Energy Dependence of Inelastic Electron Scattering Cross Section by Surface Vibrations: Experimental Measurement and Theoretical Interpretation

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We report on the first comparison of the inelastic cross section of Ni(001) surface phonons for an extended energy range with a dynamical scattering theory. Both theory and experiment indicate large modulations in the loss cross section as a function of incident energy. The intensity ratio of the S_4 and S_6 surface phonons on Ni(001) is best fitted with a 1.7%–3.3% contraction in the outermost interlayer spacing.

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Because of its high surface sensitivity and wide spectral range, high-resolution electron energy-loss spectroscopy (HREELS) has rapidly emerged as a major tool for studying vibrational properties of clean and adsorbate-covered surfaces. An experimental innovation was introduced recently by Lehwald *et al.*[1] who collected off-specular HREELS data at high incident energies, $E_i = 180$ eV and 322 eV. The combination of a short electron mean free path and large surface-localized displacements make HREELS cross sections of surface phonons and resonances much larger than that of bulk modes. For a fcc (001) surface, lattice dynamics yielded three surface modes: S_1, S_4, and S_6. The S_1 mode is a shear horizontal wave with odd polarization with respect to the (110) plane. If the scattering plane is also along the (110) direction, then a selection rule requires that this mode has a zero cross section.[2] The other two surface modes, S_4 and S_6, however, should have nonzero cross sections. Near a zone boundary, e.g., $\bar{X}$, the frequencies of the S_4 and S_6 modes occur in gaps of bulk modes. To date, only one surface mode, i.e., the S_4 mode, has been measured.[1] The S_6 surface mode, as well as other surface resonances, were not detected in this first experiment.[3] As we shall show below, measurement of the S_6 frequency provides an important check of the lattice dynamical model, while measurement of the S_6 phonon cross section provides a very sensitive structural indicator.

A theory of phonon intensities has been developed[2] which incorporates the muffin-tin approximation for the scattering potential and the additional assumption that the ions move rigidly when the nuclei are displaced through the excitation of a phonon.[4] At energies of the order of 100 eV, electrons scatter mainly from the near-core region of the atoms. Hence, we expect cross sections calculated from this rigid-ion multiple-scattering (RIMS) slab method to be rather accurate. In this Letter, we show that this is indeed the case: calculated cross sections at $\bar{X}$ and $\theta_f = 65°$ for S_4 and S_6 surface phonons in the energy range 40–250 eV indicate three regions where the S_6 mode has cross sections comparable to that of S_4. These theoretical predictions are confirmed by measurements in which the S_6 mode is observed for the first time at the predicted energies. Moreover, there is close tracking between theory and experiment in the energy dependence of the cross section. Both theory and experiment indicate large modulations in the phonon loss cross section as a function of incident energy, a behavior in marked contrast to the simple Born expression of $|\Delta\mathbf{k}\cdot\mathbf{u}|^2$, where $\mathbf{u}$ is the vibrational displacement vector and $\Delta\mathbf{k}$ is the electron momentum change. The simultaneous measurement of S_4 and S_6 modes also allows a discrimination between different structural models for the Ni(001) surface. The ratio of measured S_4/S_6 cross section is best fitted by a Ni(001) surface with a 1.7%–3.3% contraction in the outermost interlayer spacing. This is in good agreement with a recent ion-scattering result of Frenken, Van der Veen, and Allan.[5]

In Fig. 1, we show the displacement directions of the S_4 and S_6 surface phonons at $\bar{X}$. Also shown is the scattering geometry. Note that the surface unit cell convention is used and $\mathbf{q}_x$ is along the [110] direction. The phonon eigenvectors of the first five atomic layers of the two surface modes at $\bar{X}$ are listed in Table I. These eigenvectors are based on the nearest-neighbor central-force model,[6] with the force constant in the bulk adjusted to fit the maximum bulk Ni phonon fre-

