

## Phonons at the Fe(110) Surface

T. Ślęzak,<sup>1,2</sup> J. Łazewski,<sup>3</sup> S. Stankov,<sup>4</sup> K. Parlinski,<sup>3</sup> R. Reitering,<sup>5</sup> M. Rennhofer,<sup>5</sup> R. Ruffer,<sup>4</sup> B. Sepiol,<sup>5</sup> M. Ślęzak,<sup>2</sup> N. Spiridis,<sup>1</sup> M. Zajac,<sup>2</sup> A. I. Chumakov,<sup>4</sup> and J. Korecki<sup>1,2</sup>

<sup>1</sup>*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Kraków, Poland*

<sup>2</sup>*Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland*

<sup>3</sup>*Institute of Nuclear Physics, Polish Academy of Sciences, 31-342 Kraków, Poland*

<sup>4</sup>*European Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France*

<sup>5</sup>*Scattering and Spectroscopy Group, Faculty of Physics, University of Vienna, A-1090 Wien, Austria*

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The in-plane density of phonon states of clean Fe(110) surface was measured separately for the first, second, and further atomic monolayers using nuclear inelastic scattering of synchrotron radiation. The results show that atoms of the first layer vibrate with frequencies significantly lower and amplitudes much larger than those in the bulk, and that vibrational spectra along two perpendicular in-surface directions are different. The vibrations of the second layer are already very close to those of the bulk. The good agreement of the experimental results and the first-principles calculations allows for detailed understanding of the observed phenomena.

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The fascinating development of various scientific fields in the direction of nanoscale and quantum objects requires a precise understanding of the physics of surfaces, in particular, of their dynamics and thermodynamics. However, direct measurements of density of phonon states (DOS) on a clean surface were not accessible until now. Spectacular successes of surface sensitive methods, like high resolution electron energy loss spectroscopy and helium atom scattering (HAS) [1], do not change the fact that they are unable to give exact information on the complete phonon spectrum of a surface layer. Despite impressive theoretical studies of phonon dynamics at surfaces [2], in a classical textbook on surface physics giving a comprehensive discussion of the surface phonons [3] experimental determination of the phonon DOS is not even mentioned.

Recent developments in third generation synchrotron radiation sources brought their performance to the stage where the phonon spectroscopy of nanostructures and thin layers became feasible using nuclear inelastic scattering (NIS) [4]. The method gives phonon DOS which is (i) "partial"—only atoms of the resonant isotope contribute—and (ii) "projected" to the direction of the incident photons—the contributions of various branches are weighted by the squared projection of the phonon polarization vector to the incident photon's direction [5]. The large cross section of nuclear resonant scattering allows for studying phonon DOS in a film with a thickness of few atomic layers [6]. However, the most intriguing information on the phonon spectrum of a clean surface was not yet accessible and the indispensable (as shown below) spatial resolution of a single atomic layer was not yet achieved.

In this Letter we report on measurements of DOS for single atomic monolayers at and near a clean Fe(110) surface uninterruptedly maintained in ultrahigh vacuum (UHV) conditions. We studied single-crystalline Fe(110) films epitaxially grown on W(110) crystal, where the

chosen atomic monolayers were filled with the resonant <sup>57</sup>Fe isotope while the rest of the film was composed of the nonresonant <sup>56</sup>Fe atoms. Because of the ideal isotope selectivity of nuclear resonant scattering, this approach provides the resolution of a single atomic layer in a chemically homogeneous crystal. Moreover, the design of the samples nicely fits the slab geometry used in first-principles calculations. Therefore, experimental and theoretical DOS could be directly compared. As we show below, the good agreement of the experimental results and the first-principles calculations allows for detailed understanding of the atomic dynamics on a clean surface.

