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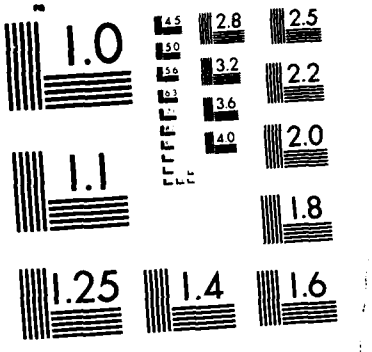

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STRUCTURE-INDUCED SURFACE VIBRATIONAL RESONANCES ON METAL SURFACES

by

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Ithaca, NY 14853

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STRUCTURE-INDUCED SURFACE VIBRATIONAL RESONANCES ON METAL SURFACES

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ABSTRACT

A new class of surface vibrational resonances are shown to exist on surfaces having a non-monotonic bulk phonon dispersion as the result of their particular geometric structure. These resonances have previously been observed by electron energy loss spectroscopy on the (110) surfaces of Cu and Ni ~~(ref. 1)~~, and analysis based on surface lattice dynamics of measurements on the Al(110) and the Fe(111) surfaces are now reported. The resonance is observed on Fe but not on Al.

INTRODUCTION

Possible relations between the geometric structure of the crystal surface and the accompanying surface vibrational modes have attracted a lot of attention in the field of surface vibrational spectroscopy (ref. 2). Recent surface lattice dynamics analysis of electron energy loss spectra from the (110) surfaces of Cu and Ni has shown that a dipole active surface vibrational resonance can arise from the non-monotonic longitudinal bulk phonon dispersion along the (110) direction (ref. 1). This non-monotonic behavior is directly related to the particular coordination of the atoms in the [110] direction for fcc crystals.

This resonance belongs to a new class of resonances since it originates from a single band of bulk phonons. The only requirement is that the non-monotonic dispersion introduces a pseudo-band gap where the density of states is depleted and that the surface force constants are not drastically different from those in the bulk. The resonances discussed previously by Allen, Alldredge and deWette (ref. 3) arise from two bulk phonon bands.

Besides reviewing this kind of surface vibrational resonance in this conference paper new measurements on the Al(110) and Fe(111) surfaces by electron energy loss spectroscopy (EELS) are analyzed in terms of surface lattice dynamics.

Another example of a structure-induced non-monotonic bulk phonon dispersion with a pronounced pseudoband gap is found in the [111] direction of a bcc crystal like Fe. A surface vibrational resonance is observed at an energy close to the calculated resonance energy. No resonance is observed on the Al(110) surface.

This negative result is speculated be due to that a good model for the surface lattice dynamics for a nearly free electron metal like Al is not obtained just by accounting for the loss of the coordination of the surface atoms in modelling of the surface force constants. On the other hand this model seems to work rather well for Cu, Ni and Fe where the localized d-electrons play an important role in determining the interatomic forces.

EXPERIMENTS

The experiments were performed in an ion, turbomolecular, and titanium sublimation pumped ultra high vacuum system with a base pressure of 4×10^{-11} Torr (ref. 4). The EELS spectrometer consists of a double pass 127° cylindrical deflection monochromator and analyzer. The EELS spectra were recorded in the specular direction at 300 K. The impact energy of the incident electrons were 3.2, 4.3, 2.9, and 3.6 eV for Cu, Ni, Fe, and Al, respectively. The incident angle was 60° with respect to the crystal normal, and the angular acceptance of the analyzer is 1.8° full width at half maximum (FWHM). The Cu sample was cleaned by Neon ion sputtering at 500 eV and annealing to 750 K. The Al and Fe crystals were cleaned extensively in previous studies (ref. 5). The cleaning procedure for this study included Neon ion sputtering at 1 and 2 keV, and annealing to 850 and 770 K, for the Fe and Al samples, respectively. The clean surfaces produced well ordered sharp LEED patterns. The most difficult contaminant to remove on the Fe and Al surfaces was found to be oxygen.