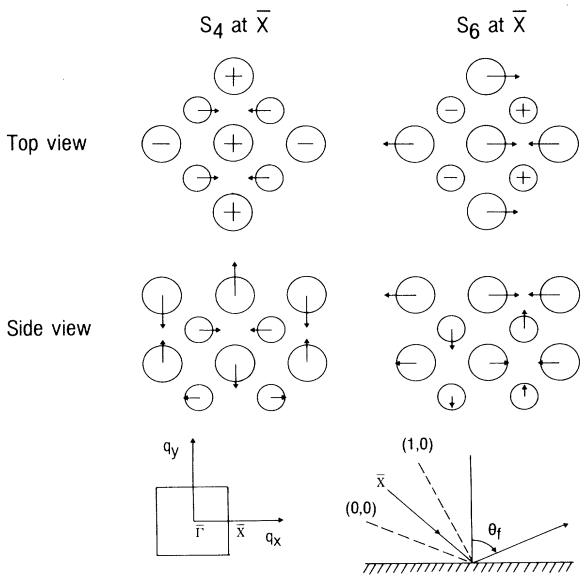

FIG. 1. Direction of atomic displacements of S_4 and S_6 modes at $\bar{X}$: plusses, up; minuses, down. In the top view, the smaller circles denote second-layer atoms. The lower right-hand figure shows the scattering plane.

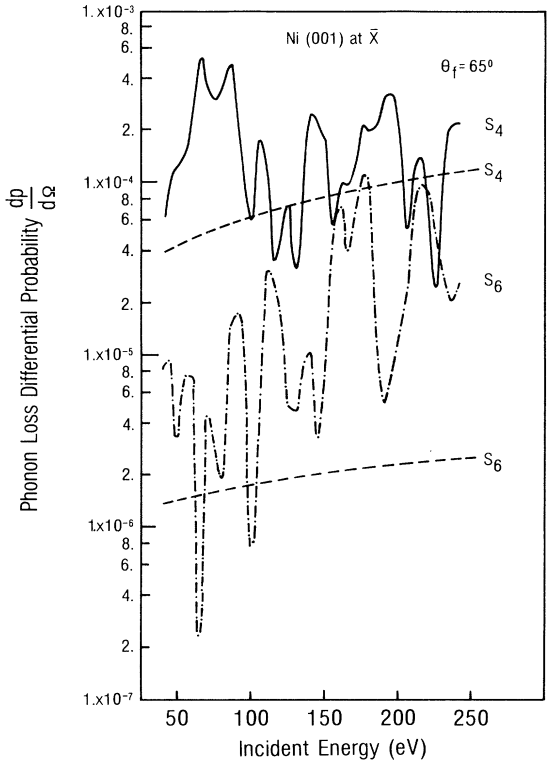

FIG. 2. Calculated differential probability for S_4 and S_6 surface phonons vs incident energy. The Born approximation results are shown by dashed lines.

quency, and the surface force constant which couples atoms in the first layer to those in the second is increased by 20%.[1,5] This lattice dynamical model was found to provide the best agreement with the measured phonon dispersion curves.[1,7]

With the eigenvectors of the S_4 and S_6 modes, the inelastic cross sections are evaluated in the 40–250-eV energy range by use of the RIMS method. The method allows the electron to scatter elastically or inelastically at each atomic layer, and is exact in terms of the number of multiple-scattering events or atomic layers included. In Fig. 2, we show the energy dependence of the calculated phonon-loss differential probability (i.e., number of phonon-loss electrons per solid angle per incident electron) for S_4 and S_6, evaluated at $\bar{X}$ and $\theta_f = 65°$. We see substantial modulations in the differential probability and at three energy intervals, E_i from 110 to 115 eV, 155 to 180 eV, and 210 to 230 eV, the two modes have comparable probabilities. Also shown (dashed lines) are estimates of the probability based on the Born approximation (BA) arbitrarily normalized to 1.0×10^{-4} at $E_i = 200$ eV for the S_4 mode. In the BA model, the probabilities are smooth functions of energy and the probability of S_6 is too small to be detected by experiment. From Fig. 2, we see that the S_6 probability is very much enhanced by multiple scattering, to a magnitude that it can easily be measured under current experimental conditions. In the multiple-scattering picture, an electron is scattered into a direction essentially parallel to the surface.

TABLE I. Eigenvectors of S_4 and S_6 surface modes at $\bar{X}$ for Ni(001). Model (a) is for a 20% increase in the force constant which couples atoms in the first and second layers and no contraction in the surface interlayer spacing. Model (b) is for the same force-constant model as in model (a) and a 3% contraction in the surface interlayer spacing.