The experiment was performed at the ID18 beam line [7] at the European Synchrotron Radiation Facility using a recently constructed UHV system. The system includes standard chambers for surface preparation and characterization and a chamber for x-ray scattering measurements. The latter enables *in situ* coherent nuclear scattering and incoherent NIS both in grazing incidence geometry (for details of the experimental methods, see Ref. [4]). The measurements were performed with the x-ray beam along both high-symmetry directions of the 2-dimensional rectangular unit cell of the (110) surface, i.e., along [001] and [110]. The energy resolution of the inelastic spectrometer was 2.8 meV; the energy dependencies of NIS were measured collecting mainly Fe *K*α fluorescence; all data were taken at room temperature.

The Fe(110) films were deposited on the atomically clean W(110) crystal from the <sup>56</sup>Fe and <sup>57</sup>Fe electron beam evaporators with thickness reproducibility of 0.05 Fe monolayer (ML). Note that one Fe(110) ML corresponds to 2.03 Å. All samples included a 20 ML <sup>56</sup>Fe(110) buffer film optimized for a flat surface by a proper temperature protocol during the growth, while further <sup>56</sup>Fe and <sup>57</sup>Fe monolayers were deposited on the buffer film at lower temperature (350 K) to prevent mixing of the

isotopes [8]. This caused a slight broadening of otherwise extremely sharp low-energy electron diffraction spots, from which the minimum width of terraces on the Fe(110) surface was estimated as 50 Å [9]. The following samples were studied: (20 ML<sup>56</sup>Fe/1 ML<sup>57</sup>Fe)—referred to as “surface” (*S*), (20 ML<sup>56</sup>Fe/1 ML<sup>57</sup>Fe/1 ML<sup>56</sup>Fe)—referred to as “subsurface” (*S* − 1), and (20 ML<sup>56</sup>Fe/3 ML<sup>57</sup>Fe/3 ML<sup>56</sup>Fe)—referred to as “deep” (*D*) layers. Immediately after preparation each sample was transferred within the UHV environment to the x-ray scattering chamber. Electronic properties of the prepared surface were determined using grazing incidence nuclear resonance scattering (NRS) with measuring time below 1 h. Then the energy dependence of NIS was measured.

Figure 1 shows the time spectra of coherent grazing incidence nuclear scattering measured with the x-ray beam along the  $[1\bar{1}0]$  direction. The spectra were analyzed consistently for both crystal orientations using the software package CONUSS [10]. The time spectra (*S* − 1) and (*D*) show a single frequency quantum beat pattern described by a well-defined hyperfine magnetic field  $B_{\text{hf}}$  oriented parallel to the beam, i.e., along the  $[1\bar{1}0]$  direction. This is consistent with the  $[001]$  to  $[1\bar{1}0]$  switching of the easy magnetization axis observed in Fe/W(110) films with thicknesses below 100 Å [11]. In contrast, the surface (*S*) spectrum shows a modulation of the beat structure, which results from a finite electric field gradient caused by the broken translation symmetry at the surface, in agreement with a conversion electron Mössbauer experiment [8].

Figure 2 shows the DOS extracted [12] from the measured energy dependencies of incoherent NIS. Because of the grazing incidence geometry, the DOS comprise predominantly the states with big in-plane components of the polarization vector. The DOS of the first surface monolayer (panel *S*) is very much different from those of two other samples, as well as from the DOS of the bulk  $\alpha$  iron. The

most striking anomalies are the suppression of the phonon peak at 35 meV and a considerable enhancement of vibrational states below 15 meV. In addition, the DOS projected to the  $[1\bar{1}0]$  and  $[001]$  directions are clearly different, which is unusual for the cubic lattice.

