

# INFLUENCE OF STRUCTURE ON SOLID-STATE REACTIONS

F. C. TOMPKINS

*Chemistry Department, Imperial College, London, S.W.7, U.K.*

## THE COMPLEXITY OF SOLID-STATE REACTIONS

The problems associated with the elucidation of the mechanisms of solid-state reactions are fundamentally more complicated than those involved in gas-phase or liquid-phase processes. In these latter reactions, mixing occurs at the molecular level so that the assumption of uniformity of concentration of the reactants at the reaction zone is generally valid; in contrast, in solid-state processes involving changes in chemical composition, one reactant (at least) diffuses into the other in order that the reaction may be initiated and subsequently propagated. For this reason, concepts involving concentrations, and mechanisms derived from an apparent experimental order of reaction, are of little intrinsic significance, and, at best, should be interpreted with caution. Furthermore, it follows that discussion of mechanism involves the rate of movement of the interphase boundary, *i.e.*, the mathematical formulation of the rate process must be expressed in terms of both spatial and time coordinates. Should the experimental results permit the concept of a geometric boundary between reactants and products, the overall rate can be defined in terms of the rate of progression of the interphase boundary, *i.e.*, as the change with time of the thickness (or weight) of the product layer. However, conclusions derived from results merely expressing the extent of the total reaction with time, *e.g.*, the amount of gas produced in a thermal decomposition study, or the change of an average macroscopic property such as density, must be, to some extent, speculative; for both the mathematical relationship and the activation energies derived from the associated temperature coefficients often change with increasing extent of reaction. Moreover, the rate equations used in describing the results are often non-discriminatory and are found to be only approximately valid over part of the time period of the process. Indeed, the derivation of activation energies from the usual Arrhenius relation, based on an exponential dependence of some rate parameter on the temperature, is often invalidated by the fact that equilibrium between the activated and non-activated species in the rate-determining process according to a Boltzmann distribution is not attained.

It therefore cannot be over-emphasized that kinetic expressions derived from overall reaction velocities are insufficient to characterize the mechanism with confidence. Auxiliary measurements aimed at determining more directly the specific parameters are then required. A classic example of an investigation which does provide sufficient experimental information to be

definitive is that of Garner and Wischen<sup>1</sup> on the thermal decomposition of barium azide. Here the kinetics and energetics of nucleus formation and of growth were separately and directly determined experimentally, and from these the kinetics and energetics of the overall decomposition (followed by pressure increase of the product, nitrogen, in a constant volume) could be predicted and experimentally confirmed.

Even when an activation energy has been validly obtained, its identification with a rate process relies on a suitable hypothesis for the mechanism of the reaction; thus, it may refer to an energy of diffusion, to a "chemical" energy to form a specific activated complex, or it may refer to a set of coupled processes such as the formation and mobility of more than one charged defect in a varying field gradient. Clearly, should the activation energy vary as the reaction progresses, then derivation of rate equations with the assumption of a rate constant invariant with time has little value; the decreasing rate may be completely determined by the increasing activation energy and relationships between the rate of progression of the reactant/product interface as a function of thickness of the product layer are spurious. A study of the effects of variables, such as temperature or oxygen pressure in the oxidation of a metal, should therefore confine attention to measurements at the same extent of reactions; alternatively, the effect of, say, temperature in two separate runs should be proved to be the same as that obtained in a separate run during which the temperature is rapidly changed at a specific time so that a short extrapolation allows comparison of the effect of the variable for the same extent of reaction.

### THE INITIAL ACT OF NUCLEATION

A solid-state reaction is a chemical process involving the rupture of old bonds and the formation of new to form a product. Consequently, the energy parameters associated with the initial act of nucleation are those relevant to the overall chemical reaction modified by the crystal environs. In other words, in a gas reaction we may confine attention to the energy changes resulting from bringing the reactants sufficiently close together so that the formation of an activated complex is energetically favourable; in a solid-state reaction there is, in addition, strong interactions with the reactant, with the product lattice, and at the interface between the old structure and the new one being formed. Consequently, a knowledge of the crystal morphology is essential in understanding the main factors contributing to the act of nucleation. Unfortunately, the site of nucleation is often at some unique locality and may or may not be in thermodynamic equilibrium with the host lattice. Thus, it may be at some point defect (or an aggregate of these), the concentration of which may be in principle calculated using statistical mechanics, or it may be at a grosser non-equilibrium defect, such as a dislocation or stacking fault. Moreover, such nuclei must reach a critical size which is controlled not only by the free energy change of the overall reaction but also by such factors as the interfacial free energy and strain energy which arise from incorporation of the one phase into the other with different spatial co-ordinates of their unit cells.

