Electron energy loss spectroscopy; history and related matters

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ABSTRACT This paper begins with some historical remarks regarding the author’s early interest in the use of electron energy loss spectroscopy to probe dynamical phenomena on crystal surfaces. We then discuss the physical nature of the interactions responsible for vibrational and spin waves losses, with attention to their role in related phenomena.

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1 Introductory remarks

Let me begin by remarking that I was very pleased indeed to receive the invitation to write for this special volume devoted to my long-time colleague and collaborator, Prof. H. Ibach. Our interactions have extended over many years now, and our conversations have ranged not only on matters directly related to our collaborative research, but on many other aspects of physics as well. I continue to be astonished at his deep understanding of a very wide range of phenomena in condensed matter physics and chemistry as well. As I think back over the many times we have discussed physics, I realize how much I have been taught by this remarkable person.

I would like to begin this paper with some comments on my own early involvements in theoretical aspects of electron energy loss spectroscopy. When I joined the faculty of the University of California at Irvine, my two senior colleagues A.A. Maradudin and R.F. Wallis were engaged in theoretical studies of diverse aspects of lattice vibrations at crystal surfaces. This was very early in my career, and at that time the field we now call surface lattice dynamics did not exist; the Maradudin/Wallis papers of the early to mid-1960s, written a bit before my arrival at Irvine, formed a unique contribution to the literature. I should also remark that at this time, a senior and well-known theorist spoke to me regarding what I might do in the near future to further my career. He commented that my two new colleagues were very able indeed, but he found it strange that they were writing all these papers on surface atom vibrations. His advice was to avoid this field since it would never be possible to measure anything whatsoever related to the vibrational properties of the outer layer of atoms on crystal surfaces. For this reason, he felt this was an inappropriate field for a young theorist to pursue, since the issues addressed by theory were of purely academic interest only.

The early Maradudin/Wallis papers now stand as seminal contributions to a large, active and important field. As a consequence of the very high resolution, momentum resolved electron loss studies of surface lattice vibrations pioneered by H. Ibach and his colleagues, along with the inelastic He scattering developed by J.P. Toennies, we now have a very large volume of fully quantitative data on surface phonons and surface vibrations on a very large number of clean and adsorbate covered surfaces. We now understand, in great detail, the nature of atomic vibrations in the outermost atomic layer of matter along with the physics which control the interatomic forces between atoms and molecules in crystal surfaces. It is impressive to scan the recent review article by Heid and Bohnen [1], which summarizes the current experimental and theoretical status of the field of surface lattice dynamics. At the time of this writing, the use of spin polarized electron loss to probe spin waves on magnetic surfaces is in its early stages [2], and we can expect this to evolve into a fascinating new field that will teach us much about magnetism at surfaces, and in ultrathin film structures.

After my arrival at Irvine, I began to study the papers written by my two colleagues and I became quite intrigued by both the theoretical techniques they had developed, and also with the nature of vibrational motions at surfaces. It was interesting to inquire how one might probe dynamics in the outer layer of a crystal, when the outermost layer sits on top of the remainder of the semi infinite material. At that time, my colleagues Maradudin and Wallis had developed the theory of the thermal diffuse scattering experienced by a particle which reflects off the surface, sampling only its outer layer [3]. The theory could be compared with the experimental studies of the Webb group [4], in which the variation of the intensity of thermal diffuse scattering with wave vector transfer was measured for electrons reflected from a silver surface.

It was clear, on physical grounds, that thermal diffuse scattering had its origin in the excitation of phonons on the surface by the probe particle. If one envisions resolving the energy of the scattered electrons which contribute to the thermal dif-
fuse background, one can directly study both surface phonons, and also obtain information on the nature of bulk phonons as they reflect off the surface. What is called for is an experiment which employs highly monoenergetic electron beams, and then one must resolve the energy loss spectrum of the electrons which contribute to the thermal diffuse background. This seemed like a rather far-fetched thing to pursue in the laboratory in that era, but at about that time very early electron loss studies of the vibrations of molecules adsorbed on tungsten surfaces were published by Propst and Piper [5]. While the resolution in these data was quite poor, nonetheless vibrations on crystal surfaces were observed.

With these thoughts in mind, in the late 1960s, my graduate student V. Roundy and I set off to explore the nature of energy loss spectrum that would result from such a measurement. A central issue in our minds was the relative importance of surface phonons, and bulk phonon contributions to the spectrum of an electron which scatters off primarily the surface layer. Our study of a model (100) surface of an fcc crystal showed that both bulk and surface modes leave their imprint on the spectrum [6], for large angle deflections now referred to as impact scattering. Our modeling of the electron phonon matrix element was very crude indeed, it should be remarked.

