High resolution electron energy loss spectroscopy: Explored regions and the frontier

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High-resolution electron energy loss spectroscopy (EELS) is rapidly being developed into one of the more useful techniques for probing physical and chemical phenomena at surfaces. Key elements of the technique include high surface sensitivity, the fact that it is a molecular sensitive rather than an atom sensitive spectroscopy, and the direct relationship that exists between experimental data and important surface parameters. New applications of EELS are currently being explored; these applications will be the primary focus of this paper. Recent work which combines EELS measurements with modeling of surface vibrations based on lattice dynamical calculations has shown that this approach can provide useful insight into structural parameters at surfaces. Other experiments aimed at refining our understanding of EELS scattering mechanisms and the selection rules that govern them have yielded some new and unexpected results which will be discussed. Finally, development of a new generation of EELS spectrometers should eventually produce improvements of two to three orders of magnitude in signal levels as well as more precise control of instrument response. These instruments will open up new applications of the EELS technique in areas including the study of technical surfaces and real time studies of surface reaction kinetics. The new spectrometers will also permit more precise studies of fundamental surface phenomena including electron scattering mechanisms.

I. INTRODUCTION

High-resolution electron energy loss spectroscopy (EELS) is rapidly being developed into one of the more useful techniques for probing physical and chemical phenomena at surfaces. Several key features account for the growing popularity of the EELS technique. One of the most important features is the high surface sensitivity and the fact that all surface species including hydrogen can be probed. Under ideal contributions, present EELS spectrometers are capable of detecting vibrational energies of adsorbed molecules at surface concentrations below 0.001 monolayer. A second important feature of EELS, and of vibrational spectroscopic techniques in general, is that these techniques are sensitive to the molecular nature of the adsorbed surface species. Vibrational energies reflect molecular composition, surface structure and the local molecular level environment, i.e., the surface adsorbate site coordination. A third important feature of EELS, which is also characteristic of the most widely used spectroscopic methods, is that qualitative features of the spectra can lead immediately to an understanding of important structural and chemical properties of atoms and molecules chemisorbed on surfaces.

A few typical examples illustrate these features of EELS. Surface cleanliness can often be checked using EELS more conveniently and at higher sensitivity than with Auger spectroscopy. EELS is quite sensitive to two of the most common residual gases found in surface analysis chambers (CO and H₂), whereas Auger spectroscopy cannot directly detect atomic hydrogen. In many cases, dissociative chemisorption of a molecule can be directly inferred simply from the number of vibrational modes observed in an EELS spectrum. Diagnosis of fragments and intermediates from surface reactions is often possible by recognizing established characteris-

tic EELS modes of CH, OH, CO, and other chemical groups. Isotopic exchange involving deuterium labeled hydrocarbon molecules can be exploited by combining EELS measurements and thermal programmed desorption measurements. Coverage induced shifts in loss peaks can be used to study coverage dependent multiple site adsorption phenomena, and in many cases, where all of the surface vibrational modes can be identified, the adsorption site symmetry can be determined. A specific example of this feature of EELS is presented in the following section. These examples, which illustrate only a few of the many applications of EELS in surface science, should give some appreciation for the usefulness of the technique which accounts for its rapid growth as a spectroscopic method.

The examples just described fall into a particular category of applications which rely only on semiempirical analysis of the spectra to arrive at useful information. In addition to these, new applications of EELS based on a more quantitative approach to the analysis of experimental data are currently being explored. Specifically, applications based on lattice dynamical modeling of vibrational data, full multiple scattering analysis of inelastic electron scattering cross sections, and other sophisticated approaches are being explored. Such approaches generally require large-scale computational exercises as well as significantly expanded efforts to obtain suitable experimental data for analysis.

Initial studies which have combined lattice dynamical modeling with EELS measurements have produced some extremely promising results. A few examples of this approach are described in this paper. These examples illustrate the potential of developing surface vibrational spectroscopy into a direct probe of surface structure.

Recent experimental and theoretical work has also yield-

ed a more thorough understanding of EELS scattering mechanisms, the energy dependence of the inelastic scattering cross sections, and the selection rules that govern them. This work also offers hope of important new applications of the EELS technique.