## STRUCTURE AND DIFFUSION PATHS

Nucleation is followed by growth and, except in diffusionless transformation, this requires transport of matter to the reaction interface through an increasing thick layer of product—the chemical reaction has therefore in many systems to wait on a rate-determining diffusion step. In such diffusion processes, the concentration and mobility of lattice defects, particularly vacancies and interstitials, play a decisive rôle whether the process is a chemical one, a phase change or an order-disorder transformation; and both the concentration and the activation energy for movement in the lattice is determined by the crystal structure. Considerable effort has been directed to the determination of the enthalpy of formation and activation energy of mobility of point imperfections, both theoretically and experimentally, for many ionic systems, *e.g.*, from the ionic conductance at various temperatures of pure and impurity-doped alkali halides.

Naturally, the decisive factor in determining the effective defect in transport is the sum of these two enthalpies. Thus, in KCl the activation energy of movement of interstitial cations in the [111] direction is about the same as that of cation vacancies, but since the energy of formation of a cation Frenkel pair is much larger than that of the Schottky pair, transport is dominated by the movement of the cation vacancies<sup>2</sup>. It is a fairly general rule that in close-packed structures the formation energy of vacancies is less than that to form interstitials so that vacancy mechanisms are far more prevalent than others; and again, although there are many exceptions, cation vacancies are normally more numerous than their anion counterpart. Direct experimental evidence for vacancy diffusion is provided by the presence of the Kirkendall effect. Inert markers are incorporated in the solid system, and owing to unequal rates of diffusion of the mobile species there is a balanced flow of vacancies leading to expansion and contraction on the two sides of the interface and a consequent movement of the inert markers.

Our present interest is the correlation of the diffusion process in relation to the broader aspects of crystal structure. We note that two types of close-packing are particularly prevalent: (i) the hexagonal, comprising two close-packed layers repeated along the hexagonal *c* axis and (ii) the cubic, which contains repeat units of the three closest-packed layers along the [111] direction. Between the atoms are octahedral interstices with a coordination number of six, and tetrahedral interstices coordinated with four atoms; the latter are twice as numerous as the former and the relative size of a spherical atom which can be fitted into these interstices is 0.414 for octahedral and 0.225 for the tetrahedral cavity for "one-atom" solids so that movement of atoms within the solid requires the presence of vacancies. The easiest diffusion path in cubic close-packed structures comprises an interpenetrating array of these tetrahedral and octahedral interstices; but in the normal lattice these may be empty or occupied. Thus, for simple binary inorganic compounds, the structure comprises the closest packing of the larger anions with the metals cations occupying the tetrahedral and/or octahedral interstices. As pointed out by Azaroff<sup>3, 4</sup>, in NaCl, the sodium ions are in the octahedral sites and since this occupancy

blocks the easiest diffusion path, then to allow movement in the lattice, a metal ion must be removed, *e.g.*, by formation of a cation vacancy. Alternatively, it may be displaced by the mobile atom by an interstitialcy mechanism as probably occurs in the silver halides. Clearly, the larger halide ion can only diffuse by an anion vacancy mechanism. These conclusions are, of course, the same as those derived from considerations of point defects.

However, interesting features arise when structures, similar to the NaCl lattice but in which the octahedral voids are only partially filled, are considered. Azaroff considers the example of  $\text{CrCl}_3$ . In this compound only one-third of these cavities are occupied and there is a continuous path comprising unoccupied octahedral voids linked with empty tetrahedral voids. Diffusion of the Cr ion can therefore proceed without the additional requirement of defect formation and the term voidal diffusion is proposed to distinguish such paths. Naturally, a corollary is that anisotropic movement may be favoured. Thus, in  $\alpha\text{-ZnS}$ , one set of the two distinct types of tetrahedral voids are empty and an easy diffusion path exists parallel to the [110] direction *via* the empty tetrahedral cavities and the octahedral ones, all of which are also empty, without the necessity to create point defects.