Quite by accident, I suppose, the first measurements of surface phonon dispersion on a crystal surface which extended to the surface Brillouin zone boundary were carried out by the Ibach group on Ni(100) [7], a (100) surface of an fcc material whose surface lattice dynamics can be modeled quite nicely by the approach used by Roundy and myself [6]. These remarkable data followed the dispersion curve of the Rayleigh surface phonon from the very low frequency of 25 cm$^{-1}$ near the zone center, out to the surface Brillouin zone boundary. It should be remarked that subsequent experiments and theoretical analyses verified two key predictions of the paper by Roundy and myself. One is that on this surface, a surface phonon exists in the gap of the projected bulk phonon density of states on the (100) surface of the fcc crystal, and this should appear clearly in the electron loss spectrum. The mode was indeed found shortly after the initial studies of the Rayleigh surface phonon on Ni(100) [8]. It is also now clear that bulk phonons which excite surface atom vibrations as they reflect off the surface influence the loss spectrum importantly [9]. To understand this in quantitative terms, it was necessary to have in hand a full and complete theory of the phonon excitation process, for large angle scatterings from the surface in the impact regime. A formalism which addressed this area was developed and implemented by S.Y. Tong and the present author and our collaborators [10–13]. This formalism has been applied with considerable quantitative success to a number of clean and adsorbate covered surfaces. The analysis in [9] is an example of such an application.

Before the calculations by Roundy and myself were completed, the remarkable and now classic experimental study of the surface phonons on ZnO reported by Ibach appeared [14]. The data was astonishing. The signal was strong, by virtue of the fact that small angle dipole scattering [15] was responsible for the signal. The key issue is that the experiment demonstrated for the first time that one could achieve energy resolution sufficient to resolve phonons on the surface of crystals. I was very excited personally when I saw this paper. H. Ibach and I met for the first time shortly after its publication. This was the beginning the many years of collaboration and interaction referred to in the opening paragraph.

In the remainder of this paper, I wish to discuss aspects of the interaction responsible for exciting phonons on crystal surfaces. Emphasis will be placed on the physical pictures which underlie these interactions, and some consequences of these interactions.

## 2 The physics of surface phonon excitation and some consequences

As remarked in Sect. 1, the mechanism responsible for excitation of the surface phonons on ZnO [14] is referred to as the dipole mechanism. As the ions near the surface of this ionic crystal vibrate, they create macroscopic electric fields which extend into the vacuum above the crystal. If the wavelength of the mode is quite long, or its wave vector small, then the field is long ranged and extends far into the vacuum above the crystal. The strong signals found in dipole scattering are the consequence. One may appreciate the long ranged nature of these fields from an elementary argument. If the two dimensional wave vector of the surface phonon is $Q_{||}$, then the electrostatic potential above the crystal sensed by the beam electron must have the spatial form $\phi(z) \exp[iQ_{||} \cdot r]/z$ where $z$ is the coordinate normal to the surface, and the subscript $//\,$ refers to the projection of a vector onto the plane parallel to the surface. The potential above the crystal must satisfy Laplace’s equation, so we must have $\phi(z) = \phi_0 \exp[-Q_{||} z]$. Hence long wavelength modes produce fields which are very long ranged in space, above the crystal. Theory [15] shows that the dipole mechanism produces strong inelastic scattering of electrons which emerge very close to the specular (or to a Bragg) direction. The “dipole lobe” typically responsible for the loss has an angular diameter of roughly $\hbar \omega_{ph}/2E$ (in radians), where $\omega_{ph}$ is the frequency of the phonon involved in the loss process, and $E$ is the energy of the electrons in the beam.

Clearly as $Q_{||}$ increases, the potential just described becomes localized to the surface so that as one moves out into the surface Brillouin zone, a full microscopic theory of the excitation process is required. Large angle scatterings outside the small angle dipole regime are referred to as impact scattering. As remarked in Sect. 1, a description based on multiple scattering theory has been developed to address this regime [10–13], and this has proved quite successful in the quantitative sense.

We wish to return to the topic of dipole scattering, and comment on some consequences of the macroscopic electric fields described above. Dipole scattering was first discussed as the mechanism responsible for surface phonon excitation on ionic crystals. However, the mechanism enters into the discussion of the excitation of diverse entities near crystal surfaces. Suppose we think of the semi-infinite crystal as simply a collection of charges, those of the nuclei associated with the various ions, and also of the electrons bound to the ions or moving about the crystal if we have a metal in mind. There are necessarily thermodynamic fluctuations in the charge density occurring in the crystal at all times. We can write the fluctuating component of the charge density as $\delta q(r, t)$. This may be Fourier analyzed with respect to the spatial coordinates paral-