I. INTRODUCTION

In the quest for new coating materials with outstanding corrosion and wear resistance properties, chromium carbide thin films are of high interest in applications for electrical contacts and decorative purposes [1, 2]. Metal carbide films produced by physical vapor deposition (PVD), show different microstructures, ranging from epitaxial single-crystal materials to nanocomposites with crystallites of the carbide in an amorphous carbon/amorphous carbide matrix [3, 4]. Completely amorphous metal carbide coatings are also found, in both binary and ternary systems such as Cr-C, Fe-C, Ni-C, and W-Fe-C [1, 5, 6]. It is an important methodological challenge to theoretically model such complex non-crystalline environments, in order to understand their structure and bonding properties.

In the case of crystalline materials, there is a multitude of successful combined experimental and theoretical studies in the literature, see for example Refs. [7, 12]. On the contrary, it is far from straightforward to model amorphous structures for studying materials properties. The lack of long-range translational symmetry provides a formidable challenge for obtaining suitable model structures of the systems. This is also the case experimentally, as the samples become X-ray amorphous with no usable diffraction peaks to determine the structure. Furthermore, in the computation of XANES and EXAFS spectra, the absence of symmetry means that the excitation response of each atom is unique and can be very distinct. As spectral measurements are effective samplings of individual excitations of atoms in different local chemical environments, an average over a large number of sites must be considered in a theoretical approach. While detailed explanation for the formation of non-crystalline phases during PVD in certain carbide systems remains unclear, it involves a significant quenching for conditions with neutral atoms and substrate temperatures below the melting point of the carbide, giving rise to limited surface mobility where atoms only find locally favorable sites. It is known that amorphous films often occur in metallic carbide systems where crystalline phases exhibit structural units that have carbon atoms in a mixture of both octahedral and prismatic sites [13].

Previous experimental studies of amorphous Cr$_{1-x}$C$_x$ films [13, 15] suggest that the films contain two components; an amorphous metal-rich carbide phase, and an amorphous carbon-rich phase. With increasing total carbon content, the amorphous carbon-rich contribution is believed to grow and incorporate the additional carbon, leaving the metal-rich phase more or less constant in carbon content [14, 19]. From C 1s X-ray photoelectron spectroscopy (XPS) measurements on the same samples as in this work, it was determined, based on quantitative estimations of carbide and a-C contributions in the spectra, that the amorphous metal carbide phase contained approximately 20-30 at.% of carbon. This is in the same compositional range as e.g. the crystalline Cr$_{23}$C$_6$ and Cr$_7$C$_3$ phases. On the other hand, the amorphous carbon phase contained approximately pure carbon with a high amount of $sp^2$-hybridized graphene-like carbon for large amounts of total carbon contents [20]. However, to identify the detailed structure and the bonding of the carbide phase in these complex non-equilibrium materials [20], more detailed experimental and theoretical studies are needed, in particular focusing on the surrounding of the metal atoms.

In this work, we investigate and compare experiments for nanocomposite Cr$_{1-x}$C$_x$ thin films with theory for completely amorphous systems as a function of carbon concentration, together with ideal crystal structures. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies are ideal tools for characterizing the structure
II. THEORY

A. Structural models

All structural models were obtained using density functional theory (DFT) \cite{26,27} utilizing the projector augmented wave (PAW) \cite{28} method as implemented in the Vienna ab-initio simulation package (VASP) \cite{29,30}. The generalized gradient approximation (GGA) \cite{31} for electronic exchange and correlation effects was used in these simulations. The atoms are first placed randomly in a supercell and then relaxed using DFT until the force on each atom is negligible \cite{29,25}. In this way a large set of structures is obtained, which together represent a specific concentration, at a comparatively low computational cost. Finally, to produce the theoretical X-ray absorption spectra, an average is taken over spectra computed at each Cr-atom site in the amorphous structure. In order to consider possible microstructures and phases within an amorphous matrix, we also consider crystalline CrCx structures that exist experimentally: cF116-Cr23C6, oP16-Cr3C, hP20-Cr7C3, hP80-Cr5C3, oP40-Cr7C3, oP20-Cr5C2, as well as the cubic B1 (octahedral) and hypothetical hexagonal hP2 (trigonal prismatic) type of CrC. All spectra are calculated by employing the computationally efficient real-space Green’s function code FEFF9 \cite{32,34}. In this way it is possible to produce the many individual spectra which are needed to represent amorphous structures. Different magnetic structures, ferromagnetic and antiferromagnetic were considered as initial configurations, although, with the exception of B1 CrC, magnetic moments relaxed to zero or almost zero during the electronic structure calculation.

The structural models used for simulations of the spectra of amorphous Cr0.67C0.33, Cr0.5C0.5, and Cr0.33C0.67 were obtained using the stochastic quenching approach \cite{23,25} in combination with DFT. Cubic supercells containing 250 atoms (Cr0.5C0.5) or 252 atoms (Cr0.67C0.33 and Cr0.33C0.67) were used, allowing for the selected concentrations to be modeled accurately. The stochastic quenching procedure was carried out in a similar procedure as in Ref. \cite{23}. The atomic positions were initiated with a random distribution in the simulation box, avoiding, for numerical stability concerns in the electronic structure calculations, pair distributions shorter than 0.8 Å, which is about 0.6 times the calculated C-C dimer distance in vacuum. This random structure is then quenched by gradually relaxing the internal atomic positions inside the supercell, until they reach locally stable positions with forces on each ion being smaller or in the order of 0.02 eV/Å.