A good example from the above viewpoint is that of  $\text{PbI}_2$  where experimentally it is found that the activation energy for diffusion within the closest-packed layers is about one-third of that for movement normal to the layers. Seith's original explanation<sup>5</sup> is doubted, because the large iodide ions are required to have a lower activation energy of diffusion than the smaller lead ion; Azaroff's theory avoids this difficulty. He suggests that lead ions diffuse parallel to the *c* axis along a chain of octahedral voids *via* a defect mechanism, which is probably an interstitialcy one since alternate octahedral cavities are normally occupied. In contrast, in a direction normal to the *c* axis there are layers of unoccupied octahedral and tetrahedral voids which allow voidal diffusion, without the requirement of defect creation; movement of Pb ions may thus proceed with a lower activation energy.

The activation energy for voidal diffusion naturally depends on whether the mobile cation is confined to a chain of unoccupied voids that are crystallographically equivalent as exist in hexagonal close-packed lattices; or whether the path consists of alternate empty tetrahedral and octahedral interstices as occurs in cubic close-packed lattices. In the former case, the magnitude of the activation energy is determined by the height of the potential barrier separating the cavities, whereas in the latter system, an additional energy term, the energy difference of the cation in octahedral and tetrahedral interstices, has to be included. Should some of the voids be fully occupied or completely unoccupied then the energy to create the mobile defect must also be added. It is easy to predict qualitatively a rough value of the ratio of activation energies in certain selected systems, should certain conditions prevail. These are: (i) the metal cation should be the dominant mobile species, (ii) the two crystals under comparison should be similar except for the type of diffusion path, (iii) the experimental activation energies for mobility should have been determined in the intrinsic range of the crystals. For these reasons,  $\alpha\text{-AgI}$  was chosen<sup>4</sup>; it exists in two polymorphic modifications, (i) the  $\beta$ -form which has a zincite structure with hexagonal close-packing of iodide ions and one-half of the tetrahedral voids

are occupied by silver ions and (ii), the  $\gamma$ -modification comprising a zinc-blende structure, *i.e.*, a cubic close-packing with half-occupancy of the tetrahedral cavities. Now, in  $\beta$ -AgI the diffusion path is by way of octahedral interstices, whereas in  $\gamma$ -AgI it comprises alternating tetrahedral and octahedral voids. No defect creation is required in  $\gamma$ -AgI since silver ions already occupy some of the tetrahedral interstices whereas in the  $\beta$ -form, silver ions must be displaced from tetrahedral interstices to the octahedral ones. The energy requirement is roughly the energy difference of the silver ion in a tetrahedral and octahedral interstice in  $\gamma$ -AgI; consequently the activation energy for diffusion in the  $\beta$ -form is greater (very roughly two-fold) than that in the  $\gamma$ -form; and indeed the ratio of the experimental values 0.61:0.38 eV is in good agreement for such a simple model.

### EFFECT OF ELECTRON DISTRIBUTION OF MOVING ION

In addition to simple geometric considerations, one must consider the effect of the crystal symmetry on the energy of the cation—and since spinels are being considered by many authors at this Conference, we select these as examples for discussion. In a spinel of general composition  $AB_2O_4$ , the divalent A atoms normally occupy one-quarter of one set of tetrahedral sites, whereas the trivalent B atoms occupy one-half of the octahedral sites. The large oxygen atoms are arranged in an approximate cubic close-packed structure, and in the unit cell there are 32 O-atoms with 64 tetrahedral sites and 32 octahedral sites. Each occupied octahedral site is surrounded by 12 nearest octahedral sites, 6 of which are occupied, and each occupied site is surrounded by 8 nearest empty tetrahedral sites. In addition, each occupied tetrahedral site is surrounded by 6 unoccupied tetrahedral and 4 unoccupied octahedral sites. From geometric consideration alone, taking  $CoCrO_4$  as an example<sup>6</sup>, the Cr ion might be expected to move from its occupied octahedral site to the neighbouring unfilled tetrahedral site and then to an unfilled octahedral one. However, the shape of the electron cloud makes the ionic radius larger to tetrahedral surroundings so that an octahedral environment is favoured; more specifically, the large  $Dq$  and the  $d^3$  configuration of this ion makes it prefer octahedral sites. Hence, it may be easier to interchange the Cr ion directly from an occupied to an unoccupied octahedral site despite the fact that the lattice has to acquire sufficient strain energy to separate the atoms surrounding the site, and the activation energy for mobility would then be the strain energy involved in this separation. On the other hand, Co ions have an electron distribution which shows no preference for either octahedral or tetrahedral voids, and it therefore requires less energy to execute a zig-zag motion from an occupied tetrahedral site to an empty octahedral and then to an unfilled tetrahedral. In this manner, a reason is provided for the fact that the Cr ion requires a higher activation energy (70 kcal/mole) for mobility than does the Co ion (51 kcal/mole), and provides an example of the insufficiency of a purely geometrical model and the dominant part played by interaction of the cation with the lattice.