The goals of the present paper are threefold: (1) to review the evolution of our present understanding of the underlying scattering mechanisms and describe some recent work which is aimed at improving our understanding of EELS scattering mechanisms and the selection rules that govern them; (2) to focus attention on successful efforts which have combined EELS results with lattice dynamical modeling to expand the interpretation of vibrational data beyond the qualitative analysis level; and (3) to attempt to anticipate the future, especially in relation to new applications which will become possible as a result of a more thorough understanding of fundamental mechanisms as well as advances in instrumentation.

II. EXPLORED REGIONS

We begin by reviewing what is known about the basic scattering mechanisms, the selection rules that govern them, and the application of lattice dynamical methods for analysis of vibrational data. We also attempt at the end of this section to briefly assess the current state-of-the-art in EELS instrumentation in relation to the present applications of the technique, and highlight some of the inadequacies which are hindering progress and new applications.

A. Inelastic electron scattering and surface vibrations

The development of high-resolution EELS started during the late 1960's and early 1970's. It was this period of time during which the effect of a surface on the phonon spectrum of crystals was a subject of considerable interest: Laramore and Duke¹ reported a detailed analysis of the temperature dependence of LEED intensities; Maradudin and Wallis,² and Allen, Alldredge, and de Wette³ developed the theory of surface lattice dynamics to a high degree of sophistication; and the first observation of surface vibrational modes of chemisorbed atoms on surfaces was reported by Propst and Piper.⁴ Shortly thereafter, Ibach reported a complete experimental investigation of inelastic electron scattering from ZnO⁵ and Si(111).⁶

In Ibach's experiments, and in work by others which quickly followed, the distribution of the inelastically scattered electrons was observed to the centered around a narrow angular cone along the specular direction. This strongly peaked angular distribution and the well-known shallow penetration depth of low energy electrons in solids indicated that the electrons which suffer vibrational losses are scattered predominantly by surface phonons with a small wave vector, i.e., $q_{\parallel} \approx 0$. The surface phonons clearly produced long range electric fields that extend well beyond the vacuum–crystal interface. The physical origin of the electric field can be viewed as a consequence of the lack of inversion symmetry at the surface which permits the existence of a dipole moment having an effective charge arising from the surface phonons.

Lucus and Sunjic⁸ presented a classical theory of the "dipole" scattering mechanism which was expanded and refined by Evans and Mills⁹ to a quantum mechanical description. Roundy and Mills¹⁰ developed a corresponding quantum mechanical description of inelastic electron scattering of slow electrons for the more general case of large momentum transfer, and explored the dependence of scattering cross sections based on their theory for various force constant models of the surface and near surface regions. These studies showed that the shape of the loss spectrum (energy dependence) is sensitive to changes in atomic force constants near the surface, and suggested that "the study of inelastic electron scattering from surface has the potential of mapping out in great detail the frequency spectrum associated with surface atoms."

These pioneering studies stimulated an explosive growth in the application of EELS in studies of surfaces. Many investigators were attracted into the field and contributed to the development of the technique. Several international conferences 11,12 and a book 13 document this growth. One of the next key developments in the evolution of EELS was a step towards realizing the full potential of the technique for mapping surface phonon bands. Vibrations parallel to the surface can produce charge separation normal to the surface yielding a dipole moment which can be probed in specular scattering geometry based on "dipole" scattering. In addition, in cases where a parallel dipole moment is not completely screened by substrate electrons, 14 inelastic losses can be detected in the large momentum transfer regime.

Off-specular scattering studies of H on W(100) by Willis, 15 and by Ho, Willis, and Plummer, 16 and of $c(2\times2)$ O on Ni(100) by Strong and Erskine 17 and Szeftel et al. 18 have now shown that inelastic scattering cross sections in the large momentum transfer (impact scattering) regime are large enough to effectively probe parallel vibrations. This permits mapping of surface and adsorbate phonon bands.

