# The Widened Lattice Interval and its Essential Role in the Behavior of Crystalline Metal[1]

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IT IS WELL RECOGNIZED that solid metals exhibit two opposed conditions: a "soft" condition which may show after thorough annealing, and a "hard" condition produced by strain (cold-work). The fact is equally familiar that these two states may pass one into the other by many gradations.

In the fully annealed, or "dead-soft," condition the x-ray diffraction lines from the metal are sharp, and the $K_\alpha$ doublet, if present, is fully resolved. The diffraction spectrum is that to be expected from a continuous and uniform lattice. After hardening by strain, on the other hand, the metal yields much-broadened lines that betray diminished regularity in the intervals between diffracting points, the atoms, or ions, of the crystal.

The irregular intervals of the hardened lattice may: (*a*) be due to its subdivision into small particles of normal crystal between which widened spacings occur; or (*b*) be produced, without separation into discrete particles, by widening of portions of occasional interplanar spacings, "parameter variation." There has been diversity of opinion among the numerous investigators as to which of these two causes is responsible for line broadening by cold-work, and it is possible that both may sometimes be present (*1*). Parameter variation can occur in various families of intersecting planes and, if it progresses far enough, will result in subdivision of the crystal into particles. The presence of such particles may hence constitute the extreme case of parameter variation, reached either locally or generally, as the manner and degree of distortion determined.

The two causes may thus differ only in degree; but in any case it is clear, merely from the x-ray studies alone, that in work-hardened metal, in contrast to (thoroughly) soft metal, *widened lattice intervals are present.*

The x-ray evidence is much supplemented and clarified if we make use of hydrogen and its ionization product, the proton, as probes for the exploration of metallic structure. Here relations are simplest for the Fe-type metals, which absorb endothermically, whereas complications are present in the case of palladium and the other exothermic absorbers. We therefore regard chiefly the endothermic systems (*2*).

## SOLUBILITIES

To begin with, we consider the metal-hydrogen solubility relations, taking as an example the well-studied instance of iron-hydrogen.

If iron of high or fairly high purity, in the state in which it is ordinarily obtained as foil or wire—that is, in somewhat cold-worked condition—is heated in hydrogen of atmospheric pressure to a temperature between 300° C and the melting point, and is allowed to come to a steady state, the quantity of hydrogen taken up by a given amount of metal is well defined.

It is reproducible within reasonable limits of error, even by different observers; it is attainable either from higher or from lower concentrations; and it increases regularly with the temperature, as is thermodynamically required for an endothermic absorption. Hence it has naturally been regarded as the true "solubility of hydrogen."

Provided, then, that we proceed in the manner just described, iron—and other metals of its (endothermic) type—Ni, Co, Cr, Cu, Pt, Ag—show a definite solubility equilibrium with hydrogen.

Suppose, however, that we proceed in a different way.

We will take iron of high purity and heat to a temperature of 800° or 1,000° C, at the same time carrying off any gas evolved with the aid of efficient pumps. When the metal, as thin foil or wire, has thus been thoroughly degassed and fully relieved of the effects of any foregoing cold-work, it approaches the state of the perfect lattice.

If we now admit hydrogen, as in the previous case, we find that the gas is not absorbed, and it is impossible to reach the solubility equilibrium. Moreover, if such thoroughly annealed and degassed iron is made cathode in an electrolytic cell, it fails to absorb, in spite of the high effective pressure at which the hydrogen is thus applied—a pressure which at usual currents is certainly equivalent to many atmospheres. As we know, less annealed iron takes up cathodic hydrogen readily and in large quantity.

We have then the fundamental fact that, whereas strained iron can establish an entirely normal solubility equilibrium with hydrogen, such a condition cannot be reached with the thoroughly annealed metal. This is established by the concordant results of several experimenters, and such evidence exists for other metals as well (*3*).

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The metal-hydrogen solubility equilibrium is therefore peculiar in that the possibility of its attainment is dependent on the previous history of the metal. Diffusion of hydrogen into the material is clearly conditioned by the strained state! This does not accord with the idea that we are dealing with a solid solution, as commonly conceived, an interstitial, or even a substitutional distribution of hydrogen within the metal; for if the hydrogen were thus contained it should evidently diffuse into perfect lattice.

