

High-frequency phonon modes on stepped and kinked Cu surfaces: Experiments and theory

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Using electron energy loss spectroscopy, we have found step-localized vibrational modes with frequencies higher than those of the bulk phonons on Cu(532) and Cu(211). From structural and lattice dynamical calculations based on many-body interaction potentials, we trace the origin of these modes to local effects involving surface relaxations and resulting stiffening of force constants between the step (or kink-site) atom and its “bulk” nearest neighbor. Such modes are not observed on Cu(511) and Cu(17,1,1), although they are predicted in the theoretical calculations. We discuss the impact of these results on systems with bond-length–bond-order correlation.

Vicinals are surfaces for which the macroscopic orientation forms a small angle with respect to a low-index plane. Ideally, they are made up of terraces separated by regularly spaced steps of monatomic height. The lower coordination and the reduced symmetry of atoms on vicinal surfaces, as compared to those in the bulk solid and on flat surfaces, lead to characteristic variations in the surface electronic charge densities which may in turn affect their reactivity and propensity to harbor localized vibrational and electronic surface excitations. Early interest in vicinals was motivated by the need to comprehend in a rather controlled manner the sensitivity of catalytic reactions¹ to atoms in step and kink sites. Attention to vicinal surfaces has been renewed in recent years, because of their technological importance as templates² for the growth of well ordered, laterally patterned nanostructures. For such technological purposes there is also the need to understand the stability of vicinal surfaces as a function of surface temperature.

The lower coordination of the step atoms compared to terrace atoms causes them to “relax” around their nearest neighbors. This means that in their minimum energy configuration the equilibrium positions of these atoms are displaced from their bulk-terminated ones. Related to surface relaxation is the anticipated smoothing of the charge densities at and near step edges and kink sites.³ It is this characteristic that leads to structural, dynamical, and electronic changes at steps and kink sites and which is ultimately related to the nature of the bonding between atoms. The presence of the surface, the step, and the kink can be thought of as perturbations of increasing complexity on an otherwise periodic system. On flat surfaces the reduction in translational symmetry in the direction perpendicular to the surface leads to localized surface vibrational modes whose frequencies are found to be lower than that of the maximum bulk phonon band. The frequencies and dispersion of these surface localized modes have been of particular interest as they serve as a measure of the changes in surface force constants from values in the bulk.⁴ Recent experiments using the He atom-surface scattering technique have also unveiled low-frequency, step-localized modes on vicinals of Cu (Ref. 5)

and Ni.⁶ On the other hand, in early efforts to measure phonons at metal surfaces Ibach and Bruchmann⁷ using electron energy loss spectroscopy (EELS) had found a mode on Pt(775) whose frequency was higher than that of the bulk phonon spectrum.

The presence of the high-frequency mode on Pt(775) was confirmed in tight-binding model calculations by Allan,⁸ who related it to the stiffening of the force constants of the step atom resulting from the contraction in the top interlayer distances. Recent studies on a number of Au, Cu, and Ni vicinal surfaces with different step-face and terrace orientations using empirical many-body potentials⁹ also predict high-frequency modes that lie above the bulk band. As in the earlier work of Jiang *et al.*,¹⁰ the complex relaxation patterns near the step atoms found in Ref. 11 show a marked contraction in the bond length between the step atom and its immediate neighbors in the bulk. A general picture thus emerges for systems in which there is a bond-length–bond-order correlation: high-frequency modes appear above the bulk band as a consequence of the relaxation at and near low-coordinated atoms. In this paper, we show how this general picture is challenged by EELS measurements in which high-frequency modes have been observed on Cu(211) and Cu(532), but not on Cu(511) and Cu(17,1,1).

