

## Origins of Surface Alloy Formation: Cu(001) $c(2 \times 2)$ -Pd as a Case Study

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We present a rigorous theoretical treatment which, in agreement with recent experiments, supports the formation of the ordered  $c(2 \times 2)$  phase of the CuPd surface alloy on the Cu(001) substrate, and does not support the formation of an ordered overlayer of only Pd atoms on such a substrate. Based on *ab initio* electronic structure of random CuPd and Pd-vacancy overlayers, we study their stability against ordering using the generalized perturbation method adapted to strongly inhomogeneous systems. The approach, the first of its kind, is general and can be applied to other metal-on-metal overlayers.

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This paper addresses the problem of origins of formation of ordered surface alloys on clean transition-metal surfaces and presents the first attempt to solve it entirely from first principles. The approach we use consists of two steps: (i) the determination of the self-consistent electronic structure of a truly semi-infinite substrate with a disordered overlayer within the local-density approximation (LDA); (ii) the study of the instability of this disordered phase towards the formation of the ordered superstructure in the framework of the generalized perturbation method adapted to the case of random overlayers. Underlying both steps is the Green's-function method, which allows a proper treatment of the infinitely extended geometry, unlike in techniques using slabs or supercells. Modern theories of compositional ordering [1-6] start from the completely disordered alloy as a reference system. The disordered state itself is naturally treated by the Green's-function technique within the coherent potential approximation (CPA) method. In this work the CPA-averaged layer-resolved Green's function is calculated in a self-consistent manner using the tight-binding linear muffin-tin orbital (TB-LMTO) basis.

The formation of surface alloys on low-index transition-metal surfaces is now well established [7-13]. Typical examples are systems such as Au on Cu(001) [7,8] or Pd on Cu(001) [9-13]. When the Cu(001) crystal is exposed to Pd or Au atoms at room temperature, a  $c(2 \times 2)$  low-energy electron-diffraction (LEED) pattern is observed which reaches its maximum intensity for a deposition of  $\frac{1}{2}$  monolayer of Pd(Au) atoms. An ordered surface alloy Cu(001) $c(2 \times 2)$ -Pd(Au) is distinguished from an ordered bulk alloy by the fact that it is limited to the top sample layer with no Pd(Au) atoms found in the bulk of the substrate.

Two structural models could account for a  $c(2 \times 2)$  LEED pattern observed in the experiment, namely, the CuPd (CuAu) mixed alloy layer like a (001) face of ordered Cu<sub>3</sub>Au, and an overlayer of Pd(Au) atoms located in the fourfold symmetrical hollows on the Cu(001) face. A dynamical LEED analysis [8,12] confirms that a pure Pd(Au) overlayer could not account for the experimental results while a buckled mixed alloy CuPd (CuAu) could.

While the buckling is notable for Au atoms, the CuPd alloy is almost planar with the Pd atoms only slightly displaced outward of the Cu atoms [12]. This is consistent with the smaller Pd (compared with Au) metallic radius. The alloy character of the Cu(001) $c(2 \times 2)$ -Pd phase is also confirmed by the photoemission experiments [12], notably by the appearance of Pd-induced features similar to those observed for the Cu-rich bulk CuPd alloys [14].

Recently considerable experimental effort was devoted specifically to the CuPd case [9-13]. The Pd coverage associated with the maximum  $c(2 \times 2)$  LEED intensity was confirmed to be  $\frac{1}{2}$  of the monolayer [13] using the Rutherford-backscattering spectrometry, which provides reliable information on the coverage of a surface by foreign atoms. The  $c(2 \times 2)$  phase was observed also for Pd coverages smaller or greater than  $\frac{1}{2}$  of the monolayer, which corresponds to the ideal ordered superstructure. These quantitative measurements of the coverage dependence of the  $c(2 \times 2)$  pattern intensity clearly indicate the strong tendency towards ordering in the CuPd surface alloy.

The ordering tendency in bulk transition-metal alloys has been shown to have a general origin in band filling arguments. It was concluded [15] that transition-metal alloys will order if the Fermi energy  $E_F$  falls near half filling of their  $d$  band and phase separate if  $E_F$  lies near either band edge. This simple tight-binding argument does not apply to alloys with  $E_F$  above the  $d$ -band complex such as CuAu. Even among alloys with an unfilled  $d$  band there are notable exceptions like the NiPt alloy. The latter case was explained recently [1] on the basis of a first-principles theory of electronic structure and the mean-field theory of concentration fluctuations [2]. This illustrated a great predictive power of the first-principles theory of ordering in alloys used in Ref. [1].

