Surface melting of copper

C. S. Jayanthi* and E. Tosatti

*International School for Advanced Studies (Scuola Internazionale Superiore di Studi Avanzati),
Miramare, I-34104 Trieste, Italy*

L. Pietronero

*Brown Boveri Research Center, CH-5405 Baden, Switzerland
and Solid State Physics Laboratory, University of Groningen, Melkweg 1, 9718-EP Groningen, The Netherlands*†

The surface instabilities of copper metal are studied by computing the quasiharmonic free energy of (100), (110), and (111) surfaces within the slab model. We find that a loose-packed surface would melt prior to a close-packed one if contractive surface relaxations are neglected. The inclusion of surface contractions can reverse the order of these instabilities in agreement with recent experiments.

Surface-state photoemission in copper has recently brought out a remarkable phenomenon.[1,2] The integrated intensity of a k-resolved surface peak decreases dramatically at a temperature for which the corresponding bulk photoemission features remain essentially unchanged. This drastic drop, occurring at values of T/T_M (T_M being the bulk melting temperature) roughly around 0.6 for the (100) face, and around 0.75 for the (110) face,[2] still awaits a proper explanation. However, this evidence is suggestive of surface anharmonicity setting up on a massive scale around these temperatures, leading eventually to loss of surface long-range order. Pietronero and Tosatti[3] (PT), by studying a semi-infinite Einstein model crystal, concluded that an instability of the first surface layer would occur at about 73% of the corresponding bulk-lattice instability temperature. The (negative) first-layer square vibration amplitude $-\langle u_1^2 \rangle$ as a function of temperature has, in the PT model,[4] a behavior rather similar to that of the experimental $\log I$ described above, with a dramatic drop just preceding the surface instability. Above the instability temperature, $-\langle u_1^2 \rangle$ of PT becomes complex, which was taken to indicate that quasiharmonic vibration of a surface atom inside the cage of its neighbors is no longer self-sustaining, and the first layer would "melt" (while still remaining attached to the second layer). Note that no real softening occurs because the phonon frequencies decrease only to a finite value at the instability.[3,4] Clearly this approach refers to the instability of the solid free energy and not to the real melting transition. However, there are good reasons to think that the two processes are related by some rescaling,[3,5] the instability actually corresponding to the maximum overheating temperature. This implies that one cannot expect to obtain the absolute value of melting temperatures; nevertheless these methods can be useful to study the relative tendencies. One important confirmation of the validity of this viewpoint comes from the molecular-dynamics studies of Broughton and Woodcock,[6,7] who find a sudden loss of crystalline order in the first surface layer of a (100) fcc Lennard-Jones (LJ) slab, at about 71% of their bulk melt-

ing temperature. This agrees even quantitatively with the results of the very simple PT model.[3] It should be noted that the melting envisaged here is a short-range phenomenon occurring on the flat surface, as opposed to, and different in principle from, the well-known roughening mechanism.[8,9] In general, one can expect roughening to be unlikely for a free low-index surface of a system with strong electronic cohesion like copper.[8]

The aim of the present work is to introduce a simple model that allows analysis for the first time of the following: (i) the face dependence of the surface melting in simple solids and (ii) the effect that surface contractions in metals have on surface melting. As a model system we consider the case of copper. The results show that if only a short-range two-body potential is used (no surface contractions) a loose-packed surface would melt prior to a close-packed one, in close analogy with Lennard-Jones systems.[6,7] The inclusion of surface contraction pushes up the surface melting temperatures of a metal and even determines a reversal in the order of melting of the various surfaces. This result is in agreement with the recent experiments mentioned above.[1,2]

The calculations are first performed using a Morse-type two-body potential $V(R)$; subsequently, additional surface forces are added to simulate the contractions of the various surfaces. The two-body potential $V(R)$ acts only between nearest neighbors and was previously optimized to reproduce the harmonic and *anharmonic* properties of bulk cooper.[10] Its depth is $\Delta V = 1310$ K. Using this potential we obtain in the quasiharmonic (QH) method a bulk instability temperature at $T_B = 1750$ K,[10] which is higher than the true bulk melting temperature, $T_M = 1356$ K. A molecular-dynamics study performed with this potential indeed leads to a stable fcc crystal, which melts just below 1000 K.[11] Clearly, the instability temperature is quite different from the true melting temperature (also different in principle, as mentioned earlier); nevertheless this method can be used with reasonable confidence to compute relative trends.[3,5] Consequently, all the results in this paper will be expressed in units of a "reduced" tem-

perature $t = T/T_B$, scaled to the bulk instability temperature.

