

## The surface phonons of Cu(111)

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### Abstract

The surface phonons of Cu(111) are studied using the effective medium theory to calculate the inter-atomic interactions. Dispersion relations in excellent agreement with experiment are derived. We find effective force constants between atoms in the first layer to be decreased by 5% and those between atoms in the first and second layer increased by 10% relative to the bulk values. These changes in force constants can be explained by the many-body nature of the interactions in a metal. Simulations of the He time-of-flight spectra do not show the longitudinal resonance observed experimentally in the first layer.

### 1 INTRODUCTION

The bulk phonons of copper are very well understood. A simple nearest neighbor force constant model gives a very good description[1]. One would therefore expect the surface phonons of copper to be simple to describe. In spite of this, there is still far from agreement about the description of the phonons of the close packed (111) face.

Detailed EELS[2] and inelastic He scattering[3] experiments exist for Cu(111). The EELS results have been interpreted by Hall et al. in terms of a simple force constant model, where the force constant  $k_{11}$  between atoms in the first layer is decreased by 15% relative to the bulk value[2]. This model gives a detailed description of the EELS spectra including the intensity of the different loss features. Contrary to this, in order to interpret the He scattering results, a model has been proposed by Bortolani et al.[4] where  $k_{11}$  is 'softened' by 67%, the force constant between atoms in 1. and 2. layer  $k_{12}$  is 'stiffened' by 59%, and with force constants reaching out to sixth nearest neighbors. The observation that warrants these large changes in force constants is a broad resonance observed in the He time-of-flight (TOF) spectra, which does not appear in simulations of the TOF spectra based on the simple nearest neighbor model using the one-phonon distorted-wave Born-approximation (DWBA). The view that the changes in the force constants are only moderate has been supported by calculations using the embedded

atom method[5], and the opposite view has been supported by calculation within the rather similar 'glue' model[7].

In the present paper we present a new analysis of the phonons of Cu(111) based on total energy - and force calculations using the effective medium theory. The calculated dispersion relations agree very well with the experiments without any fitting to the surface properties of the metal. The effective force constants  $k_{12}$  between atoms in the first and second layer and  $k_{11}$  between atoms in the first layer are calculated directly and found to be only moderately different from the bulk values. As an important part of the analysis we present an explanation of why the surface force constants are different from those in the bulk. We then calculate the He TOF spectra using the one-phonon DWBA [8, 4]. This theory does not produce the broad feature observed experimentally and ascribed to a longitudinal resonance by Bor-tolani et al.[4]. We have therefore analyzed various other possible origins of this effect, and end up concluding that the problem may lie in the simplified description of the scattering potential as pair-potentials arising from interaction with single atoms in the first layer used in the one-phonon DWBA description of the TOF spectra.

## 2 THE CALCULATION

The inter-atomic interactions are described using the effective medium theory. For a complete description of the effective medium theory we refer to Ref.[9]. The details of the present application including the choice of parameters used will be published separately together with a more complete account of the results[10]. The effective medium theory has been used successfully in a number of applications to problems in bulk and at the surfaces of metals including Cu[11]. It includes explicitly the many-body nature of the inter atomic interactions in a metal, an ingredient of vital importance for the present study, as will become clear later. The approximate nature of the theory means that we cannot claim accuracy regarding the details. On the other hand it is the simplicity of the total energy expression that makes it possible to evaluate the full dynamical matrix and diagonalize it for a metal with a surface. On top of this the theory makes it possible to give simple physical interpretations of the effects observed. The effective medium calculation is consistent with ab initio frozen phonon calculation at the zone boundary[6].

