Detection of odd symmetry shear modes at metal surfaces by inelastic electron scattering: Experiment and theory

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High resolution inelastic electron scattering measurements and full multiple-scattering calculations for Ni(100) and Ag(100) surfaces are presented and used to characterize, for the first time, shear horizontal surface phonon modes. Implications of these new capabilities for studies of surface structure, reconstruction, thin film epitaxy, and for exploring selectron rules that govern inelastic electron scattering are discussed.

I. INTRODUCTION

High resolution inelastic electron scattering spectroscopy is now regarded as one of the more important techniques for studying the structure and dynamics of surfaces.[1,2] The growing popularity of the technique and the broad range of applications that are possible, based on it, are easily understood: elastic and inelastic scattering of 1–500 eV electrons from crystal surfaces are phenomena that can be interpreted on several levels, and involve a rich variety of fundamental interactions, excitations, scattering mechanisms, conservation laws, and selection rules that underlie electron spectroscopy of solids.

At sufficiently high incident energies, typically 100 eV or higher, the electron scattering cross section is dominated by a scattering mechanism known as "impact scattering," which is characterized by a short interaction range, and which produces large-angle scattering in all directions.[3,4] Multiple scattering plays an important role in the impact scattering regime because the electron de Broglie wavelengths are comparable to a lattice spacing. At lower incident energies, long-range "dipolar" fields dominate electron scattering processes. Dipole scattering[5] is characterized by a cross section that decreases monotonically with increasing energy, and an angular pattern which is concentrated in a narrow cone around the specular direction. Simple kinematic laws[1,2] govern energy and momentum transfer between incident and scattered electrons, and surface excitations (either phonons or plasmons) that are produced by the scattering. These kinematical laws applied to measurements of the energy loss and momentum transfer in electron (and helium) scattering experiments yield the excitation spectra of surface atoms; i.e., the phonon and plasmon dispersion relations. These dispersion relations, along various directions of reciprocal space, contain detailed information related to interaction potentials and structure of the surface.[2,6]

Selection rules[7,8] that apply to scattering in the large-angle scattering regime are also of crucial importance in determining which vibrational modes can be probed in a specific scattering geometry. These selection rules are based on general symmetry conditions assumed to exist at the surface. The rules apply to surface phonons and discrete adsorbate vibrations probed under appropriate scattering conditions. A specific manifestation of the large-angle selection rules appropriate to the discussion which follows is the fact that only even symmetry surface phonons and discrete surface modes can be observed in an experiment in which the scattering is confined to a plane which contains a crystal axis of inversion symmetry.

In spite of the potential importance of large-angle scattering selection rules and the apparent opportunities to exploit their effects in separating even and odd symmetry surface vibrations, neither suitable scattering measurements nor detailed scattering analysis have been carried out to assess the extent that these scattering laws apply in actual scattering experiments. The purpose of this paper is to report the first unambiguous observation and characterization of shear horizontal vibrational modes by inelastic electron scattering and to briefly discuss the implications of these new results in view of large-angle scattering selection rules and the role shear modes play in surface phenomena.

II. EXPERIMENTAL

Unambiguous observation of odd symmetry shear modes by electron scattering was possible, based on the unique capabilities of a new inelastic electron scattering spectrometer described elsewhere.[9,10] The key feature that is required for observing odd symmetry modes is a capability to accurately measure inelastic scattering momentum transfer along a direction perpendicular to the plane of incidence. Higher detection sensitivity (achieved by multichannel detection) and high angular resolution (achieved by a novel lens system), which are features of the new spectrometer, are additional important requirements. The Ni(100) and Ag(100) crystals used in experiments reported here were aligned and cut using x-ray Laue techniques, and were cleaned *in situ* using standard surface science techniques (Ne$^+$ sputtering at 500 eV, followed by annealing). Low-energy electron diffraction (LEED) and inelastic electron scattering were used to characterize the surface structure and purity. Vacuum conditions during the experiments were typically 2×10^{-10} Torr.