For each composition, five or six volumes, with 19-25 SQ structures per volume, were used to obtain the equilibrium volume with a cubic polynomial fit. A similar number of SQ structures were then used to obtain average pair distribution functions g(r) for each bond type and to simulate spectroscopic properties. The calculations were initiated with individual Cr atoms having either spin up or spin down magnetic polarization with equal probability and a spatially random distribution in order to simulate a paramagnetic configuration. Some Cr atoms, in particular in the composition Cr0.33C0.67, retained a magnetic moment after the SQ procedure with a mean magnitude of about 0.8 \( \mu_B \) with minimum and maximum magnitudes 0.1 and 2.2 \( \mu_B \), respectively. For the composition Cr0.5C0.5, the corresponding mean value is about 0.3 \( \mu_B \) with a few of the Cr moments being around 2 \( \mu_B \). For the Cr0.67C0.33 composition most of the local moments disappear with a mean magnitude of around 0.02 \( \mu_B \). Overall, the local magnetic moments are clearly less robust as compared to similar simulations for the related amorphous CrN-system \cite{35}. A Gaussian broadening of the calculated pair distances of 0.2 Å was used in the simulations. Figure 1 shows one of the supercells (SQ1) generated by the procedure of the SQ method in order to model amorphous Cr0.5C0.5. Large blue spheres correspond to Cr and smaller brown spheres are C atoms. In order to obtain the theoretical X-ray absorption spectrum for an amorphous system, an average of all the spectra for the different SQ supercells and Cr sites was performed.

B. X-ray absorption spectra

In order to produce theoretical XANES and EXAFS spectra for the structures described above, we employ the single particle Green’s function technique within DFT \cite{26,27}. All calculations were performed utilizing the computationally efficient \textit{ab initio} real-space Green’s function (RSGF) approach of the FEFF9 code \cite{32,34}. For example, in the case of Cr0.5C0.5 the resulting Cr K-edge spectrum is an average over 22 SQ structures, each in turn an average over 125 Cr sites, amounting to 2750 spectra in total to represent the amorphous system. All the potentials are calculated self-consistently and the default Hedin-Lundquist exchange correlation potential is used. In more detail, to obtain accurate near-edge structures considering XANES, we utilized the real-space full multiple scattering (RSFMS) approach within FEFF9. Here, the potentials were calculated for the central scattering Cr atom and for the other Cr and C atoms. To take the final state effect into account, a fully screened
FIG. 1: One of the structures (SQ1) obtained by the stochastic quenching method for amorphous Cr$_{0.5}$C$_{0.5}$. The Cr-atoms are represented by large blue spheres, while C-atoms are shown as smaller brown spheres. The supercell was drawn using VESTA [36].

core-hole was used for the central scattering atom, i.e. applying the final-state rule, or core-hole approximation. Clusters with more than 550 atoms were employed in order to converge the spectral features in the different systems. For a brief overview of different methodologies for calculating XANES see Ref. [10] and references within. For EXAFS, which considers the energy region far above the near-edge, it is sufficient to use multiple scattering paths with no approximation for the core-hole [32]. Finally, the theoretical spectra were aligned with experiment by applying a rigid shift.

III. EXPERIMENTAL

Amorphous chromium carbide (Cr$_{1-x}$C$_x$) samples with different carbon content were made using direct current (DC) magnetron sputtering as described elsewhere [18, 20]. It was also found [18] that the samples contain about 2-5 at.% oxygen present. The XANES and EXAFS spectra were measured at the undulator beamline I811 on the MAX II ring of the MAX IV Laboratory, Lund University, Sweden [37]. The energy resolution at the Cr 1s edge of the beamline monochromator was better than 0.5 eV. The X-ray absorption spectra were recorded in reflection mode by collecting the fluorescence yield using a PIPS detector from -150 eV below to 1000 eV above the Cr 1s absorption edge (5989 eV) with 0.5 eV energy steps. To avoid self-absorption effects in the sample and Bragg peaks from the substrate, the incidence angle on the sample was varied in 0.25 degrees steps in a maximum range of ±3 degrees from normal incidence with a step motor.

Based on the XANES fitting results (described in the next Section), two Cr-C and two Cr-Cr scattering paths obtained from FEFF9 [32-34] were included in the EXAFS fitting procedure with hP20-Cr$_3$C$_4$ as a model system using the VIPER software package [38]. The reference energy $E_0$ was set to the pre-peak of each Cr 1s X-ray absorption spectrum as determined from the first peak of the derivative of each spectrum relative to the pure bcc-Cr reference sample. In the fitting procedure, $E_0$ was set to 5988.6 eV (25% C), +0.1 eV (42 and 47%, as compared to the 25% C sample), +0.4 eV (67% C) and +0.6 eV (85% C), respectively.

The EXAFS functions $\chi^2$ were extracted from the raw absorption data after removing remaining glitches originating from substrate diffraction peaks, subsequent background subtraction, and summarizing and averaging of 15 absorption spectra. The bond distances (R), number of neighbors (N), Debye-Waller factors ($\sigma^2$, representing the amount of disorder) and $\chi^2_r$=reduced $\chi^2$ as the squared area of the residual, were determined by fitting the back-Fourier-transform signal between $k$=0-12 Å$^{-1}$ obtained from the Fourier-transform within $R$=0.7-3 Å of the first coordination shell using a Hanning window function ) [41] and a global electron reduction factor of $S_0^2$=0.8. The calculated pairs of Cr-C and Cr-Cr 1st and 2nd scattering paths in the model were obtained using the FEFF9 code [32, 34].

IV. RESULTS AND DISCUSSION

In this Section, we start by considering theoretical XANES and EXAFS Cr K-edge spectra for the amorphous and crystal chromium carbide structures, with a comparison to measurements carried out for the thin film systems and pure Cr metal. An analysis of the XANES data was done by fitting the measured spectra with the calculations using a superposition of an amorphous phase and a smaller contribution of different crystalline phases. Using the results of the XANES fitting, an analysis of the EXAFS data was carried out for the experimental data using a standard fitting procedure for crystalline materials, in order to obtain reduced (radial) pair distribution functions (RDFs), that are compared to theoretical RDF results. Finally, the trend in the structural parameters of bond lengths and coordination numbers extracted from the EXAFS analysis are compared and discussed with theoretical values.

