*METHODOLOGICAL NOTES*

# Self-oscillation processes during the structure relaxation of palladium–metal alloys (Pd–W) saturated with hydrogen

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## Contents

**Abstract.** Some possibilities of studying real microscopic structures by x-ray kinetic techniques are considered. Taking variable-composition Pd–W alloys as examples, a comparative time dependence analysis of the x-ray diffraction pattern (i. e. of the intensity and width of diffraction maxima) is carried out for palladium–metal alloys relaxing after hydrogen saturation. It is shown that the dependences are of nonmonotonic—at some relaxation stages, of oscillatory—character. Analysis indicates that these dependences are due to the self-organisation effect operating during the diffusion evolution of an alloy structure having submicroscopic heterogeneity. The self-organisation mechanisms most likely for a system of local short-range order regions, hydrogen-containing clusters, defects, and hydrogen atoms are considered. Classes of materials allowing such phenomena are discussed.

## 1. Introduction

The phenomenon of self-organisation, which is the subject of synergy, is known to occur in various systems in physics, chemistry, biology, sociology, etc. [1] where behaviour is characterised by a number of positive-feedback hydrodynamic modes; it is the feedback property which gives rise to self-organisation. (By a hydrodynamic mode is meant, conventionally [1, 2], a long-wavelength collective fluctuation corresponding to the coherent motion of a large number of microscopically long-lived particles.) For a coherent self-organisation regime, it is necessary that the control parameter determining the system's phase diagram position becomes supercritical. As a result, the system undergoes a bifurcation transition and its behaviour changes character dramatically. In the simplest case of phase transitions, the control parameter is the temperature, the hydrodynamic modes are related to the order parameter and the associated field, and the system's rearrangement reduces to its ordering [3].

The aim of the present paper is to consider and analyse evidence [4, 5] for self-organisation processes in hydrogen-containing crystal alloys. As far as semiconductor electronic subsystems are concerned, synergetic effects have long attracted attention [6]. These effects are characterised by relatively short time scales of the order of the Maxwell relaxation time. As can be seen from Section 2, the characteristic times considered here are of the order of several days. This suggests that the self-organisation effects here are due to slow diffusion-assisted atom redistribution processes acting in a solid during structural transformations. It seems obvious at first that crystal structure defects should be considered separately. A systematic study [7] shows, however, that a defect is an autolocalised region which has undergone a structural transformation, so the characteristic behaviour of defects is determined only by their dimensionality and by the nature of their spatial distribution.

Synergetically, the distinguishing feature of such transformations is that they are generally reached by the simplest scenario of all—by a phase transition. The set of hydrodynamic modes then reduces to a single degree of freedom whose amplitude is characterised by the order parameter, which completely specifies the behaviour of all the remaining degrees of freedom (hierarchy principle) [1]. As for more complex scenarios (of Belousov–Zhabotinskii reaction type), these seem to be extremely unlikely in solid structural transformations. This, however, is only true if the latter proceed homogeneously, without giving rise to localised regions of a new phase, to defects, etc. A real experimental situation is generally much more complex: the regions, or nuclei, of the new phase may be distributed in a heterogeneous way in the volume; a structural transformation may involve considerable lattice distortions, which lead to defect multiplication during the motion of the interface boundary; etc. [8]. It is well known that even as few as two

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defects may give rise either to self-oscillations [9] or autocatalytic defect multiplication [10]. This raises the question of whether we can have a nontrivial self-organisation scenario in which some of the hydrodynamic degrees of freedom result from structural transformations and some from the redistribution of the crystal structure defects.

Basically, such a scenario resembles the following. First, the process must develop in time, and this requires a study of the time behaviour of the x-ray diffraction pattern, i. e. of the x-ray diffraction kinetics. Second, since such a scenario must also involve defect redistribution, the x-ray diffraction analysis must include the measurement of the intensity and width of the diffraction maxima. Third, the object under study must be a microheterogeneous system of regions of different composition.