Figure 1 illustrates the results of extensive EELS measurements of $c(2\times2)$ O on Ni(100). Data points at $k_{\parallel}\neq0$ rely on the impact scattering mechanism to detect loss peaks. Fairly high impact energies (up to a few hundred eV) are required to reach the zone edge and to optimize the scattering cross section. ^{18,19} Simple kinematical scattering laws are the only requirements to obtain the plots of $E(q_{\parallel})$ from the energy and direction of incident and scattered electrons. The ability to map surface phonon bands is responsible for the development of lattice dynamical modeling as a means of analyzing surface vibrational data as discussed later.

B. Cross-section effects and selection rules

Successful observation of use of impact scattering has stimulated additional theoretical efforts aimed at refining the understanding of EELS scattering cross sections and selection rules that govern time. Tong, Li, and Mills²⁰ have developed a formalism which describes EELS impact scattering cross sections over a wide range of energies and scattering geometries. A similar formalism has been developed by Aers et al.²¹ and applied to H on W (100). The formalism of Tong et al. includes an explicit description of the multiple scattering of both incident and scattered electrons from the

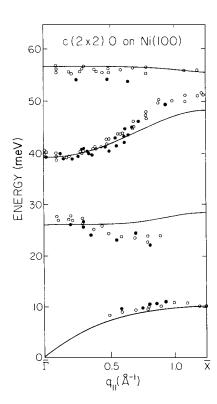


Fig. 1. Surface phonon bands of $c(2\times2)$ O on Ni(100). Experimental data: filled circles, Ref. 17, open circles Ref. 18. Solid lines, calculated phonon bands representing "best fit" to experimental data, Ref. 17. Result of fitting is that oxygen height d=0.92 Å.

substrate/adsorbate system which has permitted realistic theoretical studies of the cross-section dependence on adsorbate bond distances and adsorption sites. These calculations have suggested that precise measurement of inelastic electron differential cross sections could be used to determine the site geometry and test bond distance models. However, comprehensive experimental investigations of these predictions await improvements in electron spectrometers described in the next section of this paper.

The formalism for calculating impact scattering cross sections also contains the basis for postulating a set of impact scattering selection rules which govern the angular dependence of the scattering cross section. These rules predict null scattering along certain high symmetry directions which depend on the polarization of surface modes in relation to that direction. Figure 2 summarizes these selection rules for a simple model chemisorption system which is discussed later.

A refinement of the multiple scattering theory of impact scattering was introduced by Hall, Tong, and Mills²² which includes the effects of the surface image potential. The results of this paper also suggest an interesting breakdown of a pseudoselection rule for large angle scattering.

The predictions of these calculations for impact scattering cross sections have been experimentally observed but not tested in detail. One indication of the validity of the models has been obtained from the work of Xu et al.²³ who have shown that the calculated cross sections of the S_4 and S_6 surface phonons on Ni(100) are in fairly good agreement with experiment. Attempts to directly test the predictive capability of the multiple scattering formalism in the case of

IMPACT SCATTERING SELECTION RULES

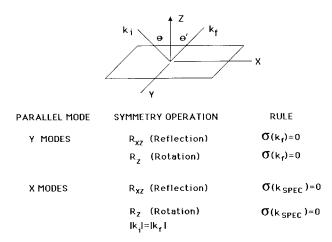


FIG. 2. Selection rules for impact scattering cross sections σ along a high symmetry direction of a surface adsorbate complex (Ref. 20). The xz plane is the scattering plane. R_{xz} represents reflection symmetry around the xz plane, R_z represents twofold rotational symmetry around the z axis. For the given symmetry, modes with eigenvector parallel to the y direction (y modes) have null cross sections for all angles θ_r in the scattering plane, and modes with eigenvector parallel to the x direction (x modes) have null cross section in the specular scattering direction ($\theta_1 = \theta_s$).

simple adsorbates has met with less success as indicated below.