The observed anomalies of atomic dynamics are strongly localized within the first atomic monolayer: Already in the second atomic layer (panel *S* − 1) most of the bulk DOS features are restored. For the deep layers (panel *D*) the only apparent difference from the bulk is a small shift of the slightly reduced 35 meV peak to lower

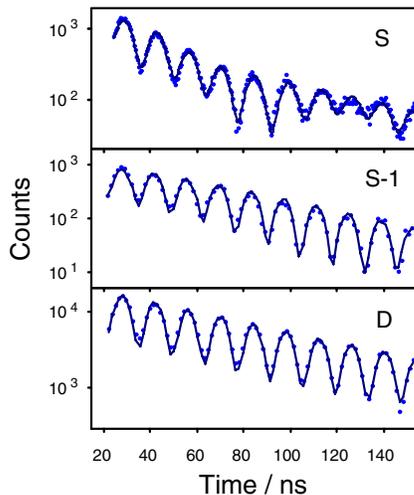


FIG. 1 (color online). Fitted NRS time spectra for the Fe(110) surface (*S*), subsurface (*S* − 1), and deep (*D*) layers measured with the x-ray beam along  $[1\bar{1}0]$  direction.

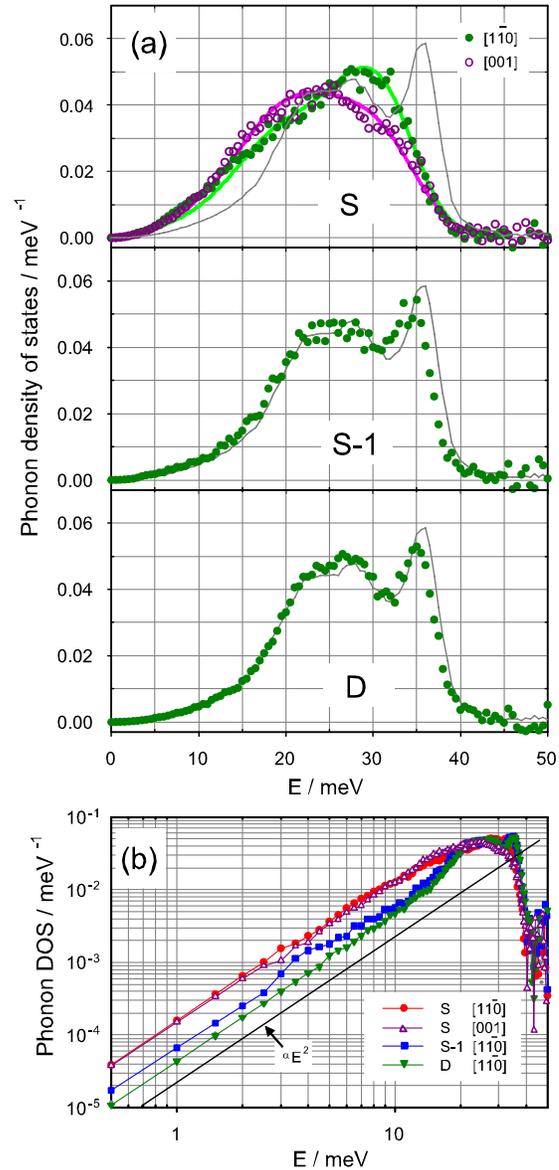


FIG. 2 (color online). (a) Measured phonon DOS for the surface (*S*), subsurface (*S* − 1), and deep (*D*) layers near the Fe(110) surface projected to  $[1\bar{1}0]$  (solid symbols) and to  $[001]$  (open symbols). The solid lines in (*S*) depict results of DFT calculations. The phonon DOS of an  $\alpha$ -<sup>57</sup>Fe foil is shown for comparison in each panel as a continuous line. (b) Double logarithmic plot of the phonon DOS collection from (a).

energies. Similar shift was observed also for a 9 nm Fe film on W(110) [13]. It possibly results from magnetostrictive effects [Fe films on W(110) are single domain in the remanent state] or residual epitaxial strains leading to a negative pressure exerted on the film.

Below  $\sim 10$  meV, the DOS are consistent with the Debye-like  $\propto E^2$  behavior [14] [Fig. 2(b)]. The functional dependence of the low-energy modes in systems with reduced dimensionality is an important and controversial issue. While Stuhr *et al.* [15] using neutron spectroscopy found that Pd surface atoms in a nano-Pd black sample perform low-energy vibrations with a local DOS essentially linear in the frequency, for different Fe-containing nanocrystals no deviation from Debye behavior was observed in inelastic neutron scattering [16,17] and NIS [18,19] experiments. From the theory point of view, a quasilinear behavior is derived only for nanosystems with high surface-to-volume ratio [20] and hence might be regarded as a surface feature. Our studies reveal that the DOS of a flat surface shows no deviation from the Debye-like  $\propto E^2$  dependence.