In this paper the vibrational modes of two classes of stepped Cu surfaces have been investigated by EELS. The choice of these vicinals is partly motivated by the fact that their terraces are nonreconstructed and hence this particular source of interaction between steps (“magic vicinals”¹¹) is suppressed, and partly because available theoretical calculations of their energetics and dynamics^{9–13} have the possibility of providing a linkage between surface relaxations, changes in surface interatomic force constants, and the observed EELS data on surface phonon frequencies. Since extraction of structural quantities from experimental data is never an easy task, any quantitative information that EELS may be able to provide on the subject would be welcome. At the same time, it is heartening that techniques like low-energy electron diffraction (LEED) which measure relaxations directly are now being applied to examine vicinal sur-

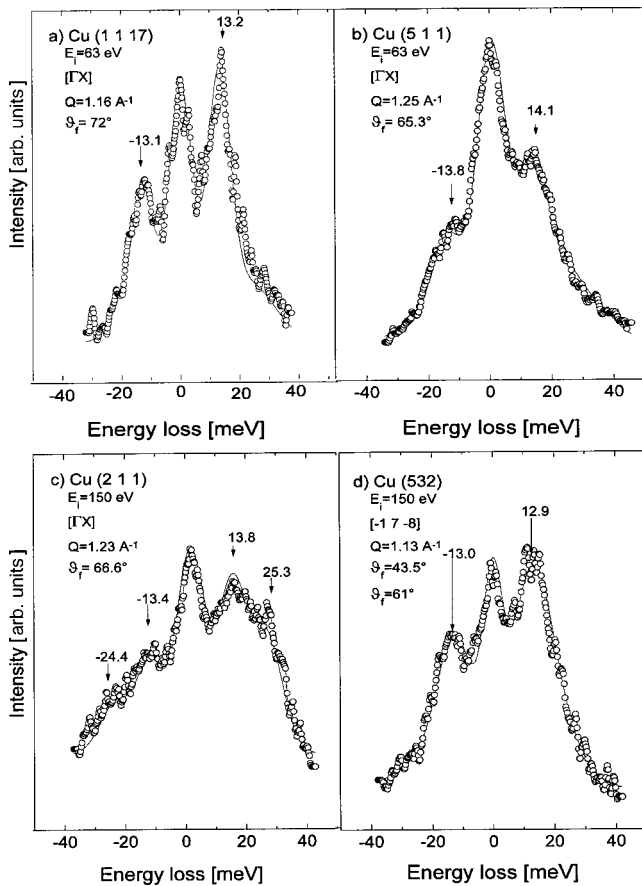


FIG. 1. Typical electron energy loss spectra recorded in impact scattering geometry.

faces. Recent LEED measurements by Seyller *et al.*¹⁴ on Cu(211) find a relaxation pattern in agreement with our calculations. Very recent relaxation data on Cu(511) using x-ray scattering¹⁵ appear to be not in complete agreement with previous results,⁹ making the subject of this paper all the more interesting. Conclusions from the present analysis of EELS data can thus complement (or raise further questions about) the structural information from LEED and x-ray scattering and lead to a broader understanding of the relationship between surface structure and dynamics.

On surfaces whose step structure is a (001) microfacet, our EELS measurements have helped identify a vibrational mode propagating along the steps with frequency well above the maximum of the surface-projected bulk phonon continuum. We associate the presence of these confined high-frequency phonons with a significant relaxation of the step atoms on surfaces with this type of microfacet. Interestingly, modes with frequencies above the bulk band are not detected in these EELS measurements, on a Cu vicinal whose step structure is a (111) microfacet. In the accompanying lattice dynamical analysis using an embedded atom method (EAM) type interaction potential, such high-frequency surface phonon modes are predicted for all four vicinal surfaces examined here. These are found to be localized step excitations resulting from an inward relaxation of atoms at and in the vicinity of steps, and possess complex displacement patterns, whose amplitudes are maximum in the second layer and decay into the bulk.