SURFACE LATTICE DYNAMICS

Geometrical structure and non-monotonic bulk phonon dispersion

Longitudinal bulk phonons propagating normal to a low index surface displaces the atomic layers rigidly normal to the surface. The lattice dynamics for these phonons reduces to one-dimensional problems due to that the high symmetry along the major crystal directions partition the dynamical matrix (ref. 6). In such a problem an interplanar force constant Φ_n is defined as the force exerted on an atom in a layer by displacing the n:th nearest neighboring layer. The resulting bulk phonon dispersion is given in terms of a Fourier series in the interplanar force constants Φ_n as,

$$\omega^2 = \frac{2}{m} \sum_n \Phi_n (1-\cos n\pi\zeta), \qquad (1)$$

where $\zeta = k_z d/\pi$ is the reduced wave vector and d is the interplanar distance. The wellknown Born-von Karman analysis uses this relation to determine the interplanar force constants from the bulk phonon dispersions measured by inelastic neutron scattering.

For Cu (and Ni) a central nearest neighboring force constant model is known to give an adequate fit to the measured phonon dispersions along the major crystal directions as shown in particular for the [110] direction in Fig. 1 (ref. 7). In this direction an atom has not only nearest neighboring atoms in the nearest neigboring layer but also in the second nearest neighboring layer as depicted in Fig. 2 (b). The strong non-monotonic behavior of the dispersion is due to that this particular coordination of the atoms and the central force constants makes Φ_2 as strong as Φ_1.

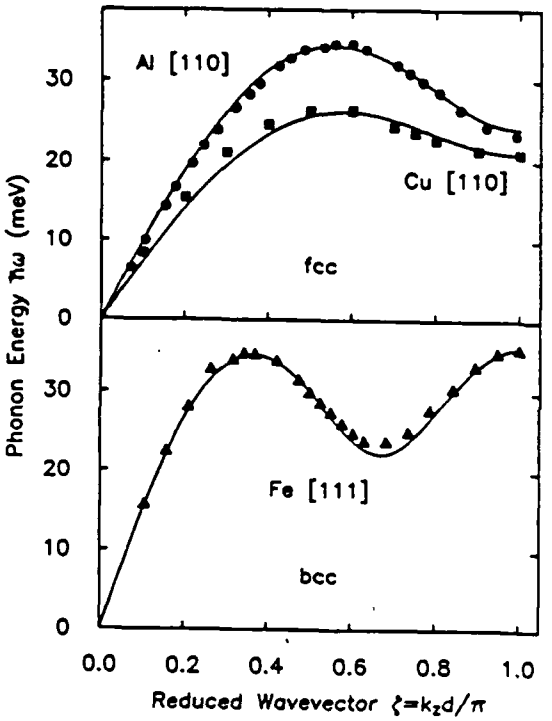

Fig. 1 Longitudinal bulk phonon dispersions (top panel) along the [110] directions for Cu (■) (ref. 7) and Al (●)(ref. 8), and (lower panel) along the (111) direction for Fe (▲) (ref. 9) obtained by inelastic neutron scattering. The solid line shows the fit of the Cu data by a central, nearest neighboring force constant model. The fit to the Al data, shown by the solid line, is obtained by a Born-von Karman analysis for the first two interlayer force constants, with the values $\Phi_1/m=147.6$ and $\Phi_2/m=216.4$ meV^2. The same analysis for the Fe data using the first three interlayer force constants give $\Phi_1/m=96.4$, $\Phi_2/m=68.4$, and $\Phi_3/m=219.1$ meV^2.

