Growth of H$_2$O layers on an ultra-thin Al$_2$O$_3$ film: from monomeric species to ice

G. Tzvetkov a,*, Y. Zubavichus b, G. Koller a, Th. Schmidt c, C. Heske c, E. Umbach c, M. Grunze b, M.G. Ramsey a, F.P. Netzer a

a Institut für Experimentalphysik, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria
b Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
c Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Received 9 May 2003; accepted for publication 15 July 2003

Abstract

Adsorption of water on an ultra-thin alumina film grown epitaxially onto NiAl(110) has been investigated by temperature-programmed desorption, work function measurements, ultraviolet photoelectron spectroscopy, and high-resolution X-ray photoelectron spectroscopy as a function of surface coverage at 100 K. At low coverages monomeric H$_2$O species are adsorbed and it is proposed that the oxygen lone pair orbitals interact weakly via polarisation forces with the Al$^{3+}$ cations of the second layer. No indication for the dissociation of H$_2$O and the formation of OH$^-$ species has been found. For intermediate coverages clustering of H$_2$O molecules occurs and the growth of a three-dimensional ice layer is observed. Care has to be exercised in photoemission experiments of ice layers, since UV photon-induced dissociation of H$_2$O in thicker ice layers is indicated.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Adsorption kinetics; Water; Aluminum oxide; Thermal desorption; Photoemission (total yield); Work function measurements

1. Introduction

The molecular-level interaction of water with solid surfaces has been extensively studied during the last three decades. The existing wealth of literature concerning this topic is summarised in the excellent reviews given by Thiel and Madey [1] and Henderson [2]. In particular, the adsorption of water on metal-oxide surfaces has found a continuous interest. This adsorption system is of fundamental importance in many fields, such as heterogeneous catalysis, geochemistry, atmospheric chemistry, electrochemistry, and corrosion science [1–3].

The adsorption of water on metal-oxide surfaces at low temperature is characterized by several general features. First, in contrast to the metal surfaces, H$_2$O molecules form strong chemisorption bonds on the oxide substrates. On perfect surfaces molecular adsorption of H$_2$O usually takes place. The prevailing interpretation is that water binds via the lone pair of the oxygen atom to the cation sites of the substrate (Lewis acidic sites).
Dissociation of H\textsubscript{2}O on oxides is dominated by defect sites (e.g., oxygen vacancies) as it was observed for surfaces such as NiO(100), Cr\textsubscript{2}O\textsubscript{3}(111) [4], SnO\textsubscript{2}(110) [5], TiO\textsubscript{2}(110) [6], etc. Secondly, H\textsubscript{2}O on oxides does not generally form hydrogen-bonded clusters at low coverages. In such a case monomeric water species can be isolated on the surface. The monomeric water adsorption has been proposed for SrTiO\textsubscript{3}(110) [7], Na\textsubscript{0.7}WO\textsubscript{3}(100) [8], TiO\textsubscript{2}(100) [9] and anatase TiO\textsubscript{2}(101) [10] surfaces.

In this work we have studied H\textsubscript{2}O adsorption on an ultra-thin epitaxial Al\textsubscript{2}O\textsubscript{3} film grown on NiAl(110). As shown in [11] the oxide film is considered to mimic the \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}(111) surface. Furthermore, the oxide film is oxygen-terminated and the sequence of layers from bulk to surface is most likely NiAl–Al–O–Al–O, i.e., two oxygen/aluminum bilayers of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}(111). This surface has been tested for H\textsubscript{2}O adsorption at both 90 and 130 K [12]. Not surprisingly, it has been found that the oxide film is rather inert toward H\textsubscript{2}O, but the authors do not present specific experimental data. Though H\textsubscript{2}O/metal-oxide systems have been the focus of many investigations, only one oxygen-terminated oxide surface has been considered, namely FeO(111), on which H\textsubscript{2}O adsorption has been thoroughly investigated. Ranke and co-workers [13,14] observed physisorbed H\textsubscript{2}O monomers and a hydrogen-bonded bilayer with an ice-like structure on the FeO(111) surface.