Figure 3 illustrates EELS spectra for β_1 H on W(100)

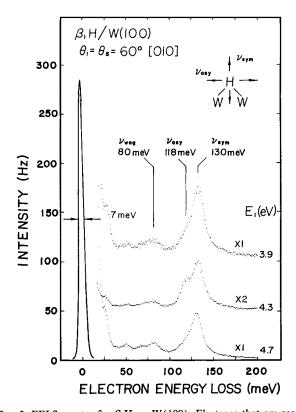


FIG. 3. EELS spectra for $\beta_1 H$ on W(100). Electrons that are scattered specularly at 60° incident angle along the [010] crystal direction spectra for three incident energies E_i are displayed. $E_i = 4.3$ eV corresponds to the condition for the (01) LEED beam to energy parallel to the surface. Corresponding spectra for deuterium exhibit the same three peaks shifted to lower energy by a factor of $\sqrt{2}$.

(the β_1 phase has two atoms per surface unit cell bridge bonded to the W atoms). The three modes, which are apparent in the spectra, correspond to the wag mode $v_w = 80$ meV, the asymmetric stretch mode $v_{\rm asy}=117$ meV, and the symmetric stretch mode $v_{\text{sym}} = 130 \text{ meV}$. The fact that two different parallel vibrational frequencies are observed for the adsorbed H supports the bridge bond assignment. Fourfold coordination of the adsorbed H would yield degenerate parallel vibrational modes. These results, which have been verified by corresponding studies using deuterium and using offspecular scattering geometry, are the first to delineate all three vibrational modes of β_1 H on W(100). Previous studies16 using 25 meV resolution were unable to resolve the 117 meV peak from the strong 130 meV dipole peak, and attibuted a 160 meV peak (which is an overtone of the wag mode) to the asymmetric stretch mode. This is a clear case where improved instrument performance was essential.

The results in Fig. 3 were obtained using novel scattering parameters which were chosen to cause the emergence of the $(0\overline{1})$ LEED beam along the scattering plane. Under these conditions, the dipole cross section is suppressed, as shown in Fig. 4, permitting impact modes to be easily observed. The results displayed in Figs. 3 and 4 contain some very interesting implications which we have not fully investigated. These features are listed below and are described in more detail (the issues are not yet resolved) in some referenced papers which are in press or to be submitted.

(1) The impact modes ($\nu_{\rm asy}$ and $\nu_{\rm wag}$) are observed in specular geometry. Application of the selection rules²⁰ (refer to Fig. 2) to the structure of $\beta_1 H$ on W(100) as it is presently understood yields the prediction that the parallel mode cross sections should vanish. Clearly, many factors

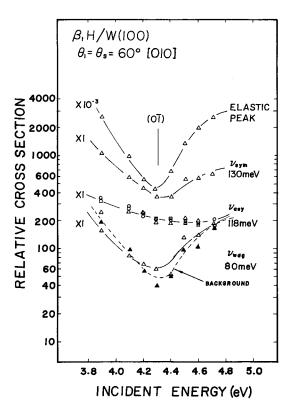


FIG. 4. Relative scattering cross sections for the elastic peak and the three loss peaks as a function of incident energy.

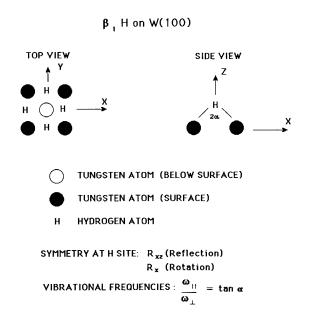


FIG. 5. Illustration of site symmetry of $\beta_1 H$ on W(100). A simple dynamical model (Ref. 13) predicts the ratio of asymmetric stretch frequency to symmetric stretch frequency for a twofold bridge site is equal to $\tan \alpha$, where 2α is the bridge bond angle.

must be considered in relation to the above results, i.e., analyzer acceptance cone, crystal alignment, possible deviations from perfect bridge geometry, etc., but the fact remains that the results raise some very interesting and important questions.