Obeying the Debye-like behavior, the low-energy part of the surface DOS is, however, a factor of  $\sim 3$  higher than that of the bulk. This trend is often observed in systems with reduced dimensionality. Its origin, however, remains strongly debated. Various explanations include specific surface modes, decrease of sound velocity, and cooperative particle dynamics [17–20]. The below presented comparison of the experimental data to first-principles calculations helps to clarify the question.

The first-principles calculations were performed with spin-polarized density functional theory (DFT) implemented in the Vienna *ab initio* simulation package (VASP) [21] using the all-electron augmented wave method within the general gradient approximation scheme with  $4 \times 4 \times 2$   $k$ -point mesh. Surface properties were derived with the filling slab approach [2,22], using the already calculated five layer Fe(110) slab [23], and a bulk section built up of six supercells, each consisting of 4 layers. Thus, the considered thick slab contained 29 Fe layers. The calculated dispersion relations and the DOS projected on two in-plane directions are shown in Fig. 3. All obtained frequencies are positive, hence the system is stable. The Rayleigh mode [the lowest dispersion curve in Fig. 3(a)] is well separated from the rest of the phonon band. The atomic vibrations in this mode are polarized perpendicular to the surface. Therefore, in contrast to a HAS experiment [24], this mode does not contribute to the surface-projected DOS measured here.

Once the phonon DOS are known, various dynamic and thermodynamic parameters can be determined. Table I shows the experimental and calculated mean force constant, mean square displacement, and vibrational entropy.

For comparison to experiment, the calculated DOS were convoluted with a Gaussian function accounting for experimental broadening of DOS features. The impressive consistence of the experimental and theoretical results

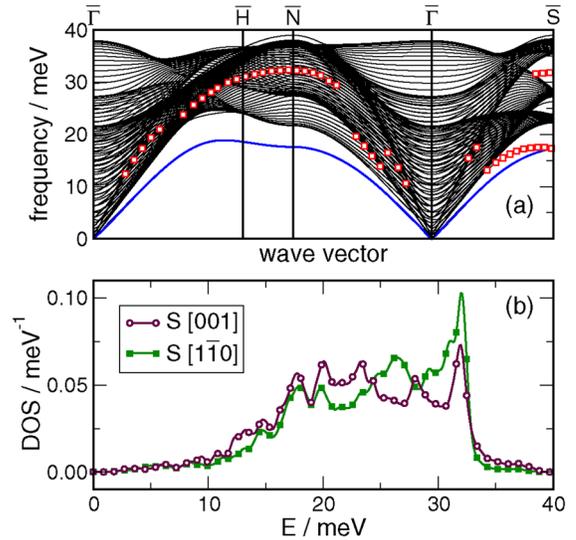


FIG. 3 (color online). (a) Dispersion curves and (b) surface DOS along  $[1\bar{1}0]$  (solid squares) and  $[001]$  (open circles) directions calculated for 29 layers Fe slab. High-symmetry points correspond to two dimensional Brillouin zone of the plane reciprocal lattice (Ref. [2]). In (a), the lowest dispersion curve is the Rayleigh mode while the open squares depict surface modes with the highest in-plane intensities.

(Fig. 2, panel S) allows for further insight into the nature of the observed phenomena. In particular, it suggests an explanation of the observed enhancement of soft vibrational states [Fig. 2(b)]. The dispersion relations reveal that the most intense surface modes are the Rayleigh mode and surface modes associated with in-plane vibrations, depicted in Fig. 3(a) with the open squares. However, beside them, the 29-layer slab also shows various additional low frequency modes. Their eigenvectors reveal that some vibrational amplitude in these modes belongs to the surface atoms. Thus, the DOS of the surface atoms are considerably augmented by the surface-specific vibrational modes, which are not present in the bulk. This possibly answers a long-lasting question on the origin of the low-energy modes in nanoscaled materials [17–20]. In addition, the surface modes are responsible for the peaks of the measured DOS in the  $\sim 30$  meV energy region.