At this stage it is worthwhile mentioning some differences between bulk and surface alloys. The most notable is the pinning up of the Fermi level at the surface by the substrate. Consequently, the charge neutrality cannot be achieved by shifting  $E_F$  to accommodate valence electrons as in the bulk case but via a reconstruction of the electronic structure in the spatial region of the

sample-vacuum interface. As a result, the properties of a few top layers differ from each other as well as from those deeper in the sample (the infinite medium). Thus a surface alloy, contrary to a bulk alloy, is spatially inhomogeneous by its nature.

The method to describe the electronic structure of disordered overlayer on the perfect substrate, needed for the present study of ordering, was described in detail elsewhere [16]. Here we just summarize its basic features. Our approach is based on the LDA and uses the first-principles TB-LMTO method to calculate the electronic structure. In this approach both intralayer and interlayer interactions are short ranged, facilitating the evaluation of the surface Green's function needed for a description of the semi-infinite nature of the problem. The potentials are treated in the atomic sphere approximation (ASA) but for the charge density we include both monopole and dipole terms in the multipole expansion, which accounts for its nonspherical shape at the surface and yields a correct value of the electrostatic surface barrier [16,17]. The effect of disorder is treated in the CPA capable of describing the surface alloy of arbitrary composition including the case of a partial coverage by foreign atoms.

Because of the semi-infinite nature of the problem, all layers can, in principle, have different local physical properties. We assume that from a certain layer on, the electronic properties of all subsequent layers are those of the corresponding infinite system, namely, either a homogeneous substrate or the vacuum. The semi-infinite sample is considered to be divided into three parts: (i) a

homogeneous substrate with no disorder, (ii) a (homogeneous) vacuum represented by empty spheres with flat potentials [18], and (iii) an intermediate region consisting of several ( $M$ ) atomic layers where all chemical and electronic inhomogeneities are concentrated. This region consists of a few substrate layers, the random overlayer, and a few layers of empty spheres of the vacuum-sample interface. Only potentials in the intermediate region are determined self-consistently during the surface calculations while those for the homogeneous bulk or vacuum are kept frozen at values found from separate calculations for corresponding infinite systems. The decomposition of the infinite system into these three regions allows an efficient solution of the electronic part of the problem by the Green's-function technique [16].

The layer-diagonal but site off-diagonal elements of the configurationally averaged overlayer Green's function  $\bar{\mathcal{G}}_{\mathbf{R}\mathbf{R}'}(z)$  (sites  $\mathbf{R} \neq \mathbf{R}'$  are limited to the overlayer), given by the electronic structure part of the calculation, are the central quantities needed in the theory of compositional ordering. For the bulk case, three variants of theory have been developed, namely, the generalized perturbation method (GPM) [3-5], the embedded cluster method (ECM) [6], and the concentration fluctuation method (CFM) [1,2]. The GPM was recently extended to random surfaces [19,20] and here we use its most general form [20] for alloys with nonuniform composition at the sample surface [21]. The central quantity is the effective, pairwise interchange interaction  $V_{\mathbf{R}\mathbf{R}'} = V_{\mathbf{R}\mathbf{R}'}^A + V_{\mathbf{R}\mathbf{R}'}^B - V_{\mathbf{R}\mathbf{R}'}^A - V_{\mathbf{R}\mathbf{R}'}^B$ , where  $A$  and  $B$  are atoms forming the surface alloy  $A_x B_{1-x}$ . Specifically [20],

$$V_{\mathbf{R}\mathbf{R}'}^{\alpha\alpha'} = -\frac{1}{\pi} \text{Im tr} \int^{E_F} \{t_{\mathbf{R}}^{\alpha}(z) \mathcal{G}_{\mathbf{R}\mathbf{R}'}(z) t_{\mathbf{R}'}^{\alpha'}(z) \bar{\mathcal{G}}_{\mathbf{R}'\mathbf{R}}(z)\}_{z=-E+i0} dE, \quad \alpha, \alpha' = A, B.$$

