EUROPHYSICS LETTERS 15 May 1987

Europhys. Lett., 3 (10), pp. 1113-1118 (1987)

The Dynamics of Cu(100) Surface Atoms at High Temperature.

G. ARMAND, D. GORSE, J. LAPUJOULADE and J. R. MANSON (*)

Service de Physique des Atomes et des Surfaces,
Centre d'Etudes Nucléaires de Saclay - 91191 *Gif-sur-Yvette Cedex, France*

(received 9 December 1986; accepted in final form 3 February 1987)

PACS. 68.30. – Dynamics of solid surfaces and interface vibrations.
PACS. 79.20R – Atomic and molecular beam interactions.

Abstract. – We present a comparison between theoretical calculation and experimental data for the thermal attenuation of helium diffraction peaks for a beam scattered from Cu(100). The calculations take into account 2-phonon exchange exactly and multiphonon exchange with a good approximation up to the highest temperatures. It is shown that there is good agreement up to $T = 450$ K with the model of crystal surface atom thermal displacements developed by Jayanthi *et al.* Above, there is a significant enhancement of these displacements which indicates either an enhancement of anharmonicity in the surface or the onset of a thermal structural roughening.

1. Introduction.

There is to date very little information about the dynamics of crystal surfaces at high temperature, especially when approaching the melting point. Indeed few experimental methods are applicable. The standard diffraction techniques of X-rays or neutrons are not sensitive to the surface and LEED is very difficult to use at high temperature because coherent elastic peaks are overwhelmed by a large diffuse incoherent background. Helium beam diffraction (HBD) is a very attractive method, since it is only sensitive to the first layer and we have indeed shown [1] that coherent diffraction peaks can be readily measured up to 1.270 K for Cu(100) (melting point 1.356 K).

However, the analysis of the thermal attenuation of elastic peaks for HBD is not so straightforward as for X-rays or neutrons. There are two difficulties:

i) the helium surface potential has a finite range, so that the helium atom interacts with more than one surface atom at any given time;

ii) the scattering is strong, so that the usual Born approximation is insufficient.

For this latter reason the calculation is difficult even in the simplifying case of a hard-wall potential [2, 3]. However, recently, two of the authors have successfully developed a

(*) Permanent address: Dept. of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634, U.S.A.

calculation of the HBD thermal attenuation which takes into account a realistic form for the potential and which is able (at least in principle) to sum up all terms in the Born series [4-6]. We shall show in this letter that these calculations are well supported by the experiments and that they allow one to draw interesting conclusions about the behaviour of the atomic thermal vibrations at high temperatures.

2. Model.

We first recall the model. The surface is taken to be flat, *i.e.* the helium surface potential is invariant for a translation along the surface. This is a good approximation for a close-packed surface such as Cu(100). Moreover, this potential is allowed to vibrate only in the normal direction, thus translational invariance is conserved. This approximation has been recently discussed by IDIODI *et al.* [7] who have shown that it is a good one for specular peaks where the influence of normal motion is strongly dominant. A very useful example of such a potential is a Morse potential, where only the repulsive part is assumed to move:

$$V(z, u(t)) = D[\exp[-2\varkappa(z - u(t))]/v_0 - 2\exp[-\varkappa z]], \tag{1}$$

where

z is the co-ordinate normal to the surface;

$u(t)$ is the thermal displacement of the potential;

$\varkappa$ is the potential stiffness;

$v_0 = \exp[2\varkappa^2\langle u^2(t)\rangle]$;

$\langle\ \rangle$ means thermal average.

The applicability of the Morse potential to HBD has been fully discussed elsewhere [8]. The intensity of diffraction peaks (here only the specular, since the potential is flat) are calculated in the T-matrix formalism by an iteration procedure. In principle all multiphonon terms can be calculated but practically only the one-phonon [4] and the two-phonon [5] ones have been calculated exactly, an approximation by resummation of the full multiphonon has also been obtained [6].

The main physical problem remains the computation of $u(t)$. It enters in the calculation through its correlation function $\langle u(t)\,u(0)\rangle$. For a crystal atom (bulk or surface) these quantities can be readily calculated from the phonon spectral density $\varrho(k, \omega)$ and the Bose-Einstein distribution $\langle n(\omega)\rangle$. The problem of relating $u(t)$ to the surface atom displacements is not yet solved by an *ab initio* calculation. We shall use here a heuristic approximation which has been first proposed by ARMAND [9]. The potential is assumed to move as the average of the four surface atoms which form a square unit cell in the case of a (100) surface of a f.c.c. crystal, in order to take into account the softness of the potential which allows an helium atom to interact simultaneously with more than one surface atom. In addition we have introduced a multiplicative parameter α in all the $\langle u(t)\,u(0)\rangle$ terms in order to take into account the following:

i) The crudeness of the four-atom average hypothesis.