Elsewhere (*2*) the solubility of hydrogen in metal has been defined as "the occlusive capacity of the metal in a fully annealed condition." To agree with all the facts, this definition is in need of supplement. It should read: "The solubility of hydrogen is the occlusive capacity of the metal (at given $t$ and $p$) in a fully annealed condition, *when some measure of cold-work and subjection to hydrogen have preceded full anneal* (*in hydrogen*)."

In other words, observance of the order of sequence —cold-work, exposure to hydrogen, full anneal (in $H_2$)—is necessary if this equilibrium is to be reached.

If the metal is not *somewhat* cold-worked, the process of interchange of hydrogen between gas-phase and solid will not begin; and if full annealing occurs before some hydrogen has been taken up, or when all hydrogen has been allowed to escape, the metal will revert to a dead-soft and (absorptively) wholly inert state.

All the foregoing is merely a statement of empirical facts well established for iron and some other metals. The only interpretation seems to be that the paths of diffusion and storage places of the hydrogen are not present in perfect lattice but are produced by strain.

In this connection it is illuminating to note that, at just above 400° C, the solubility of hydrogen in iron is of the order of 1 atom of hydrogen to 50,000 atoms of iron (*4*), or roughly 1 atom of hydrogen for 25,000 cells of the bcc metal. Strain has evidently not made the lattice interstices in general receptive to the solute, and diffusion and storage of hydrogen are confined to certain altered regions.

Since these altered regions, like the widened intervals shown by x-ray investigation, are present only in strained metal, it requires no bold leap to identify the two things; and the conclusion is fully borne out by the manner of evolution of hydrogen from metal, when the temperature is raised by steps.

Again taking iron as our example, let us suppose it to have been surcharged with hydrogen at room temperature—by cathodic treatment, by heating in the gas at higher temperature and subsequent cooling, or merely by exposure to the gas at room temperature when the metal is in severely cold-worked condition.

If, after any of these methods of supersaturation, the temperature is raised, say, to 440° C, and is kept constant, the gas comes off into a vacuum, at first rapidly and then more slowly, until after two hours or less evolution has very nearly ceased (*5*). On once more increasing the temperature, this time to 675° C, we find a similar effect: a renewed expulsion of gas, rapid to begin with, but quickly declining to a very low rate. And this may be repeated at several higher temperatures before the metal has been fully freed from hydrogen.

Supposing the normal or un-work-altered lattice interstices to be the storage place and the diffusion path of the hydrogen, we should expect heating to open these spaces all the way through the metal and so to cause complete escape of the gas into a good vacuum. Instead, each rise of temperature produces only a *limited* evolution—but does this even in iron, where increase of temperature results in a greater solubility; and the effect is, again, not confined to iron but probably characterizes all metal-hydrogen systems.

Clearly, the diffusion path is not the continuous route of the interstitial spaces, but some other system of voids which is only partly continuous but which extends to new regions of the metal as the latter is thermally expanded. This system can consist only of the network of work-altered and widened intervals of which we have found other evidences.

The x-ray results are entirely in accord; for, although they show pronounced line-broadening in the diffraction spectrum, as a consequence of cold-work, no displacement of the lines or maxima of diffraction are to be found in the cases of endothermically absorbing metals.

From all indications, then, occluded hydrogen does not enter the normal lattice, in these metals, but is confined to the widened intervals. With palladium, and the other exothermically absorbing metals such as Ta, Zr, Th, etc., the matter is less simple, since a secondary process occurs in which electrons are taken into the nucleus of the metal atom, causing distention of the "normal" lattice. Even here, however, the occurrence of a primary occlusion like that found in the Fe-type metals, is indicated by many facts.

In the metals of the simpler Fe-type, we may distinguish two temperature ranges:

1. *Above a rather ill-defined "recovery" temperature* (often from 300° to 400° C, sometimes perhaps lower) the opening of widened intervals in the lattice is a *reversible process.* Here the material is *elastic* to hydrogen pressure, and the network of work-altered intervals opens to a total volume determined by the hydrogen pressure, the temperature, and the specific nature of the metal. A solubility equilibrium can be reached; or, if the hydrogen is allowed to escape and the metal severely annealed, the widened intervals may be made to close up.
2. *Below the recovery range,* intervals are opened by strain but the process is irreversible. Here no solubility equilibrium can be reached, but work-opened intervals take up large quantities of hydrogen, even at room temperature, these being indeed the largest occlusions which occur (except during deposition of the metal, when the lattice is still in process of formation). Thus at 25° C, "pure" iron, rolled down to thin foil and not afterward annealed, has been found to take up some 45 relative volumes of hydrogen (*6*). This is 5.7 ml/g, as compared with the immeasurably small amount which would be obtained as the solubility at this temperature, if we were

warranted in extrapolating from 400°. It is not without interest to note that this occlusive capacity of severely strained iron, in massive condition, is some hundreds of times greater than the (activated) adsorption reported for this same metal in finely divided form.

