Enhanced Anharmonicity in the Interaction of Low-Z Adsorbates with Metal Surfaces

L. Wenzel, D. Arvanitis, H. Rabus, T. Lederer, and K. Baberschke
Institut für Experimentalphysik, Freie Universität Berlin, D-1000 Berlin 33, Federal Republic of Germany

G. Comelli
Sincrotrone Trieste, Padriciano 99, I-34012 Trieste, Italy

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Temperature-dependent surface extended x-ray-absorption fine-structure (SEXAFS) measurements on half a monolayer of O and N atoms on Ni(100) and Cu(100) surfaces indicate enhanced anharmonic contributions in the adsorbate-substrate pair potential, with respect to bulk values. From the temperature dependence of the SEXAFS amplitude and phase we calculate the thermal expansion coefficients. These coefficients are found to be enhanced independent of the system, establishing the observed anharmonicity as a general surface-related property. The implications of these findings for surface reconstructions are discussed.

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Extended x-ray-absorption fine-structure (EXAFS) measurements above a K edge after photon excitation constitute a well understood and widely used technique for obtaining information on the local environment of the excited atom.[1,2] Through its short-range probe character, EXAFS has proven particularly useful in the study of various systems presenting large static or dynamic disorder.[2-4] It is established that in these cases not only a reduction in the amplitude of the EXAFS oscillations occurs, but also a shift in its phase. Temperature-dependent studies of the amplitude and phase of the EXAFS oscillations provide a distinction between static and dynamic effects and a determination of the pair-distribution function or an effective pair potential of the absorber atom.[1-4] In particular, systems exhibiting high mobility, such as solids close to or above their Debye temperature[4-6] or superionic conductors,[2] yield asymmetric pair-distribution functions or anharmonic pair potentials. This establishes the harmonic approximation as insufficient in these cases for describing the relative motion between the absorber atom and its neighbors, which is probed by EXAFS.

Adsorbates on surfaces also constitute good candidates for high-mobility systems even at room temperatures. In the present Letter, we show that surface EXAFS (SEXAFS) is the technique of choice which can be successfully applied in order to study quantitatively the anharmonic contributions in the low-Z-adsorbate-metal-substrate interaction. Evidence for anharmonic interactions on surfaces have been found for Cl adsorbed on Ag(111),[7] N on Ni(100),[8] and O and S on Ni(100).[9] In the present study, we compare the temperature dependence of the SEXAFS oscillations for the prototype systems $c(2\times2)$O/Ni(100), $(\sqrt{2}\times2\sqrt{2})R45°$O/Cu(100), and $p4g(2\times2)$N/Ni(100) illustrating the interaction of half a monolayer of low-Z adsorbate atoms with a metal surface.[10] It is found that the adsorbate-substrate interaction is anharmonic and shows enhanced anharmonicity with respect to the corresponding bulk, independent of the chemical nature of the bonds. This enhanced anharmonicity for the surface systems is comparable to the one observed for the alkali halides NaBr and RbCl known as being among the most anharmonic solids studied by EXAFS.[5]

In Fig. 1(a) the SEXAFS signal $\chi(E)$ is shown for normal x-ray incidence after background subtraction. Changes in the amplitude and phase can be clearly seen for the two temperatures. After Fourier filtering, the normalized contribution $k\chi(k)$ of the first-neighbor shell only is shown in the upper part of Fig. 1(b). Comparing these contributions, the phase difference $\Delta\phi$ between the two temperatures can be obtained. It is shown in the lower part of Fig. 1(b), for discrete points, that phase differences can be seen for all three systems, being the largest for O/Cu. The fact that large nonlinear phase differences are found indicates that an EXAFS formalism suitable for describing moderate thermal disorders has to be used. Following the EXAFS literature[3-5] we use the cumulant expansion in order to generalize the ratio method. $k\chi(k)$ is given by

$$k\chi(k)=B(k,r_0,\lambda)e^{-2\sigma^2k^2}\sin\left\{2k\left[r(T)-\frac{2\sigma^2(T)}{r_0}\left(1+\frac{r_0}{\lambda}\right)\right]-\tfrac{4}{3}\sigma^{(3)}k^3\right\}, \tag{1}$$

where B is a temperature-independent factor in the amplitude. The phase difference $\Delta\phi$ of χ between two temperatures and at a fixed x-ray incidence angle Θ is then given by

$$\Delta\phi(T_1,T_2)=\phi(T_1)-\phi(T_2)=\Omega k-\tfrac{4}{3}k^3\Delta\sigma^{(3)}(T_1,T_2,\Theta), \tag{2}$$

