EUV spectroscopy of highly charged Sn\(^{13+} \text{—} \text{Sn}^{15+}\) ions in an electron-beam ion trap

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(Received 7 November 2019; accepted 13 May 2020; published 15 June 2020)

Extreme-ultraviolet (EUV) spectra of Sn\(^{13+} \text{—} \text{Sn}^{15+}\) ions have been measured in an electron-beam ion trap (EBIT). A matrix inversion method is employed to unravel convoluted spectra from a mixture of charge states typically present in an EBIT. The method is benchmarked against the spectral features of resonance transitions in Sn\(^{13+}\) and Sn\(^{14+}\) ions. Three new EUV lines in Sn\(^{14+}\) confirm its previously established level structure. This ion is relevant for EUV nanolithography plasma but no detailed experimental data currently exist. We used the Cowan code for first line identifications and assignments in Sn\(^{15+}\). The collisional-radiative modeling capabilities of the Flexible Atomic Code were used to include line intensities in the identification process. Using the 20 lines identified, we have established 17 level energies of the 4\(^p^4\)4\(^d\) configuration as well as the fine-structure splitting of the 4\(^p^5\) ground-state configuration. Moreover, we provide state-of-the-art \textit{ab initio} level structure calculations of Sn\(^{15+}\) using the configuration-interaction many-body perturbation code AMBiT. We find that the here-dominant emission features from the Sn\(^{15+}\) ion lie in the narrow 2\% bandwidth around 13.5 nm that is relevant for plasma light sources for state-of-the-art nanolithography.

DOI: 10.1103/PhysRevA.101.062511

I. INTRODUCTION

Extreme-ultraviolet (EUV) light emission near 13.5 nm wavelength from highly charged tin ions, primarily from \(4p^4\, 4d^4\) and \(4d^4\, 4f\) transitions in Sn\(^{8+}\) \text{—} Sn\(^{14+}\), is the source of light for state-of-the-art nanolithography [1–5]. Accurate knowledge of the open 4\(^d\)-subshell atomic structure of these ions provides insight for further optimization of EUV light emission of industrial laser-driven plasma sources. The electronic structure of the involved tin ions is extremely complicated, in part due to the existence of strong configuration-interaction effects. Spectroscopic accuracy remains inaccessible to even the most advanced atomic codes. Given their importance, the spectra of these charge states have been widely investigated [6–14]. Recently, however, evidence was found calling for a revision of earlier identifications of transitions in Sn\(^{5+}\) \text{—} Sn\(^{14+}\) ions [15,16]. Furthermore, no experimental atomic structure data are available on the neighboring charge state Sn\(^{15+}\), with its open 4\(^p\)-subshell 4\(^p^5\) ground-state configuration. Emission from tin ions in charge state 15+ is however readily observed from the relatively weak \(4p^3\, 5s\) transitions near 7 nm in EUV-generating laser-produced tin plasmas [17,18]. Understanding the contribution of the stronger \(4p^4\, 4d\) transitions of Sn\(^{15+}\) (as compared to its \(4p^3\, 5s\) transitions) to the industrially relevant emission feature at 13.5 nm should therefore be particularly relevant for simulations of such plasmas. New experimental tin data are thus required.

Experimental investigations are hampered by the fact that plasmas, including plasma in electron-beam ion traps (EBITs) [19–24], that are typically required to produce ions in intermediate charge states, contain a mixture of different charge states with overlapping spectral features. Charge-state-resolved spectra can be obtained using suitable subtractions of spectra acquired under various plasma conditions [25–28] or by employing genetic algorithms [29]. In this work, we employ a matrix inversion method to obtain charge-state-resolved spectra using matrix inversion techniques on convoluted, mixed-charge-state EUV spectra experimentally obtained from an electron-beam ion trap.

We focus here on the EUV spectra of Sn\(^{13+} \text{—} \text{Sn}^{15+}\). Their strongest line features are particularly closely spaced and offer a rather tractable atomic structure with a relatively limited number of strong transitions. First, as a benchmark, we use the matrix inversion method to reevaluate the \(4p^4\, 4d^4\) \text{—} (\(4p^4\, 4d^4\) \text{—} \(4p^4\, 4f\) \text{—} \(4p^5\)\((4p^5\)\)) type EUV transitions in Sn\(^{13+}\). Subsequently, we apply the method to obtain unique information on the atomic structure of the excited...
configurations $4p^2 4d$ in Sn$^{14+}$ and $4p^4 4d$ in Sn$^{15+}$. Line identifications in Sn$^{15+}$ are enabled using the semiempirical Cowan code [30], which allows for adjusting scaling factors applied to radial integrals in order to fit observed spectra using initial preliminary assignments. Identifications of lines in both Sn$^{14+}$ and Sn$^{15+}$ are further strengthened by line intensity calculations using the collisional-radiative modeling capabilities of the Flexible Atomic Code (FAC) [31]. We compare our obtained level energies with calculations performed with the Fock-Space Coupled-Cluster (FSCC) approach for Sn$^{14+}$ [16] and General-purpose Relativistic Atomic Structure Package (GRASP) calculations for Sn$^{15+}$ [32]. In this work, we also provide state-of-the-art calculations of Sn$^{15+}$ using the configuration-interaction many-body perturbation code AMBIT [33]. Its performance is gauged against published calculations as well as experimental observations.

II. EXPERIMENT

We performed spectroscopic measurements in the EUV region on tin ions over the range of charge states Sn$^{9+}$–Sn$^{20+}$ at the FLASH-EBIT facility [34] at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany. FLASH-EBIT employs a pair of superconducting Helmholtz coils to generate a 6-T magnetic field in order to guide and compress the electron beam, with a density of approximately $10^{11}$ cm$^{-3}$ (see below), down to a diameter of about 50 μm. A molecular beam of tetra-i-propyltin (C$_{12}$H$_{18}$Sn) was injected into the trap through a two-stage differential pumping system. The tetra-i-propyltin molecules are dissociated while crossing the electron beam. The electron beam rapidly ionizes and traps the Sn ions, while the lighter elements leave the trap. By adjusting the acceleration voltage, the electron-beam energy can be set to achieve preferential production of a specific charge state. Subsequently, the electron beam collisionally populates excited states from which the emission is collected.