In this connection, to observe the self-organisation scenario outlined above it is necessary to apply a special methodology which includes the search for:

(a) suitable objects in which submicroheterogeneities on about a mesoscopic scale may be expected to exist;

(b) some influences capable of enhancing or diminishing the heterogeneities, and

(c) investigation techniques allowing the study of not only the defect structure per se, but also those of its time dependent characteristics amenable to a proper comparison. It is this approach which was taken in Refs [4, 5].

The choice of the system is explained in the following way. On the one hand, it was known [11, 12] that the $Pd-W$ system with W content of about 10 at.% has local short-range order. This appears as regions a few nanometers in size which are most probably ordered as $Pd_5W$ and hence are tungsten enriched. Their volume fraction is $10^{-1}$, and they stabilise if there are excess vacancies to compensate for the ordering-induced lattice expansion (for more details, see I·6 in Ref. [3]). Clearly the appearance of these regions depletes the remaining parts of the crystallites of tungsten. On the other hand, it was known that in view of the strong $Pd-H$ affinity (discovered back in Ref. [13]), the hydrogen saturation of palladium causes a first-order, isomorphic $\alpha \rightarrow \beta$ transformation accompanied by a marked lattice expansion (the $\alpha$ phase here is a hydrogen-FCC palladium solid solution with no more than 0.02 hydrogen atoms per palladium atom; the $\beta$ phase is the same nonstoichiometric solution, but with no less than 0.6 hydrogens per palladium; the lattice periods are 3.892 and 4.025 Å, respectively; the concept of a metal-hydrogen alloy as an alloy with no definite stoichiometry was introduced in Ref. [14]). Cycling the 'saturation-degassing' process generates powerful fields of defects such as vacancies, dislocation loops, pores, etc. [15]. As a result, the $Pd-W$ alloy thus repeatedly saturated with hydrogen possesses a heterogeneous structure of mesoscopic local short-range-order regions (LSRORs) while at the same time being a heterophase mixture of the $\alpha$ phase with mesoscopic $\beta$ phase regions that vary in their defect and H-interstitial content. Since hydrogen is practically insoluble in tungsten, it may not be abundant in an LSROR. This indicates, first, that palladium-tungsten alloys are highly heterogeneous not only in composition but also in hydrogen affinity and, second, that this heterogeneity may be varied by saturating the material with hydrogen. Thus, the application of the hydrogen saturation method may either enhance or diminish heterogeneity.

From the methodological standpoint, the studies in Refs [4, 5] may be characterised as follows:

(a) the principal characteristics measured were the time dependence of the intensity and width of the x-ray diffraction maxima;

(b) measurements were carried out for a long period of time (up to three and a half months after each 'hydrogen disturbance' of the sample) and at strictly prescribed time intervals;

(c) in addition to the diffraction pattern from the samples under study, scattering from control samples with time-constant diffraction characteristics was studied.

In Section 2 we present x-ray data which show that the system described above has a very nontrivial synergetic behaviour. Namely, it displays beats caused by oscillatory modes of different periods associated with the periodic vacancy redistribution between the $\beta$ phase region and LSRORs on the one hand, and between structures such as prismatic dislocation loops on the other. Section 3 presents a synergetic analysis of such behaviour. It is found, in particular, that the volume-averaged values of the tungsten and vacancy concentrations play the role of the control parameters of the system. The variation of the concentrations leads to the bifurcation of the oscillatory regime into a relaxation one and vice versa.