In Figure 2, the large differences of the theoretical a) XANES and b) EXAFS spectra in the case of Cr$_{0.5}$C$_{0.5}$ are shown. The upper parts of the two panels a) and b) give the Cr K-edge spectra calculated over the 125 different Cr-sites (gray lines) for the SQ1 structure illustrated in Fig. 1. The averaged spectra are shown as solid black
FIG. 2: Theoretical X-ray absorption spectra at the Cr 1s-edge, a) XANES and b) EXAFS, 125 Cr-sites (gray lines), are exemplified for the structure SQ1 in Figure 1, together with the spectra for Cr$_{0.5}$C$_{0.5}$ over all 22 SQ structures. The average of the spectra are shown as black lines. The lower parts of the panels correspond to the averaged results obtained for each of the 22 SQ structures (gray lines). Finally, the resulting XANES and EXAFS spectra over the whole amorphous Cr$_{0.5}$C$_{0.5}$ structure are given by the solid black lines in the lower part of each panel. As observed in Fig. 2, the X-ray absorption fine structures are highly sensitive to the atom local environment in the amorphous matrix. Similar behavior was found at the other concentrations.

Our result in Fig. 2 contains an important message to theoreticians working with spectroscopical simulations of disordered materials, and in particular amorphous substances. It is clear that in order to give even a qualitatively reasonable description of the Cr XANES or EXAFS spectra, averaging over hundreds of atomic sites is needed. However, for a quantitative simulation of the average signal, which is what is measured experimentally, in particular for the EXAFS case it might not be enough to consider just one amorphous supercell. It can be seen in the lower curve of Fig. 2 that the computed average signals for some of the SQ supercells deviates considerably from the average line of all the samples. Thus, it might not be reliable to simulate EXAFS spectra with just one supercell, say generated with molecular dynamics and containing one- or two hundred atoms, even if the average spectra of all atoms in the supercell is considered.

In Figure 3, a comparison of theoretical a) XANES and b) EXAFS spectra is made between amorphous Cr$_{1-x}$C$_x$ and crystalline CrC$_x$ structures. In the upper parts of each panel, results for three different amorphous Cr$_{1-x}$C$_x$ structures with concentrations $x = 0.33$ (blue dashed lines), 0.5 (green line) and 0.67 (red dotted line) are shown. In the lower part of each panel, the corresponding spectra for the crystals are presented:

FIG. 3: (Theoretical X-ray absorption spectra for the Cr 1s-edge, a) XANES and b) EXAFS, are compared for amorphous Cr$_{0.67}$C$_{0.33}$ (I), Cr$_{0.5}$C$_{0.5}$ (II), Cr$_{0.33}$C$_{0.67}$ (III) and with the different crystal structures: bcc-Cr (1), cF116-Cr$_{23}$C$_6$ (2), oP40-Cr$_7$C$_3$ (3), hP80-Cr$_7$C$_3$ (4), hP20-Cr$_7$C$_3$ (5), oP20-Cr$_7$C$_2$ (6), oP16-Cr$_3$C (7), phases and cubic B1 [NaCl] (8) and hexagonal hP2 [WC] (9) type CrC.
FIG. 4: Experimental (top) and theoretical (middle) Cr 1s XANES spectra of amorphous Cr$_{1-x}$C$_x$ and crystal pure Cr are shown. The spectra were normalized below the edge and 100 eV above the absorption edge. The inset shows the experimental intensities at the pre-edge peak. At the bottom, the first derivative of the measured spectra are shown. The inset is a close-up of the first peak (marked with arrow). The edge energies $E_0$ and the chemical shifts were determined by curve fitting of the first peak of the derivative to 5989.0 eV (pure Cr), 5988.6 eV (25% C), $+0.1$ eV (42 and 47%, as compared with 25%), $+0.4$ eV (67 %) and $+0.6$ eV (85 %).

FIG. 5: An example of the fitting procedure for the measured Cr 1s XANES spectra at 25% C (red circles) with theory for amorphous Cr$_{0.67}$C$_{0.33}$ (green line) and hP20-Cr$_7$C$_3$ (blue line). Sum (black line) shows the best fit, compare with Table 1.

Typically, it is most fruitful to analyze the measured EXAFS data in the form of reduced pair distribution functions, which provide information about the average Cr-Cr and Cr-C bond lengths, which in turn can be compared with corresponding theoretical pair distribution functions. In order to evaluate the probability of different compositions, we have fitted each measured XANES spectrum with the theoretical fully amorphous 33 % C structure together with each one of the crystal structure candidates as listed in Table 1. The curve fitting analysis was done using the SPECTRAL ANALYSIS by CURVE FITTING.
TABLE I: Results from fitting of experimental XANES data with a superposition of the calculated amorphous Cr$_{0.67}$C$_{0.33}$ structure and the different crystalline structures. The values represent fitted crystalline fractions (probabilities), where 0.4 implies 40% C etc. The $\chi^2$ (squared areas under the residual) represent the quality of the fit and (*) implies more than one possible minimum.