Extreme-ultraviolet radiation emitted by the highly charged ions in the trap is diffracted by a 1200-lines/mm flat-field, grazing-incidence grating [35] and recorded on a Peltier-cooled charge-coupled device (CCD) sensor. The wavelength range covered by the spectrometer encompasses the 13.5-nm region most relevant to nanolithographic applications. A wavelength range from 12.6–20.8 nm is captured in the observation of light diffraction in first order of the grating, with lines having a full width at half maximum (FWHM) of about 0.03 nm. To achieve the best possible resolution, the camera position was alternatively set such that the 12–17 nm spectral range can be observed in second order where typically a FWHM resolution of about 0.02 nm was achieved. The spectra are corrected for small optical aberrations and background signal before projection onto the dispersive axis of the full CCD image. Corrections for camera sensitivity and grating efficiency are subsequently applied. Wavelength calibration of the spectrometer is performed by injecting oxygen into the trap and observing a set of known O$^{2+}$–O$^{4+}$ lines [36]. The calibration uncertainty of 0.003 nm (one standard deviation of the residuals) is the dominant contributor to the overall uncertainty budget for determining line centers. Calibration runs were performed on several days during the experimental campaign to combat any potential significant drift. Line positions found in the first- and second-order-diffraction measurements (see below), performed on different days and under different EBIT settings, agree well within the uncertainty estimates.

Two measurement series are performed, utilizing either the first- or second-order diffraction of the grating. Fluorescence emission from Sn$^{12+}$–Sn$^{20+}$ is observed by increasing the electron-beam energy in 5-eV steps from 320 to 695 eV while keeping the electron-beam current constant at 20 mA. The light captured on the CCD is integrated for 480 s per electron-beam energy step. In the second-order measurement series, EUV emission from tin ions in charge states 9+ up to 18+ is observed by increasing the energy of the electron beam in 10-eV steps from 210 to 560 eV. The electron-beam current in the second-order measurement series was kept steady at 10 mA. In each of the 36 steps of the electron-beam energy, an EUV spectrum was accumulated with a camera integration time of 1800 s to ensure a sufficient signal-to-noise ratio. In the following, results from the second-order measurement series are described in detail. First-order measurement results are employed for further line identifications in the wavelength range not captured in second order.

III. GENERAL FEATURES OF THE EUV EMISSION MAPS

A 2D map (wavelength, electron-beam energy) of EUV light intensities is presented in Fig. 1. An initial-charge-state identification is performed by locating known lines in the 2D map. The very bright emission feature near 13.34 nm is the resonant $4p^6 S_0$–$4p^4 4d^1 P_1$ transition in Sn$^{14+}$ [7,37]. At slightly shorter wavelength, lines from Sn$^{13+}$ can be identified [6,7,38]. From Fig. 1, it can be seen that the strong emission manifolds belonging to $4p^6 4d^m$–$(4p^4 4d^{m+1} + 4p^2 4d^{m-1} 4f^1)$ transitions in Sn$^{9+}$ ($m = 5$) to Sn$^{13+}$ ($m = 1$) shift toward shorter wavelength with increasing charge state. EUV emission from these open 4d-subshell ions have been extensively studied in the literature; see, e.g., Refs. [6–9]. Intriguingly, after emptying the 4d subshell at 14-fold charged tin, the strongest transitions for tin ions in charge state 14+ and higher shift back to longer wavelengths.

The emergence and submergence of spectral features at certain electron-beam energies can be understood from considerations of the ionization potentials of tin ions. This procedure allows for the assessment of ranges of electron-beam energies in which tin ions in a specific charge state are the dominant contributors to the EUV spectra. In each of the charge-state bands, the measured spectrum with the highest fluorescence is chosen as the representative spectrum for that charge state. In Fig. 1, the overlaid line spectra (white solid lines) are the corresponding spectra for Sn$^{11+}$, Sn$^{14+}$, and Sn$^{15+}$. From the figure it is clear that representative spectra are not free of spectral admixtures from Sn ions in adjacent charge states. Fluorescence curves are a way to assess potential admixtures of different charge states. A fluorescence curve represents the intensity of a specific line as a function of electron-beam energy. We project vertical regions of interest from the data as shown in Fig. 1. Several lines per charge state are identified in order to construct a generic fluorescence curve. We choose in the spectral map lines that are preferably isolated, mostly outside of dense spectral regions,
and compare them critically. It is found that commonly the observed energy dependencies of the line strengths are very similar for all lines associated with a particular charge state. Lines with expected blends of other charge states, showing miscellaneous energy-dependent behavior, were excluded or corrected for contributions from line blending. Individual fluorescence curves are normalized and subsequently averaged such that a generic fluorescence curve per charge is obtained. The normalized fluorescence curves of Sn$^{9+}$ to Sn$^{18+}$ ions are shown in Fig. 2. In general, the fluorescence from a certain ionic state $q$ increases rapidly once the electron-beam energy exceeds the ionization potential of the previous charge state $q-1$. Once the ionization potential of the charge state $q$ is reached, the fluorescent curve belonging to $q$ is observed to decline. The electron beam produces a strong space charge region in the trap, lowering the actual electron-beam energy in the interaction region in the center of the trap by a current-dependent value [16,39]. This effect however is partially compensated by the trapped positive ions. The net result is typically a lowering of the electron-beam energy by a few eV per mA current [16,39]. Space charge effects have a negligible influence on the onset of the fluorescence curves (cf. Fig. 2). The fluorescence curve of Sn$^{15+}$ is different from the other charge states as it shows two peaks instead of one. This can be explained by early production of Sn$^{15+}$ out of metastable Sn$^{14+}$ levels, similar to the case presented in Ref. [16]. Although weaker, a similarly early onset is also visible for Sn$^{16+}$. The relevance of early ionization via metastable levels as intermediate steps depends on a delicate balance between the lifetimes of said metastable levels and the electron-beam

![FIG. 2. Normalized intensity of spectral lines belonging to Sn$^{q+}$ ($q = 9–18$) along the variation of the set electron-beam energy. The triangles mark the threshold for producing the Sn$^{q+}$ ion at the ionization potential of charge state $q-1$ [41].]
density [40]. These features are well captured by our method below and therefore do not negatively impact it.

The fluorescence curves indicate that a tin spectrum, taken at any single electron-beam energy, contains emission features from a mixture of tin charge states. In the following, we will employ a method to retrieve charge-state-resolved spectra.