In this expression,  $t_{\mathbf{R}}^{\alpha}(z)$  [ $t_{\mathbf{R}'}^{\alpha'}(z)$ ] are the on-site  $T$  matrices of the TB-LMTO-CPA theory [16,22], and the trace, denoted by the symbol tr, extends over the orbital momentum subspace. The generalization to higher-order effective interactions, e.g., to triplets, is also possible [20]. The Fourier transform of  $V_{\mathbf{R}\mathbf{R}'}$ ,  $V(\mathbf{k}_{\parallel})$ , where  $\mathbf{k}_{\parallel}$  is a vector of the surface Brillouin zone corresponding to the sample face, provides direct information on the stability of the random overlayer phase against the formation of an ordered phase, as in the case of bulk alloys [1,2,4]. This concentration fluctuation theory of ordering in alloys can be considered as a first-principles generalization of the empirical concentration wave method of Khachaturyan [23].

The above theory is applied to the case of CuPd surface alloy. Our choice is guided by the facts that (i) the CuPd surface is almost planar [12] contrary to the case of the CuAu with pronounced buckling of Au atoms, (ii) the spin-orbit effects can be neglected, and (iii) quantitative measurements of the  $c(2 \times 2)$  spot intensity are available [13]. Points (i) and (ii) are not essential for the validity of our theory but represent a simplification of calculations. The intermediate region consists of an over-

layer, two substrate layers, and two layers of empty spheres on the vacuum side ( $M=5$ ). The fact that the CuPd surface is almost planar justifies using a radius for the Pd atoms that is equal to the Cu metallic radius [12]. The off-site elements of the overlayer Green's function are calculated by integrating  $\bar{\mathcal{G}}(\mathbf{k}_{\parallel}, z)$  over the full surface Brillouin zone [20]. Further details concerning the method to calculate  $\bar{\mathcal{G}}(\mathbf{k}_{\parallel}, z)$  can be found in Ref. [16]. We have calculated all pairwise interchange interactions up to the 11th shell of neighbors, in the real space, covering up to 3 times the nearest-neighbor distance. All triplet interactions were determined up to the 6th shell of neighbors in the real space. The quantity  $V(\mathbf{k}_{\parallel})$  was calculated by an inverse Fourier transform, by summing  $V_{\mathbf{O}\mathbf{R}}$  up to the 11th shell. This method favorably contrasts with the evaluation of  $V(\mathbf{k})$  directly in the  $\mathbf{k}$  space as done for bulk alloys in Refs. [1,2], and is justified by a fast convergence of  $V_{\mathbf{O}\mathbf{R}}$  with the shell number (see below).

For our purpose, the behavior of  $V(\mathbf{k}_{\parallel})$  is of central importance. As in the bulk case [1,2,4,23], an absolute minimum at  $\mathbf{k}_{\parallel}=0$  indicates the tendency towards phase