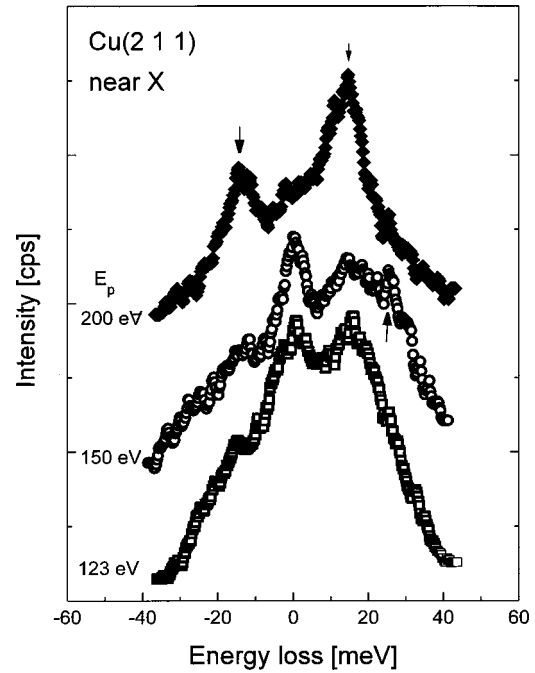


FIG. 2. Variation of the cross section with primary electron energy for inelastic scattering on Cu(211).

In the actual measurements the energy resolution is set to 6–10 meV in the specularly reflected electron beam. The incident energy is between 60 eV and 200 eV in impact scattering geometry, while in the dipole scattering mode the incident energy has been set to below 10 eV. Energy transfer spectra have been recorded within about 20 min at a base pressure of 10^{-10} Torr with the samples held at room temperature. The Cu single crystals have been prepared using established methods,¹⁶ and their orientation has been controlled with LEED. The four vicinal surfaces examined here have different local surface geometries. Terraces on Cu(211) are (111) oriented and separated by steps of monatomic height with a (001) microfacet. The steps on Cu(532) are similar to those on Cu(211) except for an additional regularly spaced kink. Cu(17,1,1) and (511) belong to a class of vicinals whose terraces are (001) oriented and separated by (111) microfaceted steps. In Figs. 1(a)–(d) we show examples of energy loss spectra recorded in the impact scattering mode for the four surfaces under investigation. These spectra are representative of those with primary incident electron energies between 50 eV and 200 eV, except for the (211) surface for which a strong variation of the cross section with incident electron energy of selected phonon modes has been observed, as shown in Fig. 2.

For the purpose of this paper, the most striking observation is the presence of a dipole-active mode (Fig. 3) on Cu(211) and Cu(532) with frequency larger than the maximum energy of the surface-projected bulk phonon continuum. The intensity of these modes, as a function of angle, scales with the intensity of the elastically scattered electrons, indicating their dipole-active character. Energy loss spectra taken in the dipole scattering regime show (Fig. 3) that such modes could not be detected in our experiments for Cu(511) and Cu(17,1,1). Due to the lack of intensity in the impact scattering region (see Fig. 1) it is difficult to comment on the presence of modes above 30 meV. Our experimental findings

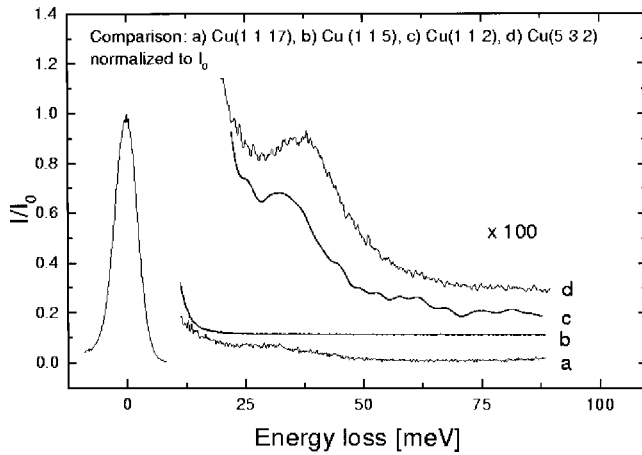


FIG. 3. Electron energy loss spectra in dipole scattering geometry on Cu(1,1,17), Cu(115), Cu(112), and Cu(532). The incident electron energy is 4.1 eV and the incident and scattering angles are 64° .

for all surfaces of interest in this paper are summarized in Fig. 4. The low-frequency surface phonons propagating parallel to the average step direction of these vicinals are found to be related to those observed on the corresponding low Miller indices (flat) surfaces. Perpendicular to the average step direction we observe in some cases the Rayleigh mode “backfolded” into the reduced Brillouin zone, as imposed by the additional periodicity of the step lattice.

