P H Y S I C A L R E V I E W L E T T E R S

Phonons in Iron: From the Bulk to an Epitaxial Monolayer

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The confinement of materials in low-dimensional structures has significant impact on propagating excitations like phonons. Using the isotope-specific ^{57}Fe nuclear resonant vibrational spectroscopy we were able to determine elastic and thermodynamic properties of ultrathin Fe films on W(110). With decreasing thickness one observes a significant increase of the mean atomic displacement that goes along with an enhancement of vibrational modes at low energies as compared to the bulk. The analysis reveals that these deviations result from atomic vibrations of the single atomic layers at the two boundaries of the film, while the atoms inside the films vibrate almost bulklike.

Intense experimental work has recently been devoted to the impact of lattice compression on the thermal and thermoelastic properties of iron [1–3], mainly due to its relevance for the geophysics of the Earth's core. Conversely, the effects of lattice expansion are less well studied even though they play an important role for the thermal properties of nanostructures like thin films and small particles. In general, lattice-expanded states are often found near surfaces and solid/solid boundaries where the atomic environment abruptly changes. In case of iron, the most prominent system is the interface between the Fe and the W(110) surface. Since the early works of Gradmann and Waller [4] it is generally accepted that the first layer of Fe on W(110) grows in a pseudomorphic fashion, i.e., with the Fe atoms aligned in registry with the W atoms of the substrate [5–7]. This means a relative stretching of the Fe lattice constant by about 10% compared to its bulk value, implying significant changes of the elastic properties in this layer and the adjacent layers. With increasing number of layers a network of misfit dislocations forms to relax the lattice strain and reestablish the bulk Fe-Fe coordination distances [8]. Thus one expects a gradual transition of the thermal properties towards those of bcc Fe, the nature of which, however, has not been revealed so far.

One route to determine elastic properties (like mean displacement, average force constant, sound velocity) and thermal quantities (like mean specific heat, vibrational entropy) is the measurement of the density of phonon states (DOS). These quantities are then calculated by a weighted integration over the DOS or they are directly derived from the raw experimental data via sum rules [9,10]. However, the measurement of vibrational properties in nanoscale environments is conceptually difficult because neither in-

elastic neutron scattering nor inelastic x-ray scattering are feasible for such tiny amounts of material. On the other hand, methods like energy-loss spectroscopy with electrons [11] or He atoms [12] typically probe only the dynamics of the topmost surface layer. The limited momentum transfer of methods using infrared or visible light usually prohibits the determination of the full density of phonon states. Therefore, none of these methods is appropriate for a systematic determination of the DOS upon the transition from the bulk to a single monolayer. Recently, nuclear inelastic scattering of x-rays has been introduced to determine the DOS of nanocrystalline Fe [13,14], Fe precipitates [15] and thin Fe films [16,17]. Common features were the observation of phonon damping and the appearance of low-energy modes. However, the internal structure and the interfaces of the investigated samples were not well enough characterized to disentangle the effects of disorder, chemical state and dimensionality on the vibrational properties. A clear separation of these influences requires well-defined crystalline systems, prepared, maintained and measured under controlled conditions, as we report in this study. Employing *in situ* high-resolution nuclear inelastic scattering under ultrahigh vacuum (UHV) conditions, we observed the DOS of ultrathin crystalline Fe films on W(110) down to thicknesses of one monolayer (ML) and determined the evolution of their elastic properties.

The experiments were performed at the nuclear resonance beamline ID18 [18] of the European Synchrotron Radiation Facility (ESRF) where a UHV chamber dedicated for preparation and measurements under UHV conditions was installed. Fe films with an isotopic enrichment of 95% in ^{57}Fe with thicknesses of 1, 2, 3, 10, and 40 ML (thickness equivalent: 1 ML = 0.2 nm) were epitaxially