The hydrogen thus absorbed brings about pronounced broadening of the x-ray diffraction lines, together with that other important effect of mechanical cold-working, hardening of the metal. Hence we see that the widened lattice intervals, once they have been produced by mechanical deformation, can be further extended merely by the entry of hydrogen, which thus itself has the effect of strain. There is also to be mentioned the closely related fact that occlusion of hydrogen is in its early stages self-accelerating.

Further illumination of the nature of the widened intervals is afforded by the variation of solubility with temperature.

A rough calculation, which has been given elsewhere (*2,* p. 258), shows that, although the (cubic) thermal expansion of iron uncharged with hydrogen, between 400° and 600° C, and therefore the approximate increase of normal interstitial volume, is of the order of only $4.9 \times 10^{-5}$ per cent per degree, the increase in its solvent capacity for hydrogen at 1 atmosphere pressure is, in the same temperature range, of the order of 1.12 per cent per degree. The growth of the volume of the widened intervals which receive the hydrogen is accordingly more than $10^4$-fold larger than that of the interstitial volume of the metal. Evidently the two volumes are relatively unconnected, and the volume of the widened spaces—shortly termed the "strain volume"—increases far more than in proportion to the other. More exact calculation, in which the volumes occupied by the atoms are taken into account, yields a qualitatively similar result.

### The Widened Intervals as Rifts

Such behavior as we have just seen would not be shown by simple defects or cavities in the lattice, for the volume of these would vary in direct proportion to any homogeneous change in the volume of the containing metal. It characterizes instead a system of tears, or "rifts," in the crystal, capable of extending relatively to the lattice, and constituting a network that grows or diminishes in volume and continuity with change of hydrogen content and pressure—and with change in the volume of the surrounding unrifted lattice (when this alters in the exothermic systems of the Pd-type).

This conception of the work-altered regions, or widened lattice intervals, in strained metals as *rifts* is consistent with a great number and variety of empirical facts that have been discussed in other places (*2, 7*), and appears at present to afford the only simple explanation of a large group of phenomena embracing particularly the dissociation pressures and electrical resistances of the metal-hydrogen systems, together with their complex hystereses and overstepping effects.

Without needless repetition of these considerations, we may content ourselves here with summarizing the conclusions to which they seem to lead with cogency, and with calling attention to some of the most strikingly indicative evidence.

### The Rift Network and its Characteristics

*A.* The behavior of the occlusion systems is inconsistent with interstitial (or substitutional!) solid solution—if we exclude the exothermic systems—but accords with the following postulates:

1. In metal with lattice already formed—
    *a.* Occluded hydrogen is held and diffuses in a rift network (and there only, in endothermic systems).
    *b.* The network, in such ready formed lattice, is initially produced solely by plastic deformation, being thus a characteristic of strained (''cold-worked'') metal.
    *c.* It must be partially formed before hydrogen can be absorbed. If the strain has been severe, gaseous hydrogen is taken up freely at room temperature. Into slightly strained metal gaseous hydrogen penetrates only when the rifts are enlarged by thermal expansion; but cathodic or chemically liberated hydrogen is absorbed at ordinary temperature even after slight strain.
    *d.* Once started mechanically, the network can be enlarged either
        (1) by further mechanical strain; or
        (2) by absorption of hydrogen—which intensifies the strained condition.
    *e.* Rifting is reversible only above a (somewhat variable) healing or recovery temperature. In the range above this, the network is elastic, a solubility equilibrium can be reached and hydrogen can keep the network open. Below the recovery range, no solubility equilibrium can be reached; but hydrogen may be absorbed in large quantities in severely strained metal.
2. During deposition of a metal—
    *a.* Rifting may be produced, and in extreme degree, by co-deposition of hydrogen (very clear for electrodeposited metal; probable also for sputtered or evaporated films, provided the H is in highly dissociated or ionized state.)