### IV. MATRIX INVERSION

For unraveling blended spectra, such as the ones of Sn\(^{\text{q+}}\) ions, we employ a matrix inversion method for charge-state-resolved EBIT spectral reconstruction. The principle of the method is analogous to that of the subtraction scheme introduced by Lepson et al. [27]. In the matrix inversion method it is hypothesized that each row in the 2D map (wavelength, electron-beam energy) of light intensities shown in Fig. 1 in fact represents a linear combination of unique spectra per charge state weighted by their respective fluorescence curve. These spectral maps can thus be represented by a matrix \(E\) of dimension \(m \times w\), where \(m\) is the number of spectral scans (electron-beam energy steps) and \(w\) is the number of wavelength bins. The matrix elements contain spectral intensities directly obtained from measurements. Fluorescence curves, such as the ones shown in Fig. 2, span a fluorescence matrix \(F\) of dimension \(m \times c\), where \(c\) is the number of distinct charge states in the EBIT spectrum. This overdetermined linear system can be described as

\[
FS = E, \tag{1}
\]

with \(S\) containing the charge-state-resolved spectra to be determined. The least-squares solution for this problem is found by utilizing the generalized inverse method [42]. The solution yields the minimum norm of the system and is found by first multiplying Eq. (1) with the transpose of the fluorescence matrix \(F\):

\[
F^TFS = F^TE. \tag{2}
\]

The matrix product \(F^TF\) is a square matrix and allows for the determination of an inverse, in the case of full column rank of \(F\) (i.e., when each column is linearly independent). The present experimental data fulfill this requirement. Subsequently, when Eq. (2) is multiplied by this inverse, the solution of matrix \(S\) is given by

\[
S = (F^TF)^{-1}F^TE. \tag{3}
\]

This solution is also referred to as the left inverse of this linear system. The resulting matrix \(S\) has dimensions \(c \times w\).

The non-negative matrix factorization (NNMF) method [43] provides an alternative route for obtaining matrices \(F\) and \(S\). NNMF enables obtaining the (positive-definite) matrices without any prior knowledge of the system, such as the fluorescence curves. Test fits to our EBIT spectra with the NNMF method were made for comparison with the spectra obtained from matrix inversion. For Sn\(^{13+}\), the NNMF spectrum looked very similar; however, a few spurious spectral features emerged when retrieving Sn\(^{14+}\) and Sn\(^{15+}\) spectra. Therefore, we do not consider NNMF in the following and accept a few small spurious features in the spectra reconstructed through matrix inversion, cf. Fig. 3, stemming from imperfections in the fluorescence curves. However, such artifacts can easily be identified and excluded.

### V. RESULTS AND LINE IDENTIFICATIONS

Charge-state-resolved spectra reconstructed by means of the matrix inversion method are presented in Fig. 3. The direct EBIT spectra at electron-beam energies at which Sn charge states Sn\(^{13+}\), Sn\(^{14+}\), and Sn\(^{15+}\) show maximum fluorescence are included in Fig. 3. From comparison of the results of the matrix inversion with the untreated direct data, it is evident that there exist large admixtures of charge states in the untreated spectra. A detailed analysis of the line identifications of Sn\(^{13+}\) to Sn\(^{15+}\) ions is presented, using the case of Sn\(^{13+}\) ions as a reference as its atomic structure is well known [6,7,38]. An analysis per charge state is laid out after a short introduction to the various atomic structure codes used to perform the line identifications.

The Hartree-Fock method with relativistic corrections incorporated in the RCN-RCN2-RCG chain of the Cowan code [30,44] is used for the calculation of wavelengths of \(4p^6\rightarrow4p^4d\) and \(4p^5\rightarrow4p^4d\) transitions in Sn\(^{14+}\) and Sn\(^{15+}\) ions, respectively. In addition to the wavelength of a transition, the line intensity is also an important identification tool. For experiments on EBITs, the electron beam may strongly affect specific line intensities, making them deviate strongly from calculated \(\alpha\) values (multiplicity times the Einstein coefficient); see, e.g., Ref. [39]. Incursion of such effects requires collisional-radiative modeling (CRm). We used the CRm capabilities available in FAC [31]. CRm calculates the relative population of levels within the atomic structure. The “line emissivity,” presented as luminosity in photons/s, is obtained from the multiplication of the relative population times the Einstein \(A\) coefficient as calculated by FAC [31].

FAC calculations here tend to overestimate level energies in comparison with experiment. Therefore, we have shifted level energies calculated by FAC to match the level energies obtained from the Cowan code. Following the conclusions in Ref. [39], in which electron-beam densities in FLASH-EBIT were investigated under similar conditions, we used a \(10^{14}\, e^{-}\cdot\text{cm}^{-3}\) electron-beam density in our CRm calculations. This density is shown to accurately predict the relative intensities of magnetic-dipole to electric-dipole transitions in Sn\(^{14+}\). Slight differences in the choice of density and possible polarization-induced emission anisotropies (such as observed, e.g., in recombination measurements in Refs. [45,46]) were investigated and are not expected to affect the final identifications. Cowan and FAC-CRm details specific to Sn\(^{14+}\) and Sn\(^{15+}\) ions are discussed in the following subsections. The resulting spectra are individually normalized per charge state. Area-under-the-curve line intensities are normalized to the strongest line for each charge state in order to allow for a straightforward comparison with the normalized line spectra.

#### A. Spectrum of Sn\(^{13+}\)

The EUV spectrum of Sn\(^{13+}\) has been studied previously in plasma discharge sources [6,7,38]. Strong lines between 13.1 and 13.6 nm have been identified as belonging to resonant transitions between levels of the first excited configuration.
FIG. 3. Charge-state-resolved spectra for Sn charge states Sn$^{13+}$–Sn$^{15+}$. Spectra determined with the matrix inversion method (described in Sec. IV) are shown in black. The untreated EBIT spectra are represented by thin gray lines and are identical to the line-out projections in Fig. 1, here normalized to the strongest line feature associated with the respective charge state. The green circular data points represent normalized $g_A$ factors for transitions previously identified in the literature [6,7]. The top panel of Fig. 3 shows our untreated (gray line) and matrix-inverted (black) EUV spectrum of Sn$^{13+}$. The matrix-inverted result is in excellent agreement with previous identifications, as shown in Fig. 3 and in Table I. Comparing the matrix-inverted and untreated spectra of Sn$^{13+}$ makes clear that spectral analysis solely based on a measurement taken at peak fluorescence for this ion would not provide sufficient detail. This demonstrates and validates the applicability of the method to the measured EBIT spectra.

