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LETTER TO THE EDITOR

Evidence for photoelectron backscattering by interstitial charge densities

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Abstract. The presence of oscillatory structures in the atomic x-ray absorption background is reported for the first time for surface-EXAFS of c(2 × 2)N/Cu(100) and (2 × 3)N/Cu(110). Systematic analysis of this feature (AXAFS) and comparison to theory yields new information on the electronic structure of the adsorbate–substrate surface bond. Also, angle and temperature dependent analysis of the AXAFS peak provides qualitative information about interstitial charge density distribution.

The extended x-ray absorption fine structure (EXAFS) technique is now well established to obtain information on the local environment of the x-ray absorbing atom by measuring the bond lengths to the neighbours and the dynamic behaviour by investigating the mean square relative displacements (MSRD) and mean cubic relative displacements (MCRD) [1]. In recent years, improvements in the data acquisition and analysis in the field of surface-EXAFS (SEXAFS) has allowed for data of a high signal to noise ratio (better than 1 to 10) for values in reciprocal space of the order of 10 Å^{-1}. Also, the systematic study of the temperature and angular dependence of the SEXAFS, and comparison to simple theoretical models and to *ab initio* calculations, has allowed for a better understanding of even small intensity oscillations at frequencies corresponding to the nearest neighbour shell or higher.

The oscillatory fine structure is defined by $\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k)$ where k is the photoelectron wavenumber, $\mu(k)$ is the x-ray absorption coefficient and $\mu_0(k)$ is the atomic x-ray absorption coefficient. In a conventional SEXAFS analysis $\mu_0(k)$ is assumed to be of non-oscillatory nature and is replaced by a smooth spline function. We will show here that $\mu_0(k)$ is not necessarily smooth but can also exhibit an oscillatory fine structure. Such fine structure originates from the scattering of the photoelectron in the periphery of the absorbing atom, as already shown by Holland *et al* in 1978 [2] where it is stated that: 'Indeed the shape of the edge up to several tens of Hartrees above the threshold is dictated in detail by scattering of the outgoing electron on the atomic potential'. This fact has been ignored for years. The problem was resumed by Rehr *et al* [3] who compared the experimental atomic x-ray absorption background of the Pr, Ce and Ba K-edges of $PrBa_2Cu_3O_7$, CeO_2 and BaO

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to *ab initio* calculations of the atomic background. These authors describe the oscillatory fine structure $\chi_e(k)$ of the atomic x-ray absorption coefficient $\mu_0(k)$ by:

$$\chi_e(k) = -\frac{1}{kr_{MT}^2}\left|f_e\right|\sin\left(2kr_{MT} + 2\delta_l^a + \phi_e\right) \tag{1}$$

where r_{MT} is the muffin-tin radius of the absorbing atom, δ_l^a is the central atom phase shift and $f_e = |f_e|\exp(\mathrm{i}\phi_e)$ is an effective curved-wave scattering amplitude of the interstitial charge density. This formula turns out to be similar to the one used for the conventional SEXAFS analysis (see for instance [1]) but with the distance to the scatterer being now the muffin-tin radius r_{MT}. This leads to an oscillation of a longer period as compared to the SEXAFS oscillations. Similar effects have been seen in magnetic EXAFS investigations. Low-frequency oscillations correlated to distances below 1 Å were also found in the spin dependent EXAFS signal similar to those presented experimentally by Schütz *et al* for Gd and Tb [4] and theoretically by Brouder *et al* for Gd [5]. However, the mere presence of features at low distances in [4, 5] cited above does not mean that they can be unambiguously associated with AXAFS. Every individual system should be examined very carefully (as shown in the present case) before arriving at a final conclusion. The analysis which has been carried out in [3] has been questioned by Filipponi *et al* [6]. The authors show in [7] that double-electron excitations corresponding to [1s4p], [1s3d] and [1s3p] double-core-hole configurations can mimic an oscillation in $\mu_0(k)$ corresponding to a distance of ≈0.8 Å in the real space. In this letter we present the first atomic EXAFS (AXAFS) investigation for the light adsorbate N on Cu(100) and Cu(110) surfaces. For N atoms the above mentioned complication of multielectron excitations does not exist. The 2s binding energy of 37.3 eV in the case of N might only be responsible for structures in the very low k-region e.g. $k = 3.1$ Å^{-1}. We show that the good signal to noise ratio of our data also at high k-values allows us to extract an oscillatory fine structure in $\mu_0(k)$ in the whole k-range up to $k = 11$ Å^{-1}.