For the surface calculations, three slabs (of 21 layers each) are generated for the (100), (110), and (111) cases, respectively. Standard slab dynamical matrices[12] are set up, allowing for the relaxation of one or two outermost layers of each surface. The quasiharmonic free energy[13]

$$F_{QH} = \frac{1}{2} \sum_{i,j} V(\langle R_{ij} \rangle) + k_B T \sum_{q,\lambda} \ln[2\sinh(\hbar\omega_{q\lambda}/2k_B T)]$$

(1)

is calculated numerically. Here, $\langle R_{ij} \rangle$ is the thermally averaged interparticle distance, and $\omega_{q\lambda}$ are slab phonon frequencies, q being the wave vector inside the surface Brillouin zone, and λ labeling the modes, $\lambda = 1, \ldots, 63$. The free energy F_{QH} depends parametrically on the first-second—layer distance, d_{12} (later we also let d_{23} vary), all other average interparticle and interlayer distances being kept fixed to the corresponding T-dependence bulk values, independently known.[10] In the absence of any external forces, the rest of the calculation consists in minimizing F_{QH} at each given temperature by varying the parameter d_{12} (and d_{23}, when its variation is allowed). A surface instability manifests itself with the gradual flattening of the minimum of F_{QH},[14] eventually becoming a saddle point at $T = T_s$, which thus defines $t_s = T_s/T_B$. Such an instability is depicted in Fig. 1 for the (111) face (where d_{23} was not allowed to vary), along with that of the corresponding bulk F_{QH}.[10] We point out that, while F_{QH} loses its

minimum at t_s, no particular surface phonon does actually go soft. In this way, for the case where surface contractions are neglected and where only d_{12} is allowed to vary, we get the surface instability temperatures as $t_s = 0.845$, 0.840, and 0.755 for (100), (111), and (110) faces, respectively. The order of these instabilities corresponds to the intuitive picture that a loose-packed surface melts before a close-packed one.[15] This order also agrees with the recent molecular-dynamics studies on the surfaces of a LJ solid,[6,7] another system with pair interactions. Such an agreement supports the validity of our model and suggests that the structure of these instabilities is linked to the general properties of the potential (two body) rather than to its detailed features. We will see in the following how the inclusion of surface contractions, arising from the nonpairwise electronic cohesive forces, has a dramatic effect on the temperatures and even on the order of these instabilities.

A suggestion that these effects may be important comes from the fact that the T dependence of the optimal value of d_{12}, denoted as $d_{12}^0(t)$, increases drastically just below t_s. This finding implies that it may be important to include the effect of surface contraction that is well known to exist for the (110) and (100) surfaces of Cu.[16] Accounting for this contraction properly would require including the (nonpairwise) electronic cohesive forces. Ma, De Wette, and Alldredge[17] have shown qualitatively how contraction can be obtained through surface Madelung forces, and Landman, Hill, and Mostoller[18] have given a discussion of surface contraction in microscopic terms. Within the present scheme we can simulate the main effect of the contraction (stiffening of surface phonons) by simply applying constant external forces f_1 and f_2 on to all atoms of the first two layers. The strength of these forces is adjusted to reproduce the experimentally known[16] contractions, $\Delta d_{12}(0)/d_{12} = -5.3\%$, -1.1%, ~ 0, and $\Delta d_{23}(0)/d_{23} = +3.3\%$, $+1.7\%$, ~ 0 for (110), (100), and (111) (Ref. 19) faces, respectively. The effect of the forces is just to add a term $\Sigma_i f_i \Delta d_{ij}$ to the variational free energy F_{QH} of Eq. (1), already calculated. Repeating the minimization of F_{QH} with this new term, we find that surface contractions have a dramatic stabilizing effect on our surfaces.

