Phonons in iron monolayers

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Abstract. The systematic investigation of the lattice dynamics from bulk to a single atomic layer of material was a great experimental challenge until now. Recently, nuclear inelastic scattering has been introduced as a unique technique capable of determining the density of phonon states of nanoscale materials in-situ with a depth resolution of one atomic layer. This became possible by setting up a dedicated ultrahigh vacuum system for samples growth and characterization directly at the nuclear resonance beamline ID18 of the ESRF. The new instrument allowed for systematic investigation of the evolution of the density of phonon states of iron from the bulk to a single atomic layer. The isotopic selectivity of the nuclear resonance absorption was employed to experimentally determine the atomic vibrations at and near the Fe(110) surface with a monolayer sensitivity. The experimental achievements stimulated a rapid progress of the ab-initio calculations of surface phonons.

1. Introduction

Recent instrumentation development [1] at the nuclear resonance beamline ID18 [2] of the European Synchrotron Radiation Facility (ESRF) in Grenoble has offered new opportunities to investigate electronic [3] and magnetic [4, 5] properties, vibrational dynamics [6–8] and diffusion phenomena [9–12] in nanoscale objects in-situ. An ultrahigh vacuum (UHV) system for deposition of thin films and nanostructures by molecular beam epitaxy and their characterization by surface sensitive techniques has been installed directly at the beamline. Thus, several nuclear resonance scattering (NRS) based techniques, such as nuclear forward scattering, nuclear inelastic and quasielastic scattering, synchrotron radiation based perturbed angular correlations, and nuclear reflectivity, can be applied to investigate the nanostructures under UHV conditions and at low/high temperatures, or during growth of the samples. In addition, the unique combination of the high penetration depth of the X-rays with the isotopic selectivity of the nuclear resonant absorption allows one to perform experiments with the ultimate depth.
resolution of one atomic layer by introducing isotopic "resonant" probe layers (a recent review can be found in [13]).

The unique combination of the UHV facility and the nuclear inelastic scattering has led to significant progress in the field of the vibrational properties of low dimensional systems. The aim of this paper is to describe the main features of the new instrument and to summarize the experimental and theoretical advances in the lattice dynamics of ultrathin epitaxial iron films.

2. UHV system for in-situ nuclear resonance scattering at ID18 of the ESRF
The overall design of the UHV system was defined by the demand for in-situ preparation and characterization of samples and their investigation by various synchrotron radiation based techniques. The UHV instrument is permanently installed into the second experimental hutch of ID18 of the ESRF, which required remote control of the entire system. Figure 1 presents schematically the new instrument, while figure 2 displays a top-side photograph [1]. The UHV set-up with a base pressure of $2 \times 10^{-10}$ mbar consists of a central distribution chamber equipped with a sample transfer mechanism and peripherally attached chambers as described in details below.

The preparation chamber, number 1 in Fig. 1 and Fig. 2, is equipped with two electron beam evaporators and an effusion cell. A four-pocket mini e-beam evaporator serves for evaporation of metals from rods and crucibles from each pocket separately, as well as, for co-deposition of different combinations of the evaporants (alloys or multilayers). A single-pocket e-beam source is used for deposition of the Mössbauer isotope $^{57}$Fe. An effusion cell is available for evaporation.

Figure 1. Schematic view of the UHV system with the preparation 1, NRS 2, distribution 3, storage 4, and load-lock 5 chambers. Number 6 marks the port where transfer chambers are connected (Ref. 1).

Figure 2. A top-side photograph of the UHV system with the preparation 1, NRS 2, distribution 3, storage 4, and load-lock 5 chambers. Number 6 shows one of the portable chambers connected to the system (Ref. 1).
of rare-earth metals. A precise calibration of the deposition rate with a thickness reproducibility of 1 Å is done by a quartz-balance monitor. The deposited structures can be characterized by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). In order to monitor in-situ the film growth, or to structurally characterize thick epitaxial films the LEED instrument can be replaced by a reflection high-energy electron diffraction (RHEED) set-up. The samples can be cooled down to about 90 K and heated up to 2300 K by a sophisticated manipulator.