| System | Sample x=0.25 | x=0.42 | x=0.47 | x=0.67 | x=0.85 |
|--------|---------------|--------|--------|--------|--------|
| a-CrC 33%C | 0.4 – 0.7 | 0.5 – 0.7 | 0.6 – 0.8 | 0.7 – 0.9 | 0.8 – 0.9 |
| bcc-Cr | 0.001 | 0.017 | 0.001 | 0.010 | 0.001 |
| Cr$_{23}$C$_6$ | 0.112 | 0.087 | 0.133 | 0.131 | 0.100* |
| Cr$_7$C | 0.010* | 0.015 | 0.010 | 0.010 | 0.010 |
| Cr$_7$C hP20 | 0.198 | 0.155 | 0.153 | 0.210 | 0.249 |
| Cr$_7$C hP80 | 0.150 | 0.152 | 0.187 | 0.200* | 0.199 |
| Cr$_7$C oP40 | 0.160 | 0.152 | 0.187 | 0.110 | 0.200 |
| Cr$_2$C | 0.100* | 0.100 | 0.132 | 0.136 | 0.100 |
| CrC NaCl (B1) | 0.060 | 0.071 | 0.081 | 0.009 | 0.067 |
| CrC WC (hP2) | 0.001 | 0.001 | 0.001 | 0.010 | 0.001 |

macro package (SPANCF) software package. In Figure 5, an example is shown for the fit (black line) of the 25% C sample (red dots) with amorphous Cr$_{67}$C$_{33}$ (green line) and hP20-Cr$_7$C$_3$ (blue line). The background was taken into account both by an integrated and a linear background (dashed lines) and the residual is shown by a thin black curve. The square of the residual was used to compare the quality of different fittings. From the fitting analysis of the XANES data in Table 1, the results show that the contribution of the amorphous Cr$_{1-x}$C$_x$ phase increases with carbon content from 40% to 90%. In all simulations the Cr$_7$C$_3$, Cr$_{23}$C$_6$ and Cr$_3$C$_2$ are the most likely crystalline-like coordination while WC, pure Cr, Cr$_3$C and B1 are unlikely.

By combining experimental and theoretical XANES and EXAFS data at the Cr K-edge in Figs. 2-5 we make several interesting observations. Both in the XANES (Fig. 4) and the EXAFS spectra, we note that the main features observed in experiment are also captured in the calculated spectra. Concerning the XANES data, it is known that the energy position and the shape of the main peak and the pre-edge depends on the chemical state of the absorbing atom. The pre-peak is due to a transition of a 1s electron to hybridized $t_{2g}$ and $e_g$ (Cr 3d - C 2p) states. On the contrary, the main peak is a pure Cr 1s $\rightarrow$ 4p dipole transition. The first derivative of the XANES in the bottom of Fig. 4 highlights the differences between the samples. The intensity of the pre-peak is a signature of the amount of p-d hybridization [40], which here decreases as a function of carbon content. Generally, the chemical state of the absorbing Cr atom is different in Cr metal, Cr$_3$C$_2$ and Cr$_2$O$_3$ [42, 43] and the spectra shift to higher energies with increasing average oxidation states that are higher than in Cr metal. Note that this could also be affected by the presence of small amounts of oxygen in the samples, up to 5 at.% [44].

The main energy shift towards higher energy with increasing C content.

It is also possible to distinguish these differences in a close study of the spectral fine structure. For instance, the samples containing 42 and 47% C show sharper resolved pre-edge peaks (Fig. 4). In the case of the calculated spectra for the amorphous systems (Fig. 2a), the individual spectrum of each and every atom is unique with a detailed fine structure of the pre-edge peak and the main line. The crystalline systems (Fig. 3a) present very distinct and sharp spectral features both at the main peak and the pre-edge. However, the spread of the different crystal spectra is smaller than the rich variation found within an amorphous structure. For the amorphous Cr$_{1-x}$C$_x$ materials, the averaged spectra over thousands of Cr atoms show more smooth features as compared with the crystallites, in agreement with measurements. Still, the overall shape of the spectra with pre-edge and main peak is similar. These spectral features are also seen for the pure Cr metal, similar to previous results [44].

Figure 6 shows experimental EXAFS data in k$^2$-space of bcc-Cr metal and the five amorphous nanocomposite Cr$_{1-x}$C$_x$ films obtained after normalizing and background removal using the VIPER software package [39]. For bcc-Cr, the main sharp oscillations occur in the 4-11 Å$^{-1}$ region. On the contrary, for the amorphous Cr$_{1-x}$C$_x$ films, the main oscillations occur in the region $k=2$-7 Å$^{-1}$, whereas for higher $k$-values the oscillations are damped out in increasing noise from about $k=12$ Å$^{-1}$. This behavior is characteristic of backscattering from light C atoms [41].

Figure 7 shows the radial distribution functions, obtained directly by Fourier transforming the measured EXAFS structure factors in Fig. 6 by the standard EXAFS procedure [38]. The quantitative analysis was made using k$^2$ weight as is normal for conductive samples with a reduced k-range between 0 and 12 Å$^{-1}$. The main peaks are dominated by the short-range order of the Cr-
C and Cr-Cr orbital overlaps observed at ~1.5 Å and ~2.2 Å, in the first coordination shell, corresponding to \( k \approx 2.6 \, \text{Å}^{-1} \) in Fig. 6. Above 2.5 Å, corresponding to \( k \geq 6 \, \text{Å}^{-1} \), a smaller peak is observed at 3–3.5 Å due to the second coordination shell. Note that the radius-values on the abscissa shown in Fig. 7 represent raw data and are shown non-phase shifted to absolute values.

Table 2 shows the results of the EXAFS fitting using scattering paths from the most probable structure (hP20-CrC3 with a large unit cell with lattice parameters \( a=b=0.96 \, \text{Å} \) and \( c=4.45 \, \text{Å} \)) from the XANES results in Table 1. For amorphous materials, it is not possible to choose a perfect model structure due to the inherent disorder, however, selecting a simpler (and less probable) model such as B1-CrC results in less accurate fitting with larger residuals. The phase shift (\( \sim +0.5 \, \text{Å} \)) is included in the fitting model for the bond lengths for easier comparison with the theoretical values. The details of the fitting procedure are described in the Experimental Section III.

