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Theoretical study of the structure and vibrational dynamics of $Cu_3Au(511)$

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Abstract
We have studied the structure and vibrational dynamics of $Cu_3Au(511)$ using embedded atom method potentials. The relaxation pattern of this surface shows a buckling in all Au-rich chains of about 0.14 Å, which is similar to that found in $Cu_3Au(100)$. The relaxation pattern of this surface is qualitatively similar to that of Cu(511), but is more pronounced in $Cu_3Au(511)$ and extends deep into the bulk. Our calculations show that the local vibrational properties of this vicinal surface is sensitive to the local atomic environment. Surface Au atoms are responsible for a large softening of the force field at the surface, yielding a substantial shift toward low frequencies of the vibrational densities of states associated with Au surface atoms. As a consequence, the excess local free energy of the Au atoms are about 43 meV/atom at 663 K.

1. Introduction

Over the last few decades LI_2 alloys have been the subject of numerous experimental and theoretical investigations because they are related to materials possessing improved mechanical properties and having important technological application in catalysis coating, high temperature engineering, etc. The Cu_3Au binary intermetallic alloy has often been selected as a model system because it exhibits a typical order–disorder transition. With the aim of obtaining a better understanding of this transition, a lot of work has been done both experimentally [1–8] and theoretically [9–17] in the area.

From studies referring to the structure [1–3] and the dynamics [10, 13–16] of both bulk and surface, it is found that in the ordered state the Au concentration in the (111) surface is 25% for all layers [8, 18, 19]. Concerning both the (001) [1–3, 8, 12, 19–21] and (110) [7, 23, 24] faces, the Au concentration in the first and second layers are essentially constant at 50% and 0%, respectively. This is compatible with the corresponding surface energies, from which it may be argued that a mixed terminal layer is energetically favoured as compared to a pure Cu layer, for these two surfaces orientations. In addition, it is found that at zero temperature the Au surface atoms present an outward displacement, while the Cu surface atoms exhibit an inward relaxation. This phenomenon is known as rippling or buckling [15, 21, 24–26, 29, 30].

In this work, we present a study of the geometry, the relaxation patterns and the dynamics of the vicinal surface of $Cu_3Au(511)$, using the interaction potential from the embedded atom method (EAM) [22]. We are interested in the local atomic environment and the effect of the existence of the Au atoms on the relaxation of Cu atoms in the layer.

In a previous study [10, 11] the structural and vibrational properties of the low Miller index surfaces of Cu_3Au have already pointed to the differential contribution of the Cu and Au atoms. Since the local environment of these atoms is expected to be even more complex and varied on the high Miller index surfaces, we have carried out examinations of the same in this work. Such systematic studies of the environment-dependent contribution to the local structural relaxations and vibrational free energy allows the determination of the role of local coordination in matters of surface and structural stability. We are further encouraged by experimental studies [5–7] of the vicinals of $Cu_3Au(100)$ which establish the stability of monoatomic and diatomic stepped surfaces of this alloy and provided us with avenues for comparison with our theoretical results.

Among the issues investigated in this work are the multilayer relaxation patterns and local relaxations, features in the local vibrational density of states and local contributions to the excess free energy. As a prototype system, we consider here $Cu_3Au(511)$ which is a vicinal of $Cu_3Au(100)$ and has three atomic chains in its terraces. In the following the geometry of the alloy surface is discussed in section 2 and the calculational details in section 3. The results for structural relaxation, calculated local vibrational density of states and contributions to the vibrational thermodynamic properties are presented in sections 4, 5 and 6, respectively. The conclusions are summarized in section 7.

2. Geometry

In the Cu_3Au crystal, each Au atom has 12 Cu nearest neighbours and each Cu has 8 Cu nearest neighbours and 4 Au nearest neighbours. This structure is a member of the LI_2 family structure. We are interested here in the (511) surface which is constructed by cutting the crystal at an angle of 15.8° from the (100) plane towards the [011] direction; $Cu_3Au(511)$ is composed of (100) terraces separated by single-atom-high steps of (111) orientation, and a step–step separation of 7.95 Å.

We have taken the x and y axes to lie in the surface plane. In our coordinate system, the x-axis is perpendicular to the step, the y-axis is parallel to the step and the z-axis is the surface normal. Figure 1 shows a view of $Cu_3Au(511)$ for which each terrace consists of three chains of atoms, labelled as corner-chain (CC), terrace-chain (TC), and step-chain (SC). The structure of the $Cu_3Au(511)$ surfaces is replicated by two types of alternating terraces: one with 50% Au(Au-rich), the Au and Cu form a checkered pattern, while the other has 0% Au(Cu-rich terrace). Each CC in the Cu-rich terrace is a neighbour of SC atom in the Au-rich terrace and vice versa. In the Au-rich terraces, each Au SC, TC and CC atom has 7, 8 and 10 Cu nearest neighbours, respectively, while each SC, TC and CC Cu atom has 3, 4 and 4 Au nearest neighbours, respectively. In the case of the Cu-rich terraces, the Cu atom in each chain has 2 Au atom nearest neighbours. The coordination of SC, TC and CC atoms on the surface is, of course 7, 8 and 10, respectively.