In the present study, the adsorption and growth of water layers on Al\textsubscript{2}O\textsubscript{3}/NiAl(110) was investigated under ultra-high vacuum (UHV) conditions. One of our motivations was to extend the quite limited knowledge of the interaction of water with oxygen-terminated oxide surfaces. Moreover, this study also presents new insights into the surface properties of the Al\textsubscript{2}O\textsubscript{3}/NiAl(110) film, which recently became an important substrate for studying model catalytic reactions [12]. Temperature-programmed desorption (TPD), work function (\(\Delta\phi\)) measurements, ultraviolet photoelectron spectroscopy (UPS), and high-resolution X-ray photoelectron spectroscopy (HR-XPS) using synchrotron radiation were employed to study the adsorption of water as a function of coverage on Al\textsubscript{2}O\textsubscript{3}/NiAl(110) at 100 K.

2. Experimental

The experiments were performed in two UHV systems equipped with standard surface preparation and different analytical tools. The UPS, TPD and \(\Delta\phi\) experiments were carried out in a custom-designed \(\mu\)-metal chamber (base pressure of \(\sim1\times10^{-10}\) mbar) in Graz. The details of the apparatus have been described elsewhere [15]. The UPS spectra were excited with He II radiation and the photoemitted electrons were collected in normal emission geometry, with a photon incidence angle of 40° with respect to the surface normal. The work function was determined by the low-energy onset of the spectra using He I radiation. The sample was biased (–9 V) to improve the secondary electron cut-off. TPD experiments were performed with a line-of-sight detection quadrupole mass spectrometer, which is surrounded by a liquid nitrogen cooled stainless steel shield in order to suppress the detection of gases desorbing from the crystal holder and chamber walls. A heating rate of 1 K/s was used in the present study.

The HR-XPS measurements were performed at the UE52-PGM undulator beamline at the BESSY II storage ring in Berlin with a Sciencia SES200 hemispherical energy analyser. The photon beam was incident at 55° relative to the surface normal and the spectra were recorded at normal emission. Photon energies of 160 and 610 eV were used for exciting electrons from the Al 2p and O 1s core levels, respectively. The combined monochromator-analyser energy resolution was better than 110 meV (\(h\nu = 160\) eV) and 140 meV (\(h\nu = 610\) eV), as determined from the width of the Fermi edge. The fitting of the O 1s spectra was performed by using Doniach–Sunjic line-shapes convoluted with a major Gaussian contribution as model functions for the individual components.

Alumina films were prepared by oxidation of a NiAl(110) single crystal surface. The oxide was formed by back filling the chamber to \(7\times10^{-9}\) mbar of oxygen for 20 min at a sample temperature of 550 K. The crystal was finally briefly annealed to \(\sim1150\) K. Usually, a complete oxidation of the surface was achieved after two oxidation/annealing cycles. According to Auger electron spectroscopy studies the thickness of such an oxide film is \(\sim5\) Å [11].
High-purity water (H$_2$O, puriss. p.a. grade) was obtained from Fluka, and was further purified by several freeze–pump–thaw cycles. Dosing of water in the chamber in Graz was carried out by a retractable pinhole doser, positioned within 4 mm from the crystal surface to get a uniform distribution of impinging molecules. The temperature of the crystal was 100 K during adsorption. The water exposures in Berlin were carried out by background dosing in the preparation chamber. All the exposures are quoted in Langmuirs (1 L = 1 × 10$^{-6}$ Torr s), with the pinhole doses calibrated against background doses. Because of the slow pumping rate of the water after background dosing in the system in Berlin, the values associated with the XPS spectra may slightly underestimate the real exposure.

3. Results and discussion

TPD measurements of water on Al$_2$O$_3$/NiAl(1 1 0) are shown in Fig. 1 for a series of different water coverages at 100 K. For the lowest exposure a desorption maximum at ~164 K appears. This peak (labelled $\beta$ and indicated by the dotted vertical line) grows with exposure without a significant shift in the temperature and eventually saturates or disappears (this is difficult to differentiate because of the overlap with the low-temperature peak) around 1 L exposure. A second desorption peak appears at ~158 K after a dose of 0.5 L H$_2$O. This peak (labelled $\alpha$) shifts to higher temperatures and has a common leading edge for increasing exposures, i.e., a feature characteristic of zero order desorption kinetics. We attribute this peak to desorption from clusters of water molecules and ice multilayers. It is worth noting that the $\alpha$ peak starts growing before saturation of the higher temperature desorption state. The observed two desorption events occur below 200 K suggesting the absence of strongly bound species on the surface. The insert (a) of Fig. 1 shows the plot of the total H$_2$O TPD peak area versus H$_2$O dose. The data form a straight line which passes through the origin, indicating a constant sticking coefficient of water on Al$_2$O$_3$/NiAl(1 1 0).