The SEXAFS data for the systems (2 × 3)N/Cu(110) and c(2 × 2)N/Cu(100) have been recorded at BESSY. The details of data collection are given in [8]. The SEXAFS has been modelled to a high degree of accuracy using the *ab initio* FEFF code as shown in [8, 9]. The local structure of the systems is shown in figure 1. In both cases the N atoms chemisorb in a fourfold hollow site. As the (2 × 3)N/Cu(110) system can be described by a pseudo c(2 × 2)N/Cu(100) overstructure the local adsorption geometry differs slightly compared to the original c(2 × 2)N/Cu(100) structure. Figure 1(a) shows that the N atom is located between four Cu atoms that form a rectangle whereas the N atom is located between the Cu atoms forming a square for the second system (figure 1(b)). Due to this distinct difference in geometry the N atoms are located in the surface plane (figure 1(c)) and at a height of 0.4 Å (figure 1(d)) on Cu(110) and Cu(100) respectively. Before discussing the AXAFS of the two systems, we want to describe the experimental SEXAFS data for N/Cu(110). The Fourier transform of the SEXAFS oscillations for normal x-ray incidence at 300 K is shown in figure 2(a). The main peak located around 1.7 Å in the Fourier transform represents the n.n. bond of the N atom to the four surrounding Cu atoms (see figure 1(a)) with bond lengths of $R_{nn} = 1.88$ Å. In this communication, we show that the peak A at 0.8 Å is due to atomic EXAFS. One has to note that the noise level seen at high distances in figure 2(a) is very low and the AXAFS peak is clearly detected. First, one has to rule out that this peak is not a spline artifact: many different splines have been tested yielding the same result. Furthermore, an automated code, AUTOBK [10] which minimizes the contributions in the Fourier transform below 1 Å calculates an oscillating atomic absorption background for the present set of data corresponding to a distance of 0.8 Å. As the backscattering amplitude

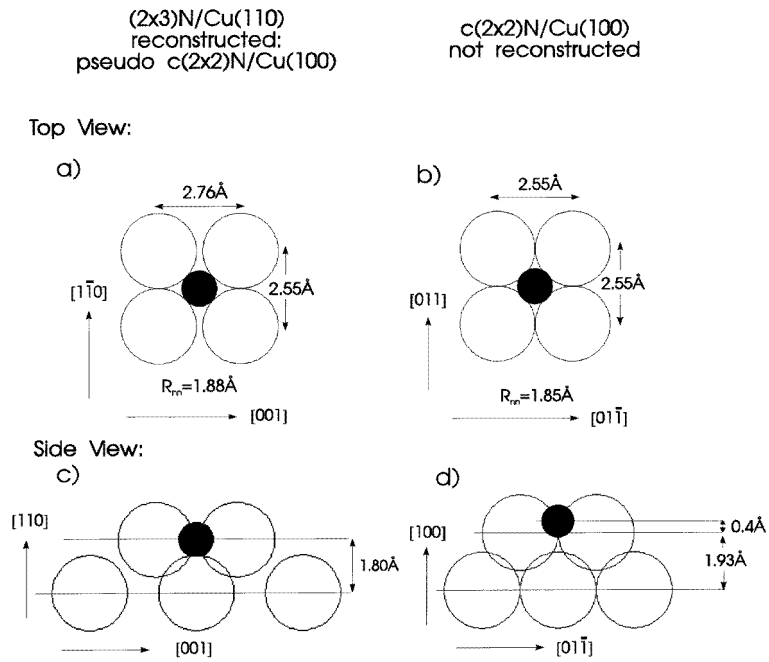

Figure 1. Local adsorption geometry of the two investigated systems N/Cu(110) (a) and (c) and N/Cu(100) (b) and (d). The N atoms are plotted as full small circles and the big circles represent the Cu atoms. See text for details.