## 2. Experimental data

Experimental data were obtained mainly by x-ray measurements in Refs [4, 5]. The electrolytic saturation and x-ray techniques are described in detail in Refs [16–18]. A special check was made to see if hydrogen atoms penetrate the sample volume throughout. For the $Pd-11.3$ at.% W alloy, the electrolytic saturation time was 15 min for a current density of 80 mA cm$^{-2}$. The hydrogen saturation regimes for the $Pd-7$ at.% W alloy are shown in Table 1. The integrated intensity, width, position, and profile of the

**Table 1.** Square of the width of the diffraction maximum (400), in degrees squared.

| Sample state | Degassing time/h | Deformed sample | Annealed sample |
|---|---|---|---|
| Initial state | — | 0.689 | 0.223 |
| First hydrogen saturation (40 mA cm$^{-2}$, 15 min) | 0 | 0.796 | 0.340 |
| | 24 | 0.776 | 0.425 |
| | 48 | — | 0.278 |
| | 140 | 0.776 | — |
| | 240 | 0.764 | — |
| | 430 | — | 0.402 |
| Second hydrogen saturation (80 mA cm$^{-2}$, 15 min) | 0 | 0.796 | 0.336 |
| | 24 | 0.776 | 0.140 |
| | 48 | 0.776 | — |
| | 72 | — | 0.336 |
| | 170 | 0.776 | — |
| | 700 | — | 0.402 |
| | 1200 | 0.764 | — |
| | 3500 | 0.780 | — |
| Third hydrogen saturation (80 mA cm$^{-2}$, 30 min) | 0 | — | 0.535 |
| | 24 | — | 0.535 |
| | 170 | — | 0.418 |
| | 800 | — | 0.472 |
| | 2500 | — | 0.518 |

diffraction maxima were measured with the x-ray diffract-ometer DRON-UM1 using monochromatic $CuK_\alpha$ radiation. Scattering on control samples (fused quartz, annealed aluminium, and palladium) was also system-atically measured.

Evidence for anomalous behaviour was first found [4] in the Pd—7 at.% W alloy. The quantity studied was the time dependence of the square of the width of the diffraction maximum (400) for the process of degassing of a hydrogen presaturated sample. The latter was taken as either deformed (following lapping and polishing) or annealed (at 500 °C for 2 h). From Table 1 it is seen that the hydrogen saturation leads to broadening of the maximum because of the increased defect density. In general, in the course of the subsequent degassing the defect content first decreases (ordinary relaxation), then anomalously increases and ultimately stabilises. The behaviour of the annealed sample once saturated is even more surprising: here the defect content also first increases, then drops to below its initial value, and then again increases to saturation. In other words, Pd—7 at.% W more often exhibits an oscillation of about half a period, but in the annealed sample which was only once saturated with hydrogen, a full period may sometimes occur.

Clearly, the above experiment does not necessarily imply the occurrence of an oscillatory regime in the system's behaviour. Rather, the discovery of the nonmonotonic property stimulated the search for an alloy with such a composition and such pretreatment and hydrogen saturation regimes as would make oscillatory behaviour possible. The answer was that, first, the tungsten content should be increased to 11.3 at.% W and, second, saturation should be repeated.

A content analysis for various types of defects was carried out by comparing the diffraction maxima (400) and (200). For the former, the increase in intensity is known [19] to be due primarily to the appearance of so-called defects of the first class, which include vacancies, small-size disloca-tion loops and other equiaxial microscopic-scale structures (clusters)†. On the other hand, the decrease in the intensity $I(200)$ is due primarily to extinction effects, which reflect the reduction in the degree of disorientation of the mosaic structure and possibly the growth of its blocks (the defects of the first class affect $I(200)$ much less than they do $I(400)$) [19]. With this in mind, we studied the time dependence of the intensity ratio $I(400)/I(200)$ taken in the semilogarith-mic scale. Its form after the third hydrogen saturation is shown in Fig. 1.

