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HIGH RESOLUTION ELECTRON ENERGY LOSS STUDIES OF SURFACE VIBRATIONS

Final Report

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L.L. Kesmodel

Indiana University

Bloomington, IN 47405

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ABSTRACT

This document summarizes technical progress made on "High Resolution Electron Energy Loss Studies of Surface Vibrations" (DE-FG02-84ER45147). The project was concerned with the measurement of surface vibrational waves (phonons) on a variety of materials, in particular the dispersion of these waves at short wavelengths. The principal experimental method employed was high-resolution electron energy loss spectroscopy (EELS) at an energy resolution of ~ 5 meV (40 cm^{-1}) and momentum resolution of $\sim .02 Å^{-1}$. New experimental information on a variety of metals, overlayer structures, ultrathin films and copper oxide materials were obtained as summarized in the document.

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SUMMARY OF PROGRESS

An experimental program for new measurements of surface phonon dispersion on a variety of materials was initiated in our laboratory in 1984 and received Department of Energy support under Grant No.DE-FG02-84ER45147. The principal experimental method employed for these studies was high-resolution electron energy loss spectroscopy (EELS). Information on surface phonons is basic to our understanding of the surface dynamics of materials and the nature of forces leading to surface relaxation, reconstruction and the modification in interatomic forces due to the adsorption of gases or thin films. Surface vibrations play a critical role in desorption and diffusion phenomena and in many materials applications such as acoustic wave devices and the technology of heat transfer across interfaces. The surface lattice dynamics is, of course, intimately connected with surface electronic and geometric structure.

Since we embarked on this program there has been marked progress in the field. The techniques of inelastic He scattering and EELS have proven to be important and quite complementary methods for probing the surface phonon structure.

Published work from our laboratory is enumerated in the accompanying References Cited [P1–P22] and includes the following materials:

— clean copper (100), copper (111)

— copper (100) with adsorbed nitrogen, oxygen and sulfur overlayers

— clean aluminum (100)

— ultrathin films of nickel and cobalt on Cu (100)

— adsorbate systems O/Ni/Cu (100) and O/Co/Cu (100)

— aluminum on Si (111)

— high T_c cuprates: $Bi_2Sr_2CaCu_2O_8$, $YBa_2Cu_3O_7$

— clean Pd (100)

— clean Ag (111)

To place this work in context we note that the He scattering measurements were largely restricted to Rayleigh mode measurements and resonance structure. Although the He data was taken at higher resolution the data often was not available at or near the zone boundary nor was any data obtained on "gap" modes (such as S_2 in Fig. 1). As is well-documented

in the literature [P4,P7] our data on Cu (111) exhibited all important modes, including the gap mode S_2 and was pivotal in resolving the issue of "lateral force constant softening" (sometimes referred to as the Bortolani-Mills Paradox) on the (111) surfaces of the noble metals. Our results indicated only a modest ($\sim$ 15 %) softening of the intralayer force constant in Cu (111) and were in sharp contrast to the model advanced by Bortolani and co-workers [1] which purported to explain the surface lattice dynamics of Cu, Ag and Au (111) surfaces in terms of dramatic intralayer force constant softening. Recent data we have obtained for the gap mode on Ag (111) is consistent with our interpretation for Cu (111) [P22]. Our phonon measurements on Cu (100) and Al (100) have also been crucial to the critical evaluation of first principles lattice dynamical calculations [P13,2].

We reported measurements of surface phonon dispersion for thin films of nickel on Cu (100) in 1989 [P8]. Our data provided the first evidence for so-called "film modes", corresponding to vibrational modes localized primarily in the overlayer film and earlier predicted in lattice dynamic calculations of Tong *et al.* [3]. The modes are expected to be a general feature of phonon dispersion in ultrathin films.