The first line in Table 2 presents the fitting results of the reference sample of pure bcc-Cr with known coordina-

\[
\begin{array}{cccccc}
\text{Sample} & \text{N}_1 & \text{N}_2 & \text{R}_1 & \text{R}_2 & \chi^2_r & S_0^0
\
\text{bcc-Cr} & 8 & 2.40 & 2.45 & 2.57 & 2.88 & 0.005
\
25\% C & 1.26 & 2.05 & 2.15 & 2.87 & 7.87 & 0.000
\
42\% C & 2.17 & 2.00 & 4.01 & 6.13 & 6.37 & 0.000
\
47\% C & 2.05 & 1.99 & 5.12 & 2.63 & 5.12 & 0.000
\
75\% C & 2.02 & 1.99 & 6.40 & 2.62 & 4.01 & 0.000
\
85\% C & 2.09 & 1.99 & 6.52 & 2.62 & 4.01 & 0.000
\end{array}
\]

\( \chi^2_r \) and \( S_0^0 \) are reduced \( \chi^2 \) and global electron reduction factor, respectively. The global electron reduction factor was \( S_0^0 = 0.8 \). The bond lengths are phase corrected \( \sim +0.5 \, \text{Å} \) in the EXAFS model fit, as opposed to the RDF data in Fig. 7.
Generally, we observe a trend of decreasing Cr-Cr coordination numbers for the first (8) and second (6) scattering paths. These nearest neighbor scattering paths represent the bond lengths space diagonal from the corner of the unit cell to the center (2.49 Å) and the edge length equal to the lattice parameter (2.88 Å). As expected, the amorphous samples on the following lines exhibit larger Debye-Waller factors than crystal bcc-Cr due to a greater amount of disorder. For comparison of the coordination numbers, the Debye-Waller factors were kept fixed for amorphous samples.

Note that while the theoretical g(r) is split into separate parts, G(r) obtained from the measurements includes all the Cr bond lengths, in particular, the Cr-Cr and Cr-C peaks in the first coordination shell.

Figure 9 shows theoretical Cr-Cr, Cr-C and C-C g(r) obtained from the optimized geometries of crystalline CrC₂ phases: cF116-CrC₂, oP16-Cr₃C, hP20-Cr₇C₃, hP80-Cr₇C₃, oP40-Cr₇C₃, oP20-Cr₅C₂, the cubic B1 (octahedral) and hP2 (trigonal prismatic, WC) type CrC and bcc-Cr. These are the same phases whose XANES and EXAFS spectra are shown previously in Fig. 3. Calculated average bond lengths and nearest neighbors are summarized in Table 3 for the amorphous systems and crystalline phases, also including C-C bonds.

As shown by the EXAFS results in Table 3, we gen-
generally observe that the crystalline bond lengths are similar to both the theoretical fully amorphous structures and measurements (Table 2), and the coordination numbers are closer to the measurements. Considering the bond lengths, \( \text{Cr}_7\text{C}_3 \) phases give the closest fit with the XANES measurements (Table 1). From the fitting of the XANES measurements to the theoretical results, we find that the dominant contribution is amorphous \( \text{CrC}_x \) carbide with a coordination that is most similar to \( \text{Cr}_7\text{C}_{3+y} \) carbide in all the samples, ranging from \( \sim 30 \) at\%. This is followed by less possible contributions of coordination similar to \( \text{Cr}_{23}\text{C}_6, \text{Cr}_3\text{C}_2 \) and \( \text{Cr}_3\text{C} \). Note that these results are in a general good agreement with the previous experimental findings by Maury et al. [19] and Nygren et al. [10].

In Table 3, a very small increase of both the \( \text{Cr-C} \) and \( \text{Cr-Cr} \) bond lengths as a function of \( C \) content is predicted in the theoretical purely amorphous structures. This is consistent with the observed increase in crystal carbide lattice parameters when they are present in nanocrystalline form in a carbon matrix [22]. This trend is possibly due to the fact that the carbon-rich environment induces charge-transfer that reduces the electron concentration around the \( \text{Cr} \) atoms with a following reduction of the strength of \( \text{Cr-Cr} \) bonding. In addition, our calculations of pure amorphous materials predict a reduction of the coordination numbers of \( \text{Cr} \) and an increase of coordination numbers of \( C \) as a function of carbon content. The predicted reduction of the coordination number of \( \text{Cr} \) is consistent with our measurements. However, an increase in the coordination number of \( C \) is only experimentally observed between the 25% and 42% samples while at higher \( C \) contents, a weak decrease is observed. This could be due to the fact that the size of the amorphous \( \text{CrC}_x \) carbide and amorphous carbon domains changes as a function of total carbon content. As observed in Transmission Electron Microscopy (TEM) [20], domain sizes are less than 1 nm for \( x=0.25 \), about 3 nm for \( x=0.47 \), and about 2 nm for the higher carbon contents. Thus, the situation in amorphous nanocomposites is more complex than in pure amorphous materials as there is also a contribution from the interface grain boundaries that changes as a function of total carbon content. Furthermore, for the \( \text{CrC}_x \) carbide phase, there are at least two different competing effects that can give rise to a change in bond length: i) at low \( C \)-content, the \( \text{Cr-rich} \) phase has vacancies that cause an increase or a decrease of the lattice constant that has a maximum for understoichiometric carbide. ii) more carbon atoms filling into the vacancies of the structure gives rise to a larger lattice parameter \( a \), see e.g., Ref. [22].

In a previous experimental study on the same samples [20], \( x=0.25 \) was observed to have the most amorphous character, in High Resolution Transmission Electron Microscopy (HRTEM). A possible interpretation is that the low carbon concentration sample can be described with a \( \text{Cr}_7\text{C}_{3+y} \) coordination with \( y \sim 0.5 \), prohibited from forming the optimal structure by carbon vacancies. The fitting with theoretical XANES spectra (Table 1) does not indicate a change in structure or a possible concentration of bcc-Cr, while having the lowest amorphous character as compared with the other samples. We find that in general, EXAFS modeling can give useful in-

**FIG. 8:** Theoretical (radial) pair distribution functions \( g(r) \) of amorphous \( \text{Cr}_{1-x}\text{C}_x \) materials at the \( C \) absorption edge. The inset shows the calculated shift of the \( \text{Cr-Cr} \) peak from 2.58 Å at 33% \( C \)-content to 2.66 Å at 67% \( C \) due to a predicted increase of the \( \text{Cr-Cr} \) distance in completely amorphous materials.