An Arrhenius analysis of the $\alpha$ TPD peak for zero order desorption kinetics above 0.7 L of H$_2$O exposure (see insert (b) of Fig. 1), i.e., where the

Fig. 1. H$_2$O (amu 18) TPD spectra from various water exposures adsorbed on an Al$_2$O$_3$/NiAl (1 1 0) surface at 100 K. The insert (a) shows the uptake curve of water obtained from the peak areas in the TPD spectra. Insert (b) shows an Arrhenius plot based on the TPD data of the $\alpha$ peak.
peak positions can be accurately determined, yields a desorption energy of 42 kJ/mol. This value can be compared with the heat of sublimation of ice multilayers, which is 42–48 kJ/mol, obtained in studies of different metal surfaces [1]. The desorption kinetics of peak $\beta$ may be safely assumed to proceed with first order. Thus, the desorption energy of water molecules in the $\beta$ state can be estimated using Redhead’s analysis [16]. Assuming a frequency factor of $10^{13}$ s$^{-1}$, a desorption energy of $\sim$43 kJ/mol is obtained. This value is only slightly greater than the desorption energy of water from ice and can be interpreted as a measure of the strength of the water–$\text{Al}_2\text{O}_3$/NiAl(1 1 0) bond.

Fig. 2(a) displays UPS spectra of the clean and water-exposed $\text{Al}_2\text{O}_3$ film. The features at 0–3 eV below $E_F$ in the clean oxide spectrum are due to the emission from the NiAl(1 1 0) substrate, whereas the oxygen-induced states appear between 4 and 13 eV. Previous studies on the NiAl valence band structure have shown that the narrow band between 0–3 eV below the Fermi level is a result of the strong hybridisation of Al p and Ni d electrons [17,18]. For low H$_2$O exposures spectral changes evolve in the region 8–15 eV below $E_F$, while the NiAl valence band at $\sim$2 eV below $E_F$ is gradually suppressed as the water coverage increases (see also Fig. 3). After a dose of 1 L one can clearly distinguish three well-separated adsorbate-induced features at $\sim$7 eV, between 8.5 and 11.6 eV, and at $\sim$13 eV below $E_F$. We attribute these features to the emission from the three highest occupied molecular orbitals (MOs) of water [19]. The first peak corresponds to emission from the non-bonding oxygen lone pair 1$b_1$ MO of water, the second feature is due to the partly bonding and partly non-bonding 3$a_1$ MO and the last one at $\sim$13 eV is caused by the bonding 1$b_2$ MO. All H$_2$O-induced signals reveal a shift to higher binding energy with increasing exposure which may be due to a reduced final state screening.

The changes in the UPS spectra induced by water adsorption are more clearly visible in the difference spectra (difference between the respective H$_2$O-exposed $\text{Al}_2\text{O}_3$/NiAl(1 1 0) spectrum and the properly attenuated clean substrate spectrum).
shown in Fig. 2(b). The difference spectrum after a 0.3 L H₂O dose already shows the “fingerprint” three-peak structure of molecular water (1b₁, 3a₁, and 1b₂ MO). As one can see the 3a₁ emission appears somewhat broad and the peak position cannot be determined accurately. At higher exposures the H₂O-induced features become better resolved and the exact peak positions and their energy separations for several coverages are listed in Table 1. For comparison the literature data for gaseous and solid water are also included. The experimental data in Table 1 clearly reveal that the peak separations (3a₁–1b₁) and (1b₂–3a₁) for the water exposures below 1 L are similar to the separations observed for the gaseous water. This suggests that the H₂O molecules are weakly bound to the surface during the first stage of adsorption on the Al₂O₃/NiAl(1 1 0) surface. Moreover, this result can be associated with our TPD data, namely the development of peak β in the same exposure range (<1 L). Thus, we assign peak β to the desorption from the weakly bound monomeric species of molecular water on the surface. In previous studies of H₂O adsorption on different surfaces the species with similar properties has been described as a two-dimensional (2D) lattice gas of water [14,22].

