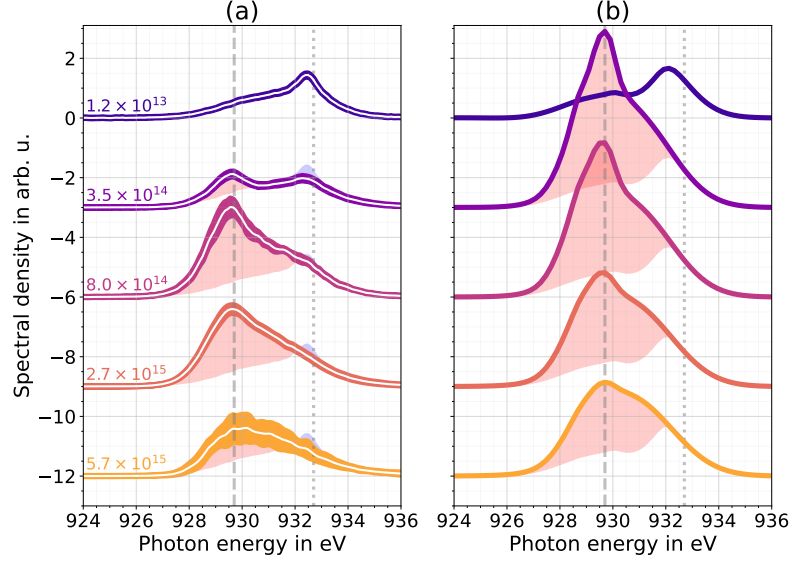


Fig. S6 Spectrally resolved transient enhancement of the scattering strength of Cu atoms. (a) Experimental measurement of the spectrally resolved scattered radiation from the multilayer structures around the Cu- L_α resonance for different intensities (in W cm^{-2}). The spectra are offset vertically by -3 arb. u. for clarity. The colored region around each spectrum represents the 99% confidence interval. The shaded red (or blue) regions correspond to stronger (or weaker) scattered intensity with respect to the cold reference spectrum measured at the low intensity $1.2 \times 10^{13} \text{ W cm}^{-2}$. The dashed and dotted lines mark the position of the Cu- L_α resonance (929.7 eV) and the Cu- L_3 edge (932.7 eV) respectively, at low intensity. (b) Corresponding forward simulation of the reflectivity spectrum. The Bragg angle fixed in the simulation is shifted by 0.05 deg with respect to the results presented in the main text.

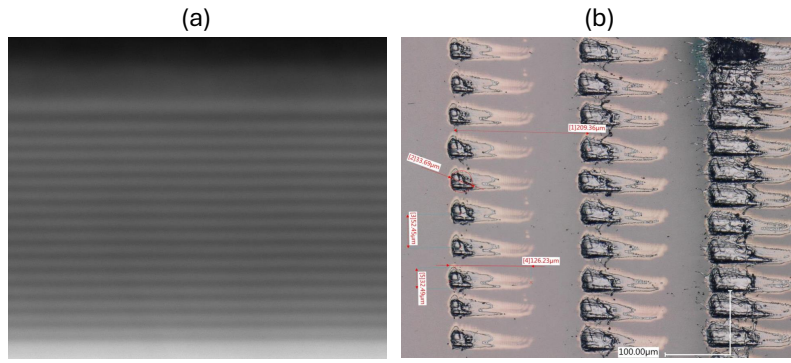


Fig. S7 Microscopic sample characterization (a) Scanning Electron Microscope (SEM) image of the cross section of the multilayer sample. The thicker and brighter bottom area is the Si substrate, the lighter lines above are the B_4C and SiC layers, which are indistinguishable due to similar density. Dark lines are the Cu layers. (b) Post-exposure optical microscope image of the surface of the sample. The three vertical lines of craters are due to exposures at different intensities.

171 References

- 172 [1] Glavic, A. & Björck, M. GenX 3: the latest generation of an established
173 tool. *Journal of Applied Crystallography* **55**, 1063–1071 (2022). URL <https://journals.iucr.org/j/issues/2022/04/00/ge5118/>. Publisher: International Union
174 of Crystallography.
- 175
- 176 [2] Parratt, L. G. Surface Studies of Solids by Total Reflection of X-Rays. *Physical*
177 *Review* **95**, 359–369 (1954). URL [https://link.aps.org/doi/10.1103/PhysRev.95.](https://link.aps.org/doi/10.1103/PhysRev.95.359)
178 [359](https://link.aps.org/doi/10.1103/PhysRev.95.359). Publisher: American Physical Society.
- 179 [3] Pietsch, U., Holý, V. & Baumbach, T. *High-Resolution X-Ray Scattering* Advanced
180 Texts in Physics (Springer, New York, NY, 2004). URL [http://link.springer.com/](http://link.springer.com/10.1007/978-1-4757-4050-9)
181 [10.1007/978-1-4757-4050-9](http://link.springer.com/10.1007/978-1-4757-4050-9).
- 182 [4] Medvedev, N. XTANT-3 (2025). URL <https://zenodo.org/records/16478661>.
- 183 [5] Frenzel, J., Oliveira, A. F., Jardillier, N., Heine, T. & Seifert, G. Semi-
184 relativistic, self-consistent charge slater–koster tables for density-functional based
185 tight-binding (dftb) for materials science simulations. <http://www.dftb.org/>. TU
186 Dresden, Dresden (2004–2009).
- 187 [6] Boyd, R. W. *Nonlinear Optics in the Two-Level Approximation* (Elsevier, 2020).