**FIG. 9:** Theoretical (radial) pair distribution functions \( g(r) \) of the different \( \text{CrC} \) single crystals at the \( C \) absorption edge: \( c\text{F}116-\text{Cr}_{23}\text{C}_6, o\text{P}16-\text{Cr}_7\text{C}_3, h\text{P}20-\text{Cr}_7\text{C}_3, h\text{P}80-\text{Cr}_7\text{C}_3, o\text{P}40-\text{Cr}_7\text{C}_3 \), \( o\text{P}20-\text{Cr}_7\text{C}_3 \), phases, cubic \( B1 \) (NaCl) and hexagonal \( h\text{P}2 \) (WC) type \( \text{CrC} \) and bcc-Cr.
formation about the local structure in amorphous materials but largely depends on the chosen model. Therefore, it is important to use *ab initio* theory as a complement.

While the present work focus on new theoretical and experimental results for the Cr K-edge, the corresponding results for the carbon K-edge can provide valuable complementary information. Therefore, it is also of interest to compare the theoretical C-C bond for the amorphous structures and crystallites (Fig. 8, 9 and Table 3) with measurements. Generally, the calculated Cr-C and Cr-Cr bond lengths were found to be rather similar between the crystallites and amorphous structures. However, the theoretical C-C bond distances are strikingly different in amorphous carbides (∼1.5 Å) compared to crystalline carbide materials (∼3 Å), which are closer to the second C-C coordination shell. As discussed in a previous work [20], these results qualitatively agree well with the relative distribution of carbon in the carbidic, CrC$_x$ phase and the amorphous carbon phase as reported in Ref. [18, 19]. For comparison, the C-C bond lengths are ∼1.5 Å in a-C, graphite and diamond [47, 49]. The experimentally observed C-C bond lengths (∼2 Å) [20] are larger than the theoretical, but significantly shorter than the bonds for the CrC crystallites in Table 3, which are similar to previous calculations [50]. Note that in this study, the Cr-C bond length (∼2.0 Å) was extracted from EXAFS modeling, while in Ref. [20] the bond length (∼2.2 Å) was only estimated directly from the RDF obtained from electron energy loss spectroscopy with lower energy resolution.

### V. CONCLUSIONS

With the combination of experiment and theory for XANES and EXAFS, we have shown that it is possible to obtain detailed information about the local structure in amorphous nanocomposite materials. Using the computationally efficient *ab initio* stochastic quenching method, we modeled fully amorphous structures, taking into account local Cr magnetic moments in the derivation. Experimentally, amorphous structures require advanced fitting procedures where the result is very sensitive to the structure of the model. Amorphous two-phase Cr$_{1-x}$C$_x$ nanocomposite films were investigated, consisting of a chromium-rich amorphous carbide phase and an amorphous carbon-rich phase. We find that the short-range coordination in the Cr-rich amorphous phase is similar to that of a hexagonal Cr$_{7}$C$_{3±y}$ structure. At total carbon contents below 30 at%, the Cr-rich phase is clearly under-stoichiometric with carbon vacancies that causes shorter Cr-Cr bond lengths and directly depend on the packing and orbital overlap with the Cr-C bonds. Furthermore, the Cr-Cr bond length in the amorphous carbide has shorter bond lengths than the more open structure of bcc-Cr metal (space diagonal=2.49 Å, lattice parameter a=2.88 Å) that indicates stronger bonds. Above 30 at% total carbon content, the structure of the amorphous Cr$_{7}$C$_{3±y}$-like domains remains, while the excessive carbons assemble in the amorphous carbon phase. The coordination numbers in the first coordination shell of Cr decreases as a function of total carbon content from 9.5 to 4.6, while the coordination number of C only weakly increases. This is associated with a smaller number and size of the Cr-rich domains causing a larger fraction of interface bonding that lacks Cr-nearest neighbors on one side. Theoretically, we also predict that the C-C bond lengths are very sensitive to the local structure, with considerably shorter bond lengths in amorphous materials (∼1.5 Å) compared to various crystals (∼2.8-3.2 Å). Generally, it is important to use theory as an assessment to investigate the trends in complex amorphous materials.

### TABLE III: Theoretical average radial distance $R$ and coordination numbers $N$ for Cr-C and Cr-Cr pairs for the Cr$_{1-x}$C$_x$ amorphous structures, bcc Cr and crystalline CrC$_x$ structures. For comparison, $R$ is also shown for C-C pairs, including the 2nd coordination shell for the amorphous structures.