- (2) The ratio of symmetric stretch mode frequency to asymmetric stretch mode frequency is related to the height of an atom above the surface by a simple classical model. Figure 5 illustrates the model for the specific case of a bridge site. The present case is especially easy to analyze because the tungsten to hydrogen mass ratio is very large. Based on the measured values of v_{sym} and v_{asy} , one obtains d=1.74 Å. This distance is quite large compared to the best estimate $(d=1.17 \text{ Å})^{24}$ based on LEED, which isn't expected to work very well for adsorbed hydrogen, and is uncomfortably large based on what one might guess based on simple chemical arguments. Thus, a second interesting question is raised by the data: Why does this simple model apparently breakdown?
- (3) The experimental results suggest the possibility of a new inelastic scattering regime which is based on an electron being trapped in a quasibound state traveling parallel to the surface.²⁵ Incident electrons can couple to this bound state through the same umklapp process which causes a LEED beam to emerge parallel to the surface. Trapped electrons can also couple back into the specular direction by a conjugate umklapp process. The impact scattering cross section would be increased by this mechanism in proportion to the lifetime of the quasibound state. The relatively strong impact scattering cross sections illustrated by Figs. 3 and 4 certainly do not rule out this possibility, but we have not obtained sufficient experimental data and have not analyzed the transmission properties of our analyzer in sufficient detail to verify the bound state hypothesis. For similar reasons, we cannot make any conclusive comments regarding the apparent disagreement between the energy dependence of the

asymmetric stretch cross section and theoretical predictions²² (refer to Fig. 4).

(4) A scattering resonance is observed in the spectra (at $\sim 26 \text{ meV}$). ²⁶ This feature is particularly interesting because we have shown that its appearance and disappearance as a function of temperature and hydrogen coverage is related to the well-known surface structural phase transformation on the W(100) surface. ²⁷

These features for the β_1 H on W(100) serve to illustrate the fact that even on the system which has been most extensively studied using EELS, there are many new phenomena to be explored, and many important issues which must be addressed.

C. Lattice dynamical modeling

A second approach to structure analysis based on EELS is to use lattice dynamical calculations for analysis of experimental data. In this case, rather than making use of the energy dependence of scattering cross sections, which depends on complex multiple scattering calculations, the approach is based on the dynamical behavior of the system. Kinematic scattering laws (conservation of energy and wave vector parallel to the surface) are all that are required to experimentally obtain a complete description of the surface lattice dynamics of an ordered overlayer system. Once $E(q_{\parallel})$, the dispersion of the surface phonon bands along a high symmetry diretion of the surface Brillouin zone has been determined by EELS, it is possible to analyze the results using surface lattice dynamics. Lattice dynamical modeling has been successfully used by Strong et al. to analyze vibrational data for $p(1\times1)$ O on Al(111)²⁸ and $p(1\times1)$ O on Ti(0001)²⁹ to verify the formation of underlayer structures. In the case of $p(1\times1)$ O on Al, the EELS data³⁰ provided striking proof of the existence of a chemisorbed phase more complicated than a single ordered oxygen overlayer. Three dipole active modes were observed at low oxygen coverages up to the point where a $p(1 \times 1)$ chemisorbed layer was reported to exist. A single dipole active mode should have been detected if a unique overlayer site were associated with the $p(1\times1)$ LEED pattern. Lattice dynamical modeling of the data²⁸ verified the simultaneous formation of overlayer and underlayer structures consistent with a $p(1 \times 1)$ structure. and yielded predictions of the scattering strengths (based on predicted vibrational amplitudes) which were in good agreement with the EELS results.

Analysis of the full phonon dispersion of $c(2\times2)$ O on Ni(100) has been used by Rahman et al.³¹ and Strong and Erskine^{17,32} to obtain the oxygen height above the surface. One can view the lattice dynamical modeling method as an *n*-parameter extension of the simple two parameter model which yields d_1 based on the ratio of v_{sym} to v_{asy} (Fig. 5). EELS data for all surface modes and for q_{\parallel} along a particular direction of the two-dimensional Brillouin zone [as shown for $c(2\times2)$ O on Ni(100) in Fig. 1] represent a large number of experimental parameters which must be fit by a correct lattice dynamical model of the surface adsorbate complex.