The lattice dynamics is obtained by calculating and diagonalizing the dynamical matrix of the system directly. The inter-atomic distances at the surface has been fully relaxed to the minimum energy configuration. A slab geometry has been used, and in order to avoid interactions between the two

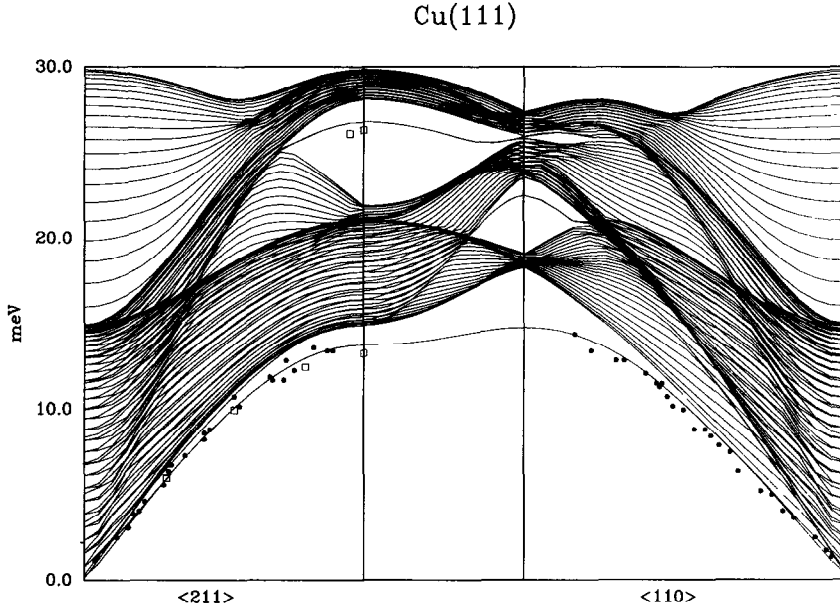


Figure 1: A comparison of the calculated and experimental dispersion relations for the Cu(111) surface. The full circles are deduced from He scattering experiments[3] and the squares from EELS experiments[2].

sides of the slab, the thickness has been varied to ensure convergence. The results shown here are for a slab of thickness 30 layers.

### 3 RESULTS AND DISCUSSION

The calculated dispersion relations are compared to experimental results for the Cu(111) surface in Fig. 1. In judging the quality of the calculated values it must be kept in mind that the parameters entering the calculation are all derived from self-consistent calculations for Cu embedded in an homogeneous electron gas and properties of the bulk. It does not contain any parameters pertaining to the surface.

Similar agreement between theory and experiment has been obtained from simple force constant models[2] by adjusting the intra-layer force constant  $k_{11}$  at the surface. We can deduce effective force constants directly from the calculated dynamical matrix, and find that the inter-layer force constant  $k_{12}$  is approximately 10% larger than the bulk value  $k_0$ , whereas  $k_{11}$  is 5% smaller

than  $k_0$ . These small changes are in rather good agreement with the direct fit to experiments by Hall et al.[2]. They found a 15% reduction of  $k_{11}$ , but did not vary  $k_{12}$ . The changes found here also agree in size with those deduced by Nelson et al.[5].

The changes in the force constants at the surface can be understood rather simply in the effective medium theory. In order to do that it is necessary to review a few simple aspects of the theory. The total energy expression derived for a noble metal like Cu is:

$$E_{tot} = \sum_i E_c(n_i) + E_{AS}. \quad (1)$$

Where the sum is over the atoms in the metal. The first term gives the energy of the perfect fcc Cu crystal as a function of volume. The argument  $n_i$  in the  $E_c$  function is the average electron density that the neighboring atoms provide at the site of atom  $i$ . The density  $n_i$  is a function of the distance of atom  $i$  from the neighbors and thus varies when the lattice constant is varied. The second term is zero for the perfect fcc crystal and measures the energy change due to density conserving (shearing) distortions of the system.

The function  $E_c(n)$  shows a single minimum at  $n_0$ [9] which defines the equilibrium density and lattice constant of the metal. The curvature of  $E_c(n)$  at  $n_0$  then defines the bulk modulus of the system. This term does not, on the other hand, contribute at all to the zone boundary phonons. Consider the second derivative of the first term in Eq.1 for one atom due to a distortion  $x$  corresponding to a zone boundary phonon:

$$\frac{d^2 E_c(n(\mathbf{r}))}{dx^2} = \frac{d^2 E_c}{dn^2} \left( \frac{dn}{dx} \right)^2 + \frac{dE_c}{dn} \frac{d^2 n}{dx^2} \quad (2)$$

For a bulk system at equilibrium  $E_c(n)$  takes its minimum value and  $\frac{dE_c}{dn} = 0$ , and for a zone boundary phonon we have  $\frac{dn}{dx} = 0$  by symmetry, making both terms zero.  $E_{AS}$  thus completely determines the zone boundary phonons, and therefore the size of the effective force constants in the bulk.