separation, while absolute minima at various high-symmetry points,  $\mathbf{k}_\parallel^*$  (surface analog of the so-called Lifshitz special points [23]), indicate the tendency to form the ordered superstructure generated by the  $\mathbf{k}_\parallel^*$  vector. In the present case, the  $c(2 \times 2)$  superstructure on the fcc (001) face is obviously generated by the vector  $\mathbf{k}_\parallel^* = (1,0)$ . The way to find the atomic arrangement of the stable overlayer superstructure is the following. We perform calculations of the electronic structure for the completely disordered phase of  $\text{Cu}_{50}\text{Pd}_{50}$  on Cu(001) and investigate the tendency towards the formation of the ordered  $c(2 \times 2)$  CuPd phase. This should manifest itself in the presence of an absolute minimum in  $V(\mathbf{k}_\parallel)$  [or, alternatively, a maximum in  $-V(\mathbf{k}_\parallel)$ ] at  $\mathbf{k}_\parallel^* = (1,0)$ . Figure 1(a) clearly demonstrates that this is the case. It is, however, equally important to rule out the possibility for the  $c(2 \times 2)$  ordered structure formed by Pd atoms sitting on the top of the Cu(001) substrate layer. Towards this end we apply the same method to a disordered overlayer of  $\text{Pd}_{50}(\text{vac})_{50}$  on Cu(001), where (vac) denotes vacancies represented by empty spheres whose potentials are determined self-consistently as in the previous case. The well-pronounced maximum in  $-V(\mathbf{k}_\parallel)$  at  $\mathbf{k}_\parallel^* = (0,0)$ , Fig. 1(b), clearly indicates that this phase does not form. The pairwise interchange interactions  $V_{0R}$  support the same picture. These pairwise interchange energies are 6.51, -0.59, -0.36, -0.18, -0.13, and -0.01 mRy for the first six neighbor shells in the  $\text{Cu}_{50}\text{Pd}_{50}$  overlayer. For  $\text{Pd}_{50}(\text{vac})_{50}$  overlayer we obtain -19.79, 1.38, -0.39, -0.03, -0.04, and 0.23 mRy. The remaining pair and all triplet interactions are of the order of 0.1 mRy or less. Clearly, the nearest-neighbor interaction dominates in both cases. The dominating positive nearest-neighbor interchange interaction implies a robust ordering tendency for the CuPd surface alloy. Small but negative second- and third-nearest-neighbor pair interactions further enhance the tendency to form the  $c(2 \times 2)$  phase (by suppressing  $AB$  pairing on these shells). Similar arguments exclude the possibility for the ordering of Pd atoms adsorbed atop the Cu(001) surface layer. Note, however, that the pairwise interactions just indicate the tendency towards ordering but are, by themselves, not sufficient to determine which superstructure will be formed. We have also calculated the effective interactions for CuPd overlayers with compositions nonstoichiometric with respect to the formation of the  $c(2 \times 2)$  superstructure. The pairwise interchange energies for the first six shells in  $\text{Cu}_{25}\text{Pd}_{75}$  are 5.59, -1.10, -0.22, -0.20, -0.02, 0.22 mRy, while in  $\text{Cu}_{75}\text{Pd}_{25}$  these are 7.70, 0.04, -0.07, 0.12, 0.0, and -0.06 mRy. The remaining pair and all triplet interactions are less than 0.15 mRy. There is a dominating tendency towards ordering also in these nonstoichiometric cases. This theoretical conclusion is in accord with a recent measurement of the Pd concentration dependence of the  $c(2 \times 2)$  LEED intensity for the CuPd surface alloy [13], where visible  $c(2 \times 2)$  LEED spots are

