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SURFACE STRUCTURE OF DEFECTS IN CRYSTALS

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Abstract

The structures of surfaces of f.c.c. crystals containing faults and defects are represented by ball models. Illustrations show the atomic arrangements of surfaces around points of emergence of dislocations, stacking faults, twin and grain boundaries. The way in which these faults and defects may modify the surface activity is discussed.

Introduction

The bulk of research in surface chemistry is concerned with mechanisms of reactions on surfaces and the identification of adsorbed and reacting species. However, a small number of workers is interested in understanding the influence of the surface itself. As an integral part of this work, it is necessary to appreciate that the structure of the surface at an atomic level may play a part in its properties, and it is therefore necessary to know the arrangement of atoms in the surface. We are concerned here with just this point, and we shall use ball models to simulate the atomic structures of surfaces. Although our discussion will be restricted to f.c.c. metals, the principle could be simply extended to other crystals.

Defects in crystals are known to control many of the mechanical properties of solids, and it has been suggested that they may also be important as active sites in the surface.[1)] Their influence in catalytic reactions has been investigated experimentally[2~4)] and the effect reviewed by THOMAS.[5)] As an aid to understanding how and when this may occur, we give here descriptions of the structures of the surfaces of crystals containing defects. We will assume that one knows the ideal atomic structure of the surface of a crystal, *i.e.* the distribution of atoms in steps and kinks, or more precisely, the distribution of atoms with various numbers of broken bonds. We shall introduce crystal defects into such a surface and describe the change of structure which they produce. Because they may have unusual chemical properties, it is important to define when surface steps are produced and to describe the nature of the steps.

We shall consider in turn point defects (vacancies, interstitials), line defects (dislocations), and planar faults (grain boundaries, stacking faults, twin boundaries), and give models or drawings of their intersections with surfaces of otherwise ideal crystals.

The surface structure of defects can be derived mathematically from a knowledge of the orientation of the surface and the vectors characterizing the defects. However, models that can be handled and modified should be of more immediate value to the practising surface chemist interested in how the surface influences the reactivity of adsorbed molecules or atoms. The models which have been constructed indicate the types of surface structures which are produced by intersecting faults, but the treatment does not include all possible combinations.

All models were constructed from balls of identical size, the diameter being a measure of the spacing between nearest neighbour atoms. An initial layer of balls was placed in a close-packed fashion in a square or hexagonal array in a tray, with suitably shaped spacers beneath part of the layer to produce the displacement of atoms appropriate for the faults intersecting a (100) or (111) surface. The models were then built up, layer by layer, by placing balls in the correct interstices of the layer beneath. The intersections of faults and defects with surfaces of various orientations were then modelled by following the instructions given in "An Atlas of Models of Crystal Surface"6) and taking into consideration the shear displacement produced by the faults. Relaxation at the surface is generally ignored because of a lack of knowledge of how it would affect the structure and because it is difficult to incorporate in a model made of inelastic balls. Also the elastic strains around dislocations are difficult to introduce into ball models and therefore a sketch is given of a surface containing a dislocation with its Burgers vector in the surface.

Description of Surfaces

Ideal Surface of a Perfect Crystal

If a plane surface is created by removing all atoms whose centres lie on one side of a plane through a crystal, the positions of the atoms left in the surface are determined by the crystal structure. The surface structure is periodic and contains a unit cell, within which the surface atoms have calculable positions and numbers of broken bonds. Thus atoms in the surface are bonded to the crystal by a number of nearest neighbour bonds which is less than the maximum. This number we call the coordination number of the surface atoms, *e.g.* all the atoms in a (111) surface of a f.c.c. crystal have a coordination number of $12-3=9$. The simplest surfaces are the close-packed planes forming the atomically smooth (100) or (111) surfaces. There is a restricted range of orientations like (110) which contain only atomic ledges, but surfaces of other orientations contain ledges of height h, and generally kinks in these ledges, and we shall call all such surfaces atomically rough. The structures of surfaces defined in this sense can be determined for any orientation and examples have been given with ball models.[6]

Point Defects

Figure 1 shows a model of a close-packed (111) surface containing a natural step S–S′ with kinks K in it. It also shows an adatom vacancy pair A_1, V_1 on the closepacked surface, created by an atom jumping from its normal position in the close-packed plane onto the surface, and a vacancy V_2 in a step and an adatom adsorbed on the step A_2. The vacancies and adatoms do not occur in ideal surfaces, but can result from atomic rearrangements, and will generally exist on real surfaces. It should be noted that if a kink atom moves