This will not be true at the surface. The  $E_{AS}$  term will still determine a large fraction of the effective force constants, but the  $E_c$  term will not be zero. Consider first a distortion of an atom in the first layer parallel to the surface. The first term in Eq.2 will still be zero due to symmetry, but for the atoms at the surface  $\frac{dE_c}{dn}$  is non-zero because the surface atoms have fewer nearest neighbors than the bulk atoms. The electron density that these atoms are embedded in is therefore smaller than the optimum value  $n_0$ .  $\frac{dE_c}{dn}$  is negative for the surface atoms and the force constant  $k_{11}$  between atoms in the first layer should therefore be smaller than the bulk value  $k_0$ . For motion

perpendicular to the surface this is still true, but here  $\frac{dn}{dx}$  is no longer zero and the first term in Eq.2 will give a contribution which is large and positive.  $k_{12}$  therefore turns out larger than  $k_{11}$  and  $k_0$ . This effect is not due to the inward relaxation of the surface but enhanced by it.

We can thus understand both why the surface force constants are different from the bulk one and why they are anisotropic from this simple picture. Note that it is the properties of the  $E_c$  function that give this effect. A pair potential description of a metal corresponds in the effective medium theory to a linear  $E_c(n)$  function. Since  $n$  is a sum of contributions from the neighbors  $E_c(n)$  will only be a pair sum if it is linear in  $n$ . This is only true for the rare gases[9]. The curvature of  $E_c(n)$  is thus a measure of the many body forces, and this is therefore what gives rise to the effect. Note also that the curvature of  $E_c(n)$  mainly stems from the contribution to the binding energy from the kinetic energy of the electrons.

#### 4 THE He TOF SPECTRUM

Our results therefore do not support the large 'softenings' suggested by Bortolani et al.[4]. On the other hand the present calculations cannot explain the He TOF spectra either. We have simulated the TOF spectra based on the one-phonon DWBA [4, 8]. A comparison to experiment[3] is shown in Fig. 2. It is seen that the low energy peak which stems from the Rayleigh mode is well described, but there is clearly a second broad structure in the experimental spectra that is not described by the theory.

In order to simulate the scattering experiment it is not enough that the dispersion relation is well described. There is no unique way of fitting force constants in order to describe the dispersion relations. The polarizations play a very important role in describing the scattering curves. Fig. 3 show the calculated polarization amplitude in the first and second layer in the  $\bar{\Gamma} - \bar{M}$  direction. In the first layer only the Rayleigh mode has any amplitude in the perpendicular ( $z$ ) direction. In the surface plane ( $x$ ) there is a broad resonance from the  $\bar{\Gamma}$  point to the gap, where it becomes a (longitudinal) gap mode. The mode at the bottom of the bulk band is polarized in the  $y$  direction and not probed in the geometry of the experiments. In the second layer there is an additional longitudinal resonance. This has virtually no amplitude in the first layer.

The longitudinal resonance is probed in the EELS experiments because the electrons penetrate several atomic layers into the surface. This mode can, however, not be observed by low energy He atoms in the present description of the scattering potential. The He atoms scatter off far from the surface. It is easy to understand how a dramatic decrease in the force constant between the