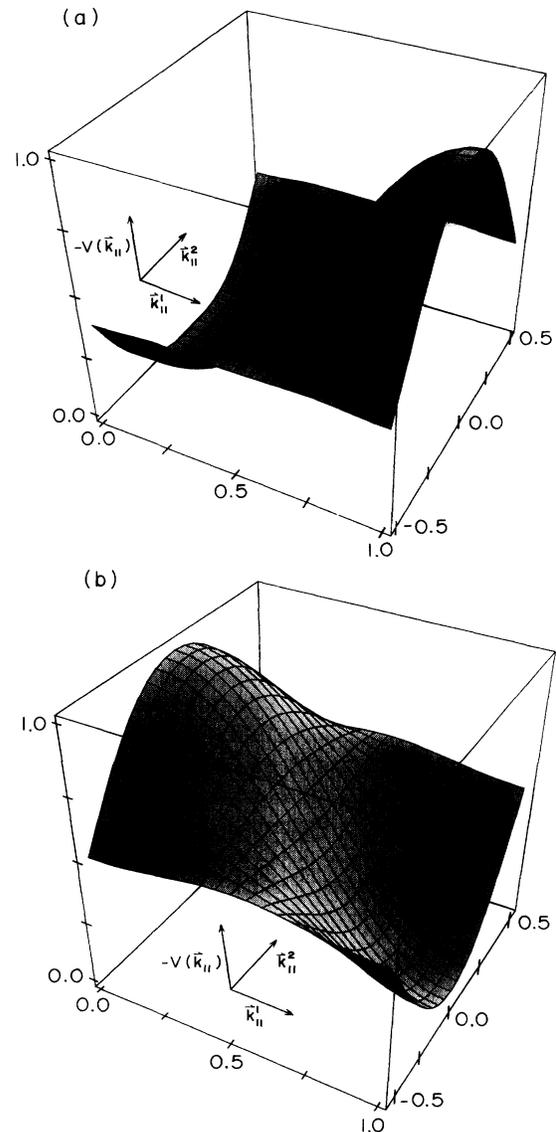


FIG. 1. The negative of the Fourier transform of the pairwise interchange interactions  $[-V(\mathbf{k}_\parallel)]$  in the relevant part of the extended surface Brillouin zone (SBZ). The irreducible part of the fcc (001) SBZ is the triangle given by points  $\mathbf{k}_\parallel = (0,0)$ ,  $(1,0)$ ,  $(\frac{1}{2}, \frac{1}{2})$ . (a) The  $\text{Cu}_{50}\text{Pd}_{50}$  overlayer on the Cu(001) substrate: The peak in  $-V(\mathbf{k}_\parallel)$  at  $\mathbf{k}_\parallel^* = (1,0)$  indicates the tendency for the disordered overlayer to order in the  $c(2 \times 2)$  phase. (b) The  $\text{Pd}_{50}(\text{vac})_{50}$  [(vac) denotes a vacancy] overlayer on the Cu(001) substrate: The peak at  $\mathbf{k}_\parallel^* = (0,0)$  excludes the possibility of the ordered  $c(2 \times 2)$  structure of Pd atoms on the Cu(001) substrate.

observed for these surface compositions. It is also interesting to compare the overlayer and the bulk effective pair interactions for the  $\text{Cu}_{50}\text{Pd}_{50}$  alloys. We just give values for the nearest-neighbor pairs: 6.5 mRy (overlayer) and 3.8 mRy (bulk). Though the detailed comparison is somewhat obscured by the fact that the surface

and the bulk alloys exist at different lattice constants, it is used here to demonstrate the enhancement of pair interactions at the surface [19,20].

In summary, we have extended the theory of ordering in bulk alloys, based on the generalized perturbation method, to the case of surface alloys. The true semi-infinite geometry is taken into account via the surface Green's-function method. The electronic structure is calculated self-consistently using the local-density approximation within the TB-LMTO method. The disorder is included via the CPA formalism adapted to strongly inhomogeneous systems like random overlayers on nonrandom substrates. We have found that the theory correctly predicts the formation of the ordered  $c(2\times 2)$  CuPd alloy on the Cu(001) substrate and excludes the formation of a  $c(2\times 2)$  overlayer of only Pd atoms. The theory predicts, in agreement with experiment, the tendency towards ordering also for the nonstoichiometric Pd coverages, less or greater than  $\frac{1}{2}$  of the monolayer.

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- [1] F. J. Pinski, G. Ginatempo, D. D. Johnson, J. B. Staunton, G. M. Stocks, and B. L. Gyorffy, *Phys. Rev. Lett.* **66**, 766 (1991).
  - [2] B. L. Gyorffy and G. M. Stocks, *Phys. Rev. Lett.* **50**, 374 (1983).
  - [3] F. Ducastelle and F. Gautier, *J. Phys. F* **6**, 2039 (1976).
  - [4] F. Ducastelle, in *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis (Kluwer, Norwell, 1989), p. 293.
  - [5] P. Turchi, G. M. Stocks, W. H. Butler, D. M. Nicholson, and A. Gonis, *Phys. Rev. B* **37**, 5982 (1988).
  - [6] A. Gonis, X. G. Zhang, A. J. Freeman, P. Turchi, G. M. Stocks, and D. M. Nicholson, *Phys. Rev. B* **36**, 4630 (1987).