The chamber for NRS experiments, number 2 in Fig. 1 and Fig. 2, is mounted on a two-circle goniometer, which serves to align the sample and to perform experiments with the focused synchrotron beam in grazing-incidence scattering geometry. The manipulator provides contacts for temperature measurement, resistive and electron-bombardment heating, and feedthrough for cooling the sample down to 90 K by flow of liquid nitrogen. In addition, the sample holder can be rotated in the range of ±180 degrees around an axis perpendicular to the sample surface, allowing for angular resolved studies. For the purpose of nuclear inelastic scattering or synchrotron radiation based perturbed angular correlation experiments an avalanche photodiode detector is placed directly above the surface of the sample.

The distribution chamber, number 3 in Fig. 1 and Fig. 2, connects the above-described chambers and serves for transferring the sample holders between them. In addition, a sample storage chamber, number 4 in Fig. 1 and Fig. 2, with the capacity to store up to 6 sample holders is an integrated part of the distribution chamber. The down-most position provides electrical contacts for resistive heating and temperature control allowing for pre-annealing of the sample holders. The load-lock chamber, number 5 in Fig. 1 and Fig. 2, serves for introducing the sample holder into the UHV system. Two additional portable chamber are also available for sample transfer and experiments at other beamlines of the ESRF.

3. Results and Discussions
In the following we present selected examples of research on the lattice dynamics of Fe monolayers.

3.1. Ultrathin Fe films on W(110)
An Fe monolayer on the W(110) surface is an established model system to study a variety of structural [14], magnetic [15] and diffusion [9, 12, 16] phenomena at the nanoscale. A flat pseudomorphic monolayer (ML) is stabilized by deposition of Fe on the atomically clean W(110) surface at 520 K. At room temperature the Fe atoms are in paramagnetic state experiencing a quadrupole interaction due to an electric field gradient induced by the broken translational symmetry at the surface [17]. The mismatch between the lattice constants of the bulk Fe and the W(110) surface of about 10% results in an enormous stretching of the pseudomorphic Fe monolayer. This implies significant changes of the elastic and thermodynamic properties of this monolayer and of the adjacent layers. Due to this large mismatch already within the second Fe layer a network of misfit dislocations forms to relax the lattice strain and to recover the bulk Fe-Fe coordination distances. Thus the interface between the Fe and the W(110) surface is a model system for investigation of the evolution of the thermodynamic and elastic properties upon transition from a strained pseudomorphic Fe monolayer towards bulk Fe.

To investigate this phenomena, the energy dependencies of nuclear inelastic absorption were measured at room temperature for various film thicknesses. Fig. 3 summarizes the derived [18] phonon density of states (DOS) for Fe films with thicknesses between 1 and 40 monolayers. The right column represents the low energy electron diffraction (LEED) patterns of the substrate, 1 ML and 40 ML thick films recorded after the sample growth. They unambiguously confirm the high single-crystalline quality of the investigated films.
Figure 3. DOS of Fe films on W(110) for thicknesses from 1 ML (1.66 Å) to a 40 ML, projected to [001] direction. The dotted line represents the DOS of the bulk bcc W convoluted with the resolution function (FWHM=3.3 meV) of the experiment. The dashed and dotted line in the DOS of the 3 ML film represent the smoothed DOS of the 2 ML film and the DOS of bulk bcc Fe convoluted with a damped harmonic oscillator (quality factor Q=7), respectively. The solid lines for the 3, 10, and 40 ML DOS result from the weighted sum of these two contributions in each case. The right column shows LEED patterns (E=96 eV) of the substrate, 1 and 40 ML (Ref. 7).

The topmost curve of the left column of Fig. 3 represents the DOS of a bulk bcc Fe, while the dotted line on the bottom plots the DOS of a bulk bcc W. The experimental data reveal that increasing the Fe coverage results in a rather sharp transition of the phonon DOS towards that of bulk Fe. Quite remarkably, already the spectrum of 3 ML film is satisfactory described as a contribution from the Fe/W interface, represented by the DOS of a 2 ML thick Fe film (dashed line), and that of bulk Fe including a significant phonon lifetime broadening (dotted line) [7]. This relatively simple model applies also for thicker films and allows one to describe the thickness evolution of the thermodynamic and spectral properties of ultra-thin films with rather good accuracy. Most likely it is valid not only for iron, but for thin films of many transition metals. For detailed discussion we refer the reader to Ref. 7.