| System       | $N_{Cr-C}$ | $R_{Cr-C}$ (Å) | $N_{Cr-Cr}$ | $R_{Cr-Cr}$ (Å) | $R_{C-C}$ (Å) |
|--------------|------------|----------------|-------------|-----------------|---------------|
| a-CrC 33%C  | 3.1        | 2.05           | 10.7        | 2.58            | 1.46/2.53     |
| a-CrC 50%C  | 4.5        | 2.06           | 8.6         | 2.63            | 1.47/2.59     |
| a-CrC 67%C  | 5.9        | 2.07           | 5.9         | 2.66            | 1.49/2.97     |
| bcc-Cr      |            |                |             |                 |               |
| Cr$_{23}$C$_6$ | 2.1      | 2.10           | 11.7        | 2.55            | 3.32          |
| Cr$_5$C     | 2.7        | 2.05           | 11.3        | 2.60            | 3.07          |
| Cr$_7$C$_3$ hP20 | 2.6      | 2.04           | 11.1        | 2.60            | 3.14          |
| Cr$_7$C$_3$ hP80 | 2.6      | 2.04           | 11.1        | 2.61            | 3.18          |
| Cr$_7$C$_3$ oP40 | 2.6      | 2.04           | 11.1        | 2.62            | 3.18          |
| Cr$_3$C$_2$  | 4.3        | 2.05           | 10.0        | 2.62            | 2.89          |
| CrC NaCl (B1) | 6         | 2.05           | 12          | 2.90            | 2.90          |
| CrC WC (hP2) | 6         | 2.04           | 8           | 2.68            | 2.68          |
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[1] Cavaleiro, A.; De Hosson, J. T. M. Nanostructured Coatings; Springer: New York, 2007.
[2] Cheng, Y. Q.; Ma, E. Atomic-Level Structure and Structure-Property Relationship in Metallic Glasses. Prog. Mat. Science 2011, 56, 379.
[3] Trindade, B.; Vittiera, M. T.; Bauer Grosse, E. In Situ High Temperature Crystallization Study of Sputter Deposited Amorphous W-Fe-C Films. Acta Metallurgica et Materialia 1995, 43, 93-99.
[4] Trindade, B.; Vittiera, M. T.; Bauer Grosse, E. Characterization of W-Me-C (Me = Fe, Co) Films and Their Structural Behaviour with Temperature. Mat. Sci. Eng. A 1994, A174, 165-171.
[5] Furlan, A.; Lu, J.; Hultman, L.; Janson, U.; Magnusson, M. Crystallization Characteristics and Chemical Bonding Properties of Nickel Carbine Thin Film Nanocomposites. J. Phys.: Condens. Matt. 2014, 26, 415501.
[6] Furlan, A.; Jansson, U.; Lu, J.; Hultman, L.; Magnusson, M. Structure and Bonding in Amorphous Iron Carbine Thin Films. J. Phys.: Condens. Matt. 2015, 27, 045002.
[7] Magnuson, M.; Butorin, S. M.; Sätche, C.; Nordgren, J.; Ravindran, P. Spin Transition in LaCoO3 Investigated by Resonant Soft X-Ray Emission Spectroscopy. Europhys. Lett. 2004, 68, 289-295.
[8] Magnuson, M.; Wilhelmsson, O.; Mattesini, M.; Li, S.; Ahuja, R.; Eriksson, O.; Högborg, H.; Hultman, L.; Janson, U. Anisotropy in the Electronic Structure of V2GeC Investigated by Soft X-Ray Emission Spectroscopy and First-Principles Theory. Phys. Rev. B 2008, 78, 035117.
[9] Magnuson, M.; Mattesini, M.; Högborg, C.; Abrikosov, I. A.; Birch, J.; Hultman, L. Electronic Structure Investigation of the Cubic Inverse Perovskite Sc3AIN. Phys. Rev. B 2008, 78, 235102.
[10] Mizoguchi, T.; Olovsson, W.; Ikeho, H.; Tanaka, I. Theoretical ELNES using One-Particle and Multi-Particle Calculations. Micros. 2010, 44, 695-709.
[11] Olovsson, W.; Tanaka, I.; Mizoguchi, T.; Radtke, G.; Puschign, P.; Ambrosch-Draxl, C. Al L2,3 Edge X-Ray Absorption Spectra in III-V Semiconductors: Many-Body Perturbation Theory in Comparison with Experiment. Phys. Rev. B 2011, 83, 195206.
[12] Olovsson, W.; Weinhardt, L.; Fuchs, O.; Tanaka, I.; Puschign, P.; Umbach, E.; Heske, C.; Draxl, C. The Be K-Edge in Beryllium Oxide and Chalcogenides: Soft X-Ray Absorption Spectra From First-Principles Theory and Experiment. J. Phys.: Condens. Matt. 2013, 25, 315501.
[13] Bauer-Grosse, E. Thermal Stability and Crystallization Studies of Amorphous TM2C Films. Thin Solid Films 2004, 447-8, 311-315.
[14] Gaskell, P. H. A New Structural Model for Amorphous Transition Metal Silicides, Borides, Phosphides and Carbides. J. Non-Crystalline Solids 1979, 32, 207-224.
[15] Bauer-Grosse, E.; Aouni, A. Glass-Forming Range and Glass Thermal Stability in Binary 3d TM2C Systems. J. Non-Crystalline Solids 2007, 353, 3644-3649.
[16] Music, D.; Kreissig, U.; Mertens, R.; Schneider, J. M. Electronic Structure and Mechanical Properties of Cr7C3. Phys. Lett. A 2004, 326, 473-476.
[17] Jiang, C. First-Principles Study of Structural, Elastic, and Electronic Properties of Chromium Carbides. Appl. Phys. Lett. 2008, 92, 041909.
[18] Andersson, M.; Högström, J.; Urbonaite, S.; Furlan, A.; Nyholm, L.; Jansson, U. Deposition and Characterization of Magnetron Sputtered Amorphous Cr-C Films. Vacuum 2012, 86, 1408 - 1416.
[19] Magnuson, M.; Levin, E.; Hultman, L.; Jansson, U. Electronic Structure and Chemical Bonding of Nanocrystalline-TiC/Amorphous-C Nanocomposites. Phys. Rev. B 2009, 80, 235108.
[20] Magnuson, M.; Andersson, M.; Lu, J.; Hultman, L.; Jansson, U. Electronic Structure and Chemical Bonding of Amorphous Chromium Carbide Thin Films. J. Phys.: Condens. Matt. 2012, 24, 225004.
[21] Cockayne, D. J. H. The Study of Nanovolumes of Amorphous Materials Using Electron Scattering, Annu. Rev. Mater. Res. 2007, 37, 159-187.
[22] Jansson U.; Levin, E. Sputter Deposition of Transition-Metal Carbide Films? A Critical Review From a Chemical Perspective. Thin Solid Films 2013, 536, 1-24.
[23] Kádas, K.; Andersson, M.; Holmström, E.; Wende, H.; Karis, O.; Urbonaite, S.; Butorin, S. M.; Nikitenko, S.; Kvashina, K. O.; Jansson, U.; Eriksson, O. Structural Properties of Amorphous Metal Carbides: Theory and Experiment. Acta Materialia, 2012, 60, 4720-4728.
Energy Minima of Liquids. Phys. Rev. E, 2009, 2009, 80, 051111.