The results reported in Table I show that not only does the contraction strongly increase the instability temperatures but surprisingly, the surface instability temperature of the loose-packed (110) surface is now *higher* than that of both (100) and (111). The physical reason why this occurs can be traced back to the surface *stiffening*, which
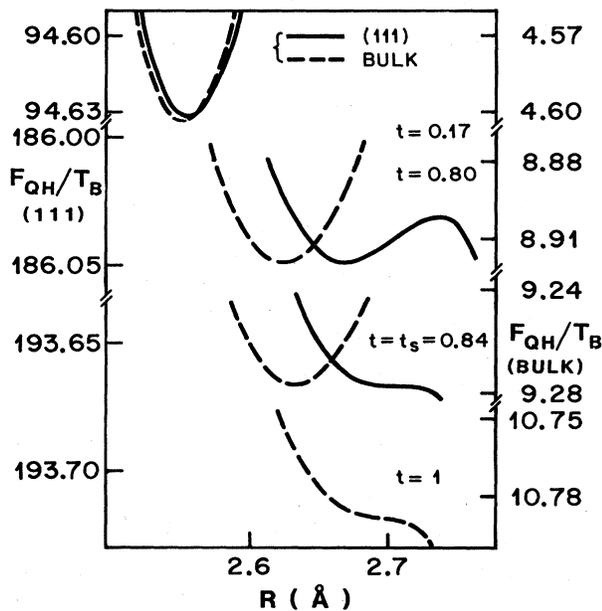
FIG. 1. Surface instabilities in the quasiharmonic free energy compared with the corresponding bulk instability. We have plotted F_{QH} as a function of R which is equal to $(\sqrt{3}/2)d_{12}$ for (111) surface and equal to nearest-neighbor distance for the bulk case. Note that the decrease of F_{QH} for very large R is unphysical.

TABLE I. Copper surface instability temperatures without and with surface relaxation (contraction).

Surface	t_s (ideal surface)	t_s (relaxed surface)
(111)	0.840	0.840
(100)	0.845	0.914
(110)	0.755	0.970
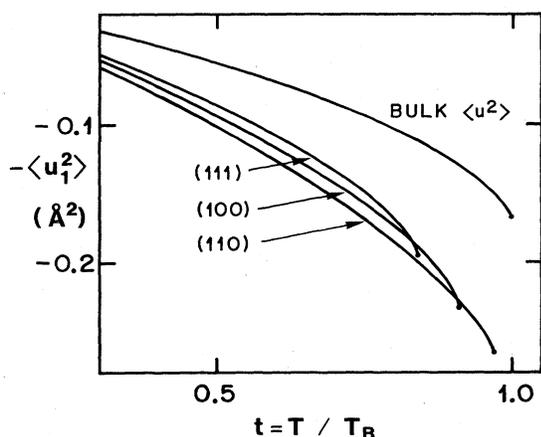
FIG. 2. Mean square first-layer vibration amplitude of Cu surfaces, calculated up to their respective t_s. The bulk behavior (from Ref. 10) is also given for comparison.

implies a reduced anharmonicity, associated with surface contraction. It should be noted at this point that these instability temperatures are very sensitive to the amount of surface contraction imposed, and they can even be shifted above the bulk intensity. In Fig. 2 we show the calculated behavior of $-\langle u_1^2 \rangle$ (Ref. 20) for the contracted faces of Cu, along with the corresponding bulk $-\langle u^2 \rangle$. In comparison with the experimental results of Refs. 1 and 2, we find that our calculation correctly predicts that the (110) surface melts later than the (100) surface, even though it is "softer" at low temperatures. We note, however, that the instability onset temperatures suggested by the experimental $\log I$ curves are substantially lower than our t_s. Comparison of Fig. 2 with He-scattering data[21] is also favorable, although these data stop too early to draw any conclusions about melting. We also present in Fig. 3 the calculated first- and second-layer temperature-dependent surface relaxations, which can in principle be measured, e.g., by Rutherford backscattering.