3. Computational details

Since our main interest lies in the local vibrational properties of vicinal alloy surfaces, a local approach in real space is needed. For this purpose the real space Green function (RSGF) method is used [23]. The essential feature of this method is that it makes no use of wavevectors and Brillouin zones. In this method one can focus on any 'local' region according to need and

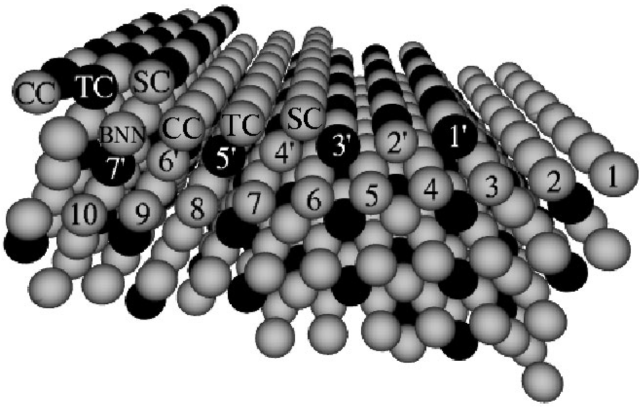

Figure 1. Top and side view of $Cu_3Au(511)$ with appropriate labelling of the atoms; the ($'$) numbered chains represent the Au rich.

analyse the effect of the rest of the system on that particular region. Also, it does not require the system to be periodic and thus it is particularly suitable for studying local vibrational density of states in complex systems with defects, disorder and reduced symmetry. The only prerequisite is that the interatomic potential between the atoms in the system be of finite range, as it is then possible to write the force constant matrix in a block-tridiagonal form. Because our purpose is to study surface atom dynamics, we set up the force constant matrix in a layer by layer manner [24]. Depending upon the range of interatomic potential and the way layers are stacked in the crystal, the number of layers to be included in a locality will be different. Once the force constant matrix is built in block-tridiagonal form, the Green function matrix corresponding to the local region of interest is then constructed following the procedure described in [25]. The normalized vibrational density of states associated with locality l is thus given by

$$N_l(\omega^2) = -\frac{1}{3n_l\pi}\lim_{\epsilon\to 0}\{\mathrm{Im}[\mathrm{Tr}(G_{ll}(\omega^2 + \mathrm{i}\epsilon))]\} \qquad (1)$$

with $N_l(w) = 2wN_l(w^2)$, where G_{ll} is the Green function matrix corresponding to locality l and n_l is the number of atoms in this locality. To describe the interactions between the atoms in the model systems, we use the embedded atom method (EAM). This is a semi-empirical potential and of many-body type [22]. Although the EAM potentials neglect the large gradient in the charge density near the surface and use atomic charge density for solids, for the six fcc metals Ag, Au, Cu, Ni, Pd and Pt, and their alloys, they seems to have done quite a successful job of reproducing many of the characteristics of the bulk and the surface systems [22, 26–30]. We have also found that the EAM potentials to be reliable for examining the temperature dependent structure and dynamics of Cu and Ag flat surfaces [27], and for describing the energetics of Cu vicinal and self diffusion processes on the (100) surfaces of Ag, Cu and Ni [31–33]. With these interactions for a model system constructed in its bulk terminated positions, the conjugate gradient method is used to relax the system to 0 K equilibrium configuration. The dynamical matrix needed for determining the Green function matrix is then obtained from analytical expressions for the partial second derivatives of the EAM potentials [22]. As mentioned above, the number of layers to be included in a locality is dictated by the range of interatomic potential and the way layers are stacked in the crystal. The range of EAM potential for Cu is such that atoms in layer 6 have negligible interactions with those in layer 13. Thus in order to have the force constant matrix in block-tridiagonal

Table 1. Multilayer relaxations of $Cu_3Au(511)$ compared with results for Cu(511) [16].

	Cu(511)	Au rich terraces	Cu
Δd_{12} (%)	−9.48	−3.8	−13.6
Δd_{23} (%)	−7.87	−28.6	−11.5
Δd_{34} (%)	+8.76	+15.7	+8.3
Δd_{45} (%)	−4.19	−6.5	−8.2
Δd_{56} (%)	−4.09	−7.0	−7.9
Δd_{67} (%)	+3.44	+5.0	+15.6
Δd_{78} (%)	−1.67	−2.0	−3.1
Δd_{89} (%)	−11.14	−2.0	−2.8
Δd_{910} (%)	−0.70	+5.8	+2.5
Δd_{1011} (%)	—	−1.1	−1.5
Δd_{1112} (%)	—	−1.3	−0.8

form, at least six layers need to be included in a locality. Since $Cu_3Au(511)$ is a vicinal of (100) which has AB stacking, in the present study we take the number of layers in a locality to be 6.

4. Relaxation of $Cu_3Au(511)$

In figure 1 we display a view of $Cu_3Au(511)$ with appropriate labelling of the atoms; light coloured spheres represent Cu atoms while dark coloured spheres represent Au atoms. In the figure we show four terraces each forming a semi-infinite plane. The atoms in the Au-rich plane are numbered with (′) to distinguish them from the atoms in the Cu-rich one.