III. RESULTS

Figure 1 illustrates the scattering geometry and defines the parameters required to characterize the scattering conditions. Electrons are incident along a [110] crystal axis at an angle θ_i measured from the surface normal $\hat{n}$. The incident energy is E_i, and incident momentum parallel to the surface is $k_{i\parallel} = 0.512\sqrt{E_i}\sin\theta_i$. Scattered electrons are detected either in the plane of incidence along the [110] axis (even scattering geometry) or out of the plane along a direction specified by θ_s and ϕ_s as shown in Fig. 1 (odd scattering geometry). In even scattering geometry, only surface modes having even symmetry under reflection around the [110] axis can be excited by the detected scattered electrons. In odd scattering geometry, both even and odd symmetry modes can be excited by the detected electrons. All previous experiments in which surface phonons have been studied have used exclusively even symmetry scattering geometry and consequently have detected only even symmetry modes.

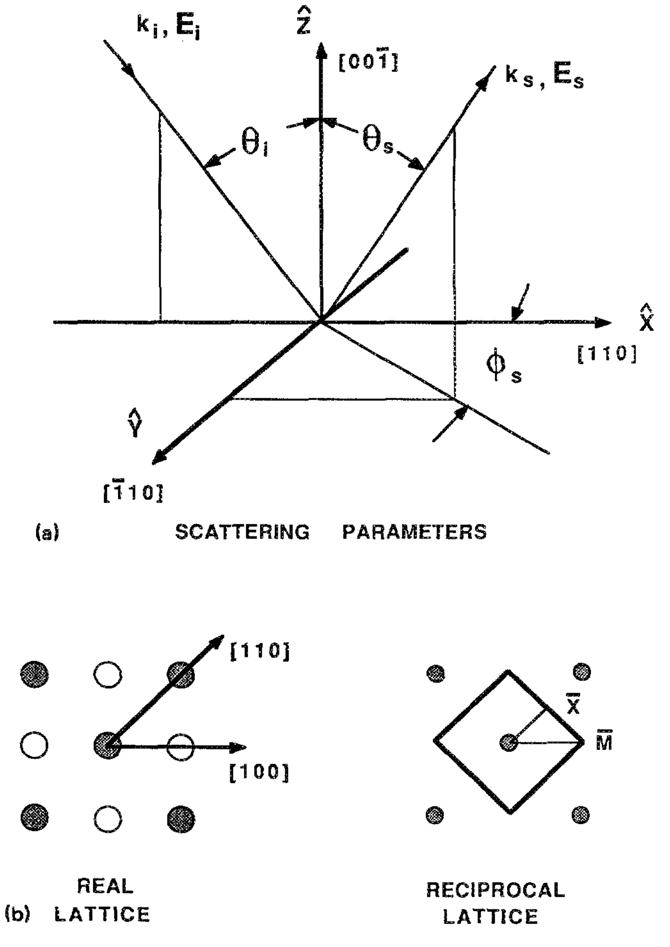

FIG. 1. (a) Scattering geometry and parameters. Surface normal is along $-\hat{Z}$ (the [00$\bar{1}$] direction). Electrons are incident at energy E_i and momentum k_i at angle θ_i measured from $-\hat{Z}$ in the X,Z plane. Scattered electrons of energy E_s and momentum k_s are measured along a direction k_s defined by θ_s and ϕ_s. For $\phi_s = 0$, scattering is confined to the X,Z plane and $\Delta k_\parallel = \Delta k_x = 0.512\sqrt{E}\,(\sin\theta_i - \sin\theta_s)$. In this geometry, only even symmetry modes are probed. For $\phi_s \neq 0$, $\Delta k_\parallel = \Delta k_{x\parallel}\hat{x} + \Delta k_{y\parallel}xy$. When $\Delta k_{y\parallel} \neq 0$, both even and odd symmetry modes can be probed. (b) Real lattice and reciprocal lattice of the (100) face of a fcc crystal.

