Solid State Communications, Vol. 63, No. 3, pp. 257–260, 1987.
Printed in Great Britain.

0038–1098/87 $3.00 + .00
Pergamon Journals Ltd.

STRUCTURE DETERMINATION OF GRAPHITIC CARBON ON Cu(1 1 0) BY MEANS OF SURFACE EXTENDED ENERGY LOSS FINE STRUCTURE

A. Santoni and J. Urban

Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, D-1000 Berlin 33, West Germany

(*Received* 21 *January* 1987 *by M. Cardona*)

Extended energy loss fine structures (EELFS) have been detected in the reflection mode above the K edge of graphitic carbon chemisorbed on a copper (1 1 0) single crystal. To explain the features of the radial distribution function of the EELFS signal a model is proposed for the geometrical structure of graphitic C on Cu(1 1 0) which reproduces well the experimental data. According to the model the graphitic carbon overlayer is positioned 1.275 Å above the Cu(1 1 0) surface and the bond length between carbon atoms in the basal plane of the hexagonal lattice turns out to be 1.47 Å.

THE EXTENDED ENERGY LOSS Fine Structure (EELFS) technique in the reflection or surface mode has been successfully employed in the past few years in the investigation of the topological structure of bulk and surface properties in polycrystalline and crystalline samples as well as their interaction with chemisorbed species (c.f. [1–6]).

In this study we present EELFS measurements above the K edge of graphitic carbon adsorbed on a Cu(1 1 0) surface.

A (1 1 0) copper single crystal was installed in an ultra-high-vacuum chamber ($P \leqslant 1 \cdot 10^{-10}$ mbar) and cleaned by ion sputtering and thermal annealing cycles. The surface was monitored by Auger spectroscopy to verify its cleanliness. After the cleaning procedure the contamination level was found to be less than 0.5% of the Cu LMM-Auger peak.

All the SEELFS spectra were detected in reflection mode at normal incidence by means of a single-pass cylindrical mirror analyser (CMA) equipped with a coaxial electron gun and operated in the second derivative mode.

By exposing the Cu(1 1 0) sample to a $2 \cdot 10^{-5}$ mbar CO atmosphere for 10 min at 298 K we were able to obtain a carbidic carbon overlayer which was monitored by Auger Electron Spectroscopy (AES). The oxygen peak at 514 eV was also present. Auger spectra of the sample at room temperature before and after the CO-exposure were taken in order to ensure that the C and O peaks were due to the CO-exposure, i.e. neither C nor O peaks could be observed prior to the CO-exposure. Following the procedure of other authors [7] who already observed the adsorption of CO on copper at room temperature and high exposures ($> 10^3$ L), we heated the sample gradually up to a temperature of 570 K. In this way the disproportionation reaction of CO, i.e. $2CO \rightarrow C + CO_2$ [8, 9], was activated and we found, by monitoring the sample by means of AES at the final temperature, that the carbon atoms on the Cu(1 1 0) surface underwent a transition from the carbidic to the graphitic state. The typical shape of the graphitic carbon Auger peak was clearly visible and no oxygen peak was detectable above noise level. The graphitic state has been found to be very stable. It did not change by heating the sample to higher temperatures or by cooling it again to room temperature.

A typical SEELFS spectrum taken above the graphitic carbon K edge is shown in Fig. 1. It was taken with a primary energy of 1600 eV, 2 μA target current and 6 $V_{p\cdot p}$ modulation amplitude.

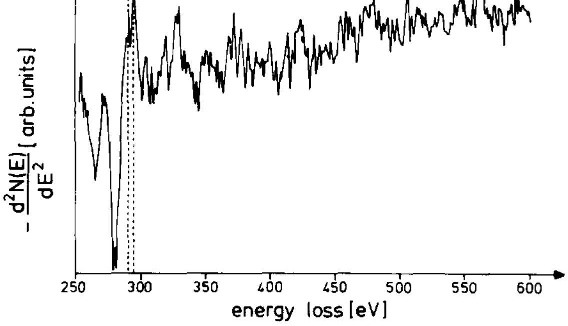

Fig. 1. SEELFS spectrum of the C–Cu system. The shape of the carbon K edge confirms the presence of the graphitic structure.