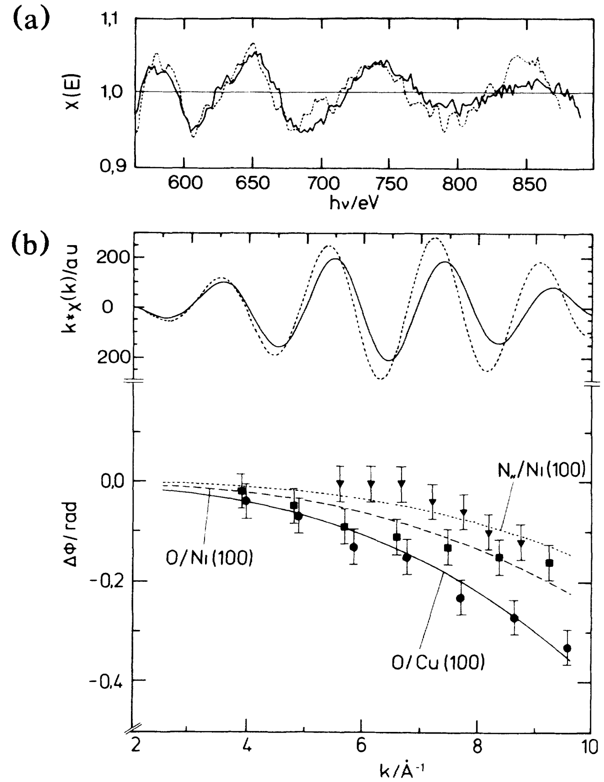

FIG. 1. (a) The SEXAFS signal, $\chi(E)$, for $(\sqrt{2}\times 2\sqrt{2})R45°$O/Cu(100), vs x-ray photon energy after background subtraction for 50 K (dashed line) and 300 K (solid line). This also includes contributions from the second and third nearest neighbor. In the upper part of (b) the SEXAFS signal due to only the nearest-neighbor shell is shown vs photoelectron wave vector k after Fourier filtering for the data shown in (a). The amplitude reduction at 300 K is accompanied by a change in the phase which increases with k. This can be better seen in the phase difference $\Delta\phi$ of the SEXAFS signal between the two temperatures vs k, shown in the lower part of (b). The lines are fits to the data points using Eq. (2). For $N_{\parallel}$/Ni the triangles correspond to the normal-incidence data probing the N bond to the first substrate layer.

with

$$\Delta\sigma^{(3)}(T_1,T_2,\Theta)=\sigma^{(3)}(T_1,\Theta)-\sigma^{(3)}(T_2,\Theta)\,,$$

Ω a small constant of approximately 5×10^{-3} Å, and $\sigma^{(3)}(T,\Theta)$ the third cumulant. The cumulant of order n is related to the nth moment of the absorber-backscatter pair-distribution function (PDF).[1-5] σ^2, the second cumulant, is the mean-square relative displacement (MSRD) between absorber and backscatterer (the so-called EXAFS Debye-Waller factor) and is related to the broadness of the PDF. A nonzero $\sigma^{(3)}$ indicates that the harmonic approximation is then not sufficient to describe the absorber-backscatter relative motion. Here we limit ourselves to temperature-dependent effects, determining only the differences $\Delta\sigma^2$ and $\Delta\sigma^{(3)}$ between room and low tempertures. $\Delta\sigma^2$ was determined from the usual logarithmic ratio plots versus k^2, as we have shown previously.[8] $\Delta\sigma^{(3)}$ was obtained by least-square fits of $\Delta\phi$ in Fig. 1(b). It should be noted that as *we only compare* the amplitude and frequency of the SEXAFS oscillations taken under the same angle of incidence but different temperatures, *our conclusions are not based on any particular structural model.*

It is of some interest to determine $r(T)$, the thermal expansion of the adsorbate-substrate bond length. Between 0 K and room temperature $\Delta r(\Delta T)$ is $\lesssim 1.0\times10^{-2}$ Å in the bulk. This is too small to be detectable in the linear rk term in SEXAFS experiments. From Eq. (1) it can be seen that the negative sign of the σ^2 term reduces this effect even more. However, the thermal expansion is clearly detectable through the k^3 term [Eqs. (1) and (2)]. In this Letter, we propose a new approach to obtain the thermal expansion, namely, by measuring independently the anharmonic $\sigma^{(3)}$ and the MSRD σ^2: Considering small corrections to the Gaussian PDF at low temperature it can be shown using the cumulants that

$$r(T)=r_0+\frac{\sigma^{(3)}}{2\sigma^2}\,, \tag{3a}$$

$$\Delta r(T_1,T_2)=C\frac{\Delta\sigma^{(3)}(T_1,T_2)}{\Delta\sigma^2(T_1,T_2)}\,, \tag{3b}$$