ii) The property of the Morse potential in which the attractive part is stationary which makes the displacements of the total isopotentials vary between $(\langle u^2\rangle)^{1/2}$ at $V = \infty$ and

ealistic form for the
he Born series [4-6].
by the experiments
ıviour of the atomic

ım surface potential
imation for a close-
vibrate only in the
oximation has been
ıe for specular peaks
ıl example of such a
ned to move:

(1)

ıssed elsewhere [8].
otential is flat) are
iple all multiphonon
two-phonon [5] ones
ull multiphonon has

rs in the calculation
ĸ or surface) these
(k, ω) and the Bose-
atom displacements
ristic approximation
ned to move as the
ıse of a (100) surface
ıtial which allows an
tom. In addition we
in order to take into

t is stationary which
$^2))^{1/2}$ at $V = \infty$ and

$2(\langle u^2 \rangle)^{1/2}$ at $V = 0$. This behaviour is not very satisfactory, since one expects from usual models that this displacement would increase as V increases.

Correction i) is independent of the incident parameters. It is expected to be quite small and we neglect it as a first approximation.

The second one ii) is more severe. Of course it depends upon incident conditions as α is expected to vary from 0.25 at very low normal energy to 1 at very large energies. Its value for each case has been calculated as follows:

The first cumulant expansion of the intensity is given by

$$\exp\left[\frac{\pi}{2p_i}\operatorname{Im}(\underset{\leftrightarrow}{F}^{(2,1)})\right],$$

where $p_i = k_i^z/\varkappa$ is the dimensionless normal component of the incident wave vector and $\operatorname{Im}(\underset{\leftrightarrow}{F}^{2,1})$ is the imaginary part of the one-phonon transition matrix element. This expression gives good intensity values at low temperature when the contribution of the two-virtual-phonon exchange is very small.

Assuming that the scattering is efficient only on the energy shell, one gets a simple approximate expression for $\operatorname{Im}(\underset{\leftrightarrow}{F}^{(2,1)})$:

$$\underset{\leftrightarrow}{f}^{(2,1)}(p_i) = \alpha 4 p_i^2 \varkappa^2 \langle u^2 \rangle \left[1 + \frac{A\sqrt{D}}{p_i} \operatorname{Im} \psi\left(\frac{1}{2} - A\sqrt{D} + ip_i\right)\right]^2$$

in which ψ is the di-gamma function, D the well depth and $A^2 = 2m/\hbar^2\varkappa^2$ with m the mass of the incident particle.

To this expression corresponds an α value determined at the normal energy corresponding to the value of p_i.

Now we determine a new p_i number, for example P_i, in such a way that

$$\underset{\leftrightarrow}{f}^{(2,1)}(P_i) = \operatorname{Im} \underset{\leftrightarrow}{F}^{(2,1)} p_i$$

and the real α value is calculated for a potential energy corresponding to p_i.

For an incident energy of 21 meV the α values so determined are close to 0.25. For higher incident energy the α value increases and is, for instance, equal to 0.47 for incident energy and angle, respectively, of 63 meV and 19 degrees.

3. Theoretical results—comparison with experimental data.

The numerical results which are presented here are related to the case of He diffracted from Cu(100) with $\varkappa = 1.05$ Å^{-1} and $D = 6.35$ meV as deduced from previous experiments [7]. The copper lattice is assumed first to be harmonic with central forces restricted to nearest neighbours. The force constant $K_c = 2.84 \cdot 10^4$ dyn · cm^{-1} is adjusted in order to obtain the correct bulk Debye temperature $\Theta_D = 350$ K [10]. A typical example is presented for an energy $E_i = 21$ meV ($k_i = 6.4$ Å^{-1}) and an incident angle $\theta_i = 73.5°$ (fig. 1). We have plotted the logarithm of the specular peak intensity *vs.* temperature for the 1 phonon, the 2 + 1 phonon, and the approximate resummation of multiphonon events. We note that the 2 + 1 and the multiphonon curves are identical up to $T = 700$ K. Above the difference is not very large thus we are quite confident in the validity of our resummation in the whole

