



Observation of a localized surface phonon on an oxide surface

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Received 23 December 1999; in final form 15 February 2000

Abstract

The vibration modes of a clean Cr₂O₃(0001) surface have been studied under ultra high vacuum conditions with high-resolution electron energy loss spectroscopy. A mode which is confined to the first few atomic layers of the oxide was detected in addition to the Fuchs–Kliwer phonons. In contrast to the Fuchs–Kliwer phonons which extend deeply into the bulk, this mode is very sensitive towards the presence of adsorbates. Full-potential linearized augmented plane-wave calculations show that this mode is an in-phase oscillation of the second-layer oxygen atoms and the Cr atoms of the two layers below. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The phonon modes of ionic surfaces have been the subject of numerous studies [1]. Several experimental methods such as high-resolution electron energy loss spectroscopy, infrared absorption and inelastic helium atom scattering have been applied [1] and different theoretical models have been developed [1] in order to calculate the energies and intensities of phonons in the experimental data. The so-called Fuchs–Kliwer phonons may be treated theoretically using dielectric theory [2] since they mainly depend on bulk properties. True surface vibrations, i.e. vibrations which are confined to the first few atomic layers cannot be described by dielectric theory since this theory relies on bulk properties. For an understanding of such vibrations a detailed microscopic

description of the surface and its phonon modes is necessary [1].

Most information on Fuchs–Kliwer phonon modes is available for MgO and ZnO [2–4]. Al₂O₃ has been studied with respect to Fuchs–Kliwer modes [5–7] but surface modes which are localized in the first few atomic layers have not been observed experimentally for corundum-type oxide surfaces. Due to the confinement of surface modes to the surface region these vibrations are very sensitive to the presence of adsorbates. Therefore they may be used as local sensors for the adsorbate/surface interaction.

Chromium oxide is known to be an effective industrial catalyst, e.g. for the polymerization of ethylene [8,9]. In recent years various investigations have been performed on the properties of different surfaces of Cr₂O₃. Among these are studies of supported chromium oxide catalysts [8], crystalline powdered samples [10–12], single-crystal surfaces [13],

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and thin oxide films grown on different substrates [14–18].

The present Letter deals with a $\text{Cr}_2\text{O}_3(0001)$ surface prepared by oxidation of a $\text{Cr}(110)$ single-crystal surface. According to LEED I/V analysis and MD simulations [18] the surface is terminated by an ordered chromium layer with an atomic density which is only half as large as that of the bulk chromium double layers. The first interlayer spacings have been found to be strongly relaxed.

2. Experimental

The investigation of the $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ system has been performed in a two-chamber ultra high vacuum apparatus with a base pressure of 2×10^{-10} Torr. The upper chamber is equipped with an Omicron 4 grid Spectaleed optics to check surface order and composition by LEED (low-energy electron diffraction) and AES (Auger electron spectroscopy), respectively. Adsorbates can be investigated by IRAS (infrared reflection absorption spectroscopy) using a modified Mattson RS-1 FTIR spectrometer. The lower chamber of the system contains a HREELS (high-resolution electron energy loss spectroscopy) spectrometer (Delta 05, VSI) with a resolution limit of 0.5 mV (4 cm^{-1}). The spectra of the chromium oxide film presented here were recorded in specular geometry with an energy resolution of 2.2–2.3 mV and a primary energy of 7.5 eV. The chromium oxide film with (0001) orientation and a thickness of $\sim 40 \text{ \AA}$ was grown on a $\text{Cr}(110)$ single-crystal surface by repeated cycles of oxidation at 800 K followed by annealing at 1000 K. Prior to oxidation the substrate was cleaned by argon ion bombardment at an elevated temperature. Details of the preparation procedure may be found in Refs. [15–18].