Mode	Model	First layer			Second layer			Third layer			Fourth layer			Fifth layer		
		e_x	e_y	e_z	e_x	e_y	e_z	e_x	e_y	e_z	e_x	e_y	e_z	e_x	e_y	e_z
S_4	a	0	0	$-0.83i$	-0.41	0	0	0	0	$0.32i$	0.13	0	0	0	0	$-0.10i$
	b	0	0	$-0.85i$	-0.40	0	0	0	0	$0.30i$	0.12	0	0	0	0	$-0.09i$
S_6	a	0.64	0	0	0	0	$0.22i$	0.54	0	0	0	0	$0.15i$	0.35	0	0
	b	0.64	0	0	0	0	$0.22i$	0.54	0	0	0	0	$0.14i$	0.36	0	0

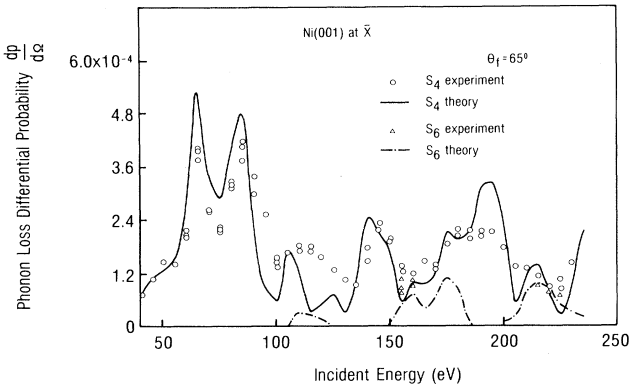

FIG. 3. Comparison between experimental and theoretical phonon-loss I-V profiles of S_4 and S_6 surface modes, at $\bar{X}$ and $\theta_f = 65°$.

Through subsequent umklapp scattering, it can couple strongly to parallel displacements of the S_6 mode. The experimental detection of the S_6 mode confirms the correctness of this picture.

For the experiment, the Ni(001) single crystal is prepared following conventional procedures. Sulfur and carbon are removed from the sample by cycles of neon bombardment and annealing. The carbon level in the sample is reduced to the extent that even after flashing to 1350 K and cooling to room temperature the concentration of carbon on the surface is below the detection limit of the cylindrical-mirror-analyzer–Auger spectrometer (carbon peak less than $\frac{1}{40}$ of the Ni 102-eV peak). Phonon-loss intensities are measured with the double-pass spectrometer used in earlier experiments.[1] Measuring intensity-energy (I-V) profiles for phonon scattering is significantly more demanding than for diffracted beams. Between the monochromator and analyzer, the electrons are accelerated and decelerated by a factor of about 100. Since the lens potentials as seen by the electrons are subject to local variations of the surface potentials on the electrodes, the long-term reproducibility of the intensities is only within a factor of 2. I-V profiles generated in different runs therefore had to be scaled by a constant factor in order to match to previous results. With this overall scaling, however, the features in the I-V profiles are fairly reproducible.

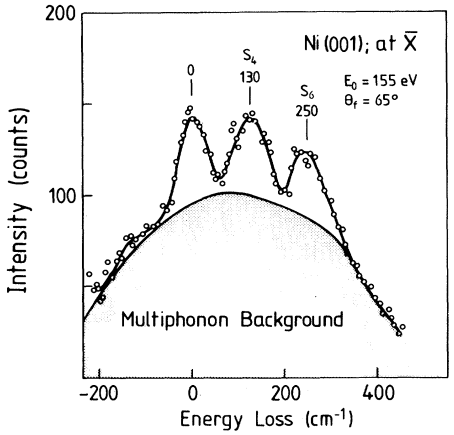

FIG. 4. Experimental loss spectrum at $\bar{X}$ ($q_{\parallel} = 1.26$ Å^{-1}) and $E_i = 155$ eV, $\theta_f = 65°$, showing both S_4 and S_6 modes. The multiphonon background is calculated in the minima between the peaks by fitting Gaussian functions to the peaks with a half-width taken from the resolution. The full curve is generated by the assumption that the multiphonon background is a smooth function of energy. Above 295 cm^{-1} the entire intensity is due to multiprocesses.