grown on the (110) surface of a tungsten single crystal [19]. The samples, being illuminated with a focused x-ray beam in grazing incidence geometry, were oriented with the in-plane [001] direction along the wavevector $\vec{k}_0$ of the incoming radiation. Energy spectra were obtained with a high-resolution (3.3 meV) monochromator scanning over an energy range of ± 60 meV around the 14.4125 keV nuclear resonance, collecting the Fe K fluorescence that was emitted with temporal delay relative to the incident x-ray pulses. All data were taken at room temperature. Figure 1 displays the DOS that were extracted from the energy spectra by using a quasiharmonic model as described in [20–23]. The right column of Fig. 1 shows selected LEED patterns to illustrate the structural quality of the films, to be discussed below.
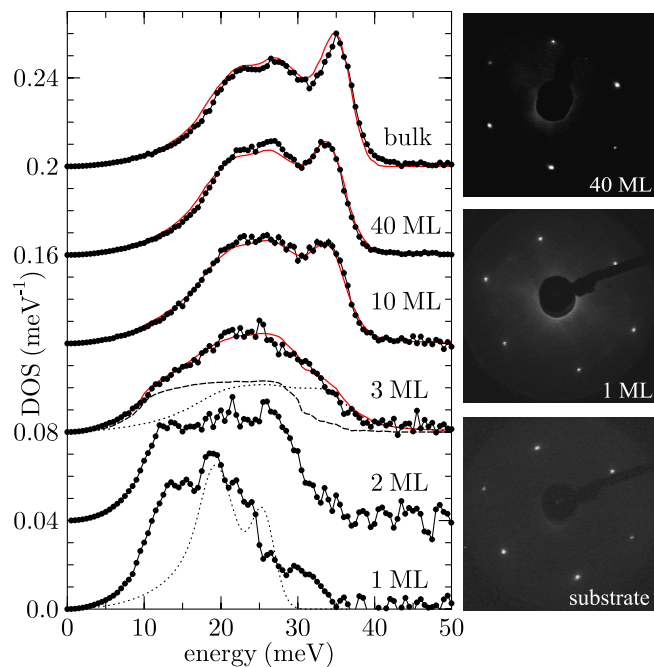

FIG. 1 (color online).   DOS of single-crystalline Fe films on W(110) for thicknesses ranging from the monolayer to a 40 ML thick film (thickness equivalent: 1 ML ≡ 0.2 nm). For clarity, the curves are displaced from another by 0.04 meV^{-1}. The solid line in the upper graph represents the density of phonon states of polycrystalline bulk α-iron, i.e., the ambient temperature bcc phase of iron [24] as calculated from neutron data and convoluted with the energy resolution function of this 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, out of which the DOS of the 3 ML film seems to be composed of. The solid lines for the 3, 10, and 40 ML DOS result from the weighted sum of these two contributions in each case. The dotted line in the lower graph represents the phonon DOS of bulk bcc W for comparison. The right column shows LEED patterns ($E = 96$ eV) of the bare substrate, 1 and 40 ML films recorded right after preparation of the films.

The DOS of bulk α-iron was obtained from the measurement at a 10 μm thick polycrystalline ^{57}Fe foil. It is virtually identical to the DOS determined by neutron scattering [24,25], showing the peaks related to the van Hove singularities of transverse and longitudinal acoustic phonons at the zone boundary, appearing at 23, 27, and 35 meV, respectively. The DOS of the 10 and 40 ML films resemble closely the DOS of bulk Fe but the spectral features are shifted to slightly lower values, e.g., the high-energy peak appears at 34 meV. This can be attributed to the expanded state of the Fe film that results from the mismatch of the W and Fe lattices and goes along with a lattice volume expansion [26] of about 2%. In addition, for the 10 ML film one observes a pronounced increase of the DOS at low energies. With decreasing thickness one observes a further increase of low-energy modes while spectral features at high energies are significantly reduced. The latter feature is most likely related to the influence of the phonon DOS of the W substrate in these energy regions that is shown as dashed line in the lower graph of Fig. 1 (convoluted with the energy resolution function of this experiment). On the other hand, the softening is caused by a decrease of the coordination number at the surface and is typical for surface phonons [27–29], but certainly also mirrors the coupling of the adsorbed iron atoms to the tungsten substrate. Moreover, spectral features seem to become significantly broader with decreasing thickness. Most probably, this results from the distribution of force constants in the strain field that is due to the large lattice misfit towards the substrate. Such a distribution leads to phonon lifetime broadening that can be described within the model of a damped harmonic oscillator [13,30], where the quality factor Q effectively relates to the width of the strain distribution: The smaller the thickness, the broader the distribution of force constants and the smaller the value of Q, as will be shown below.