*B.* Notable are the following points:

1. Rifting, being forcibly produced against the conservative forces of the lattice, changes not only the *parameters,* but also the *force-fields within the rifts,* which hence differ from those in the normal lattice interstices.
2. The stressed force-field of the rift must be highly inhomogeneous, having steep gradients which are of special effect upon atoms or ions contained within it. This probably makes the rift a place where electron exchanges occur readily.
3. The stressed field resists further changes of the kind which produced it, and so may be regarded as the chief cause of mechanical hardness.
4. The forces overcome in rift formation react upon the atoms in which they originate; and the resultant changed state of these atoms is the cause of magnetic hardness and altered atomic properties.
5. Both types of hardness are therefore dependent upon the presence of rifts; and both vanish to-

gether when the metal is heated to the temperature of rift-healing—that at which rifting becomes reversible.

6. Rifts cannot properly be regarded merely as lattice defects, since
    a. during thermal expansion they increase in greater proportion than the volume of the metal as a whole; and
    b. during volume changes of other kinds, rift volume may change in opposite sense to lattice volume.

    Neither of these things is true of any other sort of flaw or void, but only of a rift—a crack that can extend or contract relatively to the containing lattice. The rift network is therefore the important structural feature of strained metal, not a chance defect; and it is the rift field, with its consequences, rather than the arrangement of the surrounding matter, which chiefly determines the behavior of metal in the cold-worked condition.

Of the evidences of opened structure, those from x-ray diffractions are direct and seemingly unquestionable, although as we have seen, a certain ambiguity as regards arrangement attaches even to these. Other evidences either as to spatial or field characters differ much in cogency; but some appear very clear, and their number and accord lend them great cumulative weight. Among the most illuminating we may mention:

1. Hysteresis of the curves of dissociation pressure in Pd-type systems, which show the narrowing, or ''throttling,'' of the diffusion paths for hydrogen as the lattice *expands* with increasing absorption; and the subsequent opening of these paths as the lattice *contracts* when gas is withdrawn.
2. Microscopic changes in Pd-H (*8*) and Ni-H (*9*), which show, not the (submicroscopic!) rifts themselves, but structural effects such as are to be expected from rifting.
3. Magnetic changes produced by occlusion in an iron cathode (*10*), which make clear the nature of hydrogen-hardening and the fact that penetration is by special paths and not by general diffusion through the lattice.
4. Changes of electrostatic capacity and a.c.-resistance, as a result of absorption and evolution of hydrogen (*11*), which demonstrate opening and closing of structure and the ionized state of the enclosed hydrogen.
5. Certain relations between the structural patterns and the corrosive behavior of iron (*5, 12*), from which may be deduced the existence of crystallographically determined regions of sufficiently altered chemical activity to form the sites for initial chemical attack.

Studies of the absorption of highly dissociated ("atomic") hydrogen (*13*) and of the absorption or nonabsorption of the gas according to its degree of ionization (*14*) also present facts that suggest the manner of entry of the solute; and further evidence of value would doubtless be obtained—perhaps with respect to the spatial factors, and certainly concerning manner of entry, by rift or grain face—from observations upon the rate and degree of occlusion by massive metal (foil or wire), both in the soft and in the work-hardened condition, of hydrogen in these special states. Present indications are to the effect that entry is exclusively through the rifts, even with Pd-type metals, where interstitial solution, as well as rift occlusion, is undoubtedly present.

The quality of the rifts as altered force-fields is perhaps most clearly shown by fundamental phenomena of aqueous electrochemistry. Here we have the well-established facts that:

1. Hydrogen gas is not electromotively activated when brought into contact with gold, a metal which does not absorb hydrogen, and in which rifting appears to be absent under all ordinary conditions.
2. Carbon in different forms, despite its porosity and its absorption of large quantities of hydrogen, is equally incapable of acting as ''hydrogen electrode'' (*15*).
3. On the other hand, *metals* that absorb hydrogen—because of its occlusion in their rifts, as we have seen to be probable—are capable of activating the gas.

The obvious explanation of all this is that *the metallic rift* must be present, and that the essential electron transfer $H \rightleftharpoons H^+ + e$ occurs with facility *only in the rifts*. The conclusion is supported by consideration of more complicated electrochemical processes, and of accompanying changes of electrical resistance in metal-hydrogen systems.