The measured phonon loss I-V profiles are shown in Fig. 3 for the S_4 mode (circles) and, when measurable, the S_6 mode (triangles), together with the calculated results (solid and dot-dashed lines, respectively), at $\bar{X}$ and $\theta_f = 65°$. The reproducibility of the data can be seen from the relatively small scattering in the data points. There is close tracking between theory and experiment in the energy dependence of the intensities. The remaining differences may be at least partly due to the experimental difficulties mentioned above. In order to extract structural information from the data one should therefore focus on the ratio of intensities of the S_4 and S_6 modes in the spectra where both appear, since this ratio is independent of the particular focusing conditions of the lens elements. At energies and angles where the ratio is sensitive to structural parameters, it is possible to use it to discriminate between different surface models. For example, the measured intensity ratio of S_4/S_6 at 155 eV is 1.15. This ratio has been determined by subtraction of a multiphonon background as indicated in Fig. 4. In Table II, we show the calculated S_4/S_6 intensity ratio for different percent contractions of the interlayer spacing between the surface and the layer immediately below it (i.e., d_{12}). This ratio is very sensitive to d_{12} and varies, on the average, by 40% for every 1% change in d_{12}. For example, if we eliminate the 20% increase in the first-to-second layer force constant in the lattice dynamics calculation, the eigenamplitudes vary by approximately 22%. The calculated S_4/S_6 intensity ratio decreases by

TABLE II. Phonon-loss intensity ratio S_4/S_6 versus surface interlayer spacing at 155 eV and $\theta_f = 65°$.

Interlayer spacing	S_4/S_6
Experiment	1.15
No contraction ($d_{12} = 1.765$ Å)	0.57
1% contraction ($d_{12} = 1.747$ Å)	0.70
2% contraction ($d_{12} = 1.730$ Å)	0.87
3% contraction ($d_{12} = 1.712$ Å)	1.16
4% contraction ($d_{12} = 1.694$ Å)	1.65
5% contraction ($d_{12} = 1.677$ Å)	2.60

TABLE III. Experimental phonon-loss intensity ratio, with error bars, at different energies and scattering angles.

E_0	θ_f	S_4/S_6	Remark
160	60	$0.5^{+0.5}_{-0.25}$	Contribution of bulk resonance to "S_4" peak
220	65	1.4 ± 0.2	
155	65	1.15 ± 0.15	
160	65	1.2 ± 0.5	Contribution of bulk resonances to both peaks

over 30%, but this produces only a 1% change in the surface spacing contraction. Of course, the elimination of the 20% increase in the surface force constant is unreasonable because it would bring the S_4 frequency from 131 cm^{-1} (compared to an experimental value of 130 cm^{-1}) to 125 cm^{-1}, and the S_6 frequency from 252 cm^{-1} (experimental value of 250 cm^{-1}) to 247 cm^{-1}. Thus, while the eigenfrequencies are sensitive to surface force constants, the S_4 and S_6 phonon intensities are mostly sensitive to surface structure.

Data which include other energies and θ_f where the S_6 mode is observed simultaneously with S_4 are listed in Table III, together with experimental error bars. Using these data and error bars, we evaluate a reliability factor defined as

$$R = \frac{\sum_i |S_i(\text{expt.}) - S_i(\text{theory})|^2}{\sum_i |S_i(\text{expt.})|^2}, \quad (1)$$

where S_i(expt.) or S_i(theory) are the ith measured or calculated intensity ratios, respectively. A plot of R versus interlayer spacing using the upper bounds of the measured data yields a surface spacing contraction of $\leq 3.3\%$. A similar plot using the lower bounds of the measured data yields a surface spacing contraction of $\geq 1.7\%$. Thus, we conclude that the surface interlayer spacing determined from this study to be a contraction of 1.7%–3.3%, in excellent agreement with a recent ion-surface-scattering result. Since 3.3% for Ni(001) is 0.058 Å, our result is also consistent with earlier LEED studies which concluded that Ni(001) has an unrelaxed surface to within an accuracy of ± 0.1 Å.[8]

In summary, we find that the RIMS model describes the phonon cross sections accurately. Quantitative structure information can be obtained from the intensity ratios of different modes in various parts of the Brillouin zone.

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