Particular emphasis should be directed to the DOS of the epitaxial monolayer Fe on W(110) that basically reflects the local vibrational properties of the Fe atoms at the regular adsorption sites on the W(110) surface. A simple third nearest-neighbor lattice-dynamical model, which is based on a pseudomorphic arrangement of the Fe monolayer on the W(110) surface, suggests a considerable modification of the force constants in the vicinity of the surface. In order to reproduce the observed DOS, a reduction of some force constants by a factor of about 3 as compared to the average Fe-Fe and W-W bulk values and an inacceptable increase of other force constants would be required. Thus, one may be tempted to postulate deviations from the strict pseudomorphic order of the monolayer Fe on W(110). In fact, the 1-ML LEED pattern shown in Fig. 1 indicates an increase of the diffuse background and a slight asymmetric broadening of the diffraction spots which are effects indicative of disorder. With increasing thickness of the films the diffraction spots are getting

sharper, indicating the very good structural quality of the films.

Our observations indicate that prolonged exposure to residual gases leads to the rise of a peak around 30 meV. This feature, however, is very weak so that the influence of adsorbates can be neglected here, as expected from the very good vacuum conditions during this measurement. Another source for additional vibrational modes may arise from Fe atoms located at the monoatomic steps of the vicinal W surface. Since the average terrace width (determined via STM) is 30 nm, this contribution is less than 1% and thus can be neglected here as well.

The pronounced softening of the vibrational excitations close to the tungsten surface has a significant impact on the elastic properties. The mean displacement and the average force constant are displayed in Figs. 2(a) and 2(b) as function of $1/N$, where N is the number of atomic layers. Compared to the respective bulk values (points at $1/N = 0$), the average Fe-Fe force constant k for the monolayer is lower by about 45%, while the mean (in-plane) displacement, i.e., the square root of the mean square displacement, $\sqrt{\langle x^2 \rangle}$, is larger by about 53%. To a good approximation one observes a linear dependence on $1/N$ over the range from bulk Fe to 2 ML thick films. The value for the monolayer clearly falls off this linear dependence.
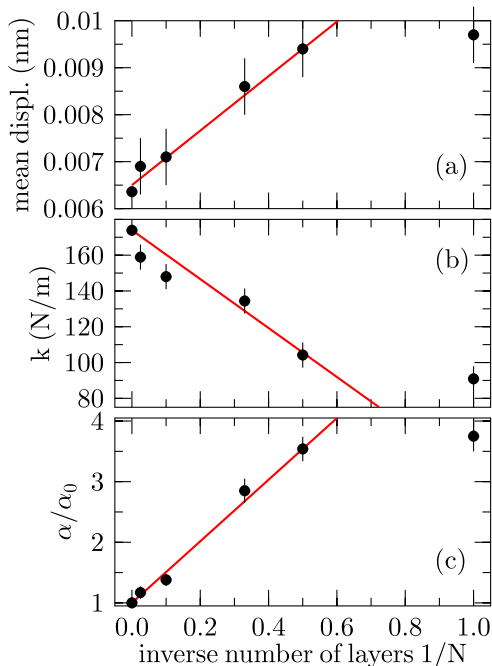
Another striking phenomenon in the measured DOS is the enhancement of vibrational modes at low energies. In order to quantify this, we have displayed the DOS for energies $5\ \mathrm{meV} < E < 13\ \mathrm{meV}$ in a double-logarithmic plot, shown in Fig. 3.