To calculate surface structural quantities and dynamics of Cu vicinals, we use EAM,¹⁷ which despite being empirical has had success in predicting several surface properties like relaxations, reconstructions, and the dispersion of the surface phonons for Ag, Cu, and Ni.^{17–19} We have used here the parametrization by Voter and Chen²⁰ in which experimental

values of the bond length and binding energy of the diatomic molecule are also included in the fitting of the potential functions, in addition to several bulk properties. For each system of interest we begin with all atoms in their bulk-terminated positions arranged in layers in the form of a slab, and allow them to relax to their minimum energy configuration, using a conjugate gradient, energy-minimization algorithm. Surface relaxations and other structural quantities of interest are then obtained. Next, with the atoms in the equilibrium configuration, the force constant matrix needed to calculate the vibrational dynamics of the system is extracted from the partial second derivatives of the EAM potentials. The secular equation with the dynamical matrix is then diagonalized in a straightforward manner to obtain the phonon frequencies and displacement patterns from the eigenvalues and eigenvectors of the diagonalized matrix. To obtain smooth spectral densities, the number of layers varies from 210 for Cu(211) to 620 for Cu(532).

Previous studies¹³ have already shown that vicinal surfaces undergo large and oscillatory multilayer relaxations that persist for several layers. As examples, we show in Fig. 5 the relaxation patterns of Cu(211) and Cu(511). There is a striking similarity in the two curves which can be traced to the local atomic environment on the two surfaces since (211) has a (111) terrace and a (001) step microfacet, while the (511) has the reverse arrangement. In the case of Cu(211), relaxations have also been calculated from first-principles electronic structure calculations²¹ and are in good agreement with our results.

Related to surface multilayer relaxations are the changes in bond lengths between the step atoms and their nearest neighbors. For the cases of Cu(211), Cu(511), and Cu(17,1,1), the step chain (SC) has a neighboring chain on the same terrace (TC), another one on the next terrace (CC),