Similarly, in many spinels, cation diffusion proceeds most easily between the open channels between tetrahedral sites. Now the position between

such sites has octahedral symmetry with respect to the oxygen ion lattice, and, if the mobile cation has a  $d^8$  configuration there arises a large octahedral stabilization energy at the top of the potential barrier to movement so that this migration barrier is lowered, thereby decreasing the activation energy for mobility along this path<sup>7</sup>. In contrast, between octahedral sites, because of the nearer distance of the lattice oxygen ions, a greater strain energy is involved, and additionally, the cation experiences greater repulsion from other cations nearby; consequently, the activation energy for movement between octahedral voids is often large. Nevertheless, such a diffusion undoubtedly takes place in spinel formation; and unless there is a large tetrahedral preference energy, will then be the rate-determining process

## SYMMETRY CONSIDERATIONS AND EXPERIMENTAL METHODS

If we consider the phase transformation of a cubic close-packed lattice to a corresponding hexagonal structure, advantage may be taken of their different symmetry elements by incorporation of a paramagnetic ion. The symmetry of the environs of this ion in the polymorphs may then be distinguished using electron paramagnetic resonance techniques. Thus, for an ion in the  $6S_{5/2}$  state in an environment of cubic symmetry, *e.g.*, in solution or in a cubic close-packed crystal, six hyperfine lines, arising from the interaction of the unpaired electrons with the  $5/2$  nuclear spin, are seen in the e.p.r. spectrum. However, in the hexagonal crystal, the ion is in a crystalline field of lower symmetry, and five groups, each containing six hyperfine lines, should be observed. The signal directly measures the concentration of the marker ions in these different states so that the kinetics of even the early stages of the reaction is experimentally accessible. One disadvantage of the method is that the concentration required is fairly high ( $\sim 0.01$  per cent) and thus incorporation may distort the lattice and so catalyse the transformation. Unfortunately, only the kinetics of the overall transformation can be obtained. Nevertheless, the technique has real potentialities and, with ingenuity, will undoubtedly be developed to answer many questions about the symmetry and nature of the environment of the diffusing ions. Thus, in the present Conference, Turkevitch and co-workers<sup>8</sup> have studied the solid-state reaction between  $MnCl_2$  and  $ZnS$  and shown from the magnitude of the hyperfine constant that probably the  $Mn^{2+}$  ion has sulphide ions as its nearest neighbours and that this ion is indeed the species dominant in the diffusion process.

Spectrophotometric methods may also be applied with advantage, either directly if the absorption bands of reactants and products can be separately identified, or indirectly by incorporation of an appropriate cation in one of the reactants. Thus, in the reaction between  $MgO$ ,  $Al_2O_3$  and  $SiO_2$  (1:1:6) at  $1000^\circ$ , a small amount of  $CoO$  was added; the product showed an absorption band due to tetrahedrally coordinated  $Co^{2+}$  but none associated with the octahedrally coordinated ion. Since  $Mg^{2+}$  and  $Co^{2+}$  exclusively occupy the tetrahedral sites, the formation of the spinel  $MgAl_2O_4$  could be followed. Similarly, Stone and Tilley report<sup>7</sup> in the present Conference that they observed a strong double band at 15000–17000

$\text{cm}^{-1}$  due to the transition  ${}^3T_{1g}({}^3F) \rightarrow {}^3T_{1g}({}^3P)$  in quenched specimens of  $\text{NiAl}_2\text{O}_4$ ; they compare this with a band of identical structure observed by McClure<sup>10</sup> in a  $\text{NiO} + \text{ZnO}$  solid solution in which the  $\text{Ni}^{2+}$  ions are known to be in the tetrahedral interstices of a close-packed oxygen lattice. They therefore conclude that the onset of the reaction to form the spinel  $\text{NiAl}_2\text{O}_4$  from the oxides  $\text{NiO} + \text{Al}_2\text{O}_3$  takes place, in part, by the migration of  $\text{Ni}^{2+}$  ions through the tetrahedral interstices.