4$p^54d^2$ and the 4$p^54d$ ground configuration. The top panel of Fig. 3 shows our untreated (gray line) and matrix-inverted (black) EUV spectrum of Sn$^{13+}$. The matrix-inverted result is in excellent agreement with previous identifications, as shown in Fig. 3 and in Table I. Comparing the matrix-inverted and untreated spectra of Sn$^{13+}$ makes clear that spectral analysis solely based on a measurement taken at peak fluorescence for this ion would not provide sufficient detail. This demonstrates and validates the applicability of the method to the measured EBIT spectra. One of the four possible transitions within the $^2D$−$^4d^2$ ($^2F$) multiplet is not observed (cf. Table I). The transition $^2D_{3/2}$−($^2F$)$^2D_{5/2}$ may be expected at a wavelength of 13.08 nm. However, according to the Cowan code calculations, it has a too low $g_A$ value to be detected. Also, the $^2D_{5/2}$−$^4d^2$ ($^4G$)$^2D_{5/2}$ transition predicted at 13.78 nm is not detected as may be expected because this $\Delta J = 0$ transition is further suppressed by configuration interaction.

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**B. Spectrum of Sn$^{14+}$**

The EUV spectrum of Sn$^{14+}$ consists of a few resonance lines. Two lines at approximately 13.34 and 16.21 nm have been observed previously [6,7,37], and are observed in our spectra as well. Additionally, three new lines in the 17–19 nm range are identified. Line positions and assignments of these five Sn$^{14+}$ transitions are presented in Table II. The assigned transitions stem from levels 2, 3, and 6 (see Table III), which are mainly of character $^3P_1$, $^3P_2$, and $^1D_2$, respectively. Excellent agreement is obtained with the fine structure determined in Ref. [16], where the fine structure of the 4$p^54d$ configuration was studied by the observation of magnetic dipole transitions in the optical regime. The level energy differences between levels 2–3 and 2–6 have been measured directly. They form Ritz combinations with transitions found in the EUV. Two of the newly assigned EUV lines in the 17–19 nm range (originating from upper levels 3 and 6) have very small $g_A$ values (on the order of 1000 s$^{-1}$) as is to be expected for $\Delta J = 2$ transitions. Notwithstanding that, these lines are observed in the EBIT spectrum because of the strongly enhanced population of their upper levels as indicated by our CRm calculations.

Fock-Space Coupled-Cluster (FSCC) predictions for the structure of Sn$^{14+}$ [16], shown in Table III, are in excellent agreement with our identifications with a root-mean-square difference with experiment below 0.1%.

Through a semiempirical adjusting of scaling factors, the Cowan code enables evaluating level energies of Sn$^{14+}$ to a high accuracy. The level energies of the 4$s^2$4$p^54d$
configuration of Sn$^{14+}$ are optimized using configuration interaction between the following configurations: $4s^24p^55d$, $4s^24p^55s$, $4s4p^24d^2$, $4s4p^54d^3$, $4s^24p^54d^4f$, $4s^24p^55g$, $4p^64d^3$, $4p^64d^4f$, and $4s4p^54f^2$. The final Cowan scaling factors are presented in Table IV, with level energies provided in Table III.

There are several other lines observed in the vicinity of the main peak at 13.34 nm in the Sn$^{14+}$ spectrum. These transitions do not belong to the $4p\rightarrow4d$ transition array. In particular, the line at 13.28 nm stands out. These additional lines may originate from transitions into the excited $4p^54d$ configuration out of the strongly mixing $4p^54f$ and $4p^64d^2$ configurations. There exist many transitions connecting these excited configurations, which prohibit a unique assignment since both expected position and line strength are strongly affected by the effects of configuration interaction. A qualitative study of the emission intensities stemming from FAC-CRM calculations tentatively suggests that the two stronger lines observed at 13.28 and 13.46 nm may be due to, respectively, $J = 4\rightarrow 3$ and $J = 3\rightarrow 4$ transitions in the $4p^64d\rightarrow4p^4d^2$ manifold. Similar transitions in the same wavelength range have been observed in charge exchange spectroscopy studies of Sn$^{15+}$ ions colliding with He [47].

The influence of the redistribution of level populations by the EBIT beam on the observed line intensity has also been observed in transitions between fine-structure levels of the $4p^54d$ configuration [16]. In Ref. [16], the strongest line at 297.7 nm ($^3P_2\rightarrow^3D_3$, intensity of 211) has a gA factor of 981, while a neighboring line at 302.9 nm ($^3D_3\rightarrow^3D_2$) with a three times higher gA factor of 2597 is detected with a more than tenfold lower intensity of 15. CRm calculations show that population of the $^3D_1$ level is strongly preferred. This leads to an inverted emissivity ratio of almost 10 to 1 instead of 1 to 10 for these transitions, in agreement with the measurements.

### C. Spectrum of Sn$^{15+}$

Sn$^{15+}$, with a bromine-like ground-state configuration ([Ar]3d$^{10}4s^24p^5$), has received little attention thus far. Its EUV spectrum in the wavelength range near 13.5 nm consists of one strong emission feature along with several weaker lines; cf. Fig. 3. These features are expected to stem from $4p^5\rightarrow4p^4d$ transitions. The peak at 13.344 nm belongs to Sn$^{14+}$ and is the strongest line in the EBIT measurements. Its contribution is seen to be incompletely removed by the method. It is the only such artifact apparent in the current spectra. The untreated spectra taken at peak fluorescence for Sn$^{14+}$–Sn$^{16+}$ are shown in the inset in the bottom panel of Fig. 3. This inset highlights the difficulty of identifying the (unresolved) lines belonging to Sn$^{15+}$ from observing line intensity changes in the untreated spectra alone. The matrix inversion method is shown to resolve the line features of the Sn$^{15+}$ ion.

To enable the identification of Sn$^{15+}$ lines (see Table II), the Hartree-Fock method with relativistic corrections (HFR) incorporated in the RCN-RCN2-RCG chain of the Cowan code was used for ab initio calculations of wavelengths arising from $4s^24p^5\rightarrow4s^24p^4d$ transitions. The following set of odd-symmetry configurations is considered: $4s^24p^54d$, $4s^24p^54df$, $4s^24p^54f$, $4s^24p^54d^2$, $4s^24p^54f^2$, $4p^54d^2$, $4p^54f^2$, and $4p^64f$. For the even symmetry, the excited $4s^24p^4d$, $4s^24p^4df$, $4s^24p^4f$, $4s^24p^4d^2$, $4s^24p^54d^2$, $4s^24p^54f$, and $4s4p^5$ configurations are included. The HFR values are improved on the basis of known data for Br-like Mo$^{17+}$ [48]. This is the heaviest system in the Br-like isoelectronic sequence for which the $4s^24p^4d$ level energies were found from an analysis of $4s^24p^5\rightarrow4s^24p^4d$ transitions [48].