The straight lines represent parabolic fits of the DOS in this energy region, i.e., $g(E) = \alpha E^2$. Since the slope is the same for all DOS curves, no deviations from the Debye law are present here. The coefficient α allows one to quantify the enhancement of the low-energy phonon DOS relative to the value α_0 for bulk Fe. The ratio α/α_0 is displayed in Fig. 2(c) vs $1/N$, showing an enhancement of low-energy modes by a factor of almost 4 for the 1- and 2-monolayer thick films relative to the bulk value. Again, one observes a linear dependence on $1/N$ over a range from the bulk down to a 2 ML thick film. Thus, one is tempted to attribute the deviations from the bulk behavior for films thicker than 1 ML to the contributions from the two atomic layers at the boundaries (the surface and the Fe/W interface). Within this model, a given elastic quantity f for a film consisting of N atomic layers can be expressed as

$$f(N) = f_b(1 - n/N) + f_n n/N \qquad (1)$$

with n being the total number of interfacial layers that contribute to the deviations from the bulk behavior. f_b is the value of the elastic quantity for bulk material and f_n is the effective value for both interfacial regions that sum up to a total of n atomic layers. The solid lines in Fig. 2 are plots according to Eq. (1) with $n = 2$, i.e., the values for f_2 are those extracted from the measurement at the 2 ML film. Consequently, this linear decomposition of elastic quantities in contributions from the boundaries and the bulk should manifest also in a similar decomposition of the DOS. Accordingly one expects, for example, the DOS of

FIG. 2 (color online). Elastic properties (mean displacement, average force constant) and the Debye enhancement factor α of Fe films on W(110) as function of $1/N$ where N is the number of atomic layers. These quantities are derived from the DOS shown in Fig. 1. Points at $1/N = 0$ mark the bulk values. The solid lines are calculations according to Eq. (1).
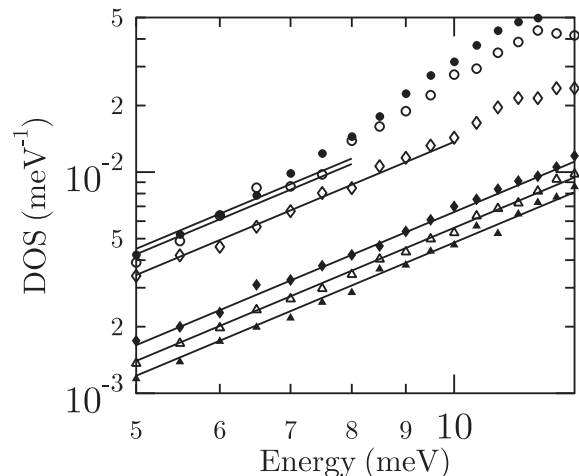

FIG. 3. Double-log plot of the low-energy region of the phonon DOS $g(E)$ displayed in Fig. 1. From bottom to top the curves belong to bulk bcc Fe and Fe films of thickness 40, 10, 3, 2, and 1 ML. Solid lines are fits according to the Debye law $g(E) = \alpha E^2$.

the 3 ML film to be a superposition of the 2 ML DOS and the DOS of bulk bcc Fe. That this is in fact the case can be seen in Fig. 1, where the solid line in the DOS of the 3 ML film is the sum of two contributions: The dashed line is a smoothed version of the 2 ML DOS and the dotted line corresponds to the DOS of bulk bcc Fe, convoluted with the energy response of a damped harmonic oscillator with a quality factor of $Q = 7$. Although the ratio found here for these two contributions (1:1) deviates from the naive expectation (2:1), one is tempted to attribute the latter contribution to the Fe atoms in the center of the 3 ML thick film (surrounded by only Fe atoms) whereby these atoms exhibit vibrational properties close to those of bulk Fe. In a similar fashion, also the DOS of the other films can be described, as indicated by the solid lines in Fig. 1. In these cases the relative contribution from the interfacial region decreases, but still makes up a significant fraction of the DOS, particularly at low energies. In addition, the effective quality factor Q that describes the vibrational damping of the bulk Fe contribution increases with increasing film thickness, assuming values of $Q = 20$ and $Q = 30$ for the 10 and 40 ML thick films, respectively.

In conclusion, we could describe the phonon density of states of thin epitaxial Fe films on W as being composed of contributions from the interfacial atomic layers and the interior of the film. Quite remarkably, the contribution from the inner part resembles closely the DOS of bulk bcc Fe including a significant phonon lifetime broadening, while the boundaries contribution basically corresponds to the DOS of a 2 ML thick Fe film. Although this model appears to be relatively simple, it allows one to describe the thickness dependence of the thermodynamic properties and the spectral properties of ultrathin films with rather good accuracy.