[25] Holmström, E.; Bock, N.; Peery, T.; Chisohl, E.; Lizárraga, R.; DeLorenzi-Venneri, G.; Wallace, D. Structure Discovery for Metallic Glasses Using Stochastic Quenching. Phys. Rev. B 2010, 82, 024203.

[26] Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. Phys. Rev. 1964, 136, 8864-B871.

[27] Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953-17979.

[28] Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Open-Shell Transition Metals. Phys. Rev. B 1993, 48, 13115-13118.

[29] Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1999, 59, 1758-1775.

[30] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865-3868.

[31] Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953-17979.

[32] Kohn, W.; Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 1965, 140, A1133-A1138.

[33] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865-3868.

[34] Rehr, J. J.; Albers, R. C. Theoretical Approaches to X-Ray Absorption Fine Structure. Rev. Mod. Phys. 2000, 72, 621-654.

[35] Arčon, I.; Mirtić, B.; Kodre, A. Determination of Valence States of Chromium in Calcium Chromates by Using X-ray Absorption Near-Edge Structure (XANES) Spectroscopy. J. Am. Ceram. 1998, 81, 222-224.

[36] Nygren, K; Andersson, M.; Högström, J.; Fredriksson, M.; Tuel, A.; Ramaswamy, V. Solid State 13C-NMR Spectral Characterization of Chromium Carbide Coatings Deposited at Low Temperature by Low Pressure Chemical Vapour Decomposition Using Dicumene Chromium. Surf. Coat. Tech. 1990, 41, 51-61.

[37] Nygren, K.; Andersson, M.; Högström, J.; Fredriksson, W.; Edström, K.; Nyholm, L.; Jansson, U. Influence of Deposition Temperature and Amorphous Carbon on Microstructure and Oxidation Resistance of Magnetron Sputtered Nanocomposite Cr-C Films. Appl. Surf. Sci. 2014, 305, 143-153.

[38] Singh, V.; Jiang, J. C.; Meletis, E. I. Cr-Diamondlike Carbon Nanocomposite Films: Synthesis, Characterization and Properties. Thin Solid Films 2005, 489, 150-158.

[39] Holmen, K.; Izu, F. VESTA 3 For Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272-1276.

[40] Nygren, K.; Andersson, M.; Högström, J.; Fredriksson, W.; Edström, K.; Nyholm, L.; Jansson, U. Influence of Deposition Temperature and Amorphous Carbon on Microstructure and Oxidation Resistance of Magnetron Sputtered Nanocomposite Cr-C Films. Appl. Surf. Sci. 2014, 305, 143-153.

[41] Singh, V.; Jiang, J. C.; Meletis, E. I. Cr-Diamondlike Carbon Nanocomposite Films: Synthesis, Characterization and Properties. Thin Solid Films 2005, 489, 150-158.

[42] Singh, D. J.; Klein, B. M. Electronic Structure, Lattice Stability, and Superconductivity of CrC. Phys. Rev. B 1992, 46, 14969-14974.

[43] Darmstadt, H.; Roy, C.; Kaliaguine, S.; Xu, G.; Auger, M.; Tuel, A.; Ramaswamy, V. Solid State 13C-NMR Spectroscopy and XRD Studies of Commercial and Pyrolytic Carbon Black. Carbon 2000, 38, 1279-1287.

[44] Li, Y.; Gao, J.; Li, Q.L.; Peng, M. F.; Sun, X. H.; Li, Y. Y.; Yuan, G.; Wen, W. J. The Electronic, Mechanical Properties and Theoretical Hardness of Chromium Carbides by First-Principles Calculations. J. Alloys Comp. 2011, 509, 5242-5249.

[45] Yamamoto, T. Assignment of Pre-Edge Peaks in K-Edge X-Ray Absorption Spectra of 3d Transition Metal Compounds: Electric Dipole or Quadrupole? X-Ray Spectrom. 2008, 37, 572-584.

[46] Egami, T.; Billinge, S. J. L. Underneath the Bragg Peaks: Structural Analysis of Complex Materials; Pergamon (Elsevier): Oxford, UK, 2003.

[47] Singh, V.; Palshin, V.; Tittsworth, R. C.; Meletis, E. I. Local Structure of Composite Cr-Containing Diamond-Like Carbon Thin Films. Carbon 2006, 44, 1280-1286.

[48] Pantelouris, A.; Modrow, H.; Pantelouris, M.; Hornes, J.; Reinen, D. The Influence of Coordination Geometry and Valency on the K-Edge Absorption Near Edge Spectra of Selected Chromium Compounds. Chem. Phys. 2004, 300, 13-22.

[49] Nygren, K.; Andersson, M.; Högström, J.; Fredriksson, W.; Edström, K.; Nyholm, L.; Jansson, U. Influence of Deposition Temperature and Amorphous Carbon on Microstructure and Oxidation Resistance of Magnetron Sputtered Nanocomposite Cr-C Films. Appl. Surf. Sci. 2014, 305, 143-153.

[50] Singh, V.; Jiang, J. C.; Meletis, E. I. Cr-Diamondlike Carbon Nanocomposite Films: Synthesis, Characterization and Properties. Thin Solid Films 2005, 489, 150-158.