TABLE I. Mean force constant  $\langle \gamma \rangle$ , mean square displacement  $\sqrt{\langle x^2 \rangle}$ , and vibrational entropy  $S_v$  derived from the experimental (Expt.) and calculated (Theor.) DOS for surface (S), subsurface ( $S-1$ ), and deep (D) layers of Fe(110) and for bulk iron.

Sample		S	S-1	D		
Beam direction		$[1\bar{1}0]$	$[001]$	$[1\bar{1}0]$	$[1\bar{1}0]$	Bulk
$\langle \gamma \rangle$ [N/m]	Expt.	138(4)	129(4)	161(4)	166(4)	172(4)
	Theor.	132.0	119.7	185.3	174.0	171.2
$\sqrt{\langle x^2 \rangle}$ [Å]	Expt.	0.083(1)	0.084(1)	0.069(1)	0.065(1)	0.065(1)
	Theor.	0.077	0.082	0.066	0.064	0.064
$S_v$ [ $k_B$ /atom]	Expt.	3.50(2)	3.61(2)	3.20(2)	3.13(2)	3.09(2)
	Theor.	3.46	3.63	2.99	3.04	3.09

Furthermore, the calculations confirm the experimentally observed differences in the DOS projected to the  $[1\bar{1}0]$  and  $[001]$  directions (Fig. 2, panel S), which originate from the broken translational symmetry along the normal of the twofold symmetry (110) surface. The missing neighbors make the surface stiffer along  $[1\bar{1}0]$  than along  $[001]$ . This observation is quantitatively confirmed by the mean force constants  $\langle\gamma\rangle$  derived from theoretical and experimental DOS (Table I). The mean force constant along  $[1\bar{1}0]$  is by 7% higher than that along  $[001]$ . The softening shifts the center of gravity of the DOS projected to  $[001]$  to lower energy relative to that for  $[1\bar{1}0]$ . This, however, does not affect the amplitude of the mean square displacements that, within the experimental error bars, is the same for both directions. This can be expected [5] because the mean square displacements are determined mainly by the low-energy parts of the DOS, which are very similar for both directions [Fig. 2(b)].

Almost identical for two orthogonal directions, the vibration amplitudes of the surface atoms by 30% exceed the bulk value, which is a consequence of the surface-specific modes. For comparison, such an increase would correspond to heating of crystal up to 530 K. The enhancement of the amplitude of atomic vibrations at surface is tightly related to surface melting, nanoscale catalysis and other surface-associated phenomena. To our knowledge, these are the first experimental data for bcc (110) surfaces. For comparison, for a close-packed face of an fcc metal, for Cu(111), the ratio  $\eta$  of surface to bulk vibrational amplitudes at room temperature has been found  $\eta_{\text{out}} = 1.35$  and  $\eta_{\text{in}} = 1.15$  for perpendicular and in-plane vibrations, respectively [25]. The present measurements for the close-packed Fe(110) surface give  $\eta_{\text{in}} = 1.29$ , while  $\eta_{\text{out}}$  is not accessible due to the experimental geometry. Similar to the DOS anomalies, the enhancement of vibrational amplitude is strongly localized within the first atomic monolayer: Already for the subsurface atoms  $\eta_{\text{in}} = 1.07$ , and it becomes  $\eta_{\text{in}} = 1.00$  in deep layers. The calculations show that anomalies in the normal-projected dynamical properties are also localized predominantly within the first atomic monolayer. Thus, the single-monolayer spatial resolution is indeed indispensable for reliable studies of surface dynamics.