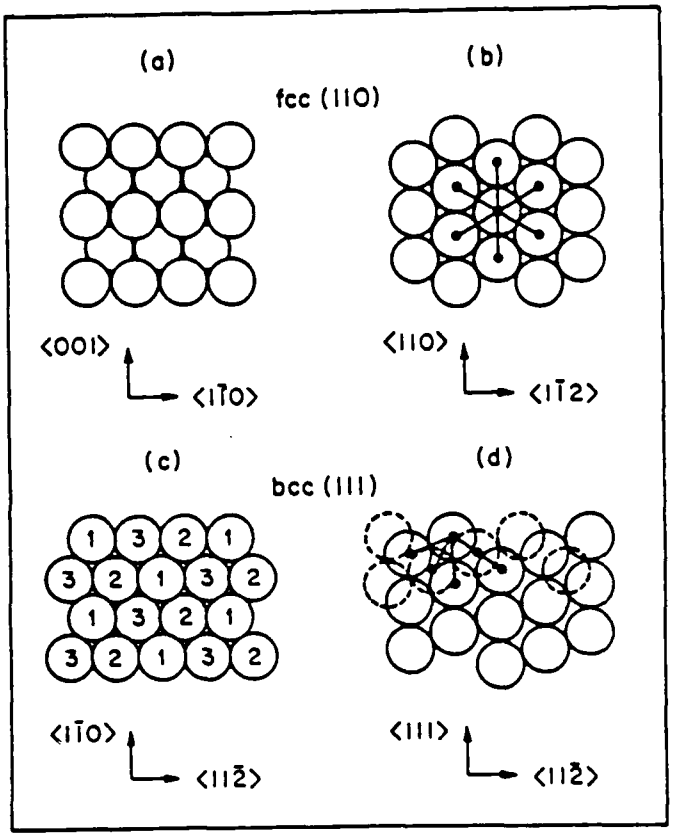

Fig. 2 Schematic diagram of the fcc(1$\bar{1}$0) and bcc(111) surfaces (a)-(b) Top and side view of the fcc(110) surface. The side view in (b) shows that an atom in a layer parallel to the surface has nearest neighbor atoms in the first and second neighboring layer. (c) Top view of the bcc(111) surface. The numbers label sequential layers of the substrate where 1 lables the surface layer. (d) The side view of the bcc(111) surface shows that an atom in a layer parallel to the surface has nearest neighboring atoms in the first and third neighboring layers. Next nearest neighboring atoms are located in the second neighboring layer.

The nearly free electron metal Al is also a face centered cubic crystal and the dispersion in the [110] direction shows a similar behavior (see Fig. 1). The non-monotonic behavior is more pronounced due to that the force constants are more long ranged so that Φ_2 is appreciably larger than Φ_1 as seen from Fig. 1. This long-range behavior is caused by the large effect of the delocalized sp-electrons on the force constants of Al.

The distance to the second nearest neighboring atoms in a body centered crystals are close to the distance to the nearest neighboring atoms and that makes it necessary to include also second nearest neighboring force constants in the description of phonon dispersions for Fe. In the (111) direction, a bcc crystal has nearest neighboring atoms even in the third nearest neighboring layer (see Fig. 2(d)) and that makes Φ_3 of comparable magnitude with Φ_1. As a consequence the phonon dispersion shows an extreme non-monotonic behavior with both a local maximum and minimum with the Brillouin zone.

Pseudo-band gaps and surface vibrational resonances

The strong non-monotonic behavior of the bulk phonon dispersions encountered here introduces a high frequency region of high phonon density of states relative to a region where the phonon density of states are depleted. This latter region will be defined as the pseudo-band gap. In the surface region the restoring forces of the layers are expected to be less than for the bulk layers due to the loss coordination of the atoms at the surface. This decrease of the restoring forces is expected to split off a mode from the high density region into the psudo band gap region where it turns into resonance. This expectation has been confirmed from surface lattice dynamics calculations in previous papers by us (refs. 1,10). Here it suffices to show the results for the dipole active density of states.