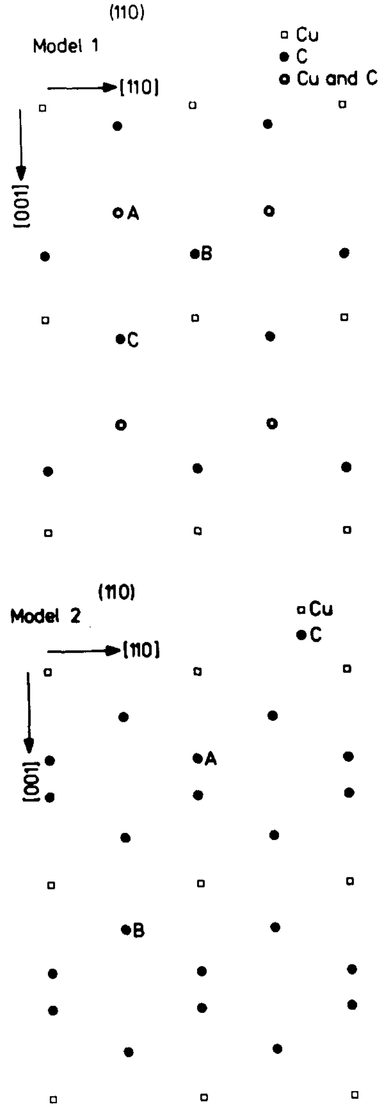

Fig. 2. The two possible models proposed for the geometrical structure of graphitic C on Cu(1 1 0).

The graphitic carbon K edge shows the two well-known features separated by about 7 eV, which are related to 1*s* → π and 1*s* → σ transitions [10].

After background removal and the usual EXAFS data analysis [11] a Fourier transform performed on the EELFS data between the limits $k_{\min} = 3.78\,\text{Å}^{-1}$ and $k_{\max} = 9\,\text{Å}^{-1}$ yielded the radial distribution function (RDF) (c.f. Fig. 3, dashed-dotted line). The RDF was calculated with phase-shift correction. The phase shift for the C-absorber and the Cu-backscatterer atom was calculated from the tabulated data of Teo and Lee [12].

The positions of the three peaks (Fig. 3) are at 1.78 ± 0.03 Å, 2.75 ± 0.03 Å and 4.18 ± 0.03 Å respectively.

In order to try to explain the features of the experimental RDF's we considered two possible models for the hexagonal structure of graphitic carbon on the Cu(1 1 0) surface. These are shown in Fig. 2. The reason for the choice of these models among other possibilities comes from the fact that they have already been successfully employed by other authors to determine the structure of graphitic C on Ni(1 1 0) [12]. In model I as well as in model II the periodicity of the hexagonal lattice matches that of the Cu(1 1 0) surface in the [1 1 0] direction if the distance between two nearest neighbour carbon atoms is assumed to be stretched from 1.42 to 1.47 Å. That means a 3.7% relaxation of the bond length. Moreover, the two models show different types of C-atoms with respect to the coordination shells of the Cu atoms, i.e. three types (A, B, C) for model I and two types (A, B) for model II respectively. Table 1 summarizes distances and coordination numbers of the coordination shells for the different types of atoms in both models.

In model I atom A shows a coordination shell with 5 Cu next neighbours because the C layer for symmetry reasons has been supposed to lie at 1.275 Å above the Cu(1 1 0) surface. This distance corresponds also to that between two Cu(1 1 0) atom planes. On the other hand no '*a priori*' preferred value exists for the distance between C-layer and Cu surface in model II. For this reason four different heights were taken into account, namely $h = 1$, 1.275, 1.6 and 2 Å.

On the basis of the features of the two models, theoretical EELFS curves were calculated by means of the usual EXAFS formula [11]. Due to the low backscattering amplitude of carbon with respect to Cu atoms [12] only C–Cu distances were considered. The Debye–Waller factor and the mean free path value have been taken to be 0.00138 Å^2 and 7 Å respectively [14]. For the copper backscattering amplitude a parametric expression was used [15].

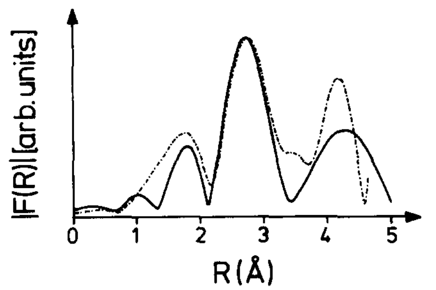

Fig. 3. Comparison between the theoretical RDF calculated from model I with phase shift correction (full curve) and the experimental RDF (dotted and dashed curve).

Table 1. Distances and coordination numbers for the different types of atoms in models I and II

MODEL I				MODEL II				
ATOM A	Shell	Distance (Å)	Coord. N	Distance (Å)				Coord. N
		h = 1.275		h = 1	h = 1.275	h = 1.6	h = 2	
	1	2.55	5	1.780	1.947	2.174	2.483	1
	2	3.606	2	2.360	2.489	2.670	2.928	1
	3	4.417	4	2.629	2.870	3.163	3.530	2
	4			3.110	3.209	3.351	3.559	2
ATOM B	1	1.664	1	1.780	1.947	2.174	2.483	2
	2	2.843	1	2.514	2.765	3.067	3.445	1
	3	2.944	2	3.299	3.393	3.528	3.726	2
	4	3.045	2	3.580	3.761	3.989	4.286	2
ATOM C	1	1.834	2					
	2	2.944	1					
	3	3.328	1					
	4	4.048	4					

Similarly to the experimental spectra, the Fourier transforms were performed between the limits k_{min} = 3.78 Å and k_{max} = 9 Å.