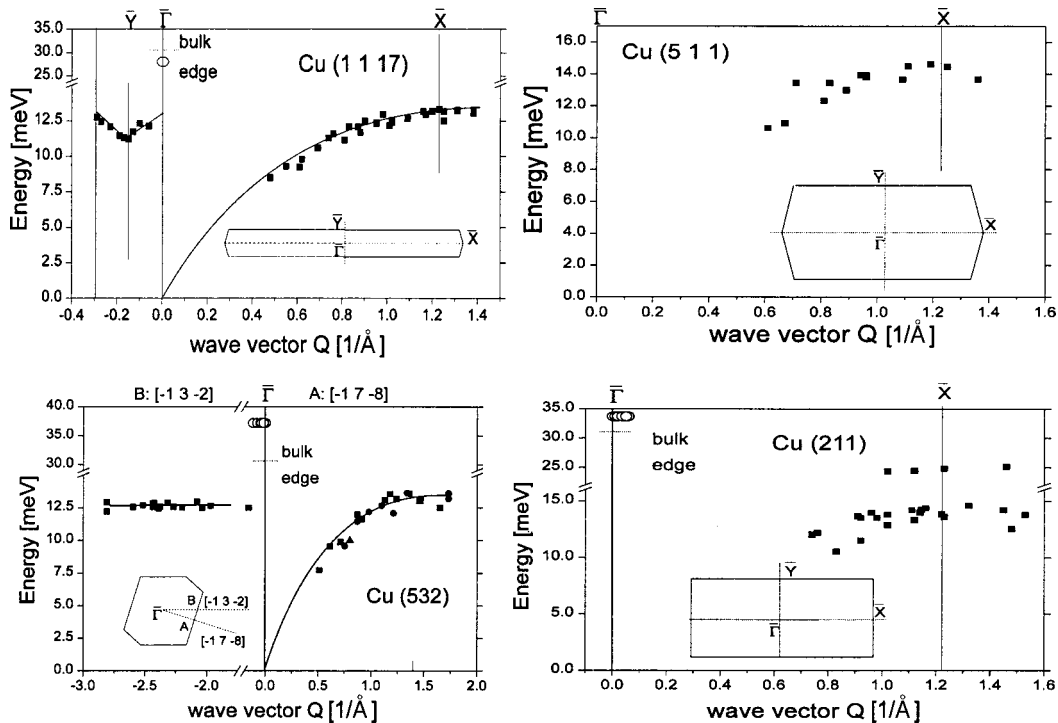


FIG. 4. Compilation of experimental results in various high-symmetry directions.

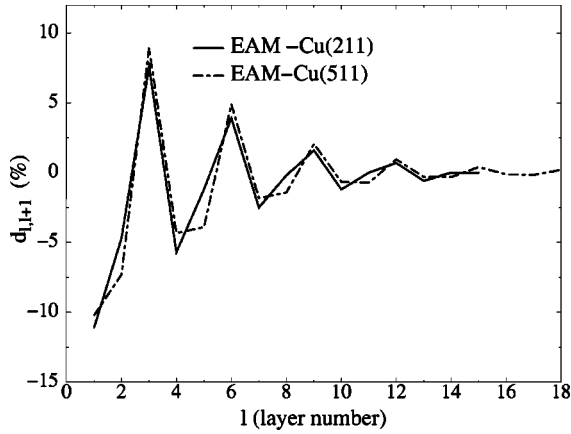


FIG. 5. Multilayer relaxation pattern for Cu(511) and Cu(211).

and one just below it (BNN) (see Fig. 6).²² The most striking feature is the shortening of the bond between SC and BNN atoms. The step atoms try to enhance their effective coordination by moving closer to their bulk nearest neighbor. In Table I, we find that the shrinkage in bond length between SC and BNN atoms is accompanied by a stiffening of the force constant between these two atoms in the direction perpendicular to the macroscopic surface. For Cu(211) this stiffening is 38.3%, for Cu(511) it is 33.3%, for Cu(17,1,1) it is 63.5%, and for the kinked surface Cu(532) it is 82.2%. Enhancement of this particular force constant is only one of the consequences of surface relaxations at and near the steps. Several other force constants are also affected. Some soften and some stiffen.⁹

Calculated phonon spectral densities at high-symmetry points in the surface Brillouin zone for all surfaces studied here show the presence of modes above the bulk band in each case. To compare the specific contributions of the step, BNN, and bulk atoms, we plot in Fig. 7 their projected vibrational density of states, at the Γ point, for Cu(211) and Cu(511). There is a striking similarity in the vibrational characteristics of the two surfaces, particularly near the top of the phonon bands. The projected density of states of the step atoms on Cu(211) shows the backfolded Rayleigh mode at an energy of 9.8 meV, in good agreement with He scattering measurements of 10.9 meV,⁵ while *ab initio* calculations find a value of 11.5 meV.²¹ At higher energies, there is another step mode with high amplitude at 25.9 meV similar to one found at 24.7 meV, in the *ab initio* calculations of Wei *et al.*²¹ A similar list of modes and their frequencies can be extracted from Fig. 7(b) for Cu(511). Note that the highest-frequency modes in Figs. 7(a) and 7(b) lie above the top of

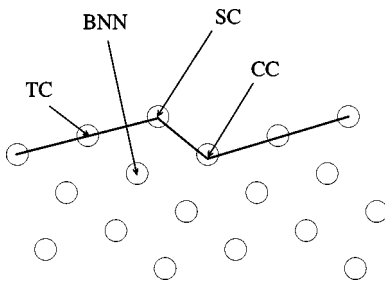


FIG. 6. Side view of a fcc vicinal surface.