and the phase shift of the interstitial charge density is not known from reference standards we carried out *ab initio* calculations of $\mu_0(k)$ using the FEFF7 program [11]. The result is shown in the inset of figure 2(a). The atomic background exhibits a clear oscillatory fine structure which has been extracted with a stiff spline function (thin line in the inset of figure 2(a)). The Fourier transform of these oscillations (dotted line in figure 2(a)) shows fair agreement to the experimental data. It has to be stressed that only the fine structure of $\mu_0(k)$ has been simulated, therefore no other peaks appear in the Fourier transform of the simulation. Here we want to indicate the importance of high-quality SEXAFS data. The SEXAFS oscillations are of the order of 10% of the edge jump ratio. This leads also to a more intense AXAFS peak for a given edge jump ratio than previously reported and makes it more reliable to analyse. In this context it is important to note that the calculations correctly reproduced the relative intensity of the AXAFS peak in all cases for the surface as well as the bulk compounds [3].

Now we focus on a more detailed discussion of the FEFF7 simulation. In these calculations the muffin tin radius r_{MT} is the only free parameter as the structural parameters have been fixed by the preceding SEXAFS analysis. The result of varying r_{MT} is given in figure 2(b). The experimental data (solid line) are compared to simulations with $r_{MT} = 0.8$ Å and $r_{MT} = 1.0$ Å. The FEFF program calculates $r_{MT} = 0.8$ Å by assuming charge neutrality for the investigated system. In this case the simulation differs both in the amplitude and in the phase which is off by 180°. We have to enlarge the muffin tin radius to $r_{MT} \approx 1.0$ Å in order to achieve good agreement of the simulation to experimental data. We interpret this effect in the following way. There is obviously a charge transfer from the Cu atoms to the N atoms. Such charge transfer is not automatically taken into account by the all

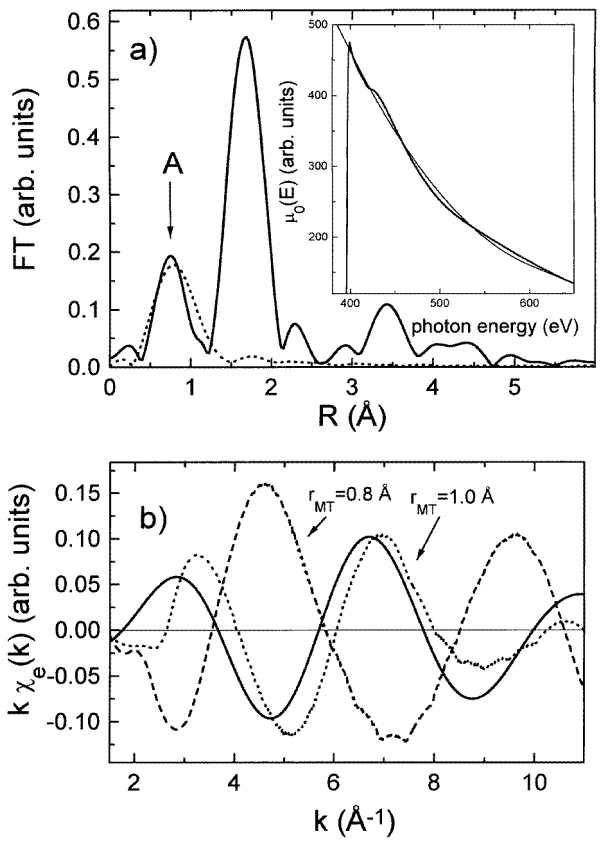

Figure 2. (a) Fourier transform FT[$k\chi(k)$] of the experimental data of the (2 × 3)N/Cu(110) system for normal x-ray incidence, 300 K (solid line). The result of the FEFF7 calculation of $\mu_0(E)$ with $r_{MT} = 1.0$ Å is also shown in the inset. Clearly visible is the oscillatory fine structure of the atomic x-ray absorption background (thick line). These oscillations have been extracted with a stiff spline function (thin line in the inset). The Fourier transform of these simulated oscillations is represented by the dotted line. (b) Back-transformed peak A of the experimental data (solid line) is compared to two simulations. The simulation for $r_{MT} = 1.0$ Å (dotted line) leads to a much better agreement with the experimental data whereas the simulation for $r_{MT} = 0.8$ Å (dashed line) differs entirely in amplitude and phase.