It is seen that after two days there is a maximum, corresponding to the minimal concentration of the defects of the first class. The next three distinct maxima are found 7, 14, and 21 days after the first one. This stage of relaxation clearly displays periodicity even though the curve in Fig. 1 is not harmonic. Another obvious feature is the fluctuation about the oscillating line. After the second saturation, the first maximum in the curve was also seen after two days. The subsequent evolution was however less

† According to Ref. [18], defects are classified based on the value of the exponent $n$ in the relation $\sigma \propto r^{-n}$, where $\sigma$ are the stresses the defect produces at a distance $r$ away. Defects of the first class, which act to reduce the intensity of diffraction maxima, have $n > 5/2$ (e.g., for vacancies $n = 3$). Defects of the second class, for which $n < 5/2$ (for a rectilinear dislocation, $n = 1$) wash out the maxima.
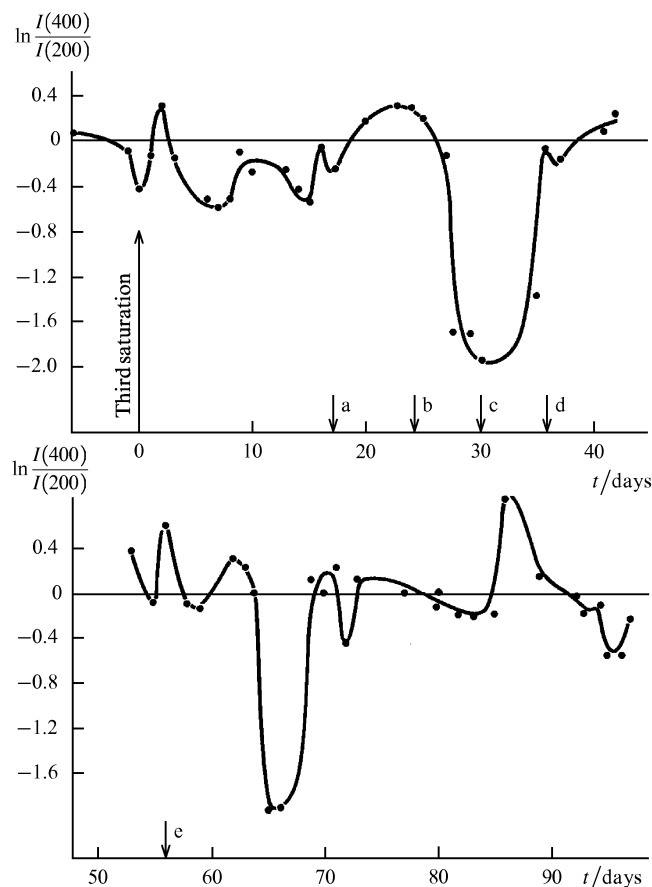


**Figure 1.** The time dependence of the logarithm of the intensity ratio of the diffraction maxima (200) and (400) in the process of degassing of a Pd—11.3 at.% W alloy subject to three hydrogen saturations.

clear than after the third saturation. Note that an increase in defect concentration soon after hydrogen saturation was also seen in the Pd—7 at.% W alloy.