We determined the equilibrium structure of $Cu_3Au(511)$ at 0 K by minimizing the total energy of the system. Two main features were found: buckling in the chains containing Au atoms and substantial changes in the interlayer separations. The buckling in the Au-rich terraces is similar to that found on the low Miller index surfaces [11, 34, 35]. We find buckling of 0.12, 0.14 and 0.15 Å for the SC, TC and CC Au rich chains, respectively. The change in the interlayer distance relative to the bulk, $\Delta d_{ij}\%$, for several layers is shown in table 1, in which the first column represents the values for Cu(511) [16] for comparison. The second column in the table is that for the Au-rich terraces, and the last column represents those for the atoms in each chain in the Cu-rich terraces. These values are obtained from the average positions of the atoms in each chain. Comparing these results with those for Cu(511) [16, 23] shows that the relaxation pattern is similar for both surfaces, although more pronounced for $Cu_3Au(511)$.

From table 1 we find a large contraction of −28.6% between the TC and CC atoms in the Au-rich terraces, together with a large upward relaxation of +15.7% between the CC and BNN atoms for the Au-rich chain. For Cu atoms in Cu-rich terraces, the relaxation pattern is similar to that of Cu(511), except for Δd_{67}, which is about five times larger for the alloy surface. The effect of the Au atoms on the multilayer relaxation of this alloy is evident from table 1. The large contraction $\Delta d_{2'3'}$, the large expansion in $\Delta d_{3'4'}$ and in Δd_{67}, are all due to the buckling of the Au atoms in the CC.

As it is clear from table 1, the relaxation pattern on $Cu_3Au(511)$ is very complex. For a better understanding of the relaxation pattern of this system, we have calculated the relative changes in the nearest neighbour distance (relative change in the bond length) between the SC atoms and their neighbours. In figure 2 we show that the maximum change in the bond length appears between the Cu(Au-rich) SC-atom and the Cu(Cu-rich) atom just underneath the SC-atom (bulk nearest neighbour-BNN). The change in bond length relative to the bulk is −6.3%. The relaxation also causes a change in the bond length between the Cu(Au-rich)

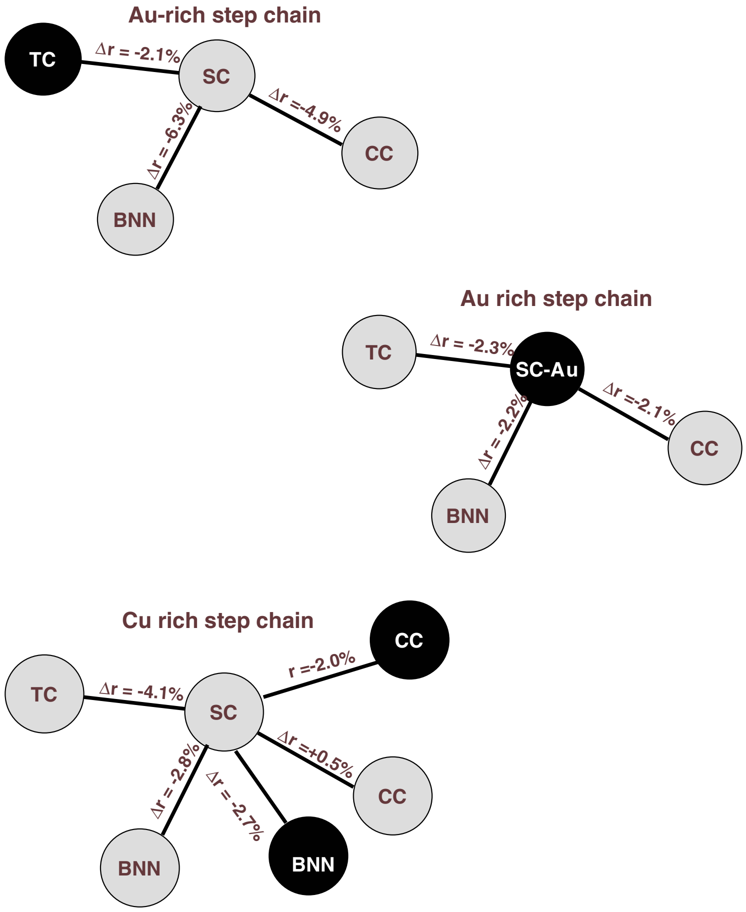

Figure 2. The relative change in the bond length of the SC atoms with their nn in $Cu_3Au(511)$. (This figure is in colour only in the electronic version)

in the SC and Cu(Cu-rich) CC atoms of −4.9%. In the case of the SC Au atoms for which all nearest neighbours atoms are Cu, the relative change in the bond length is around −2.1% with all its neighbours, while the Cu(Cu-rich) SC atom has a maximum change in the bond length of −4.1% with Cu(Cu-rich) TC atoms. The relative change in the bond length between a Cu(Cu-rich) SC atom and Cu(Au-rich) CC atoms is +0.5%. On the other hand, if the CC atoms are Au, the relative change in bond length is −2.0%. Comparisons of this result with previous work on Cu(511) [23] again leads to the conclusion that the contraction in the bond length is much more pronounced in $Cu_3Au(511)$ because of the presence of the Au atoms.