We have shown¹⁷ that starting with a general slab model for a surface-adsorbate complex, in particular $c(2\times 2)$ O on

Ni(100), and assuming only that the adsorbate site location was known (fourfold hollow site), that precise determination of the adsorbate height is achieved by requiring that the lattice model correctly reproduce the experimentally detemined surface—phonon band structure. In this sense, EELS can be regarded as a structure determination technique similar to LEED. From EELS, one obtains in addition, the force constants required to describe the dynamical system.

The general applicability of this method as a structural probe will not be established until many more adsorbate systems have been studied. There is some indication that the excellent results for $c(2\times2)$ O on Ni(100) is not accidental; the method has now been successfully applied to $c(2\times2)$ S on Ni(100).³³ These results suggest that lattice dynamical modeling of EELS data has the potential of being developed into a very useful structural tool.

Before continuing on to the next topic, it is important to point out that inelastic scattering of He atoms has also been developed into a powerful tool for studying surface phonons. Recent articles by Toennies, Lambert *et al.*, and Sibener describe the advances and results in this field.³⁴

D. Dielectric models and EELS

Before discussing new applications of EELS, we must at least mention work in a few other areas which are within the scope of the present discussion, but which cannot be covered because of space limitations. Important work is being done in areas related to the dielectric response at a surface, ³⁵ temperature dependencies, ^{36,37} vibrational linewidths and damping mechanisms, ^{37,38} and other areas closely related to surface vibrational spectroscopy. These studies will also help advance the use of EELS methods by providing a more thorough understanding of the fundamental phenomena which govern linewidths, damping mechanisms, and other features of EELS.

E. Current generation EELS instruments

We conclude this section with a very brief assessment of the current generation EELS instruments. Current state-ofthe-art single energy channel EELS spectrometers are able to achieve 3.5 meV FWHM energy resolution at 1.5×10^{-10} A target current and signal levels of $\sim 10^7$ counts/s for elastic reflection from a good single crystal sample.³⁹ The best resolution achieved by electron scattering to date appears to be in the neighborhood of 2.5 meV FWHM. These performance levels are achieved at energies where dipole losses are typically measured (i.e., below 10 eV impact energy), and are quite adequate for probing energy losses at low energies in specular scattering geometry. Peak shifts significantly smaller than the instrument resolution can be detected by the spectrometer having extremely good absolute stability, and these instruments are competitive in many respects with optical methods. There are, however, certain inadequacies in present generation EELS instruments, particularly in respect to making measurements related to the present discussion.

III. THE FRONTIER

Advances in a field of research can be stimulated by an unanticipated breakthrough or can occur as a result of persistent progress based on more effective application of accumulated knowledge. In this section an attempt is made to anticipate some of the future applications of EELS and outline some of the steps needed to advance the state-of-the-art.

A. New instrumentation

It is clear that significant advances in instrumentation is one of the most critical next steps required to advance the field. Present generation instruments have evolved to study primarily dipole scattering. Low counting rates associated with impact scattering cross sections and the need to operate spectrometers at several hundred volts in experiments which map phonon bands are two factors which must be considered in future instruments intended for such applications. A third factor is the difficulty of determining accurate scattering cross sections. Most existing EELS instruments do not incorporate the required angle-defining apertures, and no EELS spectrometer transmission function appears to have been well characterized by ray tracing even though it appears feasible. 19 These limitations render difficult the type of experiments required to obtain scattering cross sections and surface phonon band dispersion. Significant improvements in EELS spectrometers are currently feasible based on existing electron optics technology. Multichannel detection in an electron analyzer is well understood. Parallel energy detection using commercially available image detectors should yield an improvement of 50-100 in detection efficiency.⁴⁰ Recent work on electrostatic lenses⁴¹ provides a good basis for designing a more efficient lens system with large retardation/acceleration ratios and well-characterized transmission properties.