In summary, we have presented a first theoretical study of the face dependence of surface melting for a model of copper metal. We can summarize our results as follows: (1) Melting on the first layer of a metal surface can occur well below bulk melting; (2) for solids with only pair interactions a loose-packed surface melts prior to a close-packed one in analogy with computer simulations on LJ
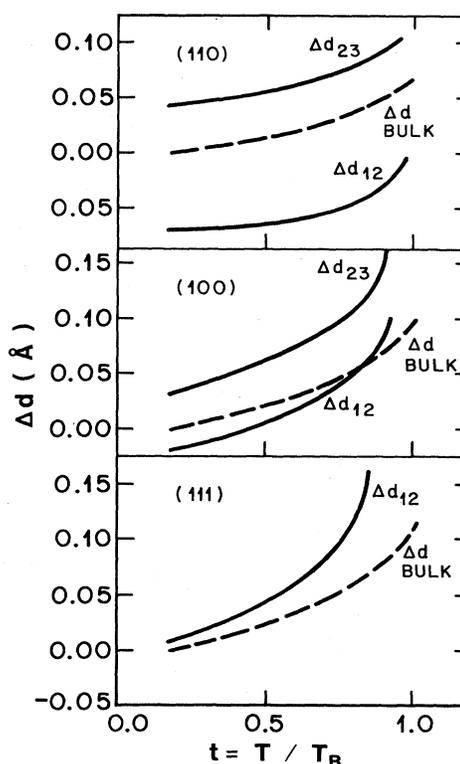
FIG. 3. Temperature dependence of the first- and second-layer relaxation.

systems;[6,7] (3) surface contractions (single layer, or multilayer) play a crucial role in determining whether a surface will melt at low temperature, high temperature, or will not melt at all. The effect of these contractions in the case of copper is particularly important because it makes the loose-packed surfaces more stable than the close-packed ones.

*Present address: Centre d'Etudes Nucléaires de Saclay, Département de Physique Générale, Service de Physique des Atomes et des Surfaces, Commissariat à l'Energie Atomique, F-91191 Gif-sur-Yvette, France.
†Present and permanent address.
[1]S. D. Kevan and D. A. Shirley, Phys. Rev. B 22, 542 (1980).
[2]R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley, Phys. Rev. Lett. 39, 302 (1977).

[3]L. Pietronero and E. Tosatti, Solid State Commun. 32, 255 (1979).
[4]L. Pietronero and E. Tosatti (unpublished).
[5]L. L. Boyer, Phys. Rev. Lett. 42, 584 (1979).
[6]J. Q. Broughton and L. V. Woodcock, J. Phys. C 11, 2743 (1978).
[7]J. Q. Broughton and G. H. Gilmer, J. Chem. Phys. 79, 5119 (1983).

[8]For a critical comparison between these two possible instabilities see the introduction of Ref. 7.

[9]See, e.g., J. D. Weeks, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980).

[10]C. S. Jayanthi, E. Tossatti, and A. Fasolino, Phys. Rev. B (to be published).

[11]E. Ercolessi (private communication).

[12]R. E. Allen and F. W. de Wette, Phys. Rev. **179**, 873 (1969).

[13]See, for example, H. R. Glyde and M. L. Klein, Crit. Rev. Solid State Sci. **2**, 181 (1971).

[14]This criterion is analogous to that of Ref. 5 where bulk melting in alkali halides was studied using the bulk lattice constant as variational parameter.

[15]B. Chatterjee, Nature **275**, 203 (1978).

[16]H. L. Davis and J. R. Noonan, Surf. Sci. **126**, 245 (1983); D. L. Adams, H. B. Nielsen, S. N. Anderson, I. Stensgaard, R. Feidenhansl, and J. E. Sörensen, Phys. Rev. Lett. **49**, 669 (1982).

[17]S. K. S. Ma, F. W. de Wette, and G. P. Alldredge, Surf. Sci. **78**, 598 (1978).

[18]U. Landman, R. N. Hill, and M. Mostoller, Phys. Rev. B **21**, 448 (1980).

[19]It is very difficult to choose correctly $\Delta d_{12}/d_{12}$ for Cu(111) from the various values given in the literature. [See, e.g., *Surface Crystallography by LEED*, edited by M. A. van Hove and S. Y. Tong (Springer, Heidelberg, 1979), p. 253.] The values seem quite small, so we decided to set $\Delta d_{12}=\Delta d_{23}=0$ for this face.

[20]We find the contribution to $\langle u_1^2 \rangle$ from the z component normal to the surface important but not dominant. In fact, the contribution of $\langle u_{1x}^2 \rangle$ and $\langle u_{1y}^2 \rangle$ also becomes important at high temperatures.

[21]J. Lapujoulade, J. Perreau, and A. Kara, Surf. Sci. **129**, 59 (1983).

[22]C. S. Jayanthi, E. Tosatti, A. Fasolino, and L. Pietronero, in The Sixth European Confernece on Surface Science (ECOSS-6), York, 1984 [Surf. Sci. (to be published)].