### DIFFUSIONLESS TRANSFORMATIONS

In principle, such processes represent the simplest type of solid-state reactions. There is no change of chemical composition, and the new crystal lattice is formed by the rotation and translation of the original crystal axes, such changes merely requiring movement of atomic dimensions. In many such transitions, the activation energy is low and the rate of propagation high. A preferred concentration is often followed and then the velocity is usually accelerated by the application of stress. The simplest concept is that, following nucleation, the transformation from one unit cell to the other proceeds through a series of activated complexes involving merely changes of bond hybridization. In some systems the energy released by the transition contributes to the energy to activate the neighbouring atom, so that an energy chain is invoked to explain the high rate of propagation. However, there are other systems where the activation energy of transformation approaches the sublimation energy of the compound; in such circumstances, the activated complex at the reaction interface has a pseudogaseous structure. It is generally thought that here again the initial act of nucleation takes place at point defects, dislocations or grain boundaries. It should be noted that the application of the phase rule, which postulates completely independent equations of state, expressed in terms of the two variables pressure and temperature, cannot be justified, since other parameters such as the interfacial free energy and strain energy make important contributions to the overall change of free energy.

Higher energy states must certainly exist at the phase boundaries; these arise from lattice distortions and, in extreme cases, to the pseudo-amorphous character at the interfacial reaction zone. For an air/crystal interface the distortion may be assessed from X-ray intensity measurements, and using the Madelung-Born theory, a crude estimate of the increase of energy made. For many oxides, this is around 2 kcal/mole, a value consistent with heat-of-solution determinations for particles of different surface/volume ratios. The energy difference between the amorphous and crystalline modifications is naturally much larger, *e.g.*, 13 kcal/mole for  $\alpha\text{-Fe}_2\text{O}_3$ . Finally, with ionic compounds, the interface is associated with electrostatic space charges of considerable magnitude, and their presence affects both the energy of formation of point defects and the energy for their mobility.

### NON-EQUILIBRIUM IMPERFECTIONS

Little has yet been said about the influence of the massive defects, dislocation, grain boundaries, stacking faults. Generally, a dislocation line is regarded as a linear discontinuity without much structure. However, the

fine structure, which is related to the crystal morphology, may well be of importance in certain solid-state reactions. As an example, in face-centred cubic crystals, the glide dislocation is often dissociated into two partial dislocations between which the normal stacking sequence is disturbed and a stacking fault, equivalent to a hexagonal layer, is formed provided the stacking fault energy is not too large. The problem is even more complicated when vacancies are present or when the close-packed layer comprises different chemical species—then the repeat distance and number of glide steps increase. These extended dislocations, which are important in discussions on plastic deformations, are indeed observed in the electron microscope. There have been few attempts to link such effects to specific problems of phase transitions and chemical reactions in solids<sup>11</sup>. Only certain aspects of the part played by dislocations will therefore be discussed briefly.

### ACCOMMODATION OF PRODUCT IN PARENT LATTICE

This aspect is of some importance in precipitation reactions and in thermal decompositions. In some systems, the optical microscope has sufficient magnification to be of value; for example, in the photolytic decomposition of silver halides, silver is seen to be preferentially precipitated on dislocations—and, indeed, the well-known decoration techniques utilized this type of experimentation. The high resolution of the electron microscope, particularly when used in conjunction with electron diffraction, may provide much more detailed information on the morphology of the products and their orientation with respect to the host lattice. Advantage can often be gained by working at low reaction rates if the interest is the specific effect of dislocations in the chemical process. Thus, with  $\text{PbI}_2$ <sup>12</sup>, preferential deposition of Pb in a finely divided crystalline or misoriented state occurs on dislocations, particularly along the edge component, at low rates of decomposition, whereas at high rates, well-developed platelets of Pb with the (111) face of its face-centred cubic lattice parallel to the (0001) plane of  $\text{PbI}_2$  separate out in cavities of about 50 Å linear dimensions that are created by loss of the iodide ion. Structural rearrangements, involving the climb of existing dislocations (utilizing anion vacancies produced by loss of iodine from the crystal), and formation of new dislocation loops, are evident. Nevertheless, in regions where no dislocations exist, the product of decomposition appears to be distributed uniformly through the crystal even at low rates of reaction. However, at high rates of decomposition, nucleation and growth occur more readily inside the cavities, and the smoothness of the interface between the bright and dark phases suggests that the Pb atom is freely mobile and that interfacial equilibrium is attained. In this example, dislocations do not appear to play the dominant rôle, although by immobilizing the cavities they help to provide a more coherent precipitate. It would be unwise to draw general conclusions since the part played by the electron beam, *e.g.*, in inducing charge effects and thereby causing mobility of the cavities, undoubtedly modify certain aspects of the mechanism. Nevertheless, the apparent importance of aggregates of vacancies as sites of nucleation and growth should be noted.