The $^3P$ term splitting of the ground-state configuration $4s^24p^5$ of Sn$^{15+}$ was predicted to be 78.35 cm$^{-1}$ [49,50] on the basis of a larger set of isoelectronic data including Pd$^{11+}$ [51], Ag$^{12+}$ [52], and Cd$^{13+}$ [53].

Starting out from this initial set of parameters, iterative refinement of the parameters allows for identification of 20 lines belonging to Sn$^{15+}$ as $4s^24p^5\rightarrow4s^24p^4d$ transitions and 17 level energies of the $4s^24p^4d$ configuration along with the $4s^24p^5\rightarrow^3P$ ground term splitting. Our value of 78.300(60) cm$^{-1}$ for the $^3P$ term splitting is in excellent agreement with predictions.

A Cowan code fit to the available level energies to obtain optimal energy parameters leads to a root-mean-square deviation from experimental level energies of 302 cm$^{-1}$. The wavelength calibration uncertainty is approximately 150 cm$^{-1}$. The final results of the optimization procedure are listed in Table III. The electrostatic energy parameters for the excited configurations were scaled by a factor 0.85 relative to their ab initio values while the spin-orbit parameters were not scaled. All configuration-interaction parameters in both parity systems were scaled by 0.85 except for the interaction

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**Table I. Comparison of observed wavelengths of EUV lines in Sn$^{13+}$ with literature values. Transitions stem from strongly mixed upper levels associated with the $4p^54d^2$ configuration (denoted by $^3D$), $4p^64f$, and $4p^55p$ decaying to the ground configuration $4p^54d$ $^3D$. Wave-function compositions of these mixed levels can be found in Ref. [7]; only the leading term is shown. Wavelength and normalized intensities (Int.) obtained in this work originate from fits to the spectrum. Superscripts on wavelengths indicate blended (bl) lines.**

| Transition   | Wavelength (nm) | Literature | Experiment | Int. |
|--------------|-----------------|------------|------------|------|
| $^3D_{5/2}\rightarrow4p^54p_{5/2}$ | 12.1339 [6] | 12.3316 [6] | 12.334 | 41 |
| $^3D_{5/2}\rightarrow4p^54p_{3/2}$ | 12.5065 [6] | 12.519 | 51 |
| $^3D_{5/2}\rightarrow4p^54p_{1/2}$ | 13.1358 [6] | 13.137 | 389 |
| $^3D_{3/2}\rightarrow4p^54p_{5/2}$ | 13.1361 [38] | 13.1821 [7] | 13.184 | 116 |
| $^3D_{3/2}\rightarrow4p^54p_{3/2}$ | 13.3014 [6] | 13.301$^{4\dagger}$ | 586 |
| $^3D_{3/2}\rightarrow4p^54p_{1/2}$ | 13.3020 [38] | 13.304$^{4\dagger}$ | 1000 |
| $^3D_{1/2}\rightarrow4p^54p_{5/2}$ | 13.3675 [6] | 13.367 | 275 |
| $^3D_{1/2}\rightarrow4p^54p_{3/2}$ | 13.4154 [7] | 13.415 | 441 |
| $^3D_{1/2}\rightarrow4p^54p_{1/2}$ | 13.4943 $^{7\dagger}$ | 13.498 | 170 |
| $^3D_{3/2}\rightarrow4p^54p_{5/2}$ | 13.5318 [6] | 13.532 | 711 |
| $^3D_{3/2}\rightarrow4p^54p_{3/2}$ | 13.5315 [38] | 13.532 | 711 |

$^{4\dagger}$Tentative assignments from Ref. [7].

$^{4\dagger}$The dominant term is indicated to be $^4f^2\mathcal{P}_{3/2}$ [7].

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TABLE II. Line transitions in Sn$^{14+}$ and Sn$^{15+}$ determined from fits to the spectra. Superscripts on line wavelengths indicate blended (bl), broad (br), or weak (w) lines. Starred (*) lines feature in the construction of the fluorescence curves. Line positions beyond 17 nm stem from measurements in first-order diffraction. Below 17 nm, line positions are established from second-order diffraction. Normalized intensities stem from the area-under-the-curve of fits to lines observed in the first-order diffraction. Normalized emissivities from FAC’s CRm module are also presented. Transitions are of type $4p^m - 4p^{m-1}d$ ($m = 6, 5$ for respectively Sn$^{14+}$ and Sn$^{15+}$); listed numbers refer to levels described in Table III. $gA$ factors stem from Cowan code calculations, except for transitions 0–3 and 0–6 in Sn$^{14+}$, which are calculated by FAC.