## He-TOF on Cu(111)

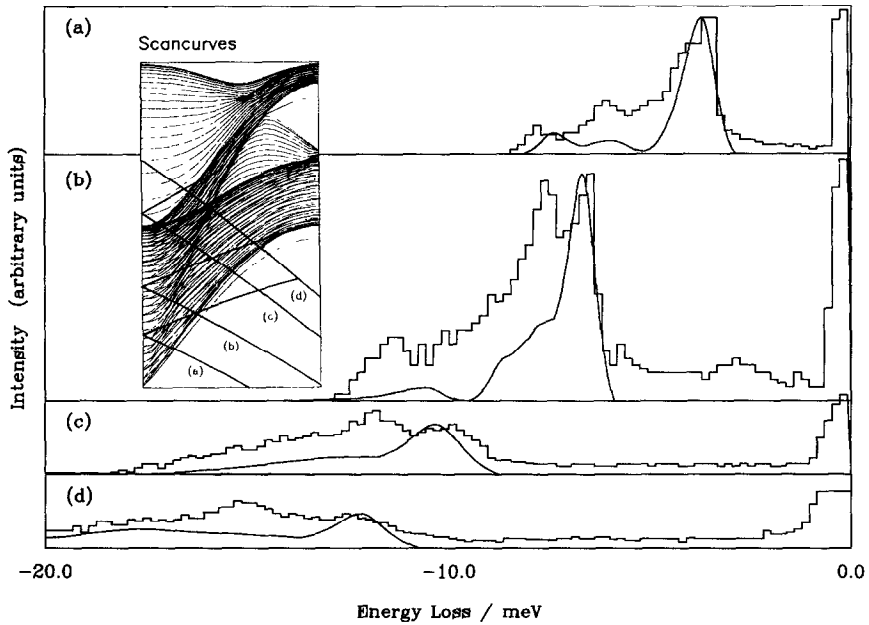


Figure 2: A comparison of the experimental He TOF spectra (histogram)[3] with those calculated from the one-phonon distorted-wave Born-approximation (full curve). The curves are normalized to the experimental intensity of the Rayleigh mode, and the instrumental broadening is the one reported in [3]

atoms in the first layer or a dramatic increase in the force constant between the first and second layer can couple the motion of the first and second layer atoms stronger and thus make the second layer longitudinal resonance visible in the first layer. There is, however, no reason to expect that this is correct from the present calculations.

We have calculated the effect of anharmonicity at the surface using 1. order perturbation theory, where we find very little effect at room temperature. The broadening of the surface phonon peaks are less than one meV and should not be expected to influence the scattering spectra, though there are to our knowledge no experiments examining the temperature dependence of the anomalous peak in the spectra. From the discrepancy between the experimental data and the one-phonon DWBA calculation we conclude that the one-phonon DWBA calculation is based on a too simplistic description of the scattering potential. One would probably also have to take into consideration the contribution to the scattering process from multiple phonon events.

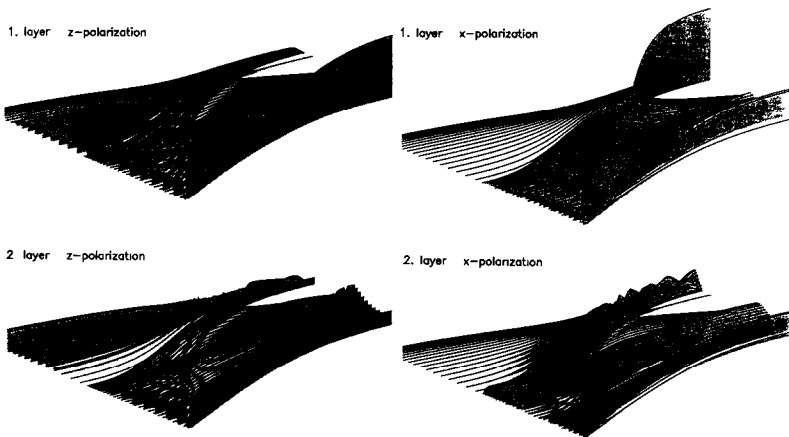


Figure 3: The calculated projected DOS in the first and second layer as a function of surface momentum and frequency in the  $\bar{\Gamma} - \bar{M}$  direction. the left panels are polarization perpendicular to the the surface and the right panels are polarizations in surface plane.

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