## DIFFUSION

The specific rôle of dislocations at phase boundaries in transport of matter is uncertain. Along grain boundaries, there is certainly enhanced self-diffusion and as a general guide the self-diffusion coefficient may be considered to have an activation energy about half that for bulk diffusion. In sub-boundaries, the diffusivity has been found to be proportional to the misorientation and hence to the density of dislocations present there. These facts suggest that dislocation lines constitute tubes of easy diffusion in which the activation energy is around one-half of that for bulk diffusion, and the tube diameter is *ca.*  $5 \times 10^{-8}$  cm. Since self-diffusion proceeds by a vacancy mechanism, the enhanced diffusivity has reference only to vacancies; it is uncertain whether they are indeed more mobile in the dislocation line, whether they are more stable than in the ideal lattice, or indeed whether they preserve their identity. With interstitials, the situation is quite different; they do retain their identity, their mobility is definitely lower than in the bulk crystal and their stability is higher. Thus, interstitial hydrogen and carbon in  $\alpha$ -iron tend to segregate on dislocation lines and the energy to move them is substantially increased.

### CREATION OF DISLOCATIONS AT THE PHASE BOUNDARY

This problem is a difficult one to approach experimentally. However, some information is available from the diffusion of impurity atoms into a single host crystal. A small impurity atom occupies a substitutional position and creates a mismatch in lattice parameters between the pure substrate and the surface layer of the mixed crystals. This mismatch is accommodated by the formation of a network of dislocations, largely comprising edge components, as soon as the concentration of impurity atoms is sufficiently high as to make the formation of dislocations energetically favourable. This diffusion-induced network of dislocations penetrates deeper as the reaction proceeds. Penetration may be effected by dislocation climb, brought about by diffusion of vacancies from the dislocation. An alternative process is by glide; two adjacent parallel dislocations split into edge dislocations of the correct orientation. These glide inwards and the dislocations recombine at lower depths so that the Burger's vector is in the plane of mismatch.

Alternatively, nucleation might be thought of as the formation of a monomolecular epitaxial layer since such a layer can be more easily deformed elastically. At first it remains adherent without dislocations but as the layer grows, there will be small regions of matching separated by larger areas of mismatch. These latter can be analysed in terms of parallel edge dislocations which cause contraction of the layer and divide it into separate nuclei, and screw dislocations with their glide plane in the boundary planes which produce a shear maintaining the layer continuous; such a mechanism could explain the advancement of a sharp interphase boundary which is experimentally observed in certain systems.

It is very evident that there are many aspects of the influence of structure on solid-state reaction which have not been included in this review. The field is vast and the selection of material is clearly a subjective one; nevertheless, many basic features are common to all reactions in the solid state.

The main theme has been that the present need is for a more critical and detailed approach, both theoretically and experimentally, now that the broader and more general features of solid reactions have been firmly established.

## References

- <sup>1</sup> Cp. A. Wischen. *Proc. Roy. Soc.* **172A**, 314 (1939).
- <sup>2</sup> K. Tharmalingam. *J. Phys. Chem. Solids* **25**, 255 (1964).
- <sup>3</sup> L. V. Azaroff. *J. Appl. Phys.* **32**, 1658 (1961).
- <sup>4</sup> L. V. Azaroff. *J. Appl. Phys.* **32**, 1663 (1961).
- <sup>5</sup> W. Seith. *Z. Elektrochem.* **39**, 538 (1933).
- <sup>6</sup> R. Sun. *J. Chem. Phys.* **28**, 290 (1958).
- <sup>7</sup> F. S. Stone and R. J. D. Tilley. *I.U.P.A.C. Symposium on Reactivity of Solids*, Paper RS 52, to be published.
- <sup>8</sup> J. Turkevitch, Larach, and P. N. Yocom. *I.U.P.A.C. Symposium on Reactivity of Solids* Paper RS 9, Elsevier, Amsterdam, in press.
- <sup>9</sup> Schmitz-Du Mont. *Proc. 4th Int. Symp. on Reactivity of Solids*, p. 718, Elsevier, Amsterdam (1961).
- <sup>10</sup> D. McClure. *J. Phys. Chem. Solids* **3**, 311 (1957).
- <sup>11</sup> Cp. J. Hornstra. On the "synchro-shear" mechanism, *J. Phys. Chem. Solids* **15**, 311 (1960).
- <sup>12</sup> A. J. Forty. *Phil. Mag.* **6**, 895 (1961).