| Ion | Experiment | Cowan | Intensity | $gA$ (1/s) | Emissivity | Transition | Terms |
|-----|-------------|-------|-----------|------------|------------|------------|-------|
| 14+ | 13.344*     | 13.343| 1 000     | $1.8 \times 10^{12}$ | 1 000      | 0–12       | $^3S_0 - ^3P_1$ |
|     | 13.3431 [7] |       |           |            |            |            |       |
|     | 13.3435 [37]|       |           |            |            |            |       |
| 16.212 | 16.214 | 137 | $5.5 \times 10^{10}$ | 71 | 0–8 | $^1S_0 - ^1D_1$ |
| 16.2103 [37]|       |       |           |            |            |            |       |
| 17.497 |       | 54  | $1.2 \times 10^{5}$ | 8 | 0–6 | $^3S_0 - ^3P_2$ |
| 17.905 |       | 63  | $1.6 \times 10^{4}$ | 15 | 0–3 | $^3S_0 - ^3P_2$ |
| 18.478 |       | 130 | $1.3 \times 10^{4}$ | 16 | 0–2 | $^1S_0 - ^1P_1$ |
| 15+ | 13.129     | 13.135| 159 | $3.0 \times 10^{11}$ | 654* | 0–20 | $^3P_{3/2} - ^3D_{5/2}$ |
| 13.393 | 13.387 | 1 000 | $2.9 \times 10^{12}$ | 1 000 | 0–19 | $^3P_{3/2} - ^3D_{5/2}$ |
| 13.416 | 13.418 | 502 | $1.5 \times 10^{12}$ | 834 | 0–18 | $^3P_{3/2} - ^3P_{3/2}$ |
| 13.477 |       |       |           |            |            |            |       |
| 13.844* | 13.844 | 334 | $8.4 \times 10^{11}$ | 469 | 0–17 | $^3P_{3/2} - ^3S_1$ |
| 14.068 | 14.064 | 89  | $2.4 \times 10^{11}$ | 77 | 0–16 | $^3P_{3/2} - ^3P_{3/2}$ |
| 14.384 br | 14.388 | 13  | $7.0 \times 10^{11}$ | 42 | 1–21 | $^3P_{3/2} - ^3P_{3/2}$ |
| 14.903 | 14.904 | 59  | $1.5 \times 10^{10}$ | 33 | 0–15 | $^3P_{3/2} - ^3P_{3/2}$ |
| 14.989 w | 14.993 | 16  | $1.7 \times 10^{10}$ | 4 | 1–18 | $^3P_{3/2} - ^3P_{3/2}$ |
| 15.278 | 15.272 | 53  | $3.6 \times 10^{10}$ | 34 | 0–14 | $^3P_{3/2} - ^3P_{3/2}$ |
| 15.510 bl | 15.503 | 119 | $2.9 \times 10^{10}$ | 57 | 0–13 | $^3P_{3/2} - ^3P_{3/2}$ |
| 15.510 bl | 15.510 | 119 | $1.1 \times 10^{10}$ | 9 | 0–12 | $^3P_{3/2} - ^3P_{3/2}$ |
| 15.528 bl | 15.527 | 120 | $6.7 \times 10^{9}$ | 39 | 1–17 | $^3P_{3/2} - ^3S_1$ |
| 15.811 | 15.805 | 42  | $9.3 \times 10^{9}$ | 40 | 1–16 | $^3P_{3/2} - ^3P_{3/2}$ |
| 16.320 | 16.330 | 140 | $5.6 \times 10^{10}$ | 118 | 0–10 | $^3P_{3/2} - ^3P_{3/2}$ |
| 16.421 | 16.414 | 81  | $5.5 \times 10^{10}$ | 82 | 0–9  | $^3P_{3/2} - ^3P_{3/2}$ |
| 16.498 | 16.492 | 103 | $2.4 \times 10^{10}$ | 103 | 0–8  | $^3P_{3/2} - ^3P_{3/2}$ |
| 16.897 | 16.894 | 56  | $3.6 \times 10^{10}$ | 49 | 0–6  | $^3P_{3/2} - ^3P_{3/2}$ |
| 17.143 | 17.152 | 61  | $5.9 \times 10^{9}$ | 47 | 0–5  | $^3P_{3/2} - ^3P_{3/2}$ |
| 18.269 | 18.271 | 121 | $1.5 \times 10^{9}$ | 21 | 0–4  | $^3P_{3/2} - ^3P_{3/2}$ |
| 18.513* | 18.507 | 225 | $4.3 \times 10^{8}$ | 182 | 0–3  | $^3P_{3/2} - ^3P_{3/2}$ |

*High emissivity resulting from a larger $gA$ factor calculated by FAC relative to that calculated with the Cowan code; see Sec. VC.

The Cowan fit to the experimental data yields $gA$ factors that can be compared to experimental line intensities. Four transitions with high $gA$ factors are expected around 13.4 nm. This quartet includes three lines to the ground state from upper levels 18, 19, and 20; cf. Table III. The fourth transition originates from level 22, the highest excited level of the $4p^4d$ configuration, which decays to the $^3P_{1/2}$ ground level. Despite its large $gA$ factor, this transition is not observed in the EBIT spectrum. CRm calculations show that the population of this upper level 22 is significantly smaller than that of neighboring levels, resulting in a low emissivity for this transition which is in line with our observations.

Typically, we find $gA$ values obtained from Cowan and FAC to be consistent within a factor of two. One exception is the $gA$ factor for the transition from level 20 ($^3D_{5/2}$) to the ground state. To understand this further, the transition is compared to the transition to the ground state from $^3D_{5/2}$ level 19 which is rather similar in wave-function composition and shows no large differences in $gA$ value between the two codes. The corresponding lines have a measured intensity ratio of 0.16 (transition 20–0/19–0), which is well explained by a $gA$ factor ratio of 0.10 (3.0 × 10$^{11} \text{s}^{-1}$/$2.9 \times 10^{12} \text{s}^{-1}$) obtained from Cowan’s code after a semiepipirical fitting of the experimental line positions. The $gA$ ratio using HFR standard scaling, before any fitting, is however 1.8 (2.2 × 10$^{12}$/$1.2 \times 10^{11}$), not too distinct from a value of 0.7 obtained from FAC calculations. It is also similar to a GRASP calculation indicating a ratio of 1.2 [32,57].
TABLE III. Energy levels of Sn$^{14+}$ and Sn$^{15+}$. Energy levels under Experiment are determined from wavelengths shown in Table II, and in addition the Cowan results from the fit to experimental data are listed. Furthermore, theoretical level energies of Sn$^{14+}$ are calculated by FSCC (reproduced from Ref. [16], and by GRASP in the case of Sn$^{15+}$ (reproduced from Ref. [32]) as well as by AMBÎT. Sn$^{15+}$ levels with $J > 5/2$ are not listed as transitions from these levels are not observed in our spectra. Up to three components of the eigenvector composition are listed for each configuration.