28 days after saturation the character of the diffraction pattern alters sharply in that the diffraction lines now display a strong broadening. If the (400) line in annealed Pd is 0.40° wide (which may be taken as an instrumental width), and if for those Pd—W alloy states which maximise its intensity we have 0.53°—0.55°, then at the instant of its sudden broadening values of 0.85°—1.1° are reached. Thus, after 28 days the diffraction broadening is 3 to 5 times greater than usual. This is clearly seen in Fig. 2, where the maximum profiles for the following states (marked by arrows on the time axis of Fig. 1) are represented: (a) the minimum in the time dependence of $I(400)/I(200)$ before the fourth maximum; (b) the fourth maximum: (c) the state corresponding to the maximum smearing of a diffraction maximum; (d) the first maximum on leaving the state of the maximum smearing of the diffraction maximum; (e) the state emerging three weeks after the preceding state. The diffraction profiles of Fig. 2 show clearly that a few days after three oscillation periods, an anomalous broadening of the diffraction profile occurs (dash-dot line). The diffraction profile then narrows again, and the value of $I(400)/I(200)$ again oscillates in time. At this stage the oscillation becomes stochastic, however. About a month after their first broadening stage is over, the lines start broadening again, and this lasts four days. After that the diffraction profile narrows again.
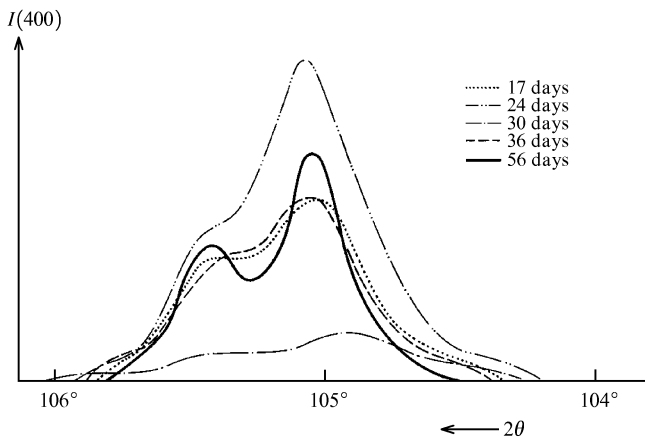
**Figure 2.** Diffraction profiles for characteristic instants during the degassing process ($2\theta$ is the scattering angle).

Thus, as the hydrogen-saturated Pd – 11.3 at.% W alloy relaxes, the intensity ratio $I(400)/I(200)$ first increases and then enters the stage of a nearly periodic variation, to be followed by the strong broadening of diffraction maxima. It should be noted that in the latter case the integrated intensities cannot be measured properly because of the loss of the 'wings' extending far away from the line. The narrowing of the maxima gives way to an aperiodic intensity variation, and then again the lines broaden and narrow.

## 3. Analysis of experimental data

The results indicate that hydrogen saturation leads to a significant increase in the initial defect concentration. During the first two days the concentration decreases to well below equilibrium values, which is the reason for the subsequent 25-day oscillations. From 28 days on, the defect content becomes so high that the oscillation process collapses and for the four days that follow the structural state of the system is unchanged. Then the oscillatory regime returns, but in a more stochastic form. This suggests that the average concentration of the defects supporting oscillation is reduced considerably at the instant of the collapse.

We will first describe the oscillatory intensity changes based on the hypothesis in Ref. [5] that the reduction of the diffraction maximum (400) is due primarily to the presence of mesoscopic LSRORs. As mentioned in the Introduction, these are clusters of the ordered phase of $Pd_5W$, no more than 10 nm in size and with a volume fraction of $10^{-1}$. The crucial point here is that the formation of these clusters is accompanied by a significant expansion of the lattice which leads to high elastic stresses [11]. Experimental conditions were such as to ensure a position on the Pd – W alloy phase diagram for which, provided there are no mechanisms for stress relaxation, the elastic energy makes the ordering process thermodynamically unfavourable. In alloys with local order, however, an excess number of vacancies are introduced at the outset (e.g., by hardening); the elastic field pulls these into an LSROR thus causing stress relaxation and leading to the stabilisation of the ordered regions (see §6 in [3] for the details). The point to bear in mind in the discussion below is that if an LSROR collapses for some

reason or another, the excess vacancies absorbed will go free and the ordered regions will appear to be their sources. When initially absorbing vacancies, they played the role of predatory beasts devouring their prey, vacancies: another example of the familiar ecological 'predator – prey' scenario [20].