Regarding the degree of ionization of hydrogen in different metals, we have preliminary indications that seem to show marked dependence on the metal. Further information on this matter is much to be desired and is probably obtainable by methods which lie to hand.

We may summarize by saying that the widened lattice intervals are evidently rifts in the crystal lattice, produced initially by plastic deformation but capable of extension or healing as conditions are varied. The rifts are apparently the distinctive characteristic of strained metal, responsible for at least some of its special properties—mechanical, magnetic, electrochemical, and presumably chemical.

The rifts have two aspects: as widened and variable lattice intervals; and as altered force-fields, although the orientation of the rift network, set by the method of deformation which produced it, must have a modifying effect. Hardening, at least, is to a large degree directional.

Existence and nature of the rifted state are demonstrated chiefly by the comportment of the metals with hydrogen, and the continued investigation of this behavior is still one of the most promising ways of extending our understanding of the whole related field; but the rifted state has an importance which extends much beyond mere problems of gas in metal, and its further study may be expected to throw light upon many properties of the metals that are of both theoretical and practical interest (*16*).

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# Technical Papers

## Structure of Pan's Crystalline Trisaccharide[1]

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Recently Pan, Nicholson, and Kolachov have described the isolation in crystalline form of a nonfermentable reducing trisaccharide (*1*) produced from maltose by the action of an enzyme system from *Aspergillus niger* (*2*). Through the kindness of Dr. Pan and his associates this trisaccharide has been placed at our disposal, and we wish to report preliminary studies pointing to its constitution.

The trisaccharide (I) was partly hydrolyzed by heating 1 ml of a 1% solution together with 0.67 ml of 0.5 *N* $H_2SO_4$ for 1 hr in a boiling water bath. An excess of $BaCO_3$ was added, the insoluble salts were removed by filtration and washed with 1.33 ml of water (II).

Further, 10 ml of a 1% solution, 0.06 g of iodine, and 0.4 ml of 1 *M* KOH were shaken together and allowed to stand for 30 min. At this point 0.2 ml more 1 *M* KOH was added, and the mixture allowed to stand overnight at room temperature. One ml of this solution was then hydrolyzed with sulfuric acid as described above (III). I, II, and III were then compared on a paper chromatogram (*3*) with the amylose series of saccharides (IV) prepared by partial acid hydrolysis of a low molecular weight amylose, the dextran series of oligosaccharides (V) similarly prepared from dextran, and a crude isomaltose preparation containing homologous, nonfermentable or difficultly fermentable higher saccharides (VI) supplied by Edna Montgomery (*4*). The chromatogram is reproduced in Fig. 1.

From a perusal of this chromatogram, it appears that Pan's trisaccharide has a considerably slower chromatographic mobility than the trisaccharide of the amylose series, yet it is by no means as slow as the trisaccharide of the dextran series. Partial acid hydrolysis produces reducing saccharides which in all probability are isomaltose and maltose, together with glucose. Partial acid hydrolysis of the aldonic acid

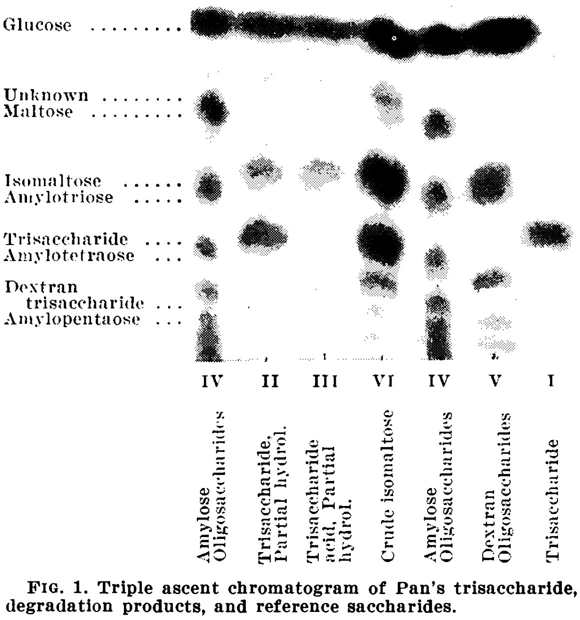

FIG. 1. Triple ascent chromatogram of Pan's trisaccharide, degradation products, and reference saccharides.

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