| Ion | Config. | Level | Experiment | Cowan | FSCC [16] | $J$ | Percentage eigenvector composition |
|-----|---------|-------|------------|-------|-----------|----|-----------------------------------|
| 14+ | $4p^6$ | 0     | 0          | 0     | 0         | $\frac{1}{2}$ | $\langle P \rangle P$ |
|     | $4p^44d$ | 1     | 532 121   | 531 833 | 0         | $\frac{1}{2}$ | 98% ($\langle P \rangle P$) |
|     |         | 2     | 541 118   | 540 795 | 1         | 89% ($\langle P \rangle P$) | 9% ($\langle P \rangle D$) |
|     |         | 3     | 558 571   | 558 339 | 2         | 63% ($\langle P \rangle P$) | 30% ($\langle D \rangle D$) | 5% ($\langle P \rangle F$) |
|     |         | 4     | 560 487*  | 560 438 | 3         | 69% ($\langle P \rangle F$) | 21% ($\langle P \rangle F$) | 9% ($\langle P \rangle D$) |
|     |         | 5     | 563 501   | 561 822 | 4         | 98% ($\langle P \rangle F$) |
|     |         | 6     | 571 490   | 571 828 | 2         | 44% ($\langle P \rangle D$) | 33% ($\langle P \rangle F$) | 11% ($\langle P \rangle P$) |
|     |         | 7     | 592 103*  | 591 945 | 3         | 63% ($\langle P \rangle D$) | 35% ($\langle P \rangle F$) |
|     |         | 8     | 616 892   | 617 525 | 1         | 84% ($\langle P \rangle D$) | 8% ($\langle P \rangle P$) | 5% ($\langle P \rangle P$) |
|     |         | 9     | 632 893   | 632 338 | 2         | 58% ($\langle P \rangle F$) | 32% ($\langle P \rangle D$) | 7% ($\langle D \rangle D$) |
|     |         | 10    | 649 941   | 649 997 | 2         | 50% ($\langle P \rangle D$) | 24% ($\langle P \rangle D$) | 21% ($\langle D \rangle D$) |
|     |         | 11    | 658 062   | 658 463 | 3         | 43% ($\langle P \rangle F$) | 29% ($\langle P \rangle F$) | 26% ($\langle D \rangle D$) |
|     |         | 12    | 749 429   | 749 449 | 1         | 92% ($\langle P \rangle P$) | 5% ($\langle P \rangle D$) | 1% ($\langle D \rangle D$) |

| Ion | Config. | Level | Experiment | Cowan | GRASP [32] | AMBÎT | $J$ | Percentage eigenvector composition$^b$ |
|-----|---------|-------|------------|-------|------------|--------|----|-----------------------------------|
| 15+ | $4p^6$ | 0     | 0          | 0     | 0          | $\frac{3}{2}$ | $\langle P \rangle$ |
|     | $4p^44d$ | 1     | 78 300    | 78 300 | 0         | $\frac{1}{2}$ | 98% ($\langle P \rangle$) |
|     |         | 2     | 540 160   | 539 988 | 3/2       | 56% ($\langle P \rangle$) | 13% ($\langle P \rangle$) | 12% ($\langle D \rangle$) |
|     |         | 3     | 540 344   | 552 374 | 3/2       | 68% ($\langle P \rangle$) | 8% ($\langle D \rangle$) | 7% ($\langle P \rangle$) |
|     |         | 4     | 547 380   | 547 330 | 3/2       | 38% ($\langle P \rangle$) | 25% ($\langle P \rangle$) | 20% ($\langle P \rangle$) |
|     |         | 5     | 583 330   | 583 015 | 3/2       | 31% ($\langle S \rangle$) | 23% ($\langle P \rangle$) | 18% ($\langle P \rangle$) |
|     |         | 6     | 591 820   | 591 934 | 3/2       | 64% ($\langle P \rangle$) | 18% ($\langle P \rangle$) | 10% ($\langle D \rangle$) |
|     |         | 7     | 604 177   | 616 910 | 3/2       | 60% ($\langle P \rangle$) | 14% ($\langle D \rangle$) | 12% ($\langle P \rangle$) |
|     |         | 8     | 606 130   | 606 367 | 3/2       | 49% ($\langle P \rangle$) | 28% ($\langle S \rangle$) | 11% ($\langle P \rangle$) |
|     |         | 9     | 608 980   | 609 246 | 3/2       | 41% ($\langle P \rangle$) | 23% ($\langle P \rangle$) | 16% ($\langle D \rangle$) |
|     |         | 10    | 612 750   | 612 365 | 3/2       | 34% ($\langle P \rangle$) | 21% ($\langle P \rangle$) | 19% ($\langle P \rangle$) |
|     |         | 11    | 620 095   | 634 622 | 3/2       | 31% ($\langle P \rangle$) | 16% ($\langle D \rangle$) | 15% ($\langle P \rangle$) |
|     |         | 12    | 644 750   | 644 728 | 3/2       | 29% ($\langle P \rangle$) | 24% ($\langle D \rangle$) | 22% ($\langle P \rangle$) |
|     |         | 13    | 644 750   | 645 021 | 3/2       | 29% ($\langle D \rangle$) | 28% ($\langle D \rangle$) | 15% ($\langle P \rangle$) |
|     |         | 14    | 654 540   | 654 802 | 3/2       | 50% ($\langle P \rangle$) | 22% ($\langle P \rangle$) | 17% ($\langle P \rangle$) |
|     |         | 15    | 671 010   | 670 948 | 5/2       | 36% ($\langle P \rangle$) | 34% ($\langle S \rangle$) | 11% ($\langle P \rangle$) |
|     |         | 16    | 710 810   | 711 019 | 3/2       | 34% ($\langle S \rangle$) | 22% ($\langle D \rangle$) | 20% ($\langle P \rangle$) |
|     |         | 17    | 722 330   | 722 341 | 3/2       | 67% ($\langle D \rangle$) | 15% ($\langle S \rangle$) | 7% ($\langle P \rangle$) |
|     |         | 18    | 745 420   | 745 278 | 3/2       | 39% ($\langle P \rangle$) | 21% ($\langle D \rangle$) | 21% ($\langle D \rangle$) |
|     |         | 19    | 746 660   | 746 998 | 3/2       | 50% ($\langle P \rangle$) | 25% ($\langle S \rangle$) | 13% ($\langle D \rangle$) |
|     |         | 20    | 761 670   | 761 325 | 3/2       | 36% ($\langle S \rangle$) | 17% ($\langle P \rangle$) | 16% ($\langle F \rangle$) |
|     |         | 21    | 773 520   | 773 307 | 3/2       | 45% ($\langle P \rangle$) | 42% ($\langle D \rangle$) | 8% ($\langle D \rangle$) |
|     |         | 22    | 820 293   | 840 862 | 3/2       | 50% ($\langle P \rangle$) | 22% ($\langle S \rangle$) | 9% ($\langle P \rangle$) |

$^a$Level energies were determined in Ref. [16] relative to level 2 by measuring transitions 3–7, 4–7, and 6–7.

$^b$All components belong to the $4p^44d$ configuration except for level 17, where the second component belongs to $4s4p^6$.