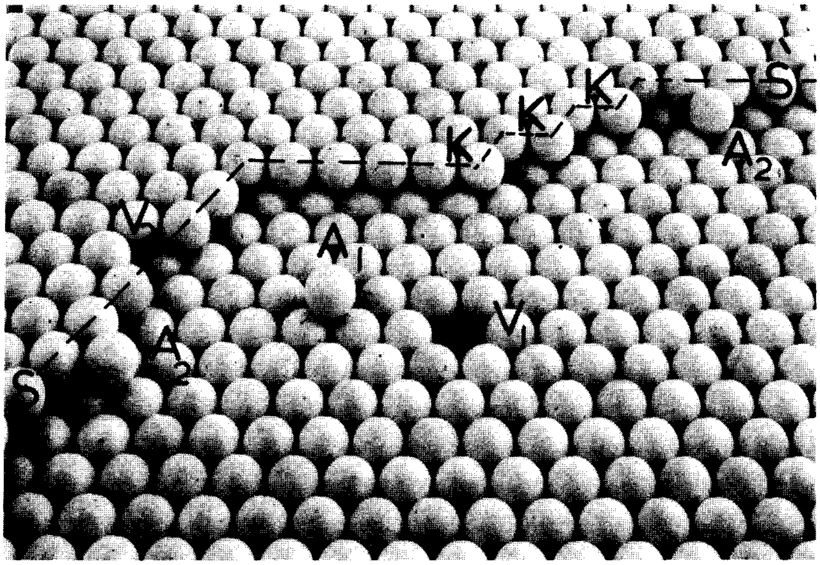


Fig. 1. Photograph of a ball model of a close-packed (111) surface in f.c.c. crystal containing a natural step S–S′ in which there are kinks K, and a vacancy V_2. V_1 is a vacancy in the close-packed plane and A_1 and A_2 represent adatoms.

away from its position in a step, it generally leaves another kink atom, and correspondingly a kink site may not be lost by adsorption of an atom at it. A surface vacancy V_1 may be created when a vacancy in the bulk diffuses to the suface, and in the presence of mobile adatoms will easily be filled. If vacancies diffuse to an atomically rough surface, and emerge on a step, they will create kinks or step vacancies. Similarly interstitial atoms will emerge as adatoms on close-packed surfaces or be incorporated on steps in atomically rough surfaces.

Dislocations

If a dislocation is introduced into a crystal, it must terminate at the surface if it does not form a closed loop or part of a network within the crystal. It creates a point of strain where it emerges at the surface and may also produce a surface step. There is no step when the Burgers vector of the dislocation is parallel to the surface ; the strain around such a dislocation in an atomically smooth surface is sketched in Figure 2. In real crystals this dislocation may split into two separated partial dislocations, thereby producing a length of step between them, of the type discussed in the section on stacking faults.

Whenever the Burgers vector is not parallel to the surface a step is formed, and Figure 3 shows a ball model of a surface containing such a step produced by a dislocation emerging at point D.

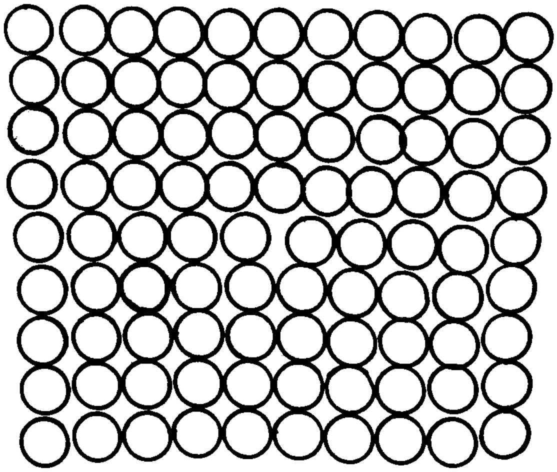


Fig. 2. Sketch of a dislocation terminating in a (100) surface of a copper crystal without producing a surface step, based on calculations by Cotterill and Doyama (7).

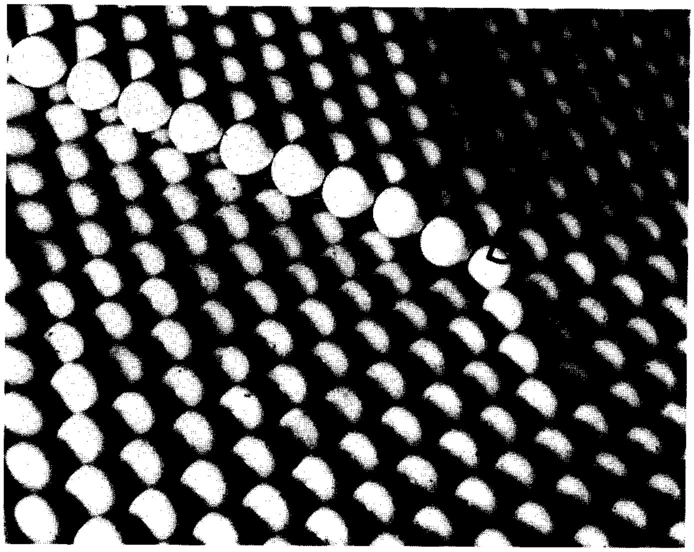


Fig. 3. Model of a dislocation terminatin in a (111) surface at D, and producing a step.

For whole dislocations the smallest Burgers vectors possible in f.c.c. crystals point along the various [110] directions and the length of these Burgers vectors is the distance from the centre of one atom to the centre of the next atom along any of these directions. When a whole dislocation moves along its slip plane, it leaves the atoms in positions equivalent to those they occupied originally and a step produced by such a dislocation is identical to a natural step except near the dislocation where its height decreases to zero (Fig. 3). Consequently, apart from near the dislocation lines, any displacements at the surface will always be of atomic dimensions.