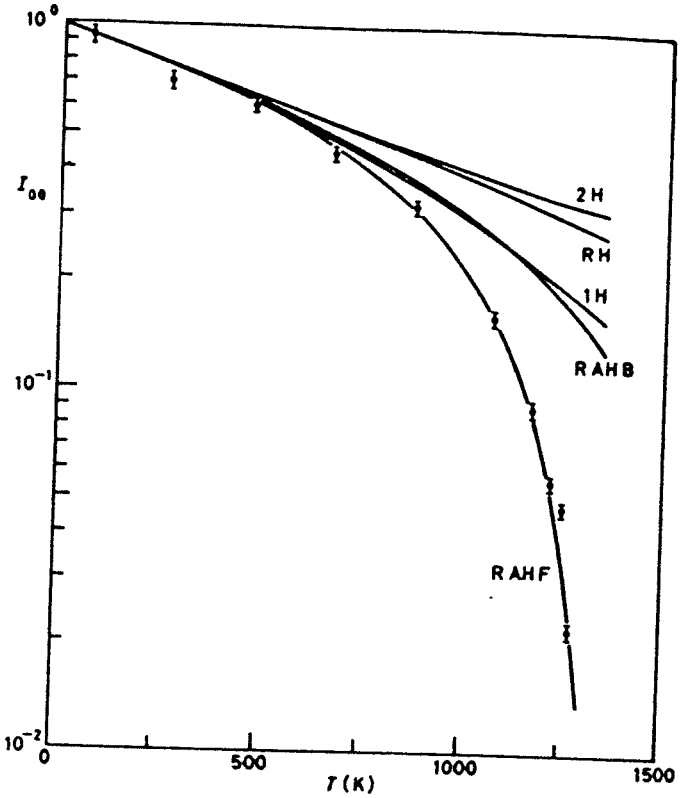

Fig. 1. – Scattering of helium by Cu(100); $E_i = 21$ meV, $\theta_i = 73.5$ °C. Logarithm of intensity *vs.* crystal temperature. • Experimental data. Calculated intensities: 1H one virtual phonon, harmonic solid; 2H two virtual phonon, harmonic solid; RH multi-virtual phonon, harmonic solid; RAHB multi-virtual phonon, anharmonicity of bulk; RAHF multi-virtual phonon, anharmonicity fitted.

temperature range. Note that the 2-phonon contribution becomes important for a temperature as low as 450 K.

The experimental results of ref. [1] are also plotted in the same figure. We observe a good agreement between the experimental and theoretical data up to $T = (250 \div 300)$ K. Above, the thermal attenuation is larger than predicted by this harmonic crystal. We have introduced the anharmonicity using a quasi-harmonic approximation and supposing that the surface anharmonicity is the same as in the bulk, as already proposed by JAYANTHI *et al.* [11]. We have in this way very much improved the agreement between the experiment and theory, as indicated by the curve marked RAHB in fig. 1. Now the two curves fit up to 600 K. Above this temperature there remains a difference: the experiment still indicates a larger thermal attenuation. We have done the same comparison for other incidence angles or energies (63 meV) and we arrive at the same conclusion.

We have to emphasize that we have thus obtained a good overall agreement between theory and experiment up to $T \simeq 450$ K without adjustable parameters. This fact makes us quite confident in the model and in the value of α which has been selected. Note that the fit for the various incidence parameters could have been slightly improved by a small adjustable of α, but we have preferred not to do so and to include the remaining discrepancies into an error bar as seen below (fig. 2).

Finally we have tentatively fitted the experimental data by adjusting for every temperature the value of the maximum crystal frequency Ω_m used in the quasi-harmonic

1500

of intensity *vs.* crystal
on, harmonic solid; 2H
l; RAHB multi-virtual
itted.

s important for a

. We observe a good
50 ÷ 300) K. Above,
crystal. We have
l supposing that the
ed by JAYANTHI *et*
een the experiment
two curves fit up to
ient still indicates a
incidence angles or

agreement between
. This fact makes us
ed. Note that the fit
proved by a small
ude the remaining