These unique results could be obtained because the experimental method combines the high penetration depth of the x rays with the isotopic sensitivity of the nuclear resonant absorption process. While the former aspect renders the technique sensitive to the full volume of the film, the latter aspect assures that the data are free of contributions from surrounding materials. Moreover, we have demonstrated that nuclear inelastic scattering at third-generation synchrotron radiation sources is sensitive to extremely small quantities of material like single atomic layers of ^{57}Fe. Therefore, this method constitutes a unique approach to reveal vibrational dynamics in layered materials with very high spatial resolution, applicable to many other materials that contain Mössbauer isotopes. Very likely the results obtained here are not restricted to Fe, but constitute a universal behavior of many transition-metal thin films and surfaces.

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[1] R. Lübbers *et al.*, Science **287**, 1250 (2000).
[2] H. K. Mao *et al.*, Science **292**, 914 (2001).
[3] J.-F. Lin *et al.*, Science **308**, 1892 (2005).
[4] U. Gradmann and G. Waller, Surf. Sci. **116**, 539 (1982).
[5] M. Albrecht, U. Gradmann, T. Reinert, and L. Fritsche, Solid State Commun. **78**, 671 (1991).
[6] H. L. Meyerheim *et al.*, Phys. Rev. B **64**, 045414 (2001).
[7] X. Qian and W. Hübner, Phys. Rev. B **60**, 16 192 (1999).
[8] H. Bethge *et al.*, Surf. Sci. **331–333**, 878 (1995).
[9] H. J. Lipkin, Ann. Phys. (Leipzig) **9**, 332 (1960).
[10] H. J. Lipkin, Phys. Rev. B **52**, 10 073 (1995).
[11] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).
[12] A. P. Graham, Surf. Sci. Rep. **49**, 115 (2003).
[13] B. Fultz *et al.*, Phys. Rev. Lett. **79**, 937 (1997).
[14] L. Pasquini *et al.*, Phys. Rev. B **66**, 073410 (2002).
[15] Y. Tsunoda *et al.*, Phys. Rev. B **66**, 214304 (2002).
[16] R. Röhlsberger *et al.*, J. Appl. Phys. **86**, 584 (1999).
[17] T. Tanaka *et al.*, J. Phys. Soc. Jpn. **74**, 1762 (2005).
[18] R. Rüffer and A. I. Chumakov, Hyperfine Interact. **97/98**, 589 (1996).
[19] The first monolayer of the samples was deposited at a substrate temperature of 520 K. To avoid island formation, the subsequent layers were prepared at a temperature of 420 K. The average deposition rate was 0.01 nm/s at a base pressure of 10^{-10} mbar.
[20] M. Seto *et al.*, Phys. Rev. Lett. **74**, 3828 (1995).
[21] W. Sturhahn *et al.*, Phys. Rev. Lett. **74**, 3832 (1995).
[22] V. G. Kohn, A. I. Chumakov, and R. Rüffer, Phys. Rev. B **58**, 8437 (1998).
[23] W. Sturhahn and V. G. Kohn, Hyperfine Interact. **123/124**, 367 (1999).
[24] H. R. Schober and P. H. Dederichs, in *Phonon States of Elements, Electron States and Fermi Surfaces of Alloys*, edited by K. H. Hellwege and J. L. Olsen, Landolt Börnstein, New Series Vol. III/13a (Springer, Berlin 1981).
[25] V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. **162**, 528 (1967).
[26] R. Popescu *et al.*, Phys. Rev. B **68**, 155421 (2003).
[27] A. Kara and T. S. Rahman, Surf. Sci. Rep. **56**, 159 (2005).
[28] J. E. Black, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (Elsevier, Amsterdam 1990), p. 179.
[29] J. Łażewski, J. Korecki, and K. Parliński, Phys. Rev. B **75**, 054303 (2007).
[30] B. Fåk and B. Dorner, Institut Laue Langevin Technical Report No. 92FA008S, 1992 (unpublished).