The dipole active projection $g^*(\omega)$ of the vibrational density of states is defined as (ref. 11),

$$g^*(\omega) = \sum_{\kappa} \left| \sum_{\ell=1}^{\infty} n^*(\ell) u_{\kappa}(\ell) \right|^2 \delta(\omega-\omega_{\kappa}) \ , \qquad (2)$$

where $u_{\kappa}(l)$ is the displacement of a layer l for an eigenmode κ with a frequency ω_{κ}, and $e^*_{tot} n^*(\ell)\sqrt{\hbar/2m\omega_{\kappa}} u_{\kappa}$, ($\sum_{\ell=1}^{\infty} n^*(\ell)^2=1$) is the contribution to the dynamic dipole-moment from layer ℓ of the mode κ. An eigenmode κ of the semi-infinite set of layers can be written as an incident plane wave plus scattered waves. Some of these scattered waves will be evanescent and localized to the surface for an incident bulk phonon with a frequency in the pseudo-band gap region. In the

calculation of $g^*(\omega)$ the interplanar force constants in the surface region are taken to be the same as for the bulk layers. This model only accounts for the loss of the coordination of the atoms at the surface.

For a finite energy resolution of about 4 meV it is more than sufficient to calculate $g^*(\omega)$ from the lattice dynamics of a slab with 180 layers by replacing the Dirac function in Eq. (2) by a Gaussian with FWHM of 4 meV. The results for $g^*(\omega)$ are shown in the insets of Figs. 3 and 4. The dipole activity is assumed to originate from the two outermost surface layers, $n^*(1)=-n^*(2)=1/\sqrt{2}$ (ref. 12).

In all cases considered a pronounced peak exists in the pseudo-band gap region. A more detailed analysis of the displacement fields for the eigen-modes κ of a semi-infinite substrate has shown that these peaks are resonances in the sense that they originates from a pole close to the real axis in the coefficients for the scattered waves of an incident phonon on the surface.

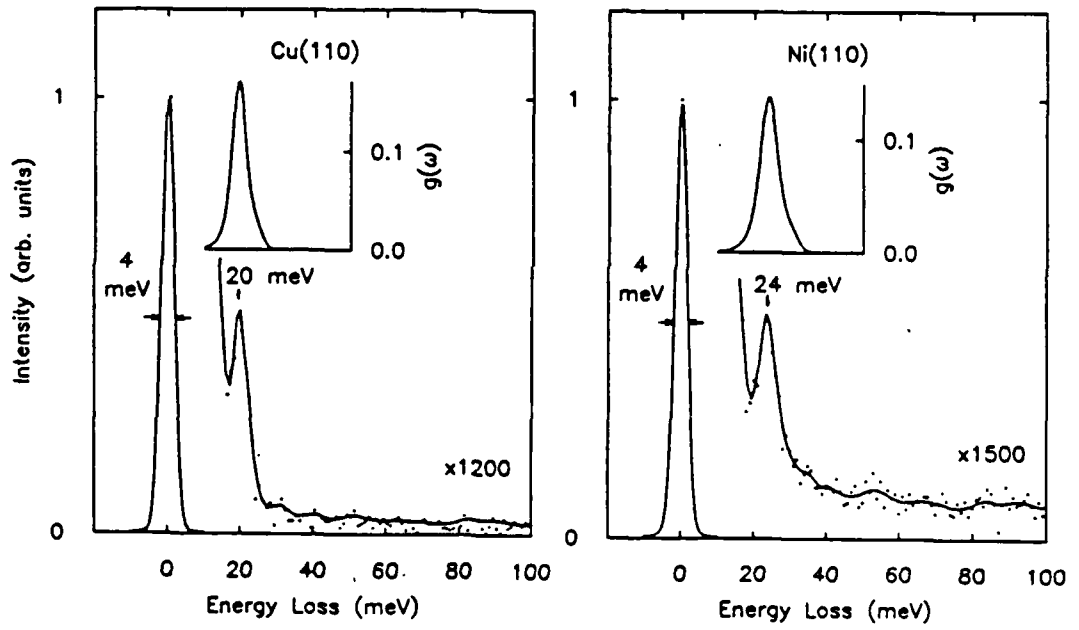

Fig. 3 Electron energy loss spectrum of the (110) surfaces of Cu and Ni. The spectra were recorded at 300 K in the specular direction. A surface vibrational resonance is observed at 20 meV and 24 meV, respectively. The insets show the dipole projected surface density of states $g^*(\omega)$, convoluted with a 4 meV FWHM Gaussian to account for the instrumental resolution. A nearest neighbor central force constant model was used for the lattice dynamics as suggested by the Born-von Karman analysis of experimental data.