In more recent work on very different materials we have reported the surface phonon spectra of the high T_c materials $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi 2:2:1:2) and $YBa_2Cu_3O_7$ (Y 1:2:3). These results include three experimental papers dealing with surface phonon spectra and related issues [P15,P17,P18] and a theoretical paper, in collaboration with D.L. Mills, which presents explicit calculations on the Bi 2:2:1:2 material [P19]. Taken together, these results provide rather definitive evidence that the *bona-fide* EELS spectra of these materials exhibit only phonon excitations, as opposed to energy-gap features [4,5].

Work in the final year of the grant has dealt with phonon dispersion measurements on Ag (111) [P22], Pd (100) [P20] and adsorption of H_2O on the Bi 2:2:1:2 material [P21]. Reprints of these recent studies [P20–P22] are appended to this report.

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FIGURE CAPTIONS

Fig. 1. Experimental and theoretical dispersion curves for surface and resonance modes on Cu(111). The experimental data are indicated by open circles and calculations by solid lines. The bulk mode boundaries are shown as cross-hatched curves [(after M.H. Mohamed, L.L. Kesmodel, B.M. Hall and D.L. Mills, *Phys. Rev. B* **37**, 2763 (1988).].

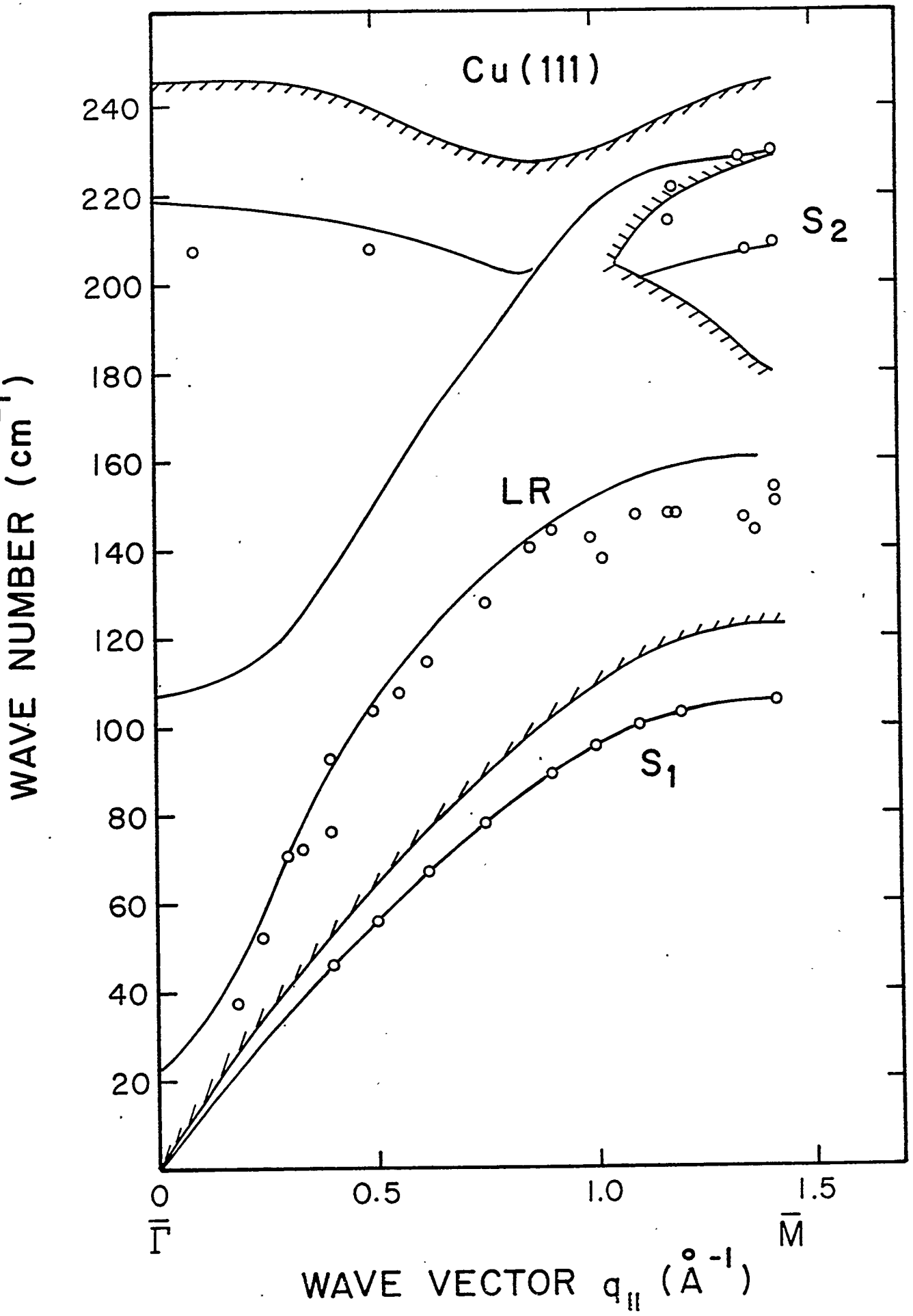
Cu (111)
240
220
200
180
160
140
120
100
80
60
40
20
WAVE NUMBER (cm^{-1})
S_2
LR
S_1
0
0.5
1.0
1.5
$\bar{\Gamma}$
$\bar{M}$
WAVE VECTOR $q_{\parallel}$ (Å^{-1})