The loss of neighbours at the surface and the consequent relaxation yield a large and complex change in the force field. In table 2 we show the force constant matrices between the step atoms and some of their neighbours. From this table we find a softening between SC–SC atoms in the force constant matrix K_{yy} and a stiffening in the force constant matrix between the SC and BNN atoms. Most of the stiffening is in the K_{zz}. These results show similar patterns in the force constant matrices of Cu(511) but generally disclose greater differences in the amount the alloy will stiffen or soften. For example the relative softening in the SC–SC atoms in Cu(511) is about 19% while it is a round 34% for $Cu_3Au(511)$ for both Au-rich and

Table 2. Force-constant matrices $K_{\alpha\beta}$ in (eV Å^{-1}/unitmass) between the SC-atom and its neighbours compared to the values in the bulk.

		Surface			Bulk		
Atoms		x	y	z	x	y	z
SC–SC(Cu(Au-rich))	x	0.037 40	0.081 00	−0.000 60	0.339 80	−0.001 60	−0.003 20
	y	−0.054 10	−3.052 80	−1.310 60	0.001 60	−4.535 70	0.000 10
	z	−0.017 50	0.397 80	−0.019 80	−0.003 20	−0.000 40	0.350 80
SC–BNN(Cu(Au-rich))	x	−0.318 7	−1.991 8	−2.805 3	−0.150 6	−0.933 8	−1.387 7
	y	−1.890 2	−2.074 0	−4.526 2	−0.885 0	−1.015 0	−2.333 1
	z	−2.709 7	−4.615 4	−6.373 7	−1.188 5	−2.132 2	−3.311 0
SC–SC(Au))	x	0.037 40	0.054 10	−0.017 50	0.339 80	−0.001 60	−0.003 20
	y	−0.081 00	−3.052 80	−0.397 80	0.001 60	−4.535 70	0.000 10
	z	−0.000 60	1.310 60	−0.019 80	−0.003 20	−0.000 40	0.350 80
SC–BNN(Au)	x	−0.178 6	−0.895 4	−1.364 3	−0.150 6	−0.933 8	−1.387 7
	y	−0.842 0	−1.039 8	−2.185 9	−0.885 0	−1.015 0	−2.333 1
	z	−1.632 4	−2.779 5	−4.074 2	−1.188 5	−2.132 2	−3.311 0
SC–SC(Cu(Cu-rich))	x	−0.217 80	0.099 50	0.068 60	0.339 80	−0.001 60	−0.003 20
	y	−0.099 50	−2.901 50	−0.987 50	0.001 60	−4.535 70	0.000 10
	z	0.068 60	0.987 50	0.010 00	−0.003 20	−0.000 40	0.350 80
SC–BNN(Cu(Cu-rich))	x	0.030 5	−1.132 0	−1.499 2	−0.150 6	−0.933 8	−1.387 7
	y	−1.178 1	−1.489 5	−3.250 2	−0.885 0	−1.015 0	−2.333 1
	z	−1.839 5	−3.799 4	−5.494 0	−1.188 5	−2.132 2	−3.311 0

Table 3. Change in the bond length and force constant relative to their bulk value for SC-BNN atoms.

Atom	Relative bond length (%)	Relative stiffening (%)
Cu(Au-rich)	−6.3	93
Au	−2.2	23
Cu(Cu-rich)	−4.1	66

Cu-rich SC atoms, in the case of relative stiffening in the force constant between SC and BNN atoms, for Cu(511) we have 35%, while for $Cu_3Au(511)$ 93% for Cu(Au-rich), 23% for Au atoms and 66% for Cu(Cu-rich) atoms.

In table 3, we have summarized the changes in the bond length relative to the bulk for the terrace atom and the corresponding changes in the force constant matrix K_{zz} relative to the bulk value for the SC and BNN. We find a correlation between these two quantities as the maximum contraction in the bond length occurs for the Cu(Au-rich) atoms (−6.3%) and the maximum stiffness is also found for the same atoms (93%).

5. Results of the local vibrational density of states calculations

In figures 3–6 we present the calculated local vibrational density of states (VDOS) for the SC, TC, CC and BNN atoms on the $Cu_3Au(511)$ surfaces, respectively. In each figure part (a) represents the Cu atoms in the Au-rich chain, part (b) the Au atoms, and part (c) the Cu atoms in the Cu-rich chain. Each VDOS is calculated along the x-, y- and z-directions. Note that there