Figure 2 displays an inelastic scattering spectra for Ni(100) in which an odd symmetry shear mode (S_1 mode) is observed. Atomic displacements that characterize the two detected surface modes are shown. Experimental parameters corresponding to the spectra shown in Fig. 2 were chosen based on the results of multiple scattering calculations of the inelastic electron scattering cross section. The calculations predicted that the S_1 and S_4 modes would exhibit approximately equal scattering cross sections under the given experimental conditions. Curve fitting analysis applied to the experimental spectra shows that the S_1 and S_4 modes contribute approximately equally to the loss and gain peaks of Fig. 2, and that the excitation energies at $\bar{X}$ are $S_1 = 15.6$ meV and $S_4 = 17.6$ meV. It is of historical interest that the S_4 mode on Ni(100) was the first surface phonon observed by inelastic electron scattering.[11] Our result for the S_4 energy at $\bar{X}$ is in excellent agreement with the value obtained by this pioneering experiment (17.4 meV).

The crystal structure of Ag is the same as Ni (both are fcc lattices). However, Ag(100) presents a more favorable situation for observing odd symmetry surface phonons because of a larger energy difference between the S_1 and S_4 modes at $\bar{X}$. In addition, under favorable scattering conditions, the odd symmetry (S_1) mode exhibits a rather large cross sec-

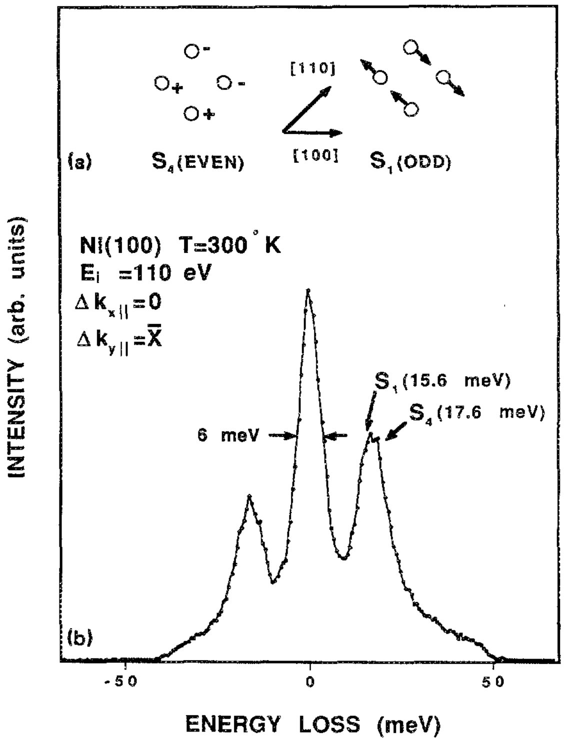

FIG. 2. (a) Eigenvectors for the S_4 and S_1 surface phonon modes. (b) Inelastic scattering spectra for Ni(100) at $\bar{X}$ of the two-dimensional Brillouin zone in "odd" symmetry geometry showing both even and odd symmetry loss and gain peaks. Full peak width of loss and gain peaks at 90% height (in comparison with elastic peak) provides evidence to two mode contribution in odd scattering geometry. Corresponding spectra taken in even symmetry geometry exhibit same widths for loss, gain, and eleastic peak. Curve fitting yields S_1 and S_4 energies.