It is clear from Section 2, however, that the oscillatory behaviour of this system is obtained only when the Pd – W alloy is saturated with hydrogen. This means that at least the 'launching' of the oscillatory process must be associated with the appearance of hydrogen enriched regions in the crystal. Regions like that must indeed arise from hydrogen saturation, because hydrogen depleted regions in the Pd – W alloy must undergo an $\alpha \to \beta$ phase transformation, with mesoscopic regions of the $\beta$ phase appearing at its initial stage. Being an interstitial solution, this phase has a much larger lattice parameter than does the initial $\alpha$ phase. Therefore, as in the case when the ordered phase of $Pd_5W$ is being formed, the appearance of $\beta$ regions involves a significant lattice expansion, which also leads to elastic stresses that require an influx of vacancies for their relaxation. Thus, in this case we also encounter the 'predator – prey' system, with $\beta$ phase regions acting as the former, and the same vacancies as the latter. The growth of the elastic energy causes these regions to lose their thermodynamic stability. In order for the elastic energy to decrease, these regions must either disintegrate, losing hydrogen in doing so, or they must decrease their specific volume by absorbing a vacancy. Since vacancies may only come from LSRORs, these latter will gradually become more and more deficient in defects, and so the reverse process, the diffusion of vacancies from $\beta$ regions into LSRORs, must set in. It is the combination of these two diffusion processes which may be the cause of the diffraction pattern oscillations in the case under study. In this situation the formation of $\beta$ phase regions has the effect of displacing the surrounding atoms. The amount of displacement depends on the atom's distance from the region. The resulting clusters lead to the weakening of the diffraction maxima. The subsequent saturation by vacancies decreases the clusters' specific volume and eliminates their ability to displace the surrounding atoms. As a consequence, the intensity of the diffraction maxima will increase, and so on. At the same time, the loss of hydrogen by the $\beta$ phase regions is a far slower process, and is not a major factor at this stage of relaxation.

What makes the present synergetic system nontrivial is that in an autonomous regime each of the 'predator – prey' pairs shows dissipative behaviour, which manifests itself in that the system monotonically (and fairly rapidly) crosses over to a steady-state regime, which is the formation of LSRORs for a hardened Pd – W alloy and of $\beta$ regions for hydrogen saturated palladium. On the other hand, the experimental data of Section 2 show that when the two pairs coexist, bifurcation into a bistable regime occurs [21]. Physically, this means that since in either pair the prey component is vacancies, the pair's predators come into food shortage conflict with one another. Even at this level of interpretation it is readily seen that such conditions may produce an oscillatory behaviour and that the problem may be treated at either of two levels of complexity: in a more complete formulation one should consider one prey and two types of competing predators, whereas in a simplified description one prey and the population difference of

the predators are enough. We next describe the analytical schemes corresponding to these two approaches.

When constructing the most complete theory one should begin by noting that the predator 'on the verge of extinction' is the source of vacancies, whereas the one increasing in population represents their sinks. Let the concentration of the former be $g$, and that of the latter, $r$. The concentration of vacancies is $n$. If the distribution over the volume is uniform, the quantities $g$, $r$, and $n$ depend only on time $t$. The set of equations for determining the dependences $n(t)$, $r(t)$, and $g(t)$ is written in the form

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{n}{t_0}\left(1 - \frac{n}{n_0} - \frac{r}{r_0} - \frac{g}{g_0}\right), \tag{1}$$

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{r}{t_r}\left(1 - \frac{n}{n^0}\right), \tag{2}$$

$$\frac{\mathrm{d}g}{\mathrm{d}t} = -\frac{g}{t_g}\left(1 - \frac{n}{n^0}\right). \tag{3}$$

Here we have introduced the time scales $t_0$, $t_r$, and $t_g$ for the variation of the corresponding quantities when in the autonomous regime; as well as the scales $n_0$ and $n^0$ for changes in the vacancy concentration, and the corresponding scales $r_0$ and $g_0$ for the sinks and sources. The first term in Eqn (1) describes the Debye vacancy generation process operating under an external influence; the second term accounts for the mutual annihilation of the vacancies due to their clustering; the third term in Eqn (1) describes the decrease in the vacancy concentration at sinks, and the last term its increase due to sources. Eqns (2) and (3) govern the sinks and sources respectively; their first terms account for the Debye relaxation, and the second ones for the growth of the concentration of the predators due to vacancy absorption. It should be kept in mind that $r$ and $g$ vary in the opposite directions, so the signs of $r$ and $g$ in Eqns (1) are different. The sign symmetry of Eqns (2) and (3) implies that in this case the $r$ and $g$ variations are measured from their respective values most distant from the common level.