with r_0 the bond length at 0 K, $\Delta r(T_1,T_2)$ the bond-length variation between T_1 and T_2, and C a constant approximately equal to $\frac{1}{3}$.[11] As we measure only the differences in $\sigma^{(3)}$ and σ^2 we use Eq. (3b) which is the high-temperature approximation of Eq. (3a). It can be shown for the systems and temperatures of interest that Eq. (3b) is within 10% a good approximation of Eq. (3a). The results for the different surface systems are shown in Fig. 2 (circles), where $\Delta\sigma^{(3)}$ is plotted versus $\Delta\sigma^2$, together with the corresponding values for bulk materials taken from EXAFS measurements between the same temperatures.[5,6,12(a)] Using Eq. (3b) *the ability to determine* $\Delta\sigma^{(3)}$ *and* $\Delta\sigma^2$ *yields directly a determination of the thermal expansion, that is to say, of the strength of anharmonicity.* The following is observed: (i) The obtained thermal expansions for the surface are much larger than the ones of the corresponding bulk compounds, found to be $12(2)\times10^{-3}$ and 1×10^{-3} Å for O/Cu and CuO, respectively, as well as $13(3)\times10^{-3}$ and 5×10^{-3} Å for O/Ni and NiO.[13] (ii) All points in Fig. 2, falling on one line through the origin, yield a comparable thermal expansion according to Eq. (3b). The observed surface $\Delta r(T_1,T_2)$ fall on one line and appear to be uncorrelated with the chemical nature of the surface bond as we are dealing with systems of more ionic (O/Ni) or more covalent (N/Ni, O/Cu) character. (iii) The solid line clearly has a higher slope than the one describing the thermal expansion of some bulk metal

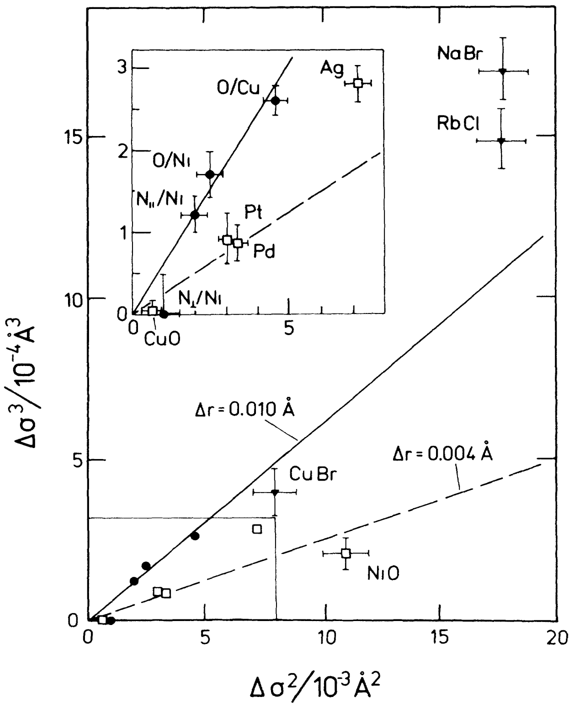

FIG. 2. The values of the third cumulant $\Delta\sigma^{(3)}$ vs $\Delta\sigma^2$, the MSRD. Data points of bulk compounds were taken for EXAFS measurements at the same temperatures as for the surface systems [squares, "normal" materials from Ref. 6 (Pt), Ref. 12(a) (Ag,Pd), and Ref. 13 (NiO); inverted triangles, "anharmonic" compounds from Ref. 5]. The adsorbate-metal systems are presented as circles (this work). The solid and dashed lines indicate different thermal expansions Δr according to Eq. (3b). Inset: Enlargement of the region close to the origin.

compounds (Fig. 2, dashed line). The only bulk materials that yield a comparable expansion are the alkali halides NaBr, RbCl, and CuBr, known as being among the most anharmonic at room temperature in the EXAFS literature.[1-5] (iv) Large Δr values for bulk materials (NaBr, RbCl, Fig. 2) are accompanied by large vibrational amplitudes (large σ^2). This is clearly not the case for our oxygen and nitrogen atoms bonded to the first substrate layer. $\Delta\sigma^2$ is as in the bulk (small), but $\Delta\sigma^{(3)}$ is much larger. Only the bonding of N to the second layer of Ni atoms ($N_\perp$/Ni) has $\Delta\sigma^{(3)} \approx 0$ Å^3 within experimental error. This is to say, it probes a harmonic potential for the vibration normal to the surface.

Since in the harmonic approximation of the atomic motion the thermal expansion is zero, the measured $\Delta r(T_1,T_2)$ can be taken as a measure of anharmonicity for the absorber-backscatterer pair potential. All the previous observations do not allow a classification of the observed enhanced anharmonicity according to bulk properties, and strongly indicate that we are dealing with a surface-related phenomenon.