The UPS spectrum after an exposure of 2.5 L shows that the 3a₁ peak is broadened, containing contributions from at least two peaks (see Fig. 2). On the basis of previous works this can be interpreted as due to the formation of hydrogen-bonded water clusters [13,14,22]. Schmeisser et al. [22] have suggested that this splitting is due to the two kinds of H₂O molecules in different bonding configuration, where one acts as a hydrogen-donor and the other one as a hydrogen-acceptor. The splitting of the 3a₁ peak is less pronounced after 6 L exposure. This is explained by the fact that at

![Fig. 3. Emission intensity of the Al(p)–Ni(d) substrate valence band (full symbols; left scale) and the H₂O 1b₁ MO (open symbols; right scale) as a function of water exposure.](image)

<table>
<thead>
<tr>
<th>Exposure (L)</th>
<th>Binding energy (eV)</th>
<th>H₂O/O₁s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1b₁</td>
<td>3a₁</td>
</tr>
<tr>
<td>0.3</td>
<td>6.6</td>
<td>–</td>
</tr>
<tr>
<td>0.5</td>
<td>6.6</td>
<td>8.8</td>
</tr>
<tr>
<td>1</td>
<td>7.1</td>
<td>9.7</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>10.1</td>
</tr>
<tr>
<td>2.5</td>
<td>7.3</td>
<td>10.1</td>
</tr>
<tr>
<td>4</td>
<td>7.4</td>
<td>10.4</td>
</tr>
<tr>
<td>6</td>
<td>7.8</td>
<td>10.9</td>
</tr>
<tr>
<td>Gaseous H₂O⁰</td>
<td>12.6</td>
<td>14.8</td>
</tr>
<tr>
<td>Solid H₂O⁰</td>
<td>8.2</td>
<td>–</td>
</tr>
</tbody>
</table>

---

*With respect to the vacuum level [20].

*From Ref. [21].
these coverages the growth of three-dimensional (3D) ice layers begins. In the bulk of an ice film all molecules are equivalent and represent donor as well as acceptor species. The 3α1 peak in the difference spectrum after 6 L H2O exposure is still broad, but this may reflect the difference of the H2O coordination at the surface and at the interface to the substrate, because the ice film is still very thin.

The attenuation of the substrate Al(p)–Ni(d) band emission intensity as a function of H2O exposure and the water-induced 1b1 signal strength are shown in Fig. 3. The substrate band emission intensity was estimated from the height of the feature at 1.7 eV, whereas the 1b1 intensity was taken from the respective heights in the difference spectra. The continuous decrease of Al(p)–Ni(d) intensity due to the covering of the substrate with adsorbate molecules and the increase of the 1b1 signal is readily seen. Apart from this correlation a small plateau is reproducibly observed between 0.5 and 1 L water exposure in both curves. Remarkably, this plateau coincides with the appearance of the α peak in the TPD spectra (Fig. 1).

The change of the work function of Al2O3/NiAl(1 1 0) as a function of water exposure at 100 K is shown in Fig. 4. A rapid drop of the work function (Δφ = –0.7 eV) after adsorption of ~1 L H2O is observed. The negative Δφ is caused by the dipole moments of the H2O molecules perpendicular to the surface, which reduce the overall surface dipole of the Al2O3/NiAl(1 1 0). This indicates that the weakly bound water molecules are most probably adsorbed in a geometry with their oxygen atoms oriented towards the substrate. Recently, the formation of physisorbed monomers of water on the oxygen-terminated FeO(1 1 1) surface has been observed [13,14]. The authors also propose an orientation of the H2O molecules with their oxygen atoms pointing towards the surface, which is caused by the attractive electrostatic interactions between the water dipoles and the Fe cations located in the second layer. We adopt this mechanism to explain the bonding of the H2O monomers on the Al2O3/NiAl(1 1 0) surface at exposures up to ~1 L and propose an electrostatic interaction between water oxygen atoms and the Al3+ cations embedded in the oxide, i.e., the cations underneath the surface O layer, as discussed below.