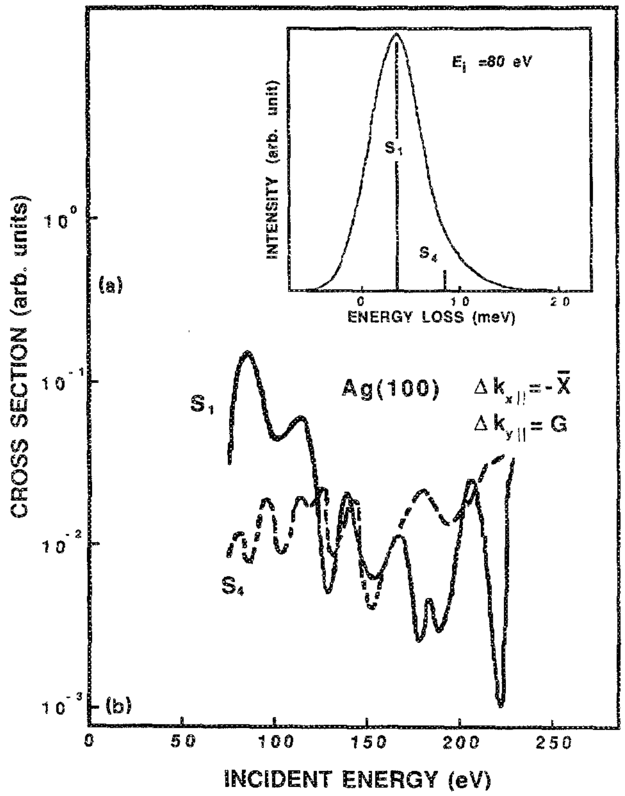

FIG. 3. (a) Calculated relative scattering cross section for S_1 and S_4 phonons and projected bulk phonons at $\bar{X}$. [Ag(100) surface at $E_i = 80$ eV]. (b) Incident energy dependence of the S_1 and S_4 mode scattering cross section of Ag(100) for $\Delta k_{x\parallel} = -\bar{X}$, $\Delta k_y = G$.

tion. Figure 3 displays the results of multiple scattering calculations of the cross section for the S_1 and S_4 surface phonons of Ag(100) at $\bar{X}$. In an energy range around 75 eV, the S_1 mode cross section is predicted to dominate the S_4 mode cross section. Unfortunately, the elastic peak completely dominates the spectra obtained in this energy range such that the loss and gain modes are obscured. For this reason, most of our data are taken at higher energies where the elastic peak is found to be suppressed.

Figure 4 displays several inelastic scattering spectra for Ag(100) at three values of $k_\parallel$ near $\bar{X}$. Both even and odd scattering geometry were used. For a specified value of $k_\parallel$, it is clear that there are two different phonon modes having significantly different energies that contribute differently to the even and odd symmetry loss spectra. Figure 5 displays an inelastic scattering cross section spectrum which exhibits both S_1 and S_4 modes. The excitation energies of the two modes at X are $S_1 = 3.3$ meV$_i$, $S_2 = 7.8$ meV, in reasonably good agreement with lattice-dynamic predictions. The spectra displayed in Figures 2, 4, and 5 and the cross section calculations (Fig. 3 and text) supporting the interpretation of the experimental results constitute unambiguous evidence of the odd symmetry modes known to exist from lattice-dynamical models of surface dynamics.

IV. DISCUSSION

We now briefly explore the consequences of this new capability to detect and characterize odd symmetry phonon modes. First, it is quite apparent that it is now possible to