When such a dislocation moves on its glide plane, it will extend the step until it moves out of the crystal or until the orientantion of the surface changes in such a way, that it becomes parallel to the Burgers vector of the dislocation. Figure 3 shows that the slip step is a continuous ledge in an atomically smooth surface. However, if it crosses a natural step a kink is incorporated into the slip step so that on flat surfaces of other orientations, slip steps will contain rows of equally spaced kinks unless the dislocation moves parallel to the existing ledges.

Partial dislocations have Burgers vectors such that as they move, atoms are shifted into new positions that are not lattice sites and thus create an area of faulty stacking. The steps created are different from natural steps and are discussed in the section dealing with stacking faults. Again the height of the

TABLE I Proportions of dislocations producing steps in the surface and kinks in a given ⟨110⟩ ledge in (111), (100) and (110) surfaces

Orientation of surface	Number of [110] directions in surface	Whole dislocations $b = \frac{1}{2} a_0 \langle 110 \rangle$		Partial dislocations $b = \frac{1}{6} a_0 \langle 211 \rangle$	
		Steps in surface	Kinks in given ⟨110⟩ ledge	Steps in surface	Kinks in given ⟨110⟩ ledge
(111)	6	6/12	10/12	21/24	24/24 $\neq$
(100)	4	8/12	10/12	24/24	24/24 $\neq$
(110)	2	10/12	10/12	20/24	24/24 $\neq$

$\neq$) In all cases the ledge is displaced by an amount which is less than that of a regular kink.

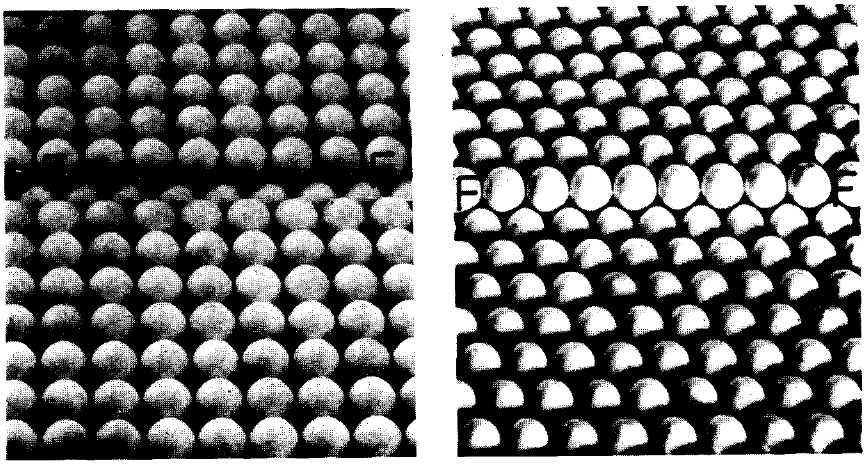
steps falls to zero at the point where the dislocation emerges at the surface.

The proportions of dislocations producing steps in some surfaces of simple orientations are given in Table 1. It shows, for example, that in f.c.c. crystals, of the 12 possible Burgers vectors of whole dislocations, only six produce steps in a (111) surface but ten produce steps in (110).

BRANDON and PERRY[8] have computed the positions of atoms in a spherical surface of a b.c.c. crystal containing a dislocation.

Stacking Faults

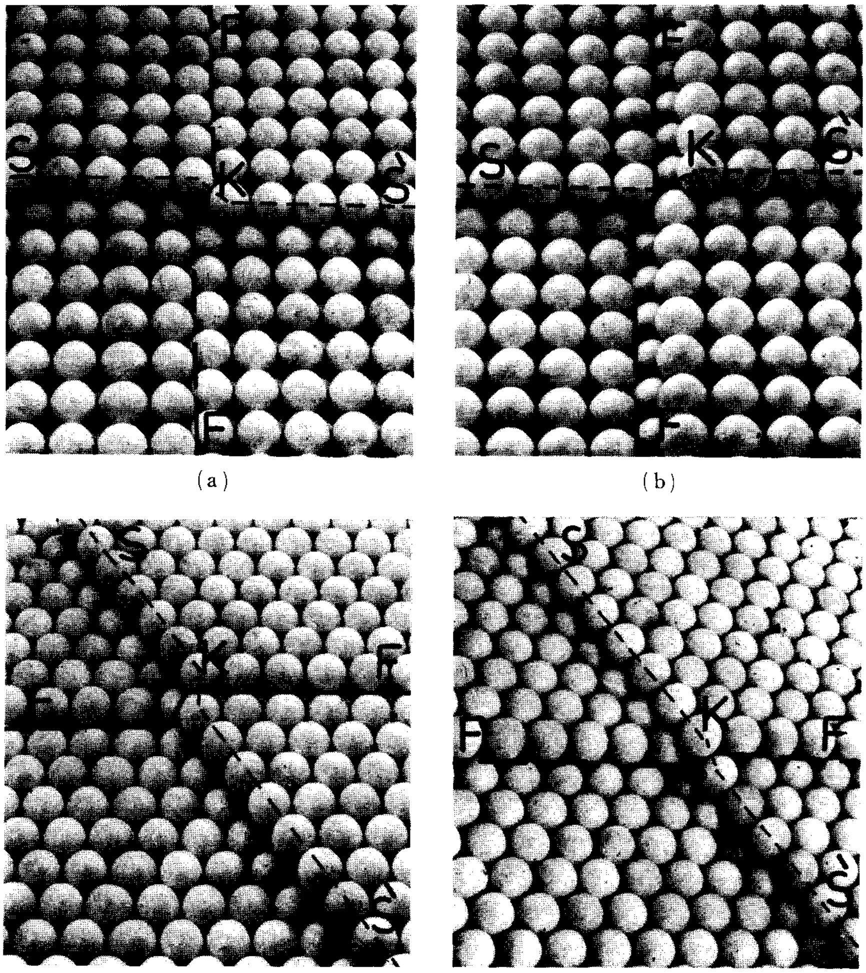
Figure 4 shows steps produced on (111) and (100) surfaces of f.c.c. crystals