TABLE I. Calculated percentage changes (Δr) in bond length, its vertical component (Δz), force constant (Δk_{zz}) between the step atom and its bulk nearest neighbor (BNN), for the four surfaces. Here $\Delta \nu$ is the shift in the frequency of the step-localized mode above the maximum bulk mode.

Surface	Δr (%)	Δz (%)	Δk_{zz} (%)	$\Delta \nu$ (meV)
Cu(211)	-2.1	-2.7	38.3	+1.0
Cu(511)	-2.2	-2.9	33.3	+1.0
Cu(17,1,1)	-2.4	-2.7	63.5	+1.8
Cu(532)	-3.5	-3.9	82.2	+2.8

the bulk band, and present a large amplitude for the BNN atom on both Cu(211) and Cu(511). The quantity of interest in this paper, the upward shift of the surface modes above the top of the bulk band, for the four surfaces of interest, is listed in Table I.

As apparent in Fig. 7, calculations show two step-localized, high-frequency modes, one of which has frequency above the bulk band, while the other is a resonance mode with frequency just below the top of the bulk band. The frequencies associated with these modes are 31.4 and 32.5 meV for Cu(211), 31.3 and 32.5 meV for Cu(511), and 31.1 and 33.0 meV for Cu(17,1,1). For Cu(532), the mode above the bulk band at 33.8 meV has a much larger amplitude than the one just below the bulk band at 30.9 meV. Analysis of the eigenvectors associated with these modes shows that the maximum amplitude of the displacement is associated with the BNN atoms, which together with the step atoms vibrate predominantly normal to the macroscopic surface plane, with the adjacent terrace and corner atoms moving mainly in the surface plane and perpendicular to the step, forming a breathing-type mode. The complex and mixed polarization associated with these modes may explain why the

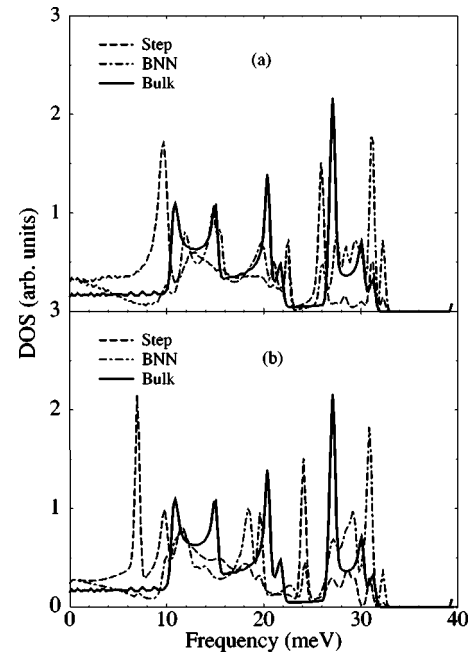


FIG. 7. Projected vibrational density of states, at Γ , for step (dashed), BNN (dot-dashed), and bulk (solid line) atoms on (a) Cu(211) and (b) Cu(511).

cross section for these modes was small in the EELS experiments on Cu(17,1,1) and Cu(511).

In summary, we have presented here arguments about the existence and origin of modes above the bulk band on several vicinals of Cu. This joint experimental and theoretical effort has raised some issues. The lattice dynamical calculations show that the high-frequency modes (above the bulk phonon band) and resonance modes just below the bulk edge are a natural feature of vicinal surfaces of metals like Cu that have a bond-length–bond-order correlation, and should be present regardless of whether the step microfacet is (001) or (111). Our EELS measurements, however, do not reveal modes above the bulk band for Cu(17,1,1) and Cu(511). We, therefore, have two possible scenarios: the modes in question exist but could not be detected in the present EELS measurements, or they do not exist and are merely artifacts of the interaction potential used in this work. It would thus be very useful to carry out calculations of the relaxations and force constant changes using more accurate techniques, like *ab initio* electronic structure calculations. The excellent agree-

ment between the structural and dynamical calculations on Cu(211) using EAM and *ab initio* methods, as discussed above, leads us to believe that the EAM potentials provide results very similar to those extracted from *ab initio* methods. However, similar comparisons may not hold for other surfaces considered here. It may also be that any model based on coordination and the bond-length–bond-order correlation is problematic when addressing subtleties in phonon spectra.