The analytical solution of the set of nonlinear equations (1)–(3) is not generally possible. One should therefore resort to a quantitative analysis using the phase space method [22]. The phase space of the system is depicted in Fig. 3a. The phase trajectory may run between the turns of a surface resembling a loose roll of paper whose axis $FF'$ is formed by the intersection of the planes $n = n^0$ and

$$g = g_0\left(\frac{n^0}{n_0} - 1\right) + \frac{g_0}{r_0}\, r.$$

Clearly, the oscillatory regime is most pronounced when the phase trajectory lies in the plane perpendicular to the axis. In the opposite — parallel — case oscillations are virtually absent. The phase diagram given in Fig. 3a helps to explain the experimental dependence shown in Fig. 1. To this end it suffices to assume that those portions of the diagram corresponding to oscillations in the intensity ratio $I(400)/I(200)$ are described by a phase trajectory in the plane perpendicular to the $FF'$ axis, the strong dips corresponding to the system's evolution along a trajectory parallel to $FF'$. As for the irregular feature mentioned in Section 2, this is easily accounted for by introducing fluctuating terms in the right-hand sides of Eqns (1)–(3) [23].
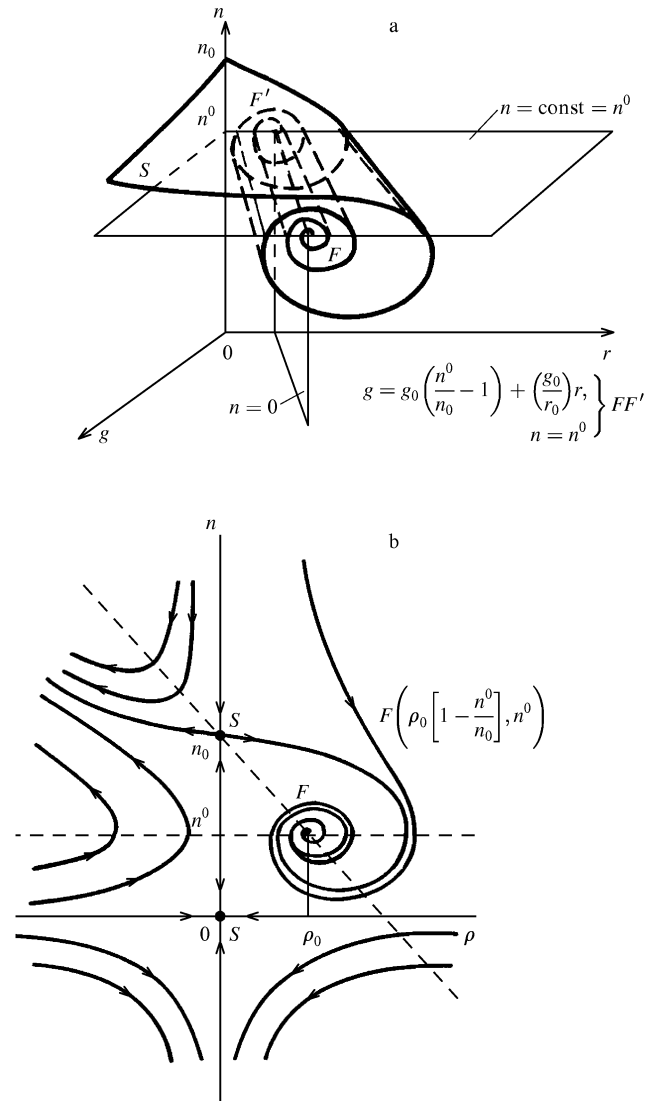


