Symmetry change due to second-order phase transitions at a surface

I. P. Ipatova, Yu. É. Kitaev, and A. V. Subashiev
A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences

(Submitted 11 June 1980; resubmitted 24 October 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **32**, No. 10, 587–590 (20 November 1980)

A group-theoretical analysis of the possible types of surface superstructures, which are formed as a result of second-order phase transitions on atomically pure surfaces of solids, is performed. The results are compared with experimental data.

PACS numbers: 68.20. + t, 64.90. + b

Various experimental methods (slow- and fast-electron diffraction, diffraction of helium atoms, and photoemission methods) make it possible to observe a structure that is different from the bulk structure on an atomically pure surface of a number of crystals.[1,2] The structural rearrangement of a surface layer of finite thickness, which is accompanied by a change of the translational and the point symmetry of the lattice, is called *surface reconstruction* (see review article [3]).

Recently, the results of several experiments[4,5] showed that surface reconstruction is reversible with temperature. It is reasonable, therefore, to associate it with phase transitions on the surface. Theoretical studies[6] also show that phase transitions at the surface always occur sooner than bulk structural transformations, and they can even occur in the case when there are no phase transitions in the bulk.

Surface reconstruction can be realized either as a first-order phase transition or as a second-order phase transition. There are, however, only a small number of experimental papers in which the order of the phase transition at the surface has been determined.[4,5]

One criterion of a second-order phase transition is the constraint imposed on the possible symmetry changes that were established by Landau and Lifshitz.[7] The change of translational symmetry in conventional, three-dimensional crystals was analyzed by Lifshitz.[8]

These conditions also make it possible to analyze the translational symmetry change produced as a result of second-order phase transitions in a thin surface layer, whose symmetry, as indicated by Wood,[9,10] must be described by 80 biperiodic groups in three-dimensional space. The validity of this approach was indirectly confirmed by Zallen,[11] where the biperiodic groups in a three-dimensional space were first used to obtain the selection rules for optical transitions and to explain the spectra in layered crystals.

The necessary condition of a second-order phase transition is the presence of intersecting symmetry elements or the inversion in the group of the wave vector **k** of the corresponding, active, irreducible representation.[7,8]

The purpose of this paper is to use this condition and Wood's tables[10] to describe the symmetry of surface structures and to establish the changes of the translational symmetry (Bravais lattice) that are possible as a result of second-order phase transitions at a surface. Since our analysis does not include the investigation of the condition under which a third-order invariant can be missing in the free-energy expansion, the second-order phase transitions, which can be described within the framework of the Potts model,[12,13] are included in this analysis.

The results of an analysis of all five plane Bravais lattices of different classes are given in Table I. The Bravais lattice is given in the first column and the crystal class of the high-symmetry phase with an inversion introduced at its center (if it was missing in the class)[1)] is given in the second column; the third column gives the superstructures of the low-symmetry phase, into which the lattice can be converted as a result of a second-order phase transition. The notations introduced by Wood[9] were used for the surface superstructures: $p(c)(n \times m)R\theta$, where the index $p(c)$ represented a primitive (centered) unit cell, n and m are proportionality constants between the new and the old translation vectors, and θ is the angle between them. The translation vectors in the oblique-angled, simple, rectangular lattice and in a square lattice were selected along the sides of the corresponding figures; they were chosen at a 120° angle to each other in the hexagonal lattice and they were drawn from the center of the unit cell to the adjacent vertices in the centered, rectangular lattice.

As we see in Table I, the transitions in all the classes with the analyzed Bravais

TABLE I.

High-symmetry phase		Low-symmetry phase
Bravais lattice	Classes	Superstructures
Oblique-angled lattice	$\bar{1}$, $2/m$	$p(2\times1)$, $p(1\times2)$, $c(2\times2)$
Simple square lattice	$2/m$, mmm	$p(2\times1)$, $p(1\times2)$, $c(2\times2)$
Centered square lattice	$2/m$, mmm	$p(2\times1)$, $p(2\times2)$, $c(2\times2)$
Square lattice	$4/m$, $4/mmm$	$p(2\times1)$, $p(2\times2)$, $c(2\times2)$
Hexagonal lattice	$\bar{3}$, $\bar{3}m$, $6/m$, $6/mmm$	$p(2\times2)$, $c(2\times2)$
	$\bar{3}m$, $6/m$, $6/mmm$	$p(\sqrt{3}\times\sqrt{3})R\,30°$

lattice are the same. The only exception is the hexagonal lattice, where the transition to the $p(\sqrt{3}\times\sqrt{3})R\,30°$ superstructure is missing in class $\bar{3}$.

It can be seen in Table I that the transformations $p(1\times1)\leftrightarrow c(2\times2)$ at the (100) W and (100) Mo surfaces[5] with a square Bravais lattice, which were identified as second-order phase transitions, are in agreement with the results obtained by us. The transformations $p(4\times5)\leftrightarrow p(2\times1)\leftrightarrow p(5\times1)$, which were identified as first-order phase transitions and observed at the (110) Si surface[4] (a simple square Bravais lattice), are also consistent with our results.

The authors thank A. L. Korzhenevskiĭ for useful discussions.

[1)]Since the wave functions with the wave vector **k** and **-k** must be used to obtain a physically irreducible (real) representation, the stars of the physically irreducible representations coincide in all the space groups which belong to the crystal classes that differ only in the presence of an inversion center.

1. E. Tosatti, Proc. 13th Int. Conf. on Physics of Semicond., edited by F. G. Fumi, Rome, 1976, p. 21.
2. W. Mönch, Surf. Sci., 86, 672 (1979).
3. I. P. Ipatova, Yu. E. Kitaev, and A. V. Subashiev, In: Problemy fiziki poluprovodnikov (po Materialam IX Zinnei shkoly po fizike poluprovodnikov) [Problems of Semiconductor Physics (Proceedings of 9th Winter School on Semiconductor Physics)], Published by A. F. Ioffe FTI of USSR Acad. Sci., Leningrad, 1979, p. 102.
4. B. Z. Ol'shanetskiĭ, S. M. Repinskiĭ, and A. A. Shklyaev, Pis'ma Zh. Eksp. Teor. Fiz. 25, 195 (1977) [JETP Lett. 25, 178 (1977)].
5. T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. 38, 1138 (1977).
6. B. P. Antonyuk, Fiz. Tverd. Tela 20, 2293 (1978) [Sov. Phys. Solid State 20, 1323 (1978)].
7. L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, Moscow,

1976.
8. E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **11**, 255, 269 (1974) [Sic].
9. E. A. Wood, J. Appl. Phys. **35**, 1306 (1964).
10. E. A. Wood, Bell Syst. Tech. J. **43**, 541 (1964).
11. R. Zallen. M. L. Slade, and A. T. Ward, Phys. Rev. **B3**, 4257 (1971); R. Zallen, In: Proc. 12th Int. Conf. on Physics of Semiconductors, Teubner, Stuttgart, 1974, p. 621.
12. E. Domany, M. Schick, and J. S. Walker, Phys. Rev. Lett. **38**, 1148 (1977).
13. M. Bretz, Phys. Rev. Lett. **38**, 501 (1977).

Translated by Eugene R. Heath
Edited by S. J. Amoretty