COMPARISON WITH EXPERIMENTS

Cu(110)

The calculated $g^*(\omega)$ displayed in Fig. 2(a), shows a pronounced resonance peak at 19.3 meV in the pseudo-band gap region. The inherent resonance width is about 3 meV and makes the convoluted spectrum slightly broader than the

instrumental resolution. Both the position and the width of the observed loss peak are in good agreement with the calculated resonance peak. This kind of agreement is rather remarkable due to the fact that large changes of the surface force constants from the bulk values are expected from the observed large multilayer relaxations on fcc(110) surfaces. A 5-9% contraction of the two outermost layers is inferred from observations by low energy electron diffraction (LEED) and high energy ion scattering (HEIS) (ref. 13). For instance, an analysis of EELS data recorded in the impact scattering regime of the dispersion for the Rayleigh phonon on Ni(100) suggests that there is a 20% increase of the surface force constant (ref. 14) accompanied withy a 3% contraction of the two outermost surface layers (ref. 15). An increase or decrease of the surface interlayer force constant with ± 15% in the surface lattice dynamics calculation would shift the peak position with 1 meV and -1.7 meV, respectively. The experimental resolution is such that the peak position can be determined within ± 1 meV. Thus there are no indications from the observed position of the loss peak that the surface interatomic forces differ from those in the bulk more than ± 15%.

The same conclusion about the surface interatomic forces could be drawn in the analysis of the analogous surface vibrational resonance observed on Ni(110) (ref. 1,10). The position of the observed loss peak simply scales with the maximum bulk phonon energy.

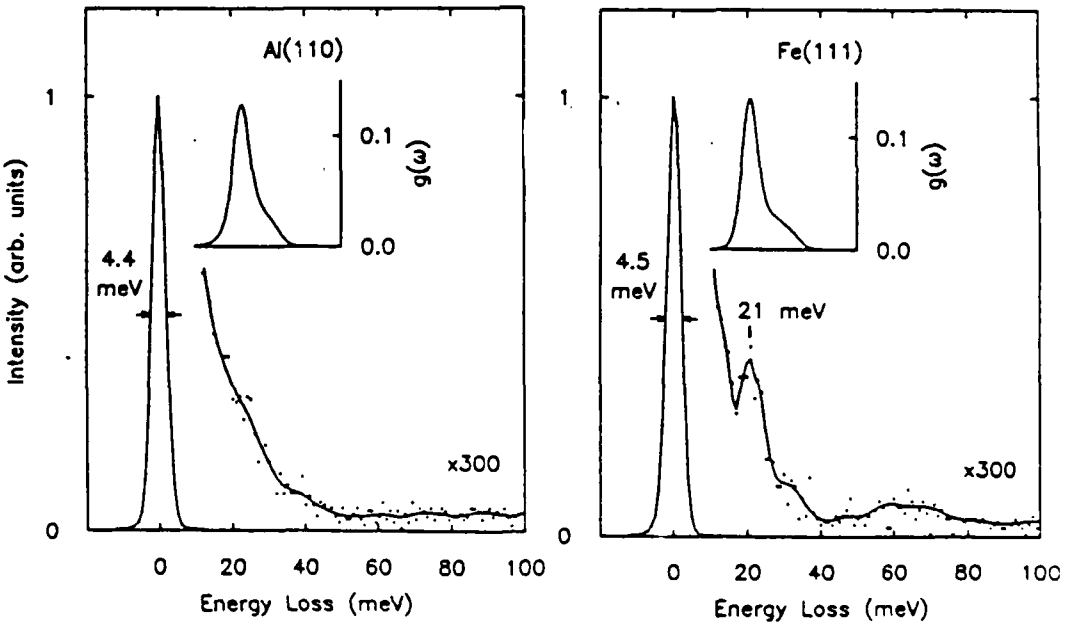

Fig. 4 Electron energy loss spectrum of (a) the Al(110) surface and (b) the Fe(111) surface. The spectra were recorded at 300 K in the specular direction. The inset shows the dipole projected to account for the instrumental resolution. The force constants were obtained from a Born-von Karman analysis of the measured lontigudinal bulk phonon dispersions. A small amount of oxygen contamination, less than 1 %, is observed for Fe(111) around 60 meV.