- [7] P. W. Palmberg and T. N. Rhodin, *J. Chem. Phys.* **49**, 134 (1968).
- [8] Z. Q. Wang, Y. S. Li, C. K. C. Lok, J. Quinn, F. Jona, and P. M. Marcus, *Solid State Commun.* **62**, 181 (1987).
- [9] G. W. Graham, *Surf. Sci.* **171**, L432 (1986).
- [10] G. W. Graham, P. J. Schmitz, and P. A. Thiel, *Phys. Rev. B* **41**, 3353 (1990).
- [11] S. H. Lu, Z. Q. Wang, S. C. Wu, C. K. C. Lok, J. Quinn, Y. S. Li, D. Tian, F. Jona, and P. M. Marcus, *Phys. Rev. B* **37**, 4296 (1988).
- [12] S. C. Wu, S. H. Lu, Z. Q. Wang, C. K. C. Lok, J. Quinn, Y. S. Li, D. Tian, F. Jona, and P. M. Marcus, *Phys. Rev. B* **38**, 5363 (1988).
- [13] T. D. Pope, G. W. Anderson, K. Griffiths, P. R. Norton, and G. W. Graham, *Phys. Rev. B* **44**, 11 518 (1991).
- [14] R. S. Rao, A. Bansil, H. Asonen, and M. Pessa, *Phys. Rev. B* **29**, 1713 (1984).
- [15] V. Heine and J. Samson, *J. Phys. F* **13**, 2155 (1983); A. Bieber and F. Gautier, *Acta Metall.* **34**, 2291 (1986).
- [16] J. Kudrnovský, I. Turek, V. Drchal, P. Weinberger, N. E. Christensen, and S. K. Bose, *Phys. Rev. B* (to be published).
- [17] H. L. Skriver and N. M. Rosengaard, *Phys. Rev. B* **43**, 9538 (1991).
- [18] W. Lambrecht and O. K. Andersen, *Surf. Sci.* **178**, 256 (1986).
- [19] G. Treglia, B. Legrand, and F. Ducastelle, *Europhys. Lett.* **7**, 575 (1988).
- [20] V. Drchal, J. Kudrnovský, L. Udvardi, P. Weinberger, and A. Pasturel, *Phys. Rev. B* (to be published).
- [21] We note that the disordered overlayer on the nonrandom substrate is one of the specific cases of more general nonuniform composition at the surface. This limit has a number of features which distinguish it from both bulk and surface cases, and its detailed study will be presented elsewhere. Most notably, the effective interactions are limited to atoms in the overlayer, and are zero otherwise. We have thus a 2D-like analog of the bulk case.
- [22] J. Kudrnovský and V. Drchal, *Phys. Rev. B* **41**, 7515 (1990); J. Kudrnovský, V. Drchal, and P. Weinberger, *Phys. Rev. B* **44**, 6410 (1991).
- [23] A. G. Khachatryan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983), Chap. 3.7.

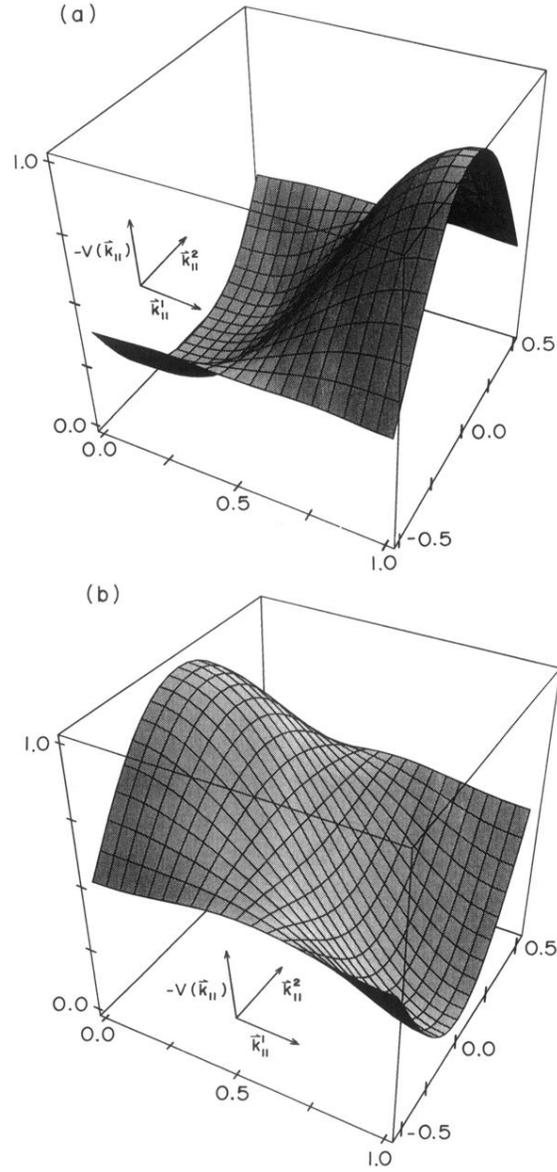


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