electron overlapped atom scattering potentials used in the program. Therefore one has to enlarge r_{MT} from 0.8 Å to 1.0 Å which is equivalent to a transfer of approximately half an elementary charge. The value for the charge transfer was estimated from n.n. distances of various inorganic crystals containing N atoms of different ionicity. The significance of the charge transfer was not taken into account in our previous publication [12]. Therefore the calculated $\chi_e(k)$ was off by π compared to the experimental data. The effect of changing r_{MT} can also be seen in the scattering potential as it is calculated with FEFF7 (see figure 3). The photoelectron which is created at the N atom site propagates along the N–Cu bond. The scattering potential along this direction is plotted around the interstitial region in figure 3. The two different muffin tin radii are visible due to the artificial jump of the scattering potential which represents the transition from the N to the Cu potential. One has to note that the artificial potential energy jump is significantly reduced by increasing r_{MT}

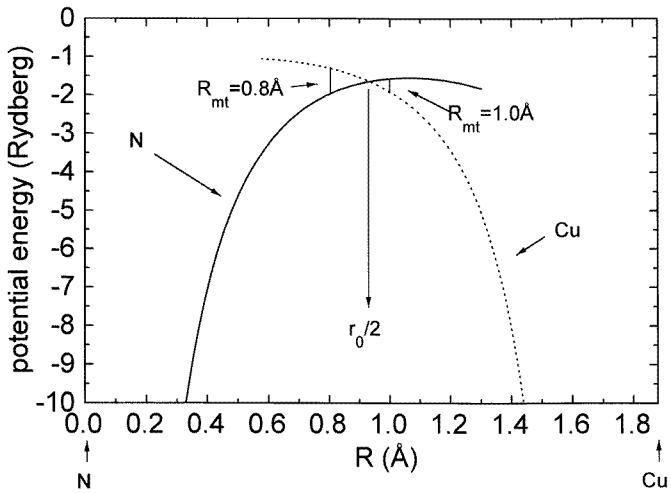

Figure 3. Scattering potential calculated by FEFF7. The photoelectron is created at the N atom which is located at $R = 0.0$ Å and moving to the Cu atom which is located at $R = 1.88$ Å. The potential of N is shown as the solid line and the dotted line represents the Cu potential. The interstitial charge density is located at approximately half the next neighbour distance. The position of the two different muffin tin radii of the N atom which have been used for the calculations are also given by an artificial jump of the potentials.

from 0.8 Å to 1.0 Å. Therefore we can rule out that the calculated AXAFS is only an artifact of the unphysical jump in the scattering potential. To exclude that the oscillations of the theoretically calculated $\mu_0(k)$ are not artifact of the spline analysis we calculated $\mathrm{d}\delta_l^a/\mathrm{d}k$ which should show the same oscillatory fine structure as the atomic x-ray absorption coefficient as was predicted in [2]. The central atom phase shifts δ_l^a have been calculated for the two cases for $r_{MT} = 0.8$ Å and $r_{MT} = 1.0$ Å. The calculated functions $\mathrm{d}\delta_l^a/\mathrm{d}k$ indeed show the same oscillatory fine structure as it is presented for $\chi_e(k)$ in figure 2(b). We also want to comment here on the amplitude of the AXAFS oscillations as a function of photoelectron wavevector k. As is seen in figure 2(b) the experimental AXAFS amplitude does not follow the theoretically predicted sharper decay, particularly visible for a muffin tin radius of 0.8 Å. This is possibly related to the fact that the actual embedded atom charge density responsible for the photoelectron backscattering has a somewhat different spatial distribution than the calculated one. Other considerations on this point are discussed when a comparison of the data of the N–Cu bonds for two different systems is given below.

Up to now we discussed AXAFS only for the N/Cu(110) system. We also see the same AXAFS peak in experimental data for the N/Cu(100) system. Therefore we want to compare the AXAFS of the two systems. In figure 4(a) the experimental and simulated Fourier transforms of the SEXAFS oscillations of the two systems are presented. The dashed and the dotted line in figure 4(a) depict the Fourier transform and the calculation of N/Cu(110) as already shown in figure 2(a). As the adsorption site is nearly the same for both systems the Fourier transform of the N/Cu(100) system shows the same features compared to N/Cu(110). But because of the small differences in the adsorption geometries which result in different n.n. distances the Fourier transform of N/Cu(100) is shifted to smaller distances. A comparison of the data for N/Cu(100) and N/Cu(110) indicates that the intensity of the AXAFS peak is stronger in the case of the reconstructed surface with the adsorbate located in the surface plane. This configuration has previously been linked