(a) (b)

Fig. 4. Stacking faults F–F intersecting atomically smooth surfaces; (a), (100); (b), (111).

by the intersection of stacking faults F–F on one of the {111} planes inclined to the surface. The planar nature of the faults ensures that the steps are straight. The height of the steps on (111) surfaces is either (1/3) h or (2/3) h, (where h is the height of a natural step) depending on the Burgers vector of the partial dislocation producing the fault. The two step heights are shown for (100) surfaces in Figure 5a and b and for (111) surfaces in Figure 5c and d. The models in Figure 5 also contain a step S–S′ on the surface to demonstrate that when a stacking fault intersects a natural step, it produces a kink



(a) (b)

(c) (d)

Fig. 5. Stacking faults F–F intersecting surfaces containing steps S–S′, anb producing kinks K; (a), (b), (100); (c), (d), (111).

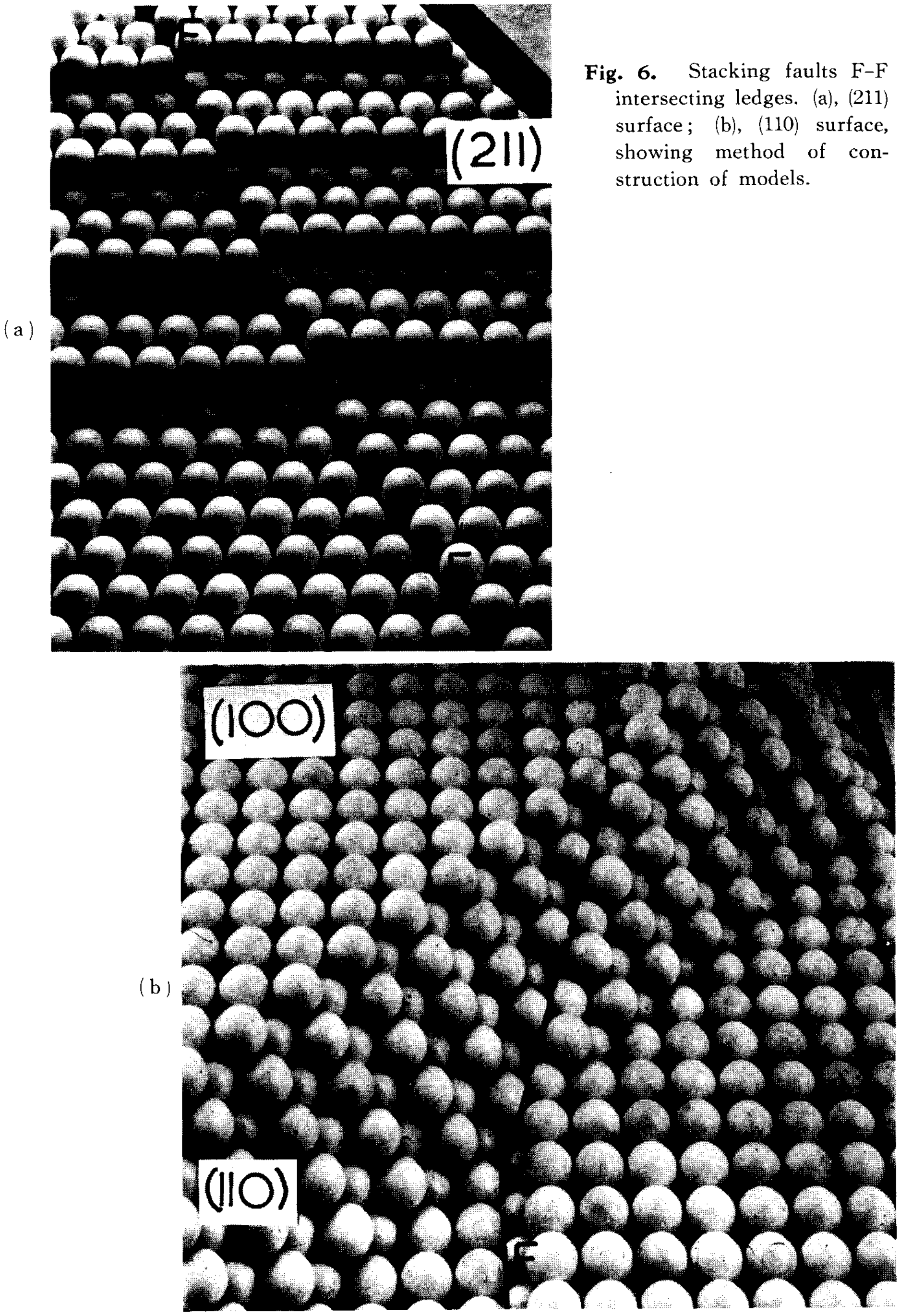
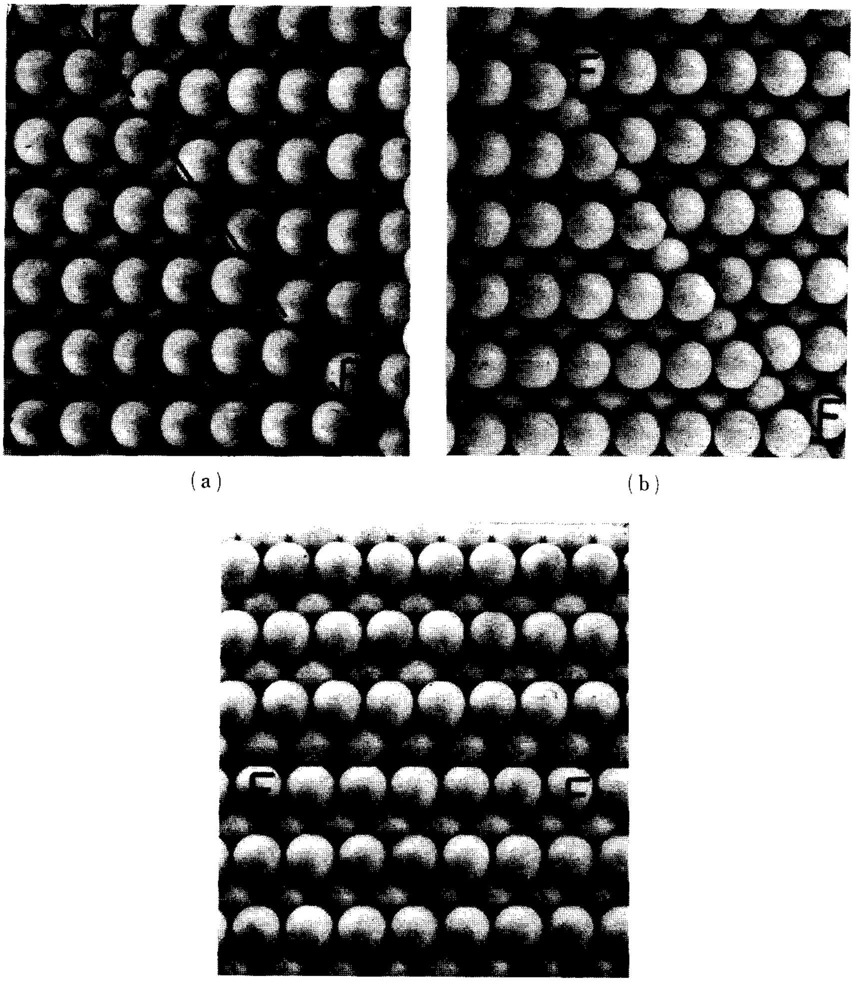