Before further discussing the previous findings we turn to a comparison of our results with other SEXAFS studies: Anharmonicity has been observed for Cl/Ag(111) (Ref. 7) and N/Ni(100),[8] but no detailed analysis was performed. Temperature-dependent studies exist also for Cl/Cu(100), S/Ni(100), and Cl/Ni(100) (Ref. 14) and for Co adsorbed on Cu surfaces.[15] In all these cases no anharmonicity was measured. In order to observe anharmonic effects, it is favorable to study adsorbate atoms that are light relative to the substrate. In this case one expects high-frequency surface modes decoupled from those of the bulk. Both facts are essential for the observation of the effect from EXAFS, where the relative movement of the atoms is measured much better for high-frequency optical modes.[1] In the SEXAFS literature anharmonicity was previously observed only for light adsorbates relative to the substrate. This is also the case here, where the atomic mass differences Δm are ~45. In the case of Cl/Ag Δm is even larger (~72). For Cl/Cu, S/Ni, and Cl/Ni the atomic mass differences are ~26 and in the case of Co/Cu only ~5. For small mass differences the expected strong coupling between the bulk and the adsorbate-related phonon modes requires full dynamical calculations in order to obtain the adsorbate vibrational amplitudes from the value of $\Delta\sigma^2(T_1,T_2,\Theta)$.[16] SEXAFS data appear much easier to interpret for large mass (force constant) differences between surface and bulk where even a simple Einstein model can yield qualitative results.[8]

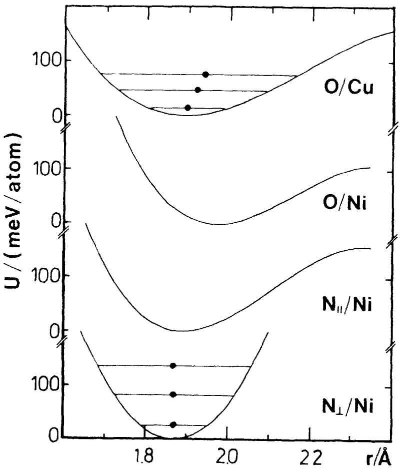

FIG. 3. The "effective" pair potentials vs interatomic distance. In the case of anharmonicity a thermal population of higher excited eigenstates yields thermal expansion, as indicated by the points which mark the mean value of the adsorbate-substrate distance.

A more compact way to illustrate the observed anharmonic effects in the adsorbate-substrate bond is the one of the effective pair potential[1-5] describing the adsorbate movement relative to its neighbors (Fig. 3). In the $N_\perp$/Ni case (Fig. 3), due to the large separation of the eigenstates (strong force constants), the first excited state remains almost unpopulated at room temperature. As a consequence no anharmonicity is observed within error. The opposite is true for the O/Cu system. There the smaller eigenstate spacing allows at room temperature a sufficient population of the first and second excited states for which the expectation value of the distance (Fig. 3, dots) is enhanced compared to the ground-state one due to the cubic contributions.

Our study of the prototype systems of low-Z-adsorbate submonolayers on metal substrates gives evidence of a surface-induced enhanced mobility of the adsorbate atoms and promises to yield a better understanding of other surface-specific phenomena. For example, in the case of surface reconstructions anharmonicity plays a key role close to the transition temperature. Anharmonic effects will keep the distortion due to the soft-mode waves finite as the system approaches the critical temperature and will determine the new structural parameters of the reconstructed system. In the case of the N/Ni system where evidence exists for a "frozen mode" reconstruction,[17,18] assuming that close to the critical temperature the whole "linear thermal expansion" is due to the tangential displacement ξ,[10,17,18] we obtain using the high-temperature approximation a critical temperature of $\sim$700 K for $\xi \sim 0.5$ Å. This value is in agreement with the experimental observation that the system always has to be activated in order to reconstruct. These are typical temperatures used in the experiment. The present study provides, therefore, the first quantitative results that will help improve *ab initio* calculations of adsorbate-induced reconstructions, and the effective pair potentials can be used as experimental input for molecular dynamics (MD).[19] The strong anharmonicity is observed only in the adsorbate-substrate bond to the first layer. The bond to the second substrate layer does not show anharmonicity at room temperature due to the strong force constant. This demonstrates that the harmonic approximation breaks down already at room temperature for the adsorbate-substrate topmost layer and has to be taken into consideration in further dynamic calculations.

In conclusion, a quantitative comparative study for low-Z elements on metal surfaces establishes the existence of a surface-enhanced anharmonicity for the first time. The present data may also help our understanding of the origin of surface structural phase transitions.

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Note added.—After submission of this manuscript, Ref. 12(b) appeared. Their results on Cu and Au fit our plot in Fig. 2 quite well. They also point out that only for EXAFS data of very high quality (fcc metals) can the thermal expansion be measured directly. In all other cases (i.e., AgBr) the mean cubic relative displacement $\sigma^{(3)}$ is much more sensitive to it. They also measured CuBr, in agreement with Ref. 5, and AgBr, which falls on the solid line of Fig. 2 close to RbCl.

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