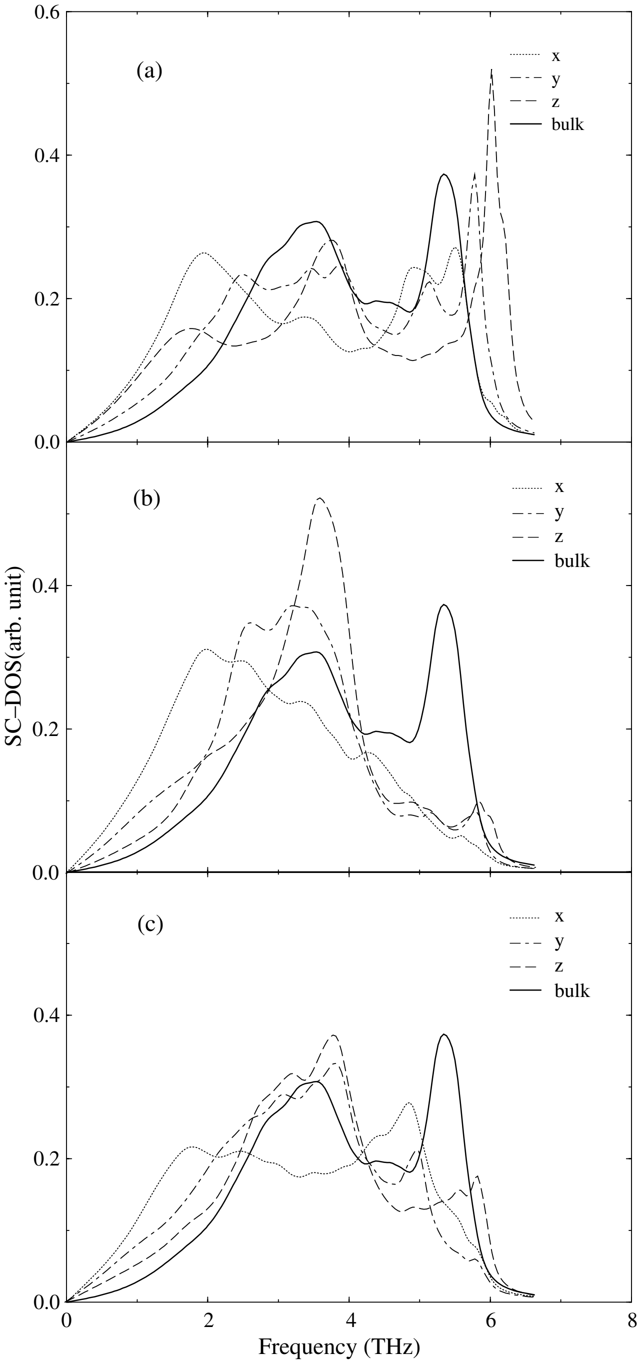

Figure 3. VDOS for step atoms (SC-DOS) for $Cu_3Au(511)$: (a) Cu atoms in the Au-rich chain, (b) the Au atoms, and (c) the Cu in the Cu-rich chain.

is a marked richness in these densities of states. In figure 3 the SC-VDOS is contrasted to the smoother VDOS for the bulk-like atom, indicating the difference in the nature of the bonding between atoms on the vicinal surface from those in the bulk. Also, the low frequency modes of