The increase of φ after 1 L H2O dose (Δφ = +0.2 eV) is somewhat surprising. It is usually assumed that negative Δφ values after water adsorption are due to the charge donation from adsorbed H2O to the surface, whereas the increase of φ is ascribed to the presence of hydroxyls on the surface, acting as electron acceptors (charge transfer from the surface to the OH− 1π orbital) [1]. Judging from our UPS and HR-XPS data (see below) we can exclude the presence of OH− from the dissociation of H2O on the Al2O3/NiAl(1 1 0) surface. The experimental data presented above indicate that at coverages below ~1 L H2O monomeric water species exist, while at higher coverages water aggregates are formed. A possible explanation of the small φ increase is that a reorganisation process of the adsorbed water species occurs at the surface. We presume that the isolated H2O molecules, present during the initial stages of exposure, form clusters after a certain coverage (~1 L H2O dose), with a concomitant change of the overall surface dipole. Referring to Fig. 3, we correlate the appearance of the small plateau in the uptake
curves with the minimum of the work function. After ~5 L H₂O dose $\phi$ remains constant indicating the growth of 3D ice.

Additional features in the UPS spectra of water-exposed surfaces appear after doses of around 10 L and higher. Fig. 5 shows the UPS spectra of the Al₂O₃/NiAl(1 1 0) surface after 10 and 15 L water doses. If one compares these spectra with the spectrum of the 6 L dosed surface two additional features at 7.2 and 11.3 eV and an overall shift towards higher binding energies can be detected. We assign the new spectral features to the 1\(\pi\) and 3\(\sigma\) orbitals of OH\(^-\), respectively. Most probably the OH\(^-\) species are created as a result of the UV irradiation of the ice films. The photon-induced dissociation of H₂O in ice films utilising synchrotron radiation or conventional light sources for photoemission studies (X-ray sources and UV-lamps) has been reported in several recent studies [23–25]. It should be mentioned that the OH\(^-\)-induced features appear in the spectra immediately after the films have been illuminated with the He II light (40.8 eV) and that their intensity increases with the duration of illumination. The presence of hydroxyls has been observed only at higher coverages, i.e., where the thick films of 3D ice exist. This suggests that the photon excited states are long lived in thicker ice layers, thus leading to dissociation, and are more rapidly quenched in the vicinity of a substrate surface.

The O 1s HR-XPS spectra of the Al₂O₃/NiAl(1 1 0) surface as a function of water exposure at 100 K are presented in Fig. 6, together with a decomposition analysis as described in the experimental section. In order to minimize the photon-induced changes in the adsorbed water layers fresh layers were prepared each time after two consecutive doses. The spectrum of the clean substrate (bottom left) shows an asymmetric peak centered at 531.2 eV. The shoulder at the high-binding-energy side (peak 2) has been observed in previous studies of the Al₂O₃/NiAl(1 1 0) system and is most probably due to the O²⁻–surface species [12]. After 0.3 L water exposure an additional feature appears at 533.7 eV (peak 3), which is due to the presence of molecular water. No evidence for the presence of OH-groups can be derived from the spectra, which would occur at ~533 eV. The peak positions of the O 1s water component and the integrated intensity ratio between water and substrate O 1s components are summarised in Table 1 (right columns). As shown in Fig. 6 the intensity of the molecular water component increases continuously with increasing water exposures. Up to ~1.5 L H₂O dose there is no shift of the water O 1s component. After 2 L H₂O dose this component is shifted by 0.2 eV to higher binding energy and after 4 L shifts further by 0.1 eV. This shift towards higher binding energy has been observed for molecular adsorption of water on various surfaces and has generally been ascribed to reduced final-state screening at larger distances from the substrate [2]. It is worth mentioning that the first shift to higher binding energy occurs at the exposure range, where the reorganisation and clustering of the monomeric H₂O species on the surface takes place. Thus the shift could also (partly) be due to a change of the initial state.

Fig. 7 shows the Al 2p HR-XPS spectra for low coverages of water on the Al₂O₃/NiAl(1 1 0)
The main component (1) of the Al 2p spectrum of Al 2O3/NiAl(1 1 0), which arises from the Al 3\(^+\) emission in the oxide layer, is centered at \(75\) eV. There is a second component (2) at \(73.4\) eV due to the interface layer between the oxide and the NiAl substrate and a third one (3) at \(72.3\) eV, which originates from Al 2p\(^{3\over 2}\) of the NiAl substrate (note the doublet due to the spin–orbit splitting).