Al(110)

Also in this case the calculated $g^*(\omega)$ shows a resonance peak in the pseudo-band gap region (see Fig. 3(a)). But this resonance is not discernible in the observed loss spectrum. The loss spectrum shows just a rather strong and featureless background. So far we have not been able to rule out the possibility that this could be due to that the strength of the dipole activity of the metal layers e^*_{tot} is too weak and that the background is instrumental. This explanation would require $e^*_{tot} < 0.015$ e and that would be in conflict with the value calculated, $e^*_{tot} = 0.045$ e, within a jellium model for Al (ref.11). The electron-hole pair background is estimated from a jellium model to be at least a factor of 10 less than the observed "loss" intensity in the energy region of the bulk phonon band and can accordingly not alone explain the observed spectrum (ref. 16).

Another perhaps more likely explanation is that the loss peak has been appreciably broadened by either shifting down to lower frequencies or shifting up in the region of high phonon density of states. Such an effect on the resonance shape has been shown by surface lattice dynamics to occur when there are large changes of the surface force constants in comparison with the bulk values (ref. 1,10). The large effects of the delocalized sp-electrons on the interatomic forces for Al suggests that the modelling of the surface interlayer force constants simply by a truncation of the bulk layers as done here, has no obvious justification in terms of the screening by the conduction electrons at the surface. For Cu and Ni, on the other hand, this kind of modelling is easier to justify due to the importance of the localized d-electrons on the interatomic forces. Thus a detailed description of the interatomic forces at the surface would be of use for Al.

Fe(111)

Besides the resonance peak at 20.6 meV in the pseudo-band gap region there is a rather large and broad contribution from the high density region of bulk phonon states in $g^*(\omega)$ (see inset in Fig. 3(b)). Both the resonance and the bulk contribution are clearly observed in the loss spectrum. The position of the observed resonance peak at 21 meV is in good agreement with the result from the truncated surface approximation for the interlayer force constants. Another noteworthy fact is that the loss peak is rather strong and a dipole intensity analysis gives that $e^*_{tot} = 0.06$ e is about twice as large as for Cu and Ni (refs. 1,12).

Surface lattice dynamics for a semi-infinite substrate reveals the presence of a second surface resonance located predominantly in the 2nd and 3rd layer with

an energy in between the energy of the 1st resonance and the top of the pseudo-band gap (ref. 10). An experimental resolution in the sub meV regime would be required to observe this 2nd resonance, however.

SUMMARY

A new kind of surface vibrational resonance has been shown to exist on surfaces with a pseudo-band gap in a single bulk phonon dispersion. In the cases considered the pseudo-band gaps are introduced by the non-monotonic longitudinal bulk phonon dispersion along the (110) direction of fcc crystals and the (111) direction of bcc crystals as the result of the particular coordination of the atoms in these directions. The resonance has been observed to be dipole active on the (110) surfaces of Cu, Ni and the Fe(111) surface but not on the Al(110) surface. We speculate that this negative result could be due to that the surface interatomic forces of a free electron-like metal is drastically different from the values obtained by simply truncating the bulk layers at the surface.

Preliminary lattice dynamics calculations sho that the resonance exists along the whole JX-direction on (110) surfaces of Cu and Ni and should also be observable at large momentum transfers by inelastic He scattering and electron impact scattering. Finally, this kind of resonance is expected to be a general phenomenon whenever a pseudo-band gap exists in the probed bulk phonon dispersion.

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