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The here-established quenching of oscillator strength of the 20–0 transition demonstrates the sensitivity of $g_A$ values to the exact wave-function composition.

The quality of the obtained complete set of Cowan code level energies is further illustrated by the identification of a particularly bright optical line observed in Ref. [16] at EBIT settings compatible with the production of Sn$^{15+}$. This line, predicted and observed at 538 nm, can be straightforwardly assigned to the yrast-type $(3^2P)D_{3/2}-(3^2P)F_{3/2}$ transition within the $4p^5d$ configuration.

**TABLE IV.** Cowan code Hartree-Fock with relativistic corrections (HFR) and least-squares-fitted (LSF) parameter values of the $4s^24p^4sd$ and $4s^24p^4d4d$ configurations respectively in Sn$^{14+}$ and Sn$^{15+}$. All parameters are given in units of cm$^{-1}$. One-standard-deviation uncertainties are given in brackets.

| Parameter | Sn$^{14+}$ | Sn$^{15+}$ |
|-----------|------------|------------|
| $E_{\text{average}}$ | HFR$^a$ | LSF | LSF/HFR$^b$ | HFR$^a$ | LSF | LSF/HFR$^b$ |
| $F^+(4p, 4p)$ | 632 080 | 629 400 (327) | $-2 680$ | 671 287 | 669 270 (98) | $-2 017$ |
| $\zeta(4p)$ | 50 300 | 51 428 (751) | 1.022 (15) | 51 881 | 53 251 (187) | 1.026 (4) |
| $\zeta(4d)$ | 5 348 | 5 823 (228) | 1.089 (43) | 5 602 | 5 788 (150) | 1.033 (27) |
| $F^+(4p, 4d)$ | 125 410 | 115 494 (1 707) | 0.921 (14) | 127 338 | 117 332 (1 054) | 0.921 (8) |
| $G^+(4p, 4d)$ | 158 897 | 142 206 (674) | 0.895 (4) | 161 200 | 144 568 (273) | 0.897 (2) |
| $\sigma$ | 100 630 | 90 060 (427) | 0.895 (4) | 102 264 | 91 712 (173) | 0.897 (2) |
| $\lambda$ | 167 595 | 147 825 (787) | 0.882 (5) |

$^a$Average energies are adjusted so that the energy of the ground level is zero in calculations with 0.85 scaling of all electrostatic parameters.

$^b$The value given for $E_{\text{average}}$ represents the difference between LSF and HFR value.

$^c$Parameters are tied at their HFR ratio at the fitting.

$^d$Interaction between $4s^24p^4sd$ and $4s^44p^6$ configurations in Sn$^{15+}$.

The AMBiT code calculations along the Br-like isoelectronic sequence (for details see text). Spline fits are drawn to guide the eye.

**FIG. 4.** Empirical adjustments of scaling factors in the Cowan code calculations along the Br-like isoelectronic sequence (for details see text). Spline fits are drawn to guide the eye.
a particle-hole excitation from the reference set along with a valence electron excitation were also included. In order to reduce the size of the CI calculation, without sacrificing accuracy, the “emu CI” technique described in Ref. [64] is used. To summarize, of the Ns valence electron excitation were also included. In order to a particle-hole excitation from the reference set along with J. SCHEERS

set are neglected. To achieve this, we place the interactions between configurations outside of this smaller set are neglected. To achieve this, we place the Ns important CSFs in the top of the CI matrix and set off-diagonal elements that correspond to interactions between higher energy states to 0. As an example, for the even-parity J = 7/2 configurations we had N = 407 271 and Ns = 40 704, reducing the number of calculated elements of the CI matrix by a factor of five.

Core-valence interactions involving the other core levels (up to 3spd) are small since the core and valence electrons are well separated in energy. In the CI+MBPT method these are treated perturbatively up to second order by modifying the Slater integrals [58]. In the diagrammatic expansion we included virtual orbitals up to 30spdfg and all orbitals that were frozen at CI level.

The AMBiT calculations are done at a level similar to previous work on Sn7+ [16]. This case also has five valence electrons; however, we are now interested in high-energy transitions between configurations, rather than levels within a multiplet (4d6 in the case of Sn7+). The results are shown in Table III. We find a systematic offset in the AMBiT 4p4d energy levels compared to experiment of 2100(900) cm−1, which originates from the relaxation of the 4p orbitals in the different configurations and is not completely accounted for by the CI and MBPT approach. Our overall relative accuracy is ~0.3%, which compares favorably with the previous theory 2.6% [32]; cf. Table III. The accuracy of AMBiT very nearly enables the direct identification of the observed lines without the need of semiempirical scaling parameters as in the case of the Cowan code, particularly so when correcting for the observed systematic shifts in level energies.

VI. CONCLUSION

We study the extreme-ultraviolet spectra near 13.5 nm wavelength of Sn13+−Sn15+ ions as measured in an electron-beam ion trap. A matrix inversion method enables the reevaluation of resonance transitions in Sn13+ and Sn14+ ions. In the latter ion, three additional EUV lines confirm its previously established level structure.

For Sn15+ we present the first line spectrum and use the Cowan code for line identification and assignments. These assignments are furthermore strengthened by the collisional-radiative modeling capabilities of the Flexible Atomic Code, thus including line emissivities in the identification process by modeling the EBIT plasma. Using the 20 lines identified, we establish 17 level energies of the 4p4d configuration as well as the fine-structure splitting of the 4p5 ground state. We find that strong 4p−4d transitions lie in the small 2% bandwidth around 13.5 nm that is so relevant for plasma light sources for state-of-the-art nanolithography. Furthermore, we provide state-of-the-art ab initio calculations of Sn15+ using the configuration-interaction many-body perturbation code AMBiT and find it to be in excellent agreement with the experimental data at a 0.3% average deviation. These AMBiT calculations outperform other theory work by almost an order of magnitude.

ACKNOWLEDGMENTS

Part of this work was carried out at the Advanced Research Center for Nanolithography, a public-private partnership between the University of Amsterdam, the Vrije Universiteit Amsterdam, the Netherlands Organization for Scientific Research (NWO), and the semiconductor equipment manufacturer ASML. This project has received funding from European Research Council (ERC) Starting Grant No. 802648 and is part of the VIDI research program with Project No. 15697, which is financed by NWO. J.S. and O.O.V. thank the MPIK in Heidelberg for the hospitality during the measurement campaign.

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