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- ¹G. A. Somorjai and M. A. Van Hove, *Prog. Surf. Sci.* **30**, 210 (1989).
- ²J. Pond, A. C. Gossard, A. Lorke, and P. M. Petroff, *Mater. Sci. Eng.*, **B 30**, 121 (1995); M. S. Miller, H. Weman, C. E. Pryor, M. Krishnamurthy, P. M. Petroff, H. Kroemer and J. L. Merz, *Phys. Rev. Lett.* **68**, 3464 (1992).
- ³R. Smoluchowski, *Phys. Rev.* **60**, 661 (1941).
- ⁴H. Ibach and T. S. Rahman, *Chemistry and Physics of Solid Surfaces V*, Springer Series in Chemical Physics Vol. 35 (Springer-Verlag, Berlin, 1991), p. 455.
- ⁵G. Witte, J. Braun, A. Lock, and J. P. Toennies, *Phys. Rev. B* **52**, 2165 (1995).
- ⁶L. Niu, D. D. Koleske, D. J. Gaspar, and S. J. Sibener, *J. Chem. Phys.* **102**, 9077 (1995).
- ⁷H. Ibach and D. Bruchmann, *Phys. Rev. Lett.* **41**, 958 (1978).
- ⁸G. Allan, *Surf. Sci.* **85**, 37 (1979).
- ⁹S. Durukanoglu, A. Kara, and T.S. Rahman, *Phys. Rev. B* **55**, 13 894 (1997), and references therein.
- ¹⁰P. Jiang, F. Jona, and P. M. Marcus, *Phys. Rev. B* **35**, 7952 (1987).
- ¹¹A. C. Redfield and A. Zangwill, *Phys. Rev. B* **46**, 4289 (1992); S. Papadia, M. C. Desjonqueres, and D. Spanjaard, *ibid.* **53**, 4083 (1996).
- ¹²A. Kara, S. Durukanoglu, and T. S. Rahman, *J. Chem. Phys.* **106**, 2031 (1997).
- ¹³Z. J. Tian and T. S. Rahman, *Phys. Rev. B* **47**, 9751 (1993).
- ¹⁴Th. Seyller, R. D. Diehl, and F. Jona, *J. Vac. Sci. Technol. A* **17**, 1635 (1999).
- ¹⁵D. A. Walko and I. K. Robinson, *Phys. Rev. B* **59**, 15 446 (1999).
- ¹⁶H.-J. Ernst, R. Folkerts, and L. Schwenger, *Phys. Rev. B* **52**, 8461 (1995); L. Schwenger, R. Folkerts, and H.-J. Ernst, *ibid.* **55**, R7406 (1997).
- ¹⁷For a review of the embedded atom method, see M. S. Daw, S. M. Foiles, and M. I. Baskes, *Mater. Sci. Rep.* **9**, 251 (1993).
- ¹⁸T. S. Rahman, in *Condensed Matter Theories*, edited by J. Clark, K. Shoaib, and A. Sadiq (Nova, New York, 1994), Vol. 9, p. 299.
- ¹⁹K. P. Bohnen and K. M. Ho, *Surf. Sci. Rep.* **19**, 99 (1993), and references therein.
- ²⁰A. F. Voter and S. P. Chen, in *Characterization of Defects in Materials*, edited by R. W. Siegel, J. R. Weertman, and R. Sinclair, MRS Symposia Proceedings No. 82 (Materials Research Society, Pittsburgh, 1987), p. 175.
- ²¹C. Y. Wei, S. P. Lewis, E. J. Mele, and A. M. Rappe, *Phys. Rev. B* **57**, 10 062 (1998).
- ²²S. Y. Tong, C. H. Li, and D. L. Mills, *Phys. Rev. B* **24**, 806 (1981).