djusting for every
the quasi-harmonic

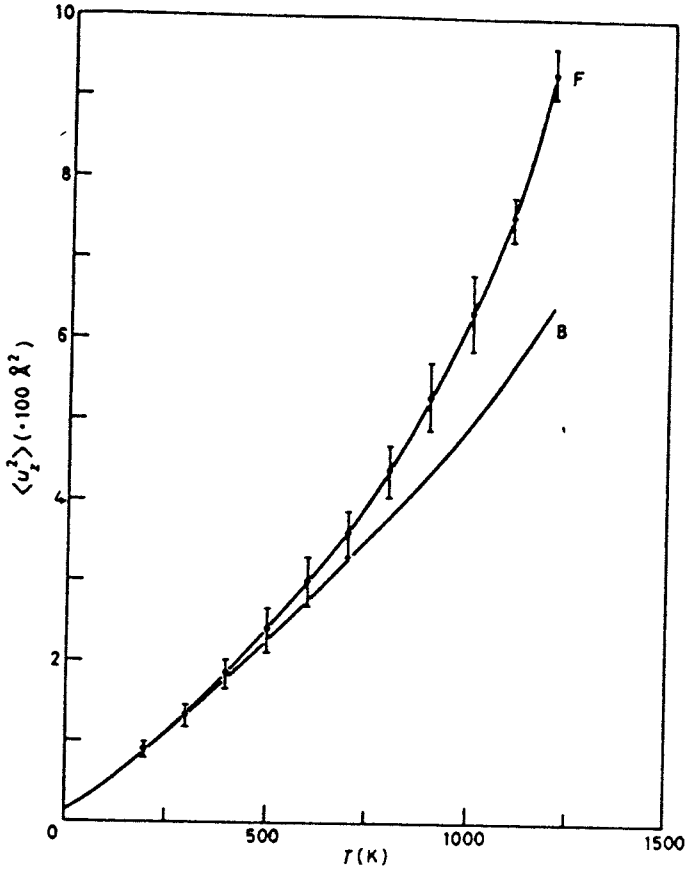

Fig. 2. – Calculated mean-square displacement normal to the surface of a surface atom $\langle u_z^2 \rangle$ as a function of crystal temperature. B with bulk anharmonicity. F with anharmonicity fitted to the experimental data. The error bar is given by the different fitted Ω_m values on experimental data for various incident energies and incident angles. The ratio $\langle u_{eff}^2 \rangle / \langle u_z^2 \rangle$ is equal to 0.425, where $\langle u_{eff}^2 \rangle$ is the potential mean-square displacement (4 atoms).

scheme. The result is also shown in fig. 1 as the curve marked RAHF. In fig. 2 instead of Ω_m itself we have plotted the value of the corresponding mean square displacement of surface atoms *vs.* temperature. As stated above these values are in good agreement with the values calculated by JAYANTHI *et al.* up to $T = 600$ °C. Above, there is a significant increase which is definitely larger than the error bars.

This enhancement has to our knowledge never been observed experimentally.

4. Discussion.

There are two immediate suggestions for the mechanisms involved:

i) If the atoms are assumed to stay in their crystalline position up to the melting point the data indicate a significant enhancement of surface atom vibration, *i.e.* an enhancement of surface anharmonicity. In this case the missing part of the elastic intensity has to be found in an enhanced inelastic background.

ii) It is also possible that the atoms do not remain in their original lattice site. In this case the enhancement of $\langle u^2 \rangle$ would be due to the beginning of thermal roughening. Then the missing part of the intensity would go into a diffuse elastic background as far as their jumping rate from one site to another is slow with respect to the helium collision time. If not, a contribution to the inelastic background would be also expected.

The shape of the background which has been found to be approximately Lorentzian does not help to distinguish between these mechanisms, since both are able to produce quasi-Lorentzian shapes. Moreover, it is expected that both can occur simultaneously, especially near the melting point. A time-of-flight analysis of the background is thus needed in order to decide. This is now technically possible and we are developing a machine which will be able to do that.

Our results are consistent with those of Frenken and Van der Veen [12] obtained by Rutherford back-scattering on Pb(110). Upon heating, they have observed first a defect solid or partially ordered liquid followed by a complete surface melting near the bulk melting point. The disappearance of the coherent signal above $T = 1.273$ K is not inconsistent with the occurrence of surface melting.

5. Conclusion.

Thus we can draw from this letter two conclusions:

1) We have now a good model to describe thermal attenuation of HBD up to very high temperature.

2) We have shown that for Cu surfaces there is a significant enhancement of the surface atom displacements which is not predicted by usual calculations. It may be due either to an enhancement of anharmonicity or to the onset of a surface roughening (or both).

REFERENCES

[1] GORSE D. and LAPUJOULADE J., *Surf. Sci.*, 162 (1985) 847.
[2] GARCIA N., MARADUDIN A. A. and CELLI V., *Philos. Mag. A*, 45 (1982) 287.
[3] LAPUJOULADE J., *Surf. Sci.*, 134 (1983) L-529.
[4] ARMAND G. and MANSON J. M., *Phys. Rev. Lett.*, 53 (1984) 112.
[5] ARMAND G., MANSON J. R. and JAYANTHI C. S., *J. Phys. (Paris)*, 47 (1986) 1357.
[6] ARMAND G., MANSON J. R. and JAYANTHI C. S., *Phys. Rev. B*, 34 (1986) 6627.
[7] IDIODI J., BORTOLANI V., FRANCHINI A., SANTORO G. and CELLI V., to be published.
[8] GORSE D., SALANON B., FABRE F., KARA A., PERREAU J., ARMAND G. and LAPUJOULADE J., *Surf. Sci.*, 147 (1984) 611.
[9] ARMAND G., LAPUJOULADE J. and LEJAY Y., *Surf. Sci.*, 63 (1977) 143.
[10] ARMAND G., *J. Phys. (Paris)*, 38 (1977) 989.
[11] JAYANTHI C. S., ARMAND G. and MANSON J. R., *Surf. Sci.*, 154 (1985) L-247.
[12] FRENKEN J. W. M. and VAN DER VEEN J. F., *Phys. Rev. Lett.*, 54 (1985) 134.