Fig. 6. Stacking faults F–F intersecting ledges. (a), (211) surface; (b), (110) surface, showing method of construction of models.



(a) (b)

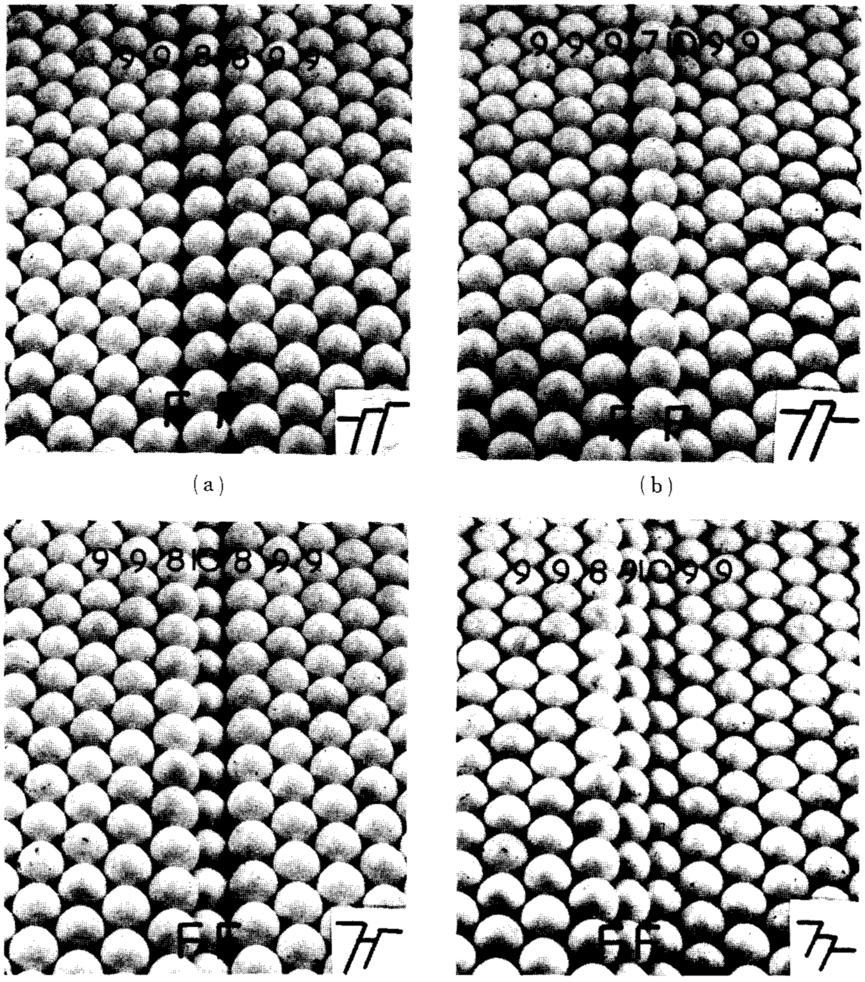
(c)

Fig. 7. Three possible arrangements in (110) surface intersected by stacking faults F–F.

which is different from those which occur naturally.