Figure 1

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Surface phonon dispersion along $\overline{\Gamma}\overline{X}$ on Pd(100)

Lieming Chen, L.L. Kesmodel *

Department of Physics, Indiana University, Bloomington, IN 47405, USA

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Abstract

High resolution electron energy loss spectroscopy was used to measure the dispersion of the Rayleigh wave along the ⟨110⟩ direction on the Pd(100) surface. It was found that the phonon frequency (2.7 THz) at zone boundary was lower than that calculated by the slab method using bulk force constants (3.0 THz). The result is anomalous from that investigated at $\overline{X}$ on other fcc transition metal surfaces. The experimental data can be fit by a considerable softening (40%) of the surface interlayer force constant. The phonon softening is qualitatively in agreement with the LEED analysis which revealed a surface expansion by 3% instead of the inward relaxation found on most fcc (100) transition metal surfaces.

1. Introduction

Surface phonons have been intensively studied both experimentally and theoretically. The phonon dispersion has been measured on clean and adsorbate covered metal surfaces by inelastic He-atom scattering and high resolution electron energy loss spectroscopy (HREELS). The experimental data are usually different from theoretical results calculated according to the bulk force constants. For most fcc transition metal (100) surfaces investigated so far, the phonon frequencies of the Rayleigh wave near the surface zone boundary $\overline{X}$ or $\overline{M}$ are significantly higher than the frequencies calculated by slab models using bulk force constants. To fit the experimental data, the force constant k_{12} between the atoms in the surface layer and their nearest neighbors in the layer below or the force constant within the first layer has to be increased. For Cu(100) or Ni(100), an increase of 20% of the force constant k_{12} between the first and second layer was found [1–3]. The surface force constant stiffening is related to the contraction of the first and second layer spacing, which is 3.2% for Ni(100) and up to 2% for the Cu(100) as revealed by ion scattering experiments [4] and LEED analysis [5], respectively. In the case of Ag(100), no significant deviation from the bulk force constants has been observed (k_{12} increased by only 5%) [6], with slightly inward relaxation of 1.3% [7]. The increase of the force constants near the fcc (100) surface was thought to be a general phenomenon, because the first interlayer spacing contraction is usually observed or theoretically predicted on fcc (100) surfaces.

Recently, the anomalous multilayer relaxation for Pd(100) has been found by Quinn et al. from LEED analysis [8]. The interlayer spacing for Pd(100) is an expansion by 3% instead of a contraction. This result contradicts the trend on fcc (100) surfaces and may suggest some new physical mechanism. Motivated by this anomalous phenomenon, we have measured

* Corresponding author. Fax: +1 812 855 5533.

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