3. Computational method

The computations were carried out with the full-potential linearized augmented plane-wave method (FP-LAPW) [19] parametrizing the exchange-correlation potential in the local spin-density approximation [20]. The muffin-tin radii chosen for oxygen and

chromium were sufficiently small (1.6 a.u.) to avoid overlapping spheres even for strong surface relaxations. The wavefunctions were expanded with a maximal angular momentum of $l_{\text{max}}^{\text{wf}} = 10$ and the energy cutoff for the FP-LAPW basis was taken to be 19 Ry, while plane waves with energies up to 81 Ry were used for the Fourier expansion of the potential. We described the $\text{Cr}_2\text{O}_3(0001)$ surface by means of a slab-supercell with hexagonal symmetry which contains four oxygen layers, three chromium double layers, and two chromium single layers terminating each side of the slab. The interaction between the two crystal film surfaces is small enough. This can be estimated from the splitting of electronic surface states. For the pair of $3d_{z^2}$ -like states originating from the first-layer Cr atoms the splitting does not exceed 0.2 eV. Brillouin zone integrals were evaluated by using three special points.

The lattice constants, internal parameters, and vibrational energies of the A_{1g} modes determined for rhombohedral bulk Cr_2O_3 are $a = 4.91 \text{ \AA}$, $c = 13.56 \text{ \AA}$, $u = 0.3497$, and $v = 0.552$, $\nu_1 = 37.7 \text{ meV}$, and $\nu_2 = 68.3 \text{ meV}$, assuming ferromagnetic ordering. These numbers compare well with experimental data [21,22]. The lattice parameters calculated for the antiferromagnetic phase, which has a slightly lower energy, differ by $< 2\%$. Therefore, we restrict our study of $\text{Cr}_2\text{O}_3(0001)$ to computations for spin-parallel ordering which are less extensive.

The relaxation of the $\text{Cr}_2\text{O}_3(0001)$ surface involves several layers of the material. The first-layer Cr atoms exhibit a strong inward relaxation of 0.63 \AA along the [0001] direction, while the second-layer O atoms are shifted downwards by 0.1 \AA . This reduces the first-layer separation by 59% with respect to the non-relaxed surface. The next four interlayer distances are changed by 1%, -38% , 10%, and -4% with respect to the ideal bulk-derived values. This agrees with the results of previous theoretical [23,24] and experimental [18] investigations.

The computation of the slab-phonon vibrations is restricted to modes, which can be determined without abandoning any symmetry of the relaxed slab-supercell. Cr atoms are displaced only in the [0001] direction, while O atoms are allowed to move along and perpendicular to the surface normal. We calculate forces for a set of configurations which span the

10-dimensional subspace of the A_{1g} modes. The derived matrix of interatomic coupling constants is diagonalized to obtain the eigenvectors and eigenfrequencies.

4. Results and discussion

Fig. 1 displays an electron energy loss spectrum of the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface recorded

at 90 K and spectra measured after the surface has been exposed to different doses of carbon monoxide at 90 K. The spectrum of clean $\text{Cr}_2\text{O}_3(0001)$ is characterized by losses at 21.4, 51.7, 78.6, and 88.5 meV and combinations of these losses at higher energies. The latter three modes are Fuchs–Kliwer phonon modes characteristic for this surface [16,17]. At ~ 85 meV a fifth state may be identified in the shoulder of the loss at 88.5 meV. It is likely that this shoulder also represents a Fuchs–Kliwer phonon