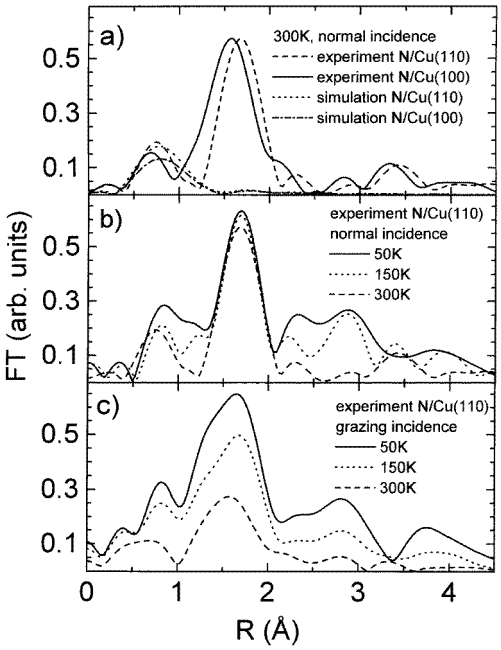

Figure 4. (a) Fourier transform of the experimental data for c(2 × 2)N/Cu(100) for normal x-ray incidence, 300 K (solid line). Also this system exhibits a clearly visible AXAFS peak which is smaller compared to the experimental Fourier transform of the (2 × 3)N/Cu(110) system (dashed line). This trend is also reproduced by the calculations for N/Cu(100) (dot–dashed line) and N/Cu(110) (dotted line). (b) and (c) temperature and angular dependence of the SEXAFS data of the N/Cu(110) system.

to a more covalent state of the adsorbate-substrate atom nearest neighbour bonds [8]. In such a case one would intuitively expect the electronic charge responsible for the formation of the adsorbate–substrate atom bond to be more localized along the adsorbate–substrate atom inter-nuclear axis. In contrast in the case of the unreconstructed surface with a more isotropic bond one expects the electronic charge related to the outermost shells to have a more delocalized distribution. Under these conditions one would expect the localization of the charge to lead to a stronger backscattering much as in the case of 'normal' EXAFS for localized core levels. The data of figure 4(a) seem to support this qualitative picture and indicate the importance of further systematic studies of the AXAFS phenomenon, to establish it as a 'direct' probe of the electronic nature of the adsorbate–substrate bond.

Now we want to discuss the temperature and angular dependence of the AXAFS contribution as shown in figure 4(b) and (c). The whole temperature dependence of the SEXAFS is described in detail in [8]. First we want to describe the data for a sample temperature of 50 K. Comparing the absolute position of the AXAFS peak for normal and grazing incidence it turns out that there is no change in the position. As a first approximation we therefore assume that the interstitial charge density is located in a half sphere around the N atom. In the temperature dependence of the AXAFS peak we observe first an overall tendency of the AXAFS peak to decrease in intensity faster than the first neighbour peak. The data of figure 4(c) allow us also to observe the effects of a strongly anharmonic motion on the AXAFS. The AXAFS peak of the data recorded at 300 K at grazing incidence is much broader than the one at normal incidence (figure 4(b)). This allows one to think

that the interstitial charge density is much more delocalized in this case as compared to the normal incidence data. This observation is compatible to the much larger amplitude of vibration along the surface normal.

An observation of a systematic AXAFS contribution for two systems N/Cu(100) and N/Cu(110) and a reasonable temperature dependence of the effect provides an unambiguous proof that there is an oscillatory fine structure in the atomic x-ray absorption coefficient as predicted in [2]. The study clearly points out the absolute necessity of high-quality data and measurements at low temperatures for the reliable analysis of the AXAFS feature. Light adsorbates turn out to be good model systems for this kind of investigation because no multielectron excitations can mimic the long-range oscillatory fine structure. *Ab initio* calculations have been performed showing fair agreement to the experimental data although the only free parameter, the muffin tin radius of the N atoms, had to be enlarged in order to consider charge transfer from the Cu atoms to the N atoms.

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