**Figure 3.** Three-dimensional (a) and two-dimensional (b) phase portraits representing the behaviour of the system.

Next we present the abridged description of the experimental situation. This follows immediately from Eqns (1)–(3) if the concentrations of the sources and sinks for the vacancies are not treated as independent but are instead assumed to be related by $\rho = r - g$, which gives the difference between the populations of the competing predators. Subtracting Eqns (2) and (3) term-by-term we arrive at the set

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{n}{t_0}\left(1 - \frac{n}{n_0} - \frac{\rho}{\rho_0}\right), \tag{4}$$

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\rho}{t^0}\left(1 - \frac{n}{n^0}\right), \tag{5}$$

where we have put $t_r = t_g = t^0$. The physical meaning of the terms on the right-hand side of Eqns (4) and (5) is evident from the discussion of the corresponding terms in the set (1)–(3). The advantage of the abridged scheme is that it goes over from three-dimensional phase space to a two-dimensional picture (as clearly illustrated in Figs 3a, 3b). The two-dimensional portrait, in particular, permits a more detailed description of the system's behaviour.

From Fig. 3b it is seen that the phase plane $\rho n$ has three special points, namely the focus $F$ with coordinates

$$\rho_F = \left(1 - \frac{n^0}{n_0}\right)\rho_0\,, \qquad n_F = n^0$$

and the saddle points $(0,0)$ and $(0, n_0)$. For physically reasonable values of the variables $\rho$, $n > 0$, whatever the initial volume fraction of LSRORs and the initial vacancy concentration, the evolution of the system is characterised by a phase trajectory spiraling to the focus point $F$. Such behaviour corresponds to an oscillatory crossover to the steady-state regime $\rho = \rho_F$, $n = n_F$ with a frequency

$$\omega = t_0^{-1}\left[\frac{t_0}{t^0}\left(1 - \frac{n^0}{n_0}\right) - \left(\frac{n^0}{2n_0}\right)^2\right]^{1/2} \qquad (6)$$

and a decrement

$$\alpha = \frac{n^0}{2n_0}\,t_0^{-1}\;. \qquad (7)$$

Thus, a pronounced oscillatory regime is possible only when the sources and sinks of vacancies have sufficiently short relaxation times:

$$t_0 < \left(\frac{n_0}{n^0}\right)^2 t_0\;. \qquad (8)$$

This explains why the oscillatory regime is attained for sufficiently small phase clusters—i.e. for mesoscopic LSRORs—and is not for macroscopic units. In the former case the formation time $t^0$ is sufficiently short, whereas in the latter the growth in the size of the inclusions makes it much longer. On the other hand, Eqn (8) requires that the mutual vacancy annihilation (characterised by the parameter $n^0$) be less intense than the absorption of vacancies by the LSRORs (parameter $n^0$). If the vacancies do not cluster $(n_0 = \infty)$, the upper saddle $(0, n_0)$ goes off to infinity, the focus $F$ becomes the centre, and the helix turns change into closed curves around it. It is in this case that we come to the classical formulation of the 'predator–prey' problem [20]. The evolution of the system in this case corresponds to the motion along one of the closed curves with a frequency $\omega = (t_0 t^0)^{1/2}$ and a decrement $\alpha = 0$.

The data in Fig. 1 show that the period of the oscillations is 7 days and their collapse interval is from 21 to 28 days. Hence the quantities (6) and (7) are related by $\omega/\alpha = 3/4$. As a result, for the parameters of the model (4)–(5) we obtain the estimate

$$\left(\frac{n_0}{n^0}\right)^2 \frac{t_0}{t^0} \gtrsim 10\;, \qquad (9)$$

showing that condition (8) has a safety factor of ten. Hence, in estimating the frequency from Eqn (6) the subtracted term under the radical may be neglected, and after substituting a period of 7 days we find $t_0 