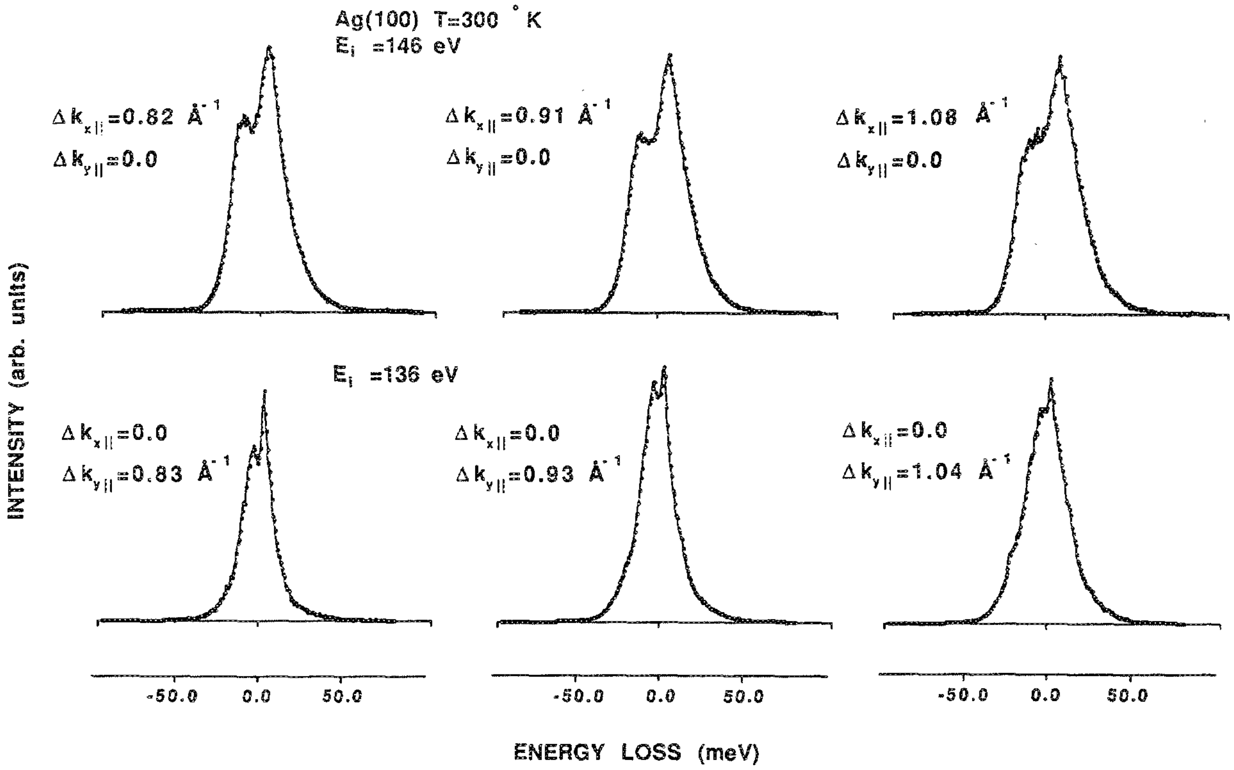

FIG. 4. Inelastic electron scattering spectra for Ag(100) along $\bar{\Gamma} - \bar{X}$ for even and odd symmetry geometry. Energy separation of the S_4 loss and gain peaks (upper spectra, $k_{y\parallel} = 0$, even geometry) is considerably greater than for the S_1 loss and gain peak separation (lower spectrum, $k_{y\parallel} \neq 0$, odd geometry).

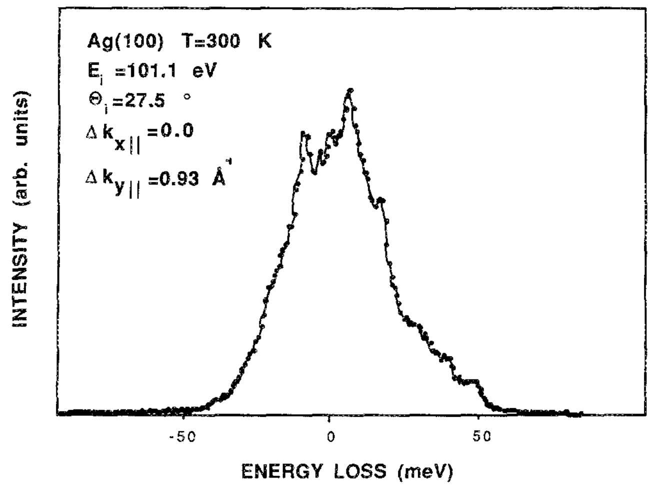

FIG. 5. Inelastic scattering spectra for Ag(100) along $\bar{\Gamma}-\bar{X}$ for odd scattering geometry. At this energy, both the S_1 and S_4 modes appear in the spectra. The presence of the elastic peak makes it more difficult to resolve these features than those in the spectra shown in Fig. 4.

test, in detail, the selection rules that govern electron scattering from crystal surfaces. Selection rules provide an important means of judging atomic-level symmetry, and a means of testing mode assignments. Second, the relatively good agreement between general properties of calculated and measured inelastic electron cross sections for both even and odd symmetry modes (which we have not been able to address in the present paper) is an indication that meaningful cross section calculations are feasible for both even and odd symmetry modes, and that these calculations combined with measurements offer an additional structure sensitive probe.

The most promising new applications of the expanded capabilities for probing surface phonons are likely to occur in the area of semiconductor surfaces and epitaxial films. In these systems, lateral reconstructions resulting from covalent bonds, strain layers resulting from epitaxy, and related effects raise important questions regarding atomic level forces that govern the phenomena. Many of the issues pertain to in-plane features of the structure and in-plane strain, which are most sensitive to shear horizontal surface modes.

Based on the initial success of our first studies of shear horizontal modes on metal surfaces, one can judge that the new capability to detect and characterize shear horizontal modes will expand the utility of inelastic electron scattering, and will introduce an important new dimension to the variety of problems that may be addressed using the technique.

ACKNOWLEDGMENTS

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