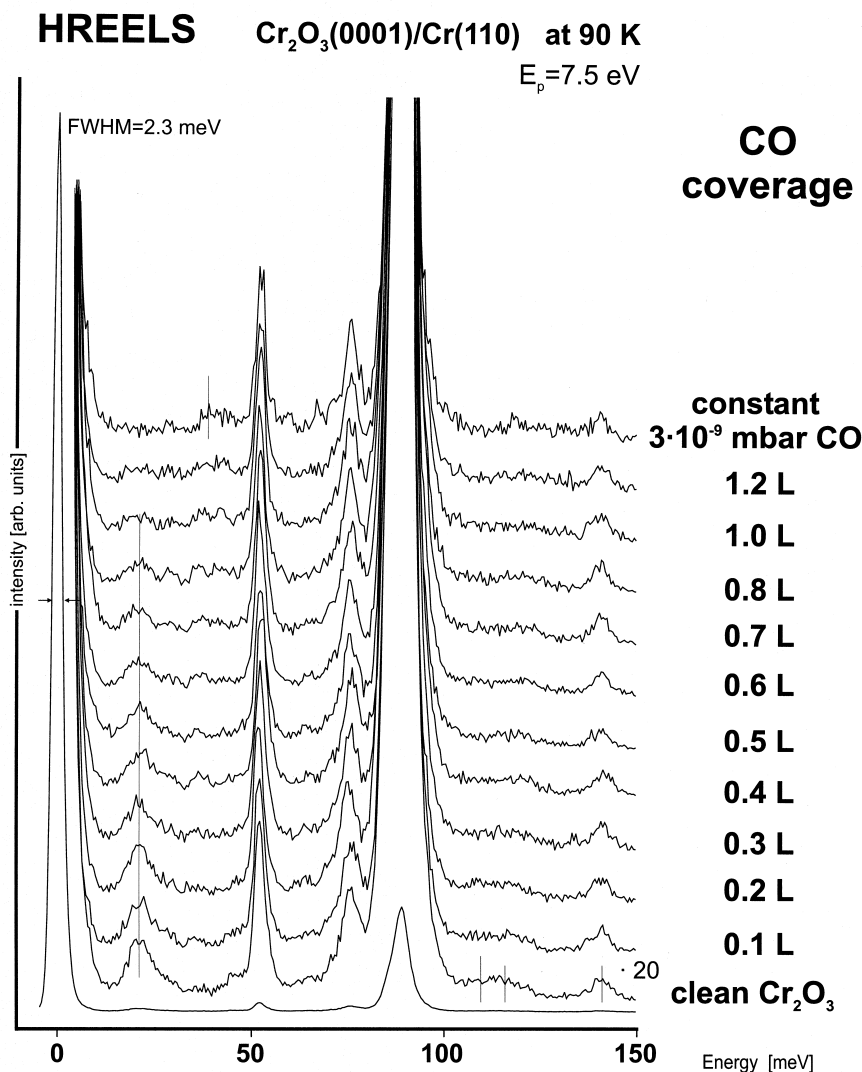


Fig. 1. HREELS spectra of the clean and CO covered $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface recorded at 90 K. (Since the CO slowly desorbs under the influence of an electron beam the last spectrum is recorded at a constant CO pressure [13].)

since there are six infrared active phonon modes of bulk Cr_2O_3 [25,26]. The intensity and position of the Fuchs–Kliwewer phonons are not notably influenced by adsorbates on the surface since their vibrations extend deeply into the bulk [2].

In addition to the Fuchs–Kliwewer phonons, the spectra of the clean $\text{Cr}_2\text{O}_3(0001)$ surface exhibit a peak at 21.4 meV. In previous HREELS investigations this feature could not be identified due to limited spectrometer resolutions [16,17]. Fig. 1 demonstrates that the loss peak at 21.4 meV is attenuated with increasing CO coverage until it is not visible any more at full coverage. We note that oxygen adsorption leads to a similar effect (not shown here).

Adsorption induces chemical and geometrical changes at the surface. Since the vibration of a surface mode involves only atoms in the surface region it is very sensitive to the presence of adsorbates. Therefore the attenuation of the loss at 21.4 meV upon adsorption of CO and O_2 identifies this vibration as a surface mode. In contrast, Fuchs–Kliwewer phonons are not expected to be notably influenced by adsorbates. The adsorbate covered surface will exhibit a more or less different surface phonon spectrum which is most likely the reason for the disappearance of the surface phonon mode upon adsorption. The rather weak peak at ~ 40 meV in the HREEL spectrum recorded at highest CO coverage may be due to the vibration of the CO molecules against the substrate [4]. However, it cannot be excluded that this peak is the counterpart of the surface phonon of the clean surface.