The structures produced by stacking faults intersecting surfaces of other orientations are more complex, but can still be seen in models based on the (100) or (111) layers. Examples of the construction of (110) and (211) surfaces containing a fault are shown in Figure 6a and b. All the possible arrangements of stacking faults intersecting a (110) surface are given in Figure 7.

The stacking faults in Figures 4–7 are all "intrinsic" *i.e.* they can be



(a) (b) (c) (d)

Fig. 8. The four possible arrangements in a (111) surface intersected by extrinsic stacking faults F–F. The numbers are coordination numbers. The inserts in the right hand corners show sections through the faults.

thought of as resulting from a close-packed plane of atoms being removed from the crystal. Extrinsic faults (the addition, rather than the extraction of an extra plane) produce steps which are similar in nature, but they contain an extra row of close-packed atoms. Examples are shown in Figure 8, which contains all the possible arrangements of extrinsic faults intersecting a (111) surface.

Twin Boundaries

Figure 9 shows a twinned region included within a (100) surface. It is bounded by coherent (CTB) and non-coherent (NCTB) twin boundaries. Twins can be considered to be introduced into a f.c.c. crystal by moving twinning (partial) dislocations and creating intrinsic stacking faults on adjacent (111) planes. The twinning dislocations form the non-coherent boundaries and the model (Fig. 9) shows that here the atomic fit across the boundary is bad. However, the atoms forming the coherent boundary belong equally to both lattices and no misfit exists. The displacement of the layer adjacent to the coherent boundary is the same as that across a stacking fault, but the orientation changes across the boundary and therefore subsequent layers are in different positions. If the plane of a (100) surface is extended into the twinned region, it exposes a surface which is 16° from (111), *i.e.* a (221) surface which consists of equally spaced ledges on a (111) surface (Fig. 10). A similar situation exists on a (111) surface, where the twin exposes a (511) surface. which consists of similar ledges on a (100) surface. As with a stacking fault the row adjacent to the coherent twin boundary may be displaced by either (1/3) h or (2/3) h. If a coherent twin boundary crosses a natural step, it creates kinks of configurations similar to those generated in natural steps by stacking faults (Fig. 5).

Figure 11 shows a model of the special case of twinning on the plane

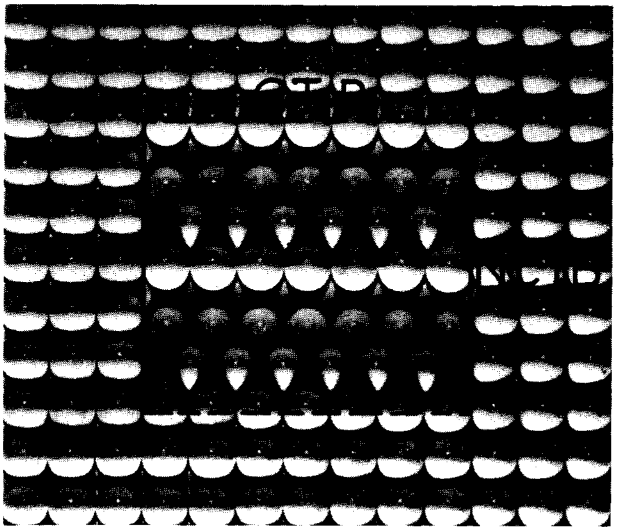


Fig. 9. Twin included in a (100) surface; CTB, coherent twin doundary; NCTB, noncoherent twin boundary.

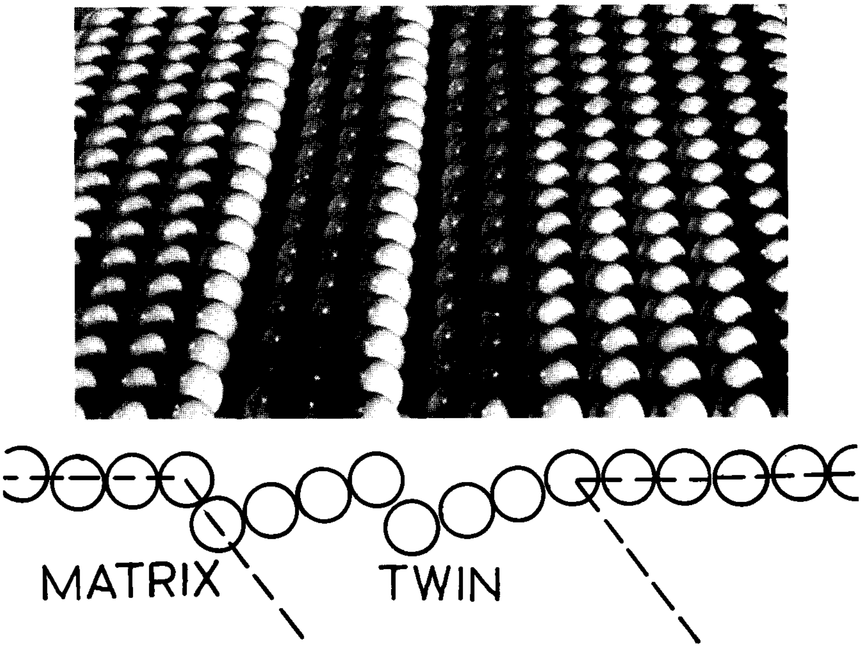


Fig. 10. A thin twin inclined to a (100) surface, showing atomic ledges and structure of the CTB.