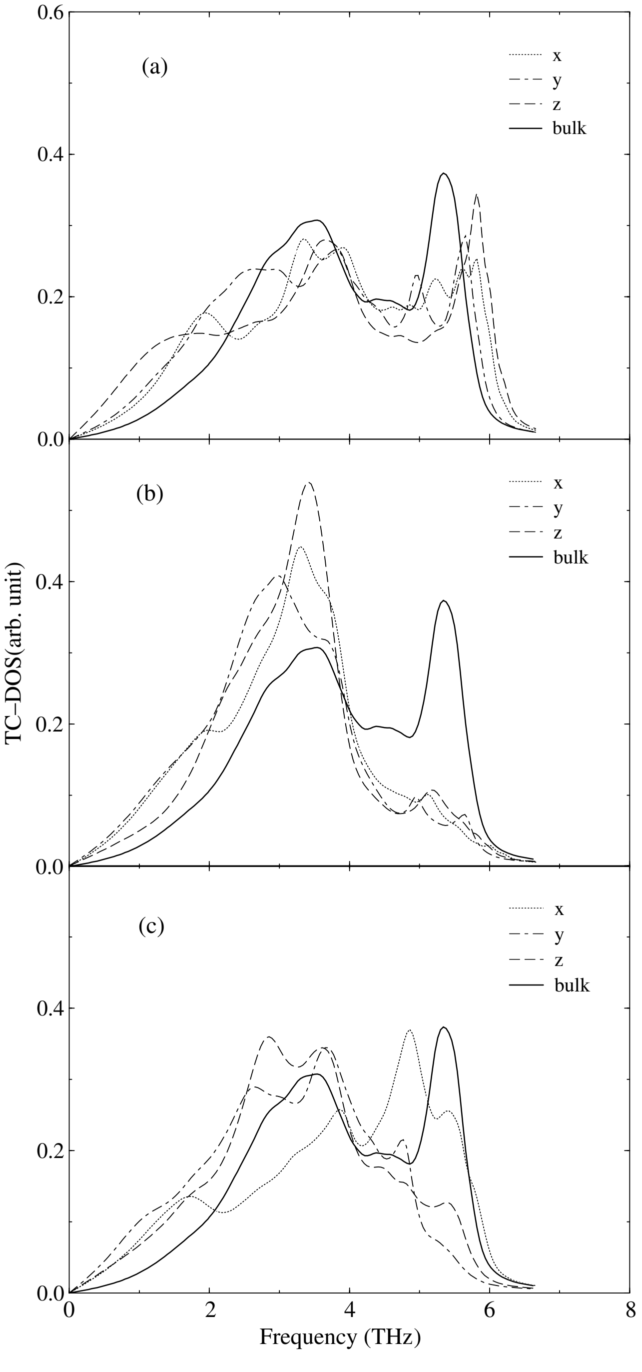

Figure 4. VDOS for terrace atoms (TC-DOS) for $Cu_3Au(511)$: (a) the Cu atoms in the Au-rich chain, (b) the Au atoms, and (c) the Cu in the Cu-rich chain.

step atoms are shifted towards lower frequencies as compared to the corresponding bulk modes (dark solid curve) in all directions. In figure 3(a) most softening appears along the x-direction, which may be traced to the loss of neighbours for the SC-atoms, in agreement with previous

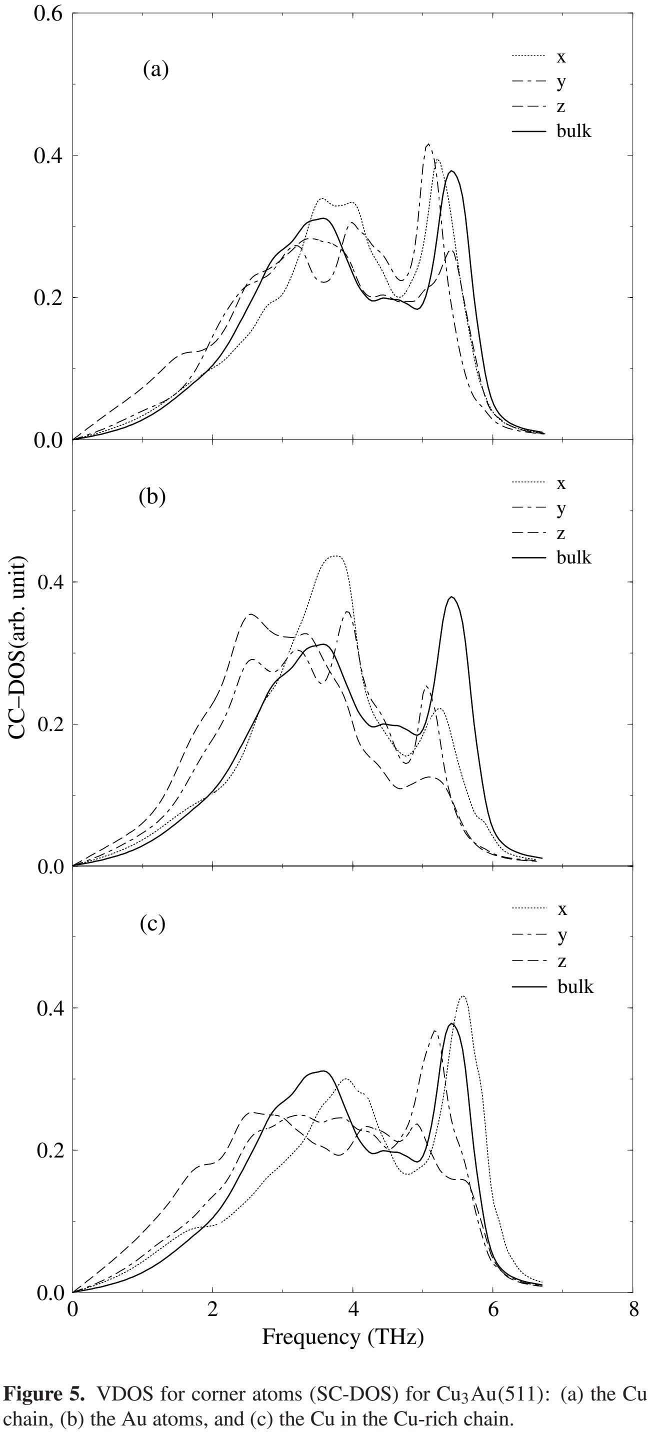

Figure 5. VDOS for corner atoms (SC-DOS) for Cu$_3$Au(511): (a) the Cu atoms in the Au-rich chain, (b) the Au atoms, and (c) the Cu in the Cu-rich chain.

theoretical work on Cu(511) [23]. The buckling of the Au atoms plays an important roll in shifting the modes. Figure 3(a) shows that the most stiffening of the frequency of the modes is along the z-direction, while figures 3(b) and (c) indicate very small shift. In figure 4(a),