A vibrational surface state has been theoretically predicted also for $\text{TiO}_2(110)$ [27]. However, this has not been experimentally verified yet. Surface-localized vibrations have also been found for $\text{KTaO}_3(001)$ [28–30].

In the region above the most intense Fuchs–Kliwewer phonon at 88.5 meV mainly combinations of the phonon losses are found. At 139.8 meV the combination of the 88.5 and 51.7 meV phonon bands shows up and the rather weak peak at ~ 110 meV can be attributed to the combination of the 88.5 meV phonon and the 21.4 meV surface phonon. Consequently, the loss at 110 meV disappears upon CO adsorption. The small loss peak at ~ 118 meV can be assigned to a vibration of oxygen atoms bonded

to the surface terminating chromium ions [31]. Oxygen is known to diffuse from the chromium metal substrate to the surface. At this point it is interesting to note that, in the infrared spectra of well-sintered polycrystalline $\alpha\text{-Cr}_2\text{O}_3$ samples, an attenuation of the band at 882 cm^{-1} (110 meV) induced by CO adsorption was observed before [11]. This band was attributed to a mode with surface character (adjacent to a bulk mode at $\sim 944\text{ cm}^{-1}$ corresponding to the 118 meV peak in Fig. 1).

In Fig. 2 is compared the HREEL spectra of $\text{Cr}_2^{16}\text{O}_3(0001)/\text{Cr}(110)$ and $\text{Cr}_2^{18}\text{O}_3(0001)/\text{Cr}(110)$ recorded at 300 K. The frequencies of the Fuchs–Kliwewer phonons are shifted towards lower frequency by 4.5–6% which is close to the square root of the isotope mass ratio (5.7%). This is in the expected range since these modes originate from the optical phonons which are dominated by the vibration of oxygen ions [26]. For the surface phonon mode at 21.4 meV the shift is significantly smaller (2.3%).

In order to identify the nature of the surface vibrational mode at 21.4 meV we carried out FP-LAPW calculations. Three modes have been found which are mainly polarized normal to the surface with particularly large displacements in the first two layers with energies of 13.51, 24.13, and 57.26 meV. The mode at lowest energy is dominated by a vibration of the outermost Cr layer. The other two modes are characterized by oscillations of the second-layer O atoms with smaller contributions from displacements of the atoms in the 1st, 3rd, 4th, and 5th layer. All of the three phonon modes have a rather large penetration depth. Their vibrational frequencies increase substantially when the atoms in deeper layers are kept fixed at their relaxed positions. Because of the finite size of our 12-layer slabs, the computed vibrational energies are overestimated by a few percent in the case of the mode at 13.51 meV and by $\sim 10\%$ in the case of the states at 24.13 and 57.26 meV. The forces converge too slowly in FP-LAPW calculations for alternating spin polarization, so that our computations of slab modes had to be restricted to the ferromagnetic phase. The effect of magnetic coupling on the vibrational frequencies cannot be estimated directly, since we find slightly smaller lattice constants for the bulk of Cr_2O_3 using antiferromagnetic ordering.