Lens designs which incorporate more than a pair of input and output lens elements (which are common in existing EELS spectrometers) will be required. Optimum image characteristics cannot be achieved by a single pair of lenses in systems which require retardation ratios of the order of 1000 to 1. Some new EELS instrument designs are already being tested. 42,43 Although it appears that it will be much more difficult to vastly improve the performance of electron monochromators, additional effort to pinpoint the fundamental limiting factors in high current monochromators is justified. Recent work at the National Bureau of Standards⁴⁴ has shown that significant improvements may be possible in high current monochromators based on the performance of a negative electron affinity GaAs source. Currents in excess of 1 μ A at 31 meV FWHM resolution have been achieved. This is at least one order of magnitude above the current obtained from conventional sources at the same energy resolution. Of course, the added flux will be useless if the fundamental limitation of EELS monochromators is associated with space charge at the exit slit or some similar effect which is not source related.

B. Technical surfaces

One of the most promising applications of EELS is the study of chemical processes at technical surfaces such as polycrystalline films and supported metal catalysts. These applications will require more efficient spectrometers because of low signal levels associated with poor reflectance properties of the surface. Counting rates for loss peaks observed from technical surfaces will be comparable to offspecular measurements of crystal surfaces.

C. Chemical dynamics

Assuming that significant improvements in spectrometer performance can be achieved (a factor of 10³ is not unreasonable), the observation of chemical processes at surfaces which occur on a time scale of milliseconds will be feasible. Experiments which combine EELS with pulsed molecular beam excitation to study surface chemical dynamics are already being conducted by Ho at Cornell, and by Ellis and coworkers at AT&T Bell Labs.

IV. CONCLUSION

This paper has attempted to highlight some of the developments and some recent investigations in the field of EELS which are related to scattering mechanisms and the use of advanced techniques for data analysis based on lattice dynamics and scattering cross-section calculations. Even within the limited scope of the stated objectives of the paper, a complete accounting of the work has been impossible within the length limitations imposed here. However, at least two points should be clear from the discussion. First, EELS has emerged as one of the most important probes of physical and chemical processes at surfaces. Second, in spite of the very rapid and impressive development of the technique, there remain many opportunities for advancing the state-of-theart, in both applications and fundamental understanding of the underlying physical phenomena. The subfield of EELS should continue to be one of the most interesting and dynamic areas of surface science for many years.

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¹G. E. Laramore and C. B. Duke, Phys. Rev. B 2, 4783 (1970).

²A. A. Maradudin and R. F. Wallis, Phys. Rev. 148, 945 (1966).

³R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. B 4, 1648, 1661, 1682 (1971).

⁴F. M. Propst and T. C. Piper, J. Vac. Sci. Technol. 4, 53 (1967).

⁵H. Ibach, Phys. Rev. Lett. **24**, 1416 (1970).

⁶H. Ibach, Phys. Rev. Lett. 27, 253 (1971).

⁷Early review articles trace the development of the EELS technique. H. Froitzheim, in *Topics in Current Physics*, edited by H. Ibach (Springer,

- New York, 1976), Vol. 4; D. L. Mills, Prog. Surf. Sci. 8, 143 (1977).
- ⁸A. A. Lucas and M. Sunjic, Phys. Rev. Lett. 26, 229 (1971).
- ⁹E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1972).
- ¹⁰V. Roundy and D. L. Mills, Phys. Rev. B 5, 1347 (1972).
- ¹¹ Vibrations at Surfaces, edited by R. Caudano, J. M. Gilles, and A. A. Lucas (Plenum, New York, 1982).
- ¹² Vibrations at Surfaces, edited by C. R. Brundle and H. Morawitz (Elsevier, Amsterdam, 1983).
- ¹³H. Ibach and D. L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations (Academic, New York, 1982).
- ¹⁴D. Sokcevic, Z. Lenac, R. Brako, and M. Sunjic, J. Phys. B 28, 273 (1977).
- ¹⁵R. F. Willis, Surf. Sci. 89, 457 (1979).
- ¹⁶W. Ho, R. F. Willis, and E. W. Plummer, Phys. Rev. Lett. **40**, 1463 (1978); Phys. Rev. B **21**, 4202 (1980).
- ¹⁷R. L. Strong and J. L. Erskine, Bull. Am. Phys. Soc. 27, 372 (1982); Phys. Rev. Lett. 54, 346 (1985).
- ¹⁸J. M. Szeftel, S. Lehwald, H. Ibach, T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. Lett. **51**, 268 (1983).
- $^{19}R.\ L.$ Strong and J. L. Erskine, Rev. Sci. Instrum. 55, 1304 (1984).
- ²⁰S. Y. Tong, C. H. Li, and D. L. Mills, Phys. Rev. Lett. 44, 407 (1980); Phys. Rev. B 24, 806 (1981).
- ²¹G. Aers, J. B. Pendry, T. B. Grimley, and K. L. Sebastian, J. Phys. C 14, 3995 (1981).
- ²²B. M. Hall, S. Y. Tong, and D. L. Mills, Phys. Rev. Lett. **50**, 1272 (1983).
- ²³M. L. Xu, B. M. Hall, S. Y. Tong, M. Rocca, H. Ibach, S. Lehwald, and J. E. Black, Phys. Rev. Lett. 54, 1171 (1985).
- ²⁴M. A. Passler, B. W. Lee, and A. Ignatiev, Surf. Sci. 150, 263 (1985).
- ²⁵E. G. McRae, Rev. Mod. Phys. 51, 541 (1979).
- ²⁶J. P. Woods and J. L. Erskine, J. Vac. Sci. Technol. (these proceedings).
- $^{\rm 27} For a recent review, refer to: A. J. Melmed and W. R. Graham, Appl. Surf.$