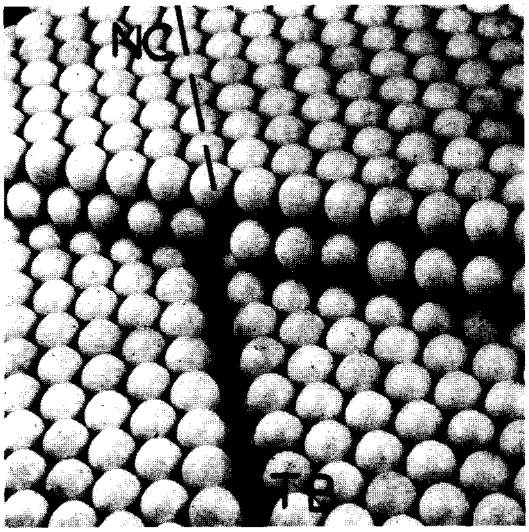


Fig. 11. Noncoherent twin boundary NCTB, intersecting a (111) surface, showing the continuous plane at the back and the misfit in the next two layers beneath it.

parallel to the surface, which can occur whenever the surface orientation is (111). In this case only the non-coherent twin boundaries can intersect the surface. The model shows the intersection with three consecutive layers. In the foreground the atomic misfit across the boundary is indicated in the model by a gap in a ⟨110⟩ direction. A similar gap occurs in the next layer. However, as the back half of the model shows, every third layer can cross the boundary without misfit. Thus in a (111) surface lines of misfit occur except that the boundary would disappear in every third layer.

Grain Boundaries

Disorientation between grains in polycrystalline solids produces atomic misfit at the common boundaries of grains. If the difference in orientation is small, the boundary can be considered to consist of an array of dislocations which may be of different types. Therefore such a boundary may be a source of steps which will run across the surface of the grains to account for the misorientation.

A number of models have been suggested for large angle boundaries, but it is not clear which is the more accurate.[9] The boundary intersects the

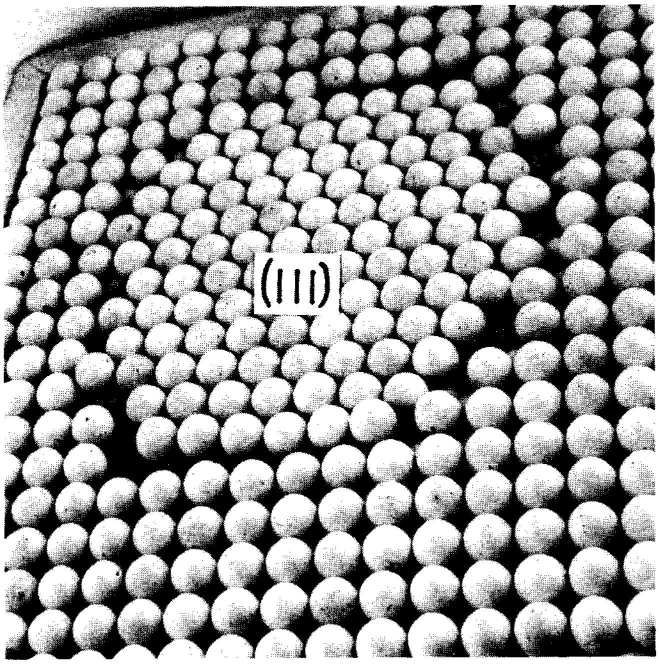


Fig. 12. Model of grain boundary, showing the atomic misfit.

surface in a line which will contain atoms with various numbers of missing neighbours, and hence may have bonding properties approximating those of atoms in steps. The extent of the misfit can be seen by the gaps in ball models, such as Figure 12 which shows a grain with a (111) surface surrounded by a (100) grain.

Real Surfaces

We have started by defining an ideal surface in a perfect crystal and then shown how the atomic arrangement in such a surface is modified by the introduction of faults and crystal defects. If one knows the orientation of the surface and the nature and vectors characterizing the defects one can in principle determine the ideal surface structure at the intersection, and construct a model.

However, in real crystals surface diffusion causes rearrangements of the surface and leads to deviations from the ideal structure. It produces the point defects which we have already mentioned. BURTON *et al.*10) have shown that the relative concentrations of the adatoms and vacancies can be obtained from thermodynamic considerations and that the creation of A_1, V_1 pairs is not likely at temperatures much below the melting point of the material, and that A_2, V_2 pairs are more easily produced (see Fig. 1). Similarly surface diffusion will lead to the breaking up of the straight slip steps and the ideally sharp intersections of different slip steps become rounded.11) The steps produced by dislocations may subsequently wander across the surface and it is therefore difficult to know how many surface atoms are affected by dislocations.