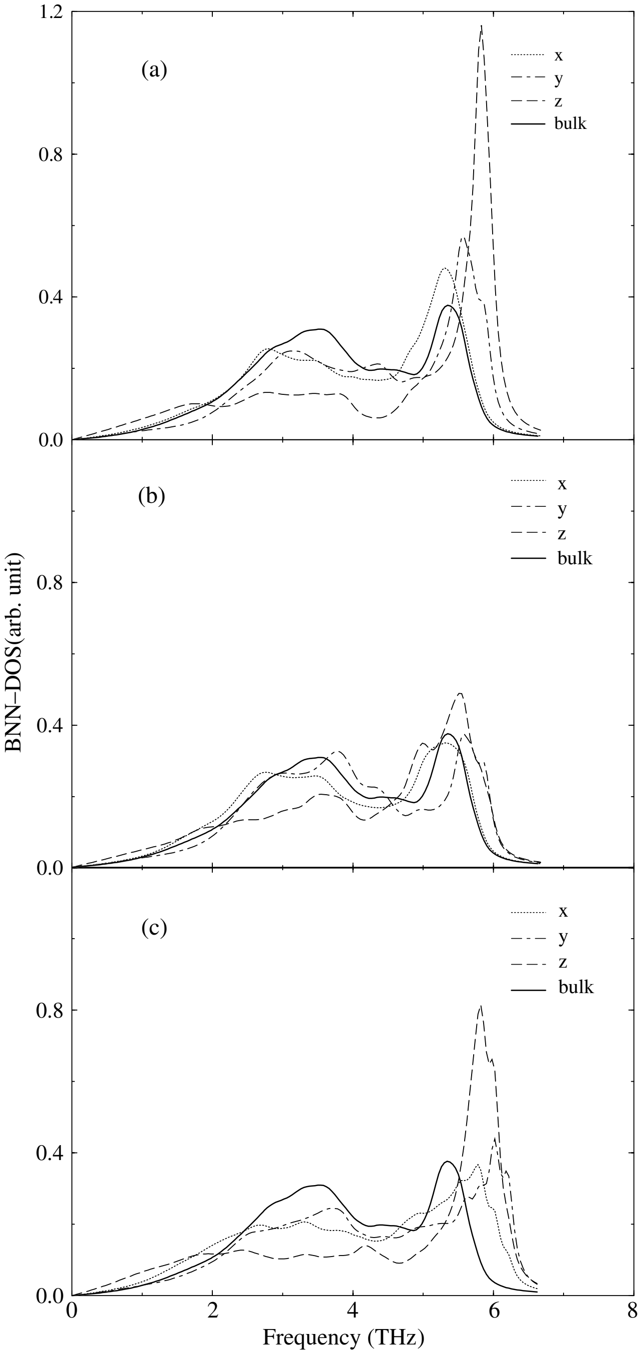

Figure 6. VDOS for bulk nearest neighbour atoms (BNN-DOS) for $Cu_3Au(511)$: (a) the of Cu atoms in the Au-rich chain, (b) the Au atoms, and (c) the Cu in the Cu-rich chain.

for the density of states for Tc atoms, both softening and stiffening are pronounced along all directions, while in figure 4(b) the softening appears in both the y- and x-directions and no stiffening appears beyond the bulk value; figure 4(c) shows equal softening along all direction

Table 4. Local contribution to the excess vibrational free energy at 300 and 663 K.

	Atom	300 K	663 K
	SC	−15 meV	−31 meV
Cu in Au-rich	TC	−14 meV	−29 meV
	CC	−6 meV	−13 meV
	SC	−17 meV	−43 meV
Au	TC	−21 meV	−43 meV
	CC	−12 meV	−43 meV
	SC	−10 meV	−21 meV
Cu in Cu-rich	TC	−9 meV	−16 meV
	CC	−4 meV	−3 meV

and we find no stiffening. In figures 5(a)–(c) for the CC atoms in the respective types of chains we find that the modes soften the most along the z-direction and find a small stiffening in figure 5(c) along the x-direction similarly.

As we go deeper into the bulk, the softening in the three modes is reduced, as seen in figure 6 for the BNN atoms for which the modes become bulk-like. We find a dramatic stiffening along the z-direction in figure 6(a), a smaller amount in figure 6(b), while in figure 6(c) we find a large stiffening in both the z- and y-directions. These results indicate that the stiffening is related to the nature of the relaxation of Cu_3Au. The softening that we find in these calculation is related to the shortening in the bond length between the SC atoms and their neighbour shown above.

6. Vibrational thermodynamic properties

Once the local vibrational density of states is calculated, we can easily determine the local thermodynamic functions of the system. We present the vibrational free energy in the harmonic approximation as given by

$$F_{\mathrm{vib}} = 3k_{\mathrm{B}}T \int_0^{\infty} \ln\left(2\sinh\left(\frac{\hbar w}{2k_{\mathrm{B}}T}\right)\right) N(w)\,\mathrm{d}w, \tag{2}$$

where F_{vib}, is the vibrational free energy along the Cartesian direction α and $N(w)$ is the calculated vibrational density of states for the local region of interest.