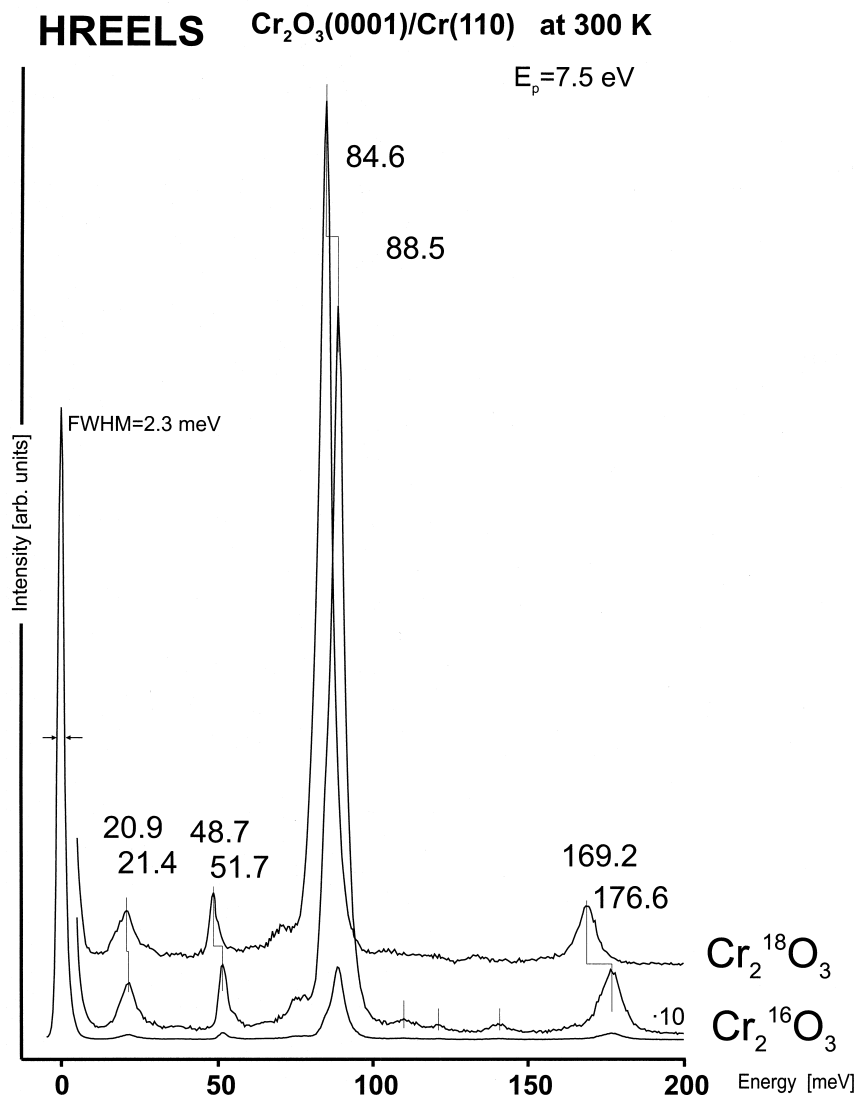


Fig. 2. HREELS spectra of the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface for the preparation with different oxygen isotopes recorded at 300 K.

We assign the loss peak found in the experimental data at 21.4 meV to the slab mode at 24.13 meV, which is dominated by a vertical in-phase vibration of the outermost O layer and the two Cr layers below. The first-layer Cr atoms move in the opposite direction with a smaller amplitude. No indications of the mode with a calculated energy of 13.51 meV could be detected in the data, which may be due to a small cross-section, whereas the mode at 57.26 meV

may be hidden underneath the Fuchs–Kliwer mode at 51.7 meV. The assignment of the slab mode at 24.13 meV to the experimentally found surface mode at 21.4 meV is supported by an additional calculation of the slab modes with the mass of all oxygen atoms changed from 16 to 18 a.u. This reduces the mode's frequency by 2.4% to 23.56 meV which is almost the same decrease as experimentally found. The relative energy changes of the other slab phonon modes are

clearly different. The energy of the mode at 13.51 meV decreases only by 0.4%, while the high-frequency modes reduce their energy by ~ 5 –6%.

5. Summary and conclusions

We have found a surface phonon mode on a single-crystal $\text{Cr}_2\text{O}_3(0001)$ surface which apparently is due to a vibration of the outermost surface layers. This conclusion could be supported by FP-LAPW calculations. Due to the confinement of the surface phonon to the surface region it is highly sensitive towards the presence of adsorbates, which leads to a complete attenuation of the corresponding energy loss upon adsorption of CO or O_2 .

Acknowledgements

We are grateful to a number of agencies that have supported our work: Deutsche Forschungsgemeinschaft (DFG - FR 1426/2-1), Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF), Fonds der chemischen Industrie and the VIGONI program sponsored by the DAAD and the CRUI.

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