Figure 3 shows the RDF obtained from model I with phaseshift correction (full curve). The maxima peak at 1.78 ± 0.03, 2.71 ± 0.03 and 4.20 ± 0.03 Å respectively. These values are in excellent agreement with the experimental ones reported above. The relative amplitudes of the peaks are also quite well reproduced.

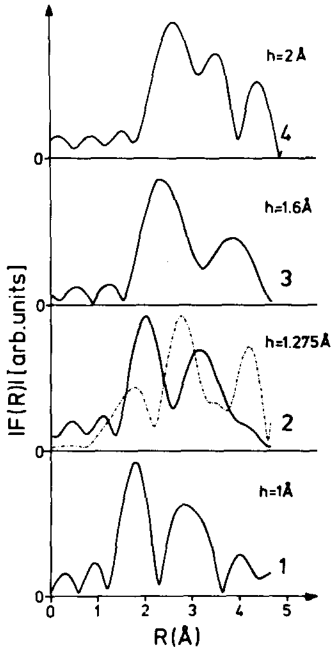

Fig. 4. Theoretical RDF's calculated from model II for different h-values. The experimental RDF is also shown on the curve calculated for h = 1.275 Å for comparison (i.e. curve 2, dotted and dashed line).

In Fig. 4 (curves 1, 2, 3 and 4) the RDF's calculated from model II for the four reported heights are shown. As it becomes evident from the figure, neither the peak position nor the relative amplitudes agree with the experimental data.

In conclusion, we propose model I as one of the possible descriptions of the structure of graphitic carbon on Cu(1 1 0). According to this model the C-overlayer is positioned at a distance of 1.275 Å above the Cu(1 1 0) surface. The carbon atoms form a hexagonal structure with a threefold symmetry axis in the middle of the rectanguilar p-two-dimensional Cu(1 1 0) lattice. The bond length between carbon atoms in the basal plane of the hexagonal lattice was found to be 1.47 Å, which means a 3.7% relaxation in comparison to the bond distance in graphite.

Acknowledgements — One of the authors (A.S.) would like to thank the Max-Planck-Gesellschaft for a post doctoral fellowship. The authors are indebted to Prof. Dr. E. Zeitler for his continued interest and support.

REFERENCES

1. M. De Crescenzi, G. Chiarello, E. Colavita & R. Rosei, *Solid State Commun.* **44**, 845 (1982).
2. L. Papagno, L.S. Caputi, M. De Crescenzi & R. Rosei, *Phys. Rev.* **B26**, 2320 (1982).
3. M. De Crescenzi, F. Antonangeli, C. Bellini & R. Rosei, *Phys. Rev. Lett.* **50**, 1949 (1983).
4. R. Rosei, M. De Crescenzi, F. Sette, C. Quaresima, A. Savoia & P. Perfetti, *Phys. Rev.* **B28**, 1161 (1983).

5. S. Polizzi, F. Antonangeli, G. Chiarello & M. De Crescenzi, *Surf. Sci.* **136,** 555 (1984).
6. A. Santoni, D.B. Tran Thoai & J. Urban, *Solid State Commun.* **58,** 315 (1986).
7. K. Jagannathan, A. Srinivasan, M.S. Hedge & C.N.R. Rao, *Surf. Sci.* **99,** 309 (1980).
8. P.R. Wentrcek, B.J. Wood & H.J. Wise, *J. Catal.* **43,** 366 (1976).
9. M. Araki & V. Ponec, *J. Catal.* **44,** 439 (1976).
10. R.F. Willis, B. Feuerbacher & B. Fitton, *Phys. Rev.* **B4,** 2441 (1971).
11. See for example: *EXAFS Spectroscopy — Techniques and Applications* (Edited by Teo and Joy), Plenum Press (1982).
12. B.K. Teo and P.A. Lee, *J. Am. Chem. Soc.* **101,** 2815 (1979).
13. L. Papagno & L.S. Caputi, *Phys. Rev.* **B29,** 1483 (1984).
14. P.A. Lee & G. Beni, *Phys. Rev.* **B15,** 2862 (1977).
15. B.K. Teo, P.A. Lee, A.L. Simons, P. Eisenberger & B.M. Kincaid, *J. Am. Chem. Soc.* **99,** 3854 (1977).