Figure 7 shows the vibrational free energy for SC, TC, CC and BNN atoms as a function of temperature. Here (a) represents the Cu atoms in the Au-rich chain, (b) the Au atoms, while (c) is for Cu atoms in the Cu-rich chain. From the figure we note that within the harmonic approximation for all cases the SC atoms have the lowest vibrational free energy while the BNN atoms have the largest value at all temperatures, also the differences between the surface atoms and bulk increases as a function of temperature. The local contribution to the excess (from the bulk) vibrational free energy for SC, TC and CC atoms, at 300 and 663 K (critical temperature at which Cu_3Au start to disorder), for Cu(Au-rich), Au and Cu(Cu-rich) are summarized in table 4. The striking contribution of the Au atoms (43 meV/atom at 663 K) to the excess vibrational free energy of this alloy vicinal surface is obvious from the table.

7. Conclusions

In summary, we have explored the local structural and vibrational properties of $Cu_3Au(511)$ using the embedded atom method for the interaction potentials and the real-space Green function technique for the evaluation of the phonon density of states. From an investigation of multilayer relaxations of this surface, qualitatively $Cu_3Au(511)$ has the same pattern of

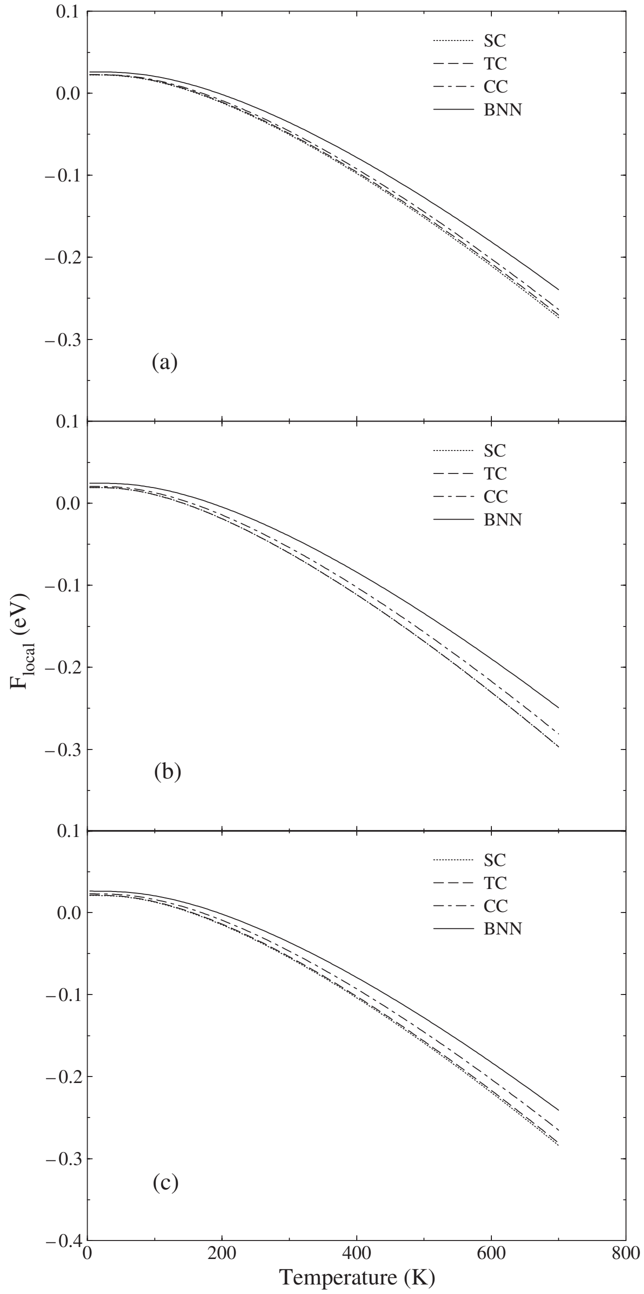

Figure 7. Calculated vibrational free energy (F_{vib}) for the SC, TC, CC and BNN atoms on $Cu_3Au(511)$: (a) Cu atoms in the Au-rich chain, (b) Au atoms, and (c) Cu in the Cu-rich chain.

relaxation as Cu(511), but these relaxations have larger values in the Au-rich chains between CC and BNN atoms of $Cu_3Au(511)$. In table 1 we show a large contraction in the relaxation between the TC and CC atoms in the Au-rich terraces. Deeper in the crystal in the Cu-rich chains we find a large expansion between the sixth and seventh layers. All of these results can be explained in terms of the buckling in the Au atoms in the CC.

Our calculations of the relative change in bond length depend on the concentration of the Au atoms in $Cu_3Au(511)$. We find a strong contraction in the bond length between SC-BNN in Cu(Au-rich) atoms while we find a slight expansion of 0.5% between SC(Cu-rich) and CC(Cu(Au-rich) with a contraction in the bond length of 2.5% between SC(Cu-rich) and CC(Au) which show the effect of the Au atoms in $Cu_3Au(511)$. We find a relationship between the change in the bond length, and the change in the force constant matrix K_{zz}, relative to the bulk value, for the SC and BNN, for which we find the maximum contraction takes place in the Cu(Au-rich) atoms. The calculated VDOS show deviation from the bulk VDOS, indicating large environment dependent softening and stiffening in the frequencies of the modes. More importantly, we find the calculated excess free energy of the Au atoms for SC, TC and CC at 663 K to be -43 meV/atom.

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