Examination of the position of the Al 2p oxide component shows that upon water adsorption a shift towards lower binding energy occurs (after \(2\) L exposure \(\Delta E = -0.5\) eV). Second, the Al atoms in the “interface layer” are influenced by the presence of the H\(_2\)O molecules on the surface, and, third, the NiAl components become attenuated. The shift of the oxide component (1) in the Al 2p spectrum to lower binding energy is the result of an interaction of the first layer of H\(_2\)O molecules with the Al\(^{3+}\) ions in the second layer. Charge transfer between the H\(_2\)O molecules and the Al cations is not expected because the interaction is weak (see above), but the H\(_2\)O molecules can be-

![Image of O 1s HR-XPS spectra](image_url)

Fig. 6. O 1s HR-XPS spectra of the clean and water exposed Al\(_2\)O\(_3\)/NiAl(1 1 0) surfaces taken at 100 K. The circles are the measured data and the dashed lines are the components determined by the fitting procedure. The solid lines through the data points are the results of the fitting, and the residuals are shown below each spectrum with enlarged scale (×4). The position of the water-induced component in the O 1s spectra (component 3) is indicated by the dotted line. All spectra are normalized to equal peak heights.

![Image of Al 2p HR-XPS spectra](image_url)

Fig. 7. Al 2p HR-XPS spectra of the Al\(_2\)O\(_3\)/NiAl(1 1 0) surface exposed to H\(_2\)O at 100 K. All spectra are normalized to equal peak heights.
come polarised thus reducing the effective positive charge on the Al ion (causing an initial state shift of the Al 2p level to lower binding energy). Moreover, the adsorbed H 2O molecules are polarisable which may lead to an enhanced dynamical final state screening of the Al core hole and thus to a reduction of the apparent Al 2p binding energy. Both effects suggest an adsorption geometry of the first layer H 2O molecules with the oxygen atoms above the second layer Al cations. A sketch of the suggested adsorption sites is shown in Fig. 8 with the “four-layer” model of the alumina film adopted from Ref. [26]. As can be seen from the figure, the H 2O oxygen atoms and their lone pair orbitals are oriented toward the surface, electrostatically interacting with the Al 3+ cations through the hollow sites of the outermost oxygen layer. This adsorbate configuration agrees well with the observed work function change.

4. Summary

It has been shown that water adsorbs non-dissociatively on the oxygen-terminated epitaxial Al 2O 3 layer on NiAl(1 1 0) at 100 K. On the basis of our TPD, UPS, Δφ, and HR-XPS results we propose the following picture of the adsorption and growth of water layers on Al 2O 3/NiAl(1 1 0):

(1) In the initial stages of H 2O adsorption (<1 L of H 2O exposure) the individual molecules are weakly bound to the surface. The Δφ and HR-XPS data imply that the isolated species are adsorbed with the oxygen end towards the substrate, electrostatically interacting with the Al 3+ cations underneath the surface oxygen layer (see Fig. 8) leading to a reduction of the surface dipole.

(2) Above 0.5 L of H 2O exposure the isolated water molecules start to condense into hydrogen-bonded clusters. The presence of the latter is deduced from the UPS data which show the splitting of the feature due to emission from the 3a 1 MO of water. According to the Δφ measurements the formation of H 2O clusters in the 1–2 L H 2O dose range proceeds with a concomitant change of the overall surface dipole.

(3) Further exposure (>4 L H 2O dose) induces the formation of 3D ice multilayers. A photon-induced dissociation of H 2O in thick ice films (>6 L of H 2O exposure) with UV-light has been observed.

Acknowledgements

We would like to thank Dr. B. Casu and A. Schöll (Uni Würzburg) for the valuable technical assistance. Furthermore, we are indebted to the BESSY staff for the support, in particular to Dr. W. Braun for his help and many discussions. This work has been supported by the Austrian Science Foundation and the German BMBF (contracts no. 05 KS1VHA and 05 KS1WW1/6).
References