In summary, we have measured density of phonon states for single atomic monolayers at and near a clean Fe(110) surface. The results show that atoms of the first layer vibrate with frequencies significantly lower and amplitudes much larger than those in the bulk. Furthermore, the DOS projected to the two orthogonal in-surface directions are different. These anomalies are strictly localized at the surface—already the second monolayer shows almost the bulk properties. Very good agreement of the experimental results and the first-principles calculations allows for detailed understanding of the observed phenomena. Besides a new insight to surface dynamics, the results have implications for physics of nanoparticles, catalysis, and other surface-associated phenomena.

The precise measurements of a single-monolayer DOS, which up to now was not accessible with any other technique, can be extended to other nuclear isotopes, in particular, to rare-earth materials. Furthermore, it allows for investigations of systems with even lower dimensionality as nanowires and, possibly in the near future, of nanodots and other quantum-scale objects. Another challenge would be to study dynamical aspects of surface reconstruction and surface structural transitions.

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- [1] J. P. Toennies, in *Surface Phonons*, edited by W. Kress and F. W. de Wette, Springer Series in Surface Sciences Vol. 21 (Springer, Berlin, 1991), p. 111.
  - [2] R. Heid and K.-P. Bohnen, *Phys. Rep.* **387**, 151 (2003).
  - [3] M. C. Desjonquères and D. Spanjaard, *Concepts in Surface Physics* (Springer-Verlag, Berlin, 1996), 2nd ed.
  - [4] R. Röhlberger, *Nuclear Condensed Matter Physics with Synchrotron Radiation*, Springer Tracts in Modern Physics Vol. 208 (Springer-Verlag, Berlin, 2004).
  - [5] V. G. Kohn, A. I. Chumakov, and R. Rüffer, *Phys. Rev. B* **58**, 8437 (1998).
  - [6] T. Tanaka *et al.*, *J. Phys. Soc. Jpn.* **74**, 1762 (2005).
  - [7] R. Rüffer and A. I. Chumakov, *Hyperfine Interact.* **97–98**, 589 (1996).
  - [8] J. Korecki and U. Gradmann, *Phys. Rev. Lett.* **55**, 2491 (1985).
  - [9] M. Albrecht, H. Fritzsche, and U. Gradmann, *Surf. Sci.* **294**, 1 (1993).
  - [10] W. Sturhahn, *Hyperfine Interact.* **125**, 149 (2000).
  - [11] U. Gradmann, J. Korecki, and C. Waller, *Appl. Phys. A* **39**, 101 (1986).
  - [12] V. G. Kohn and A. I. Chumakov, *Hyperfine Interact.* **125**, 205 (2000).
  - [13] S. Stankov *et al.* (to be published).
  - [14] Central peak in NIS spectra was subtracted using instrumental function measured in parallel for each spectrum. The residual level of inelastic scattering was obtained with sufficient statistical accuracy.
  - [15] U. Stuhr *et al.*, *Phys. Rev. Lett.* **81**, 1449 (1998).
  - [16] H. Frase, B. Fultz, and J. L. Robertson, *Phys. Rev. B* **57**, 898 (1998).
  - [17] A. F. Yue *et al.*, *Phys. Rev. Lett.* **93**, 205501 (2004).
  - [18] B. Fultz *et al.*, *Phys. Rev. Lett.* **79**, 937 (1997).
  - [19] L. Pasquini *et al.*, *Phys. Rev. B* **66**, 073410 (2002).
  - [20] A. Kara and T. S. Rahman, *Phys. Rev. Lett.* **81**, 1453 (1998).
  - [21] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11 169 (1996).
  - [22] K. Parlinski, *Phys. Rev. B* **74**, 184309 (2006).
  - [23] J. Łażewski, J. Korecki, and K. Parlinski, *Phys. Rev. B* **75**, 054303 (2007).
  - [24] G. Benedek, J. P. Toennies, and G. Zhang, *Phys. Rev. Lett.* **68**, 2644 (1992).
  - [25] K. H. Chae, H. C. Lu, and T. Gustafsson, *Phys. Rev. B* **54**, 14 082 (1996).