- Sci. 11/12, 470 (1982).
- ²⁸R. L. Strong, B. Firey, F. W. de Wette, and J. L. Erskine, Phys. Rev. B 26, 3483 (1982).
- ²⁹R. L. Strong and J. L. Erskine, J. Vac. Sci. Technol. A 3, 1428 (1985).
- ³⁰J. L. Erskine and R. L. Strong, Phys. Rev. B 25, 5547 (1982).
- ³¹T. S. Rahman, D. L. Mills, J. E. Black, J. M. Szeftel, S. Lehwald, and H. Ibach, Phys. Rev. B 30, 589 (1984).
- ³²R. L. Strong and J. L. Erskine, Phys. Rev. B 31, 6305 (1985).
- ³³S. Lehwald, M. Rocca, H. Ibach, and T. S. Rahman, Phys. Rev. 31, 3477 (1985).
- ³⁴J. P. Toennies, J. Vac. Sci. Technol. A 2, 1055 (1984); W. R. Lambert, P. L. Trevor, R. B. Doak, and M. J. Cardillo, *ibid*. 2, 1066 (1984); S. Sibener (to be published).
- ³⁵J. A. Stroscio and W. Ho, Phys. Rev. Lett. **54**, 1573 (1985); S. Andersson and B. J. N. Persson, *ibid*. **50**, 2028 (1983).
- ³⁶N. J. DiNardo, J. E. Demuth, W. A. Thompson, and Ph. Avouris, Phys. Rev. B 31, 4077 (1985).
- ³⁷J. W. Gadzuk, Chem. Phys. Lett. **80**, 5 (1981); M. Persson and B. Hellsing, Phys. Rev. Lett. **49**, 662 (1982).
- ³⁸Y. J. Chabal, Phys. Rev. Lett. **55**, 845 (1985); J. Vac. Sci. Technol. (these proceedings).
- ³⁹L. L. Kesmodel, J. Vac. Sci. Technol. A 1, 1456 (1983).
- ⁴⁰F. Hadjarab and J. L. Erskine, J. Electron. Spectrosc. Relat. Phenom. 36, 227 (1985).
- ⁴¹G. Martinez, M. Sancho, and F. H. Read, J. Phys. E 16, 632 (1983); G. Martinez and M. Sancho, *ibid.* 16, 625 (1983).
- ⁴²S. D. Kevan and L. H. Dubois, Rev. Sci. Instrum. **55**, 1604 (1984).
- ⁴³R. Frauchy and H. Ibach, Surf. Sci. 155, 15 (1985).
- ⁴⁴C. S. Fegerle, D. T. Pierce, A. Seiler, and R. J. Celotta, Appl. Phys. Lett. 44, 866 (1984).