**HIGH RESOLUTION ELECTRON ENERGY LOSS
STUDIES OF SURFACE VIBRATIONS**

Progress Report 1993

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ABSTRACT

New experimental investigations of surface vibrational properties of materials with high-resolution electron energy loss spectroscopy (EELS) are reported. This document summarizes progress over the last three year project period on surface phonon measurements on copper (001); silver (111); ultrathin magnetic films ; aluminum on silicon (111); and copper-oxide based superconductors.

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A. SUMMARY OF RESEARCH

Introduction

This project is devoted to new experimental investigations of surface vibrational properties on clean metal, semiconductor and superconductor surfaces. Adsorbed layers including metal films on these materials have also been studied as part of the project. The principal experimental method employed for the measurement of surface phonon excitations and their dispersion is high-resolution electron energy loss spectroscopy (EELS). This section gives an overview of progress made during the current three year project period from November 1, 1990 to the time of this writing. More details for projects which are continuing are given in the renewal proposal which accompanies this document. Publications are listed in the bibliography, and those which have not yet appeared in print are appended to this report.

Copper-Oxide Based High Temperature Superconductors

High-resolution EELS is becoming increasingly used to study the Cu-O-based high temperature (high T_c) superconductors [1-2]. EELS is highly sensitive to the first few atomic layers, allowing in principle measurements of the superconducting energy gap and other excitations (phonons, plasmons) which may be associated with superconductivity on a very localized scale. Furthermore, the momentum carried by the electrons enables EELS to probe a range of momentum space not accessible with infrared spectroscopy.

We have undertaken a study of surface phonons and other low-energy excitations on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi:2:2:1:2) single crystals and have also recently begun similar measurements on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y:1:2:3) single crystals. This study necessitated several equipment modifications, detailed in a later section, predicated by the need to achieve

low temperatures ($\sim 45\text{K}$) and to cleave these samples in ultrahigh vacuum (UHV). Most of the Bi:2:2:1:2 samples were acquired in a collaboration with Dr. J.E. Demuth and Dr. D.B. Mitzi of the IBM Research Division and some samples were provided by Dr. W.C. Lee and Dr. D.M. Ginsberg of the University of Illinois.

We recently reported initial results of new measurements of surface phonons on the Bi:2:2:1:2 samples [3]. The surface phonons occur at 50 meV (400 cm^{-1}), 80 meV (645 cm^{-1}), and 26 meV (210 cm^{-1}) for small momentum transfer ($\bar{\Gamma}$ of Surface Brillouin Zone (SBZ)). These modes have been interpreted as surface analogs of bulk optical phonons, i.e. Fuchs-Kliwer modes, although definitive assignments have not yet been made. The temperature dependence of the frequency of these modes in the range from 45K to 146K appears to be weak, although further work on this issue and the temperature dependence of linewidths needs to be addressed as discussed in the renewal proposal.

We have also recently obtained the first surface phonon data on the Y:1:2:3 superconductor as will be reported in the near future [4].

Surface Phonons on Cu (001), Ag (001) and Ag (111)

A collaborative study with S.Y. Tong, K.M. Ho, K.P. Bohnen and co-workers was completed for (001) surfaces and provides a very satisfactory explanation of the surface phonon dispersion in the context of first principle phonon calculations [5]. In this work we reported the first measurements of the gap mode S_6 at $\bar{X}$ in the SBZ for Cu (001).

We have also obtained new EELS data on surface phonon dispersion on Ag (111) wherein the gap mode (S_2 at $\bar{M}$) has been measured for the first time. However, we have withheld publication until a satisfactory comparison with theory (collaboration with S.Y. Tong) can be achieved.

Surface Phonons on the Al/Si(111) System

In 1991 we reported measurements of phonon excitations associated with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of aluminum adsorbed on Si (111) [6]. We also identified phonons associated with higher coverage structures of Al $((\sqrt{7} \times \sqrt{7})R19.1^\circ$ and (7×7)). This study was restricted to zero momentum transfer ($\bar{\Gamma}$) and it was found that certain phonon energies were in agreement with calculations by Northrup [7]. Recently, we have measured the dispersion of these modes along a high symmetry axis ($\bar{\Gamma}\bar{K}$) of the SBZ [8]. We have shown that by use of force constants from the *ab initio* electronic structure calculation of Northrup it is possible to account for the mode dispersion in a semi-quantitative way, with no adjustable parameters. These results provided an encouraging test of the electronic structure calculation and illustrated the usefulness of simple lattice dynamical models.

Ultrathin Magnetic Films

In 1989 we reported the first observation of localized film modes for ultrathin epitaxial films (nickel on a copper (001) substrate) [9]. There is strong current interest in the structure and magnetic properties of such films. In 1990–91 we expanded on this study with further data and a theoretical analysis [10]. The analysis showed substantial softening of the force constants in the nickel film compared to bulk values. The analysis also showed the sensitivity of the EELS cross-sections to geometrical parameters of the film.

In a related study, we were able to correlate the low frequency phonon modes of oxygen adsorption on ultrathin films of cobalt and nickel on a copper (001) substrate with the film growth mechanism [11]. Results for nickel indicated rather ideal growth whereas the spectra for cobalt were more complex, indicating the presence of cobalt clusters at coverages below two monolayers.

Equipment Development

Substantial modifications were made to the two UHV Systems which house the EELS spectrometers employed in this research. For the high T_c superconductor studies several modifications were required. The system was fitted with a liquid-helium cooled sample holder which can be rotated about a vertical axis (polar rotation) and translated in three orthogonal directions. Furthermore, the sample can be transferred from atmosphere to UHV and cleaved under UHV conditions after mounting on the sample holder. Under these conditions a sample temperature of $\sim 45\text{K}$ can be reached, i.e., well below the typical superconducting transition temperature of $\sim 90\text{K}$.

A second UHV system has been primarily used for the phonon dispersion measurements on metals and ultrathin films. The system employs a spectrometer which has a fixed angle between the analyzer and monochromator. Off-specular measurements necessary for dispersion are accomplished by rotations of the sample about a vertical axis, which in this system is offset from the primary rotation axis of the sample manipulator. Equipment modifications have involved the re-design and replacement of the old sample holder with a device which gives more precise control of the sample rotation and which also permits transfer of the sample from ambient to UHV conditions.

B. PERSONNEL

Graduate research assistant Lieming Chen was supported during the current grant period and is continuing on the project for his doctorate degree. Prasad Akavoor has received partial support and is expected to receive his doctorate in the summer of 1993. Dr. Robert Phelps has been supported full time as a postdoctoral associate since December of 1991.

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