3.2. Fe(110) surface
Combining the nuclear inelastic scattering spectroscopy with the UHV sample preparation and characterization facility allowed us to study the vibrational properties of a clean Fe surface layer-by-layer.

In order to investigate the electronic properties and the lattice dynamics at and near the Fe surface single crystalline epitaxial Fe(110) films were deposited on an atomically clean W(110) crystal from $^{57}$Fe and $^{56}$Fe e-beam evaporators. The samples consisted of a 20 ML $^{56}$Fe(110) buffer film optimized for a flat surface growth, while the $^{57}$Fe monolayers were deposited on the buffer film at lower temperature (350 K) to prevent mixing of the isotopes [19]. The following samples were studied: 20 ML $^{56}$Fe/1 ML $^{57}$Fe referred to as a "surface" (S), 20 ML $^{56}$Fe/1 ML $^{57}$Fe/1 ML $^{56}$Fe referred to as a "subsurface" (S-1), and 20 ML $^{56}$Fe/3 ML $^{57}$Fe/3 ML $^{56}$Fe referred to as a "deep" (D) layers [6].

Fig. 4 shows the phonon DOS obtained for the surface, subsurface, and deep layers from the measured nuclear inelastic scattering dependencies at room temperature. The surface sample was measured with the wave vector of the X-ray beam parallel to the [110] (solid circles) and [001] (open circles) crystallographic directions. For comparison the DOS of an α-Fe foil (grey
Figure 4. Measured phonon DOS for the surface (S), subsurface (S-1), and deep (D) layers near the Fe(110) surface projected to [110] (solid symbols) and to [001] (open symbols). The solid lines in (S) plot the results of DFT calculations. The DOS of an Fe foil is shown with solid line (Ref. 6).

Figure 5. (a) Dispersion curves and (b) surface DOS along [110] (solid squares) and [001] (open circles) directions calculated for 29 layers Fe slab. The high-symmetry points correspond to the two dimensional Brillouin zone of the plane reciprocal lattice. In (a), the lowest dispersion curve is the Rayleigh mode while the open squares depict surface modes with the highest in-plane intensities (Ref. 6).

First-principles calculations were performed with spin-polarized density functional theory implemented in the Vienna ab initio simulation package (VASP) [20]. The calculated [6,21] dispersion relations and the DOS projected on two in-plane directions are shown in Fig. 5 (a) and (b) respectively. The lowest curve in Fig. 5 (a) mark the well separated Rayleigh mode, while the open circles represent the most intense in-plane surface modes. Due to geometrical considerations (the nuclear inelastic scattering experiment is performed at grazing incidence scattering geometry) the derived phonon DOS are in-plane direction projected, therefore, not influenced by the very active Rayleigh mode, characterized with vibrations perpendicular to the surface. The observed anomalies at the surface arise from the surface-specific modes due to the broken translational symmetry. Moreover, these modes result in vibrational anisotropy, (Fig. 4 panel (S)), perfectly reproduced by the calculated phonon DOS (Fig. 5 (b)). For detailed discussion we refer the reader to Ref. 6.
4. Conclusions

The nuclear inelastic scattering was employed to systematically investigate the lattice dynamics of thin and ultrathin iron films by measuring the density of phonon states of strained iron films and of the native iron Fe(110) surface in-situ. The experimental results revealed a significant deviation of the lattice dynamics of the Fe films from that of the bulk in a close vicinity to the substrate. The transition to the bulk-like lattice dynamics is rather sharp and takes place within several atomic layers. On the other hand, the anomalous dynamics observed for the native Fe surface is localized at the first atomic layer only. The second layer already vibrates in a bulk-like manner. These observations are in total agreement with the first-principles phonon calculations. These results have been achieved after setting up of an ultrahigh vacuum system directly at the nuclear resonance beamline ID18 of the ESRF. The instrument allows one to deposit by molecular beam epitaxy a variety of nanostructures like thin and ultrathin films, nano-islands and -wires, multilayers and stoichiometric oxides. After characterization by Auger electron spectroscopy, low-energy electron diffraction or by reflection high-energy electron diffraction the electronic and magnetic properties, vibrational dynamics, and diffusion phenomena can be investigated by the nuclear resonance scattering techniques in-situ, i.e. under UHV conditions.

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