On a macroscopic scale minimization of the surface energy produces observable grooves at coherent and non-coherent twin boundaries and at grain boundaries which will slightly increase the total area of exposed surface and also produce a change of orientation at the surface intersection of these boundaries. Adsorbed impurities and chemical reactions occurring at the surface may either reduce or enhance the rate of surface diffusion and can also lead to the development of characteristic surface structures.12)

The concentrations of defects in real crystals can be varied widely and depend upon the physical conditions during preparation of the crystals. By using single crystals, grain boundaries can be avoided and suitably oriented bicrystals can provide specimens with grain boundaries of defined orientation. In metal crystals prepared by solidification from the melt followed by slow cooling, one can expect some dislocations (10^5 to $10^7\,\mathrm{cm}^{-2}$) and point defects. Deformation can increase the concentrations of dislocations ($\geqslant 10^{10}\,\mathrm{cm}^{-2}$) and some stacking faults may be formed as well as aditional point defects. In some metals deformation may also produce twins. Subsequent annealing will lower the concentrations of dislocations ; the point defects may aggregate or migrate to the surface, and twins may be formed by recrystallization.

On the other hand thin films of metals prepared by vapour deposition in vacuum usually contain much higher concentrations of all these defects, even when single crystals are formed epitaxially. Typical values which have been reported for silver films[3,13)] show that 1 cm^2 of film surface was intersected by 10^8 to 10^{12} dislocations, 10^3 to 10^4 cm of stacking faults or coherent twin boundaries, and 10^3 to 10^4 cm of non-coherent twin boundaries.

There are a number of ways of determining the defect concentrations in metal crystals, but if one is interested in the influence of surface structure and defects on chemical reactivity, then only those methods which give the number of defects intersecting the surface are of interest in the first instance. As we have pointed out, the surface structure of the defects depends upon the surface orientation and the nature of the defect, and therefore both these factors must be determined. Ideally, atomically smooth surfaces seem to be necessary for experimental work of this type, and epitaxially grown films provide, up to now, the closest approach to this situation, in spite of their high defect concentrations.

Chemical Reactivity

The important characteristic distinguishing different atoms in a surface is the number of bonds they make with the adjacent atoms (coordination number), or the complementary quantity, the number of dangling bonds which are free to associate with other atoms or molecules. Surface sites can likewise be characterized by the available coordination there, *i.e.* the number of neighbours to which an adatom can bond at this site. Thus natural surface steps containing kink sites are places where atoms similar to those in the substrate can bond more strongly and consequently they are the sites which trap atoms in crystal growth, for example.

Field emission microscopy shows that atomically rough surfaces give up electrons more readily than atomically smooth surfaces, because of their lower work function. However, kink atoms, or more precisely, atoms with low coordination numbers also show up brightly in field ionization micrographs, and they are therefore able to polarise adsorbed atoms or accept electrons readily. Thus the probability of electron transfer is favoured by atoms with low coordination numbers to the crystal.

If the properties of faults are controlled by these factors, the coordination numbers of atoms at the point of emergence of the faults are important.

TABLE II Coordination numbers of atoms in surfaces intersected by planar faults.

Orientation	Normal surface			Stacking fault	
	Plane	Ledge	Kink	Step	Kink
(111)	9	7	6	8	7, 6
(100)	8	7	6	8, 9	7
(110)	7, 11	7	6	7	7
(211)	7, 9, 10	6, 7, 8	5, 6, 7, 8	7, (8, 9), (9, 10)	5, 6, 7, 8, 9

Table II lists the coordination numbers for a variety of faults intersecting atomically smooth surfaces and natural steps. The coordination number of atoms in ideal surfaces without faults are included for comparison.

From a study of this Table, it can be seen that stacking faults, and dislocations producing steps provide rows of atoms with lower and higher coordination than exists otherwise in atomically smooth surfaces. Thus they could provide a linear site for the adsorption or release of atoms, the effect being smaller for stacking faults and coherent twin boundaries than for grain boundaries, non-coherent twin boundaries or dislocation steps.

With the above argument in mind, it seems reasonable to expect that the steps associated with stacking faults would not be particularly active, because they introduce only slight changes to the coordination numbers of surface atoms. Atoms in the core of a dislocation are more strongly affected, and those in an associated step even more so. This discussion ignores the possibility of impurities collecting on the faults and defects and thereby altering their chemical activity, *e.g.* the ability to produce etch pits at dislocations.[14,15] It is an inherent part of the argument that atomically rough surfaces are chemically more active than atomically smooth ones because they have a higher concentration of both active atoms and sites.

An examination of ball models shows that although some surfaces with orientations close to the atomically smooth (111) or (100) may be described as consisting of atomic steps separated by facets of (111) or (100), this is not so for other orientations, which may be atomically so rough that there are no or very few (111) or (100) sites. In surfaces such as these the introduction of further steps or kinks by faults becomes trivial because their concentration is already so high. Consequently we should expect the activity of these very rough surfaces to be insensitive to defects. However, their effect might be important in atomically smooth surfaces particularly if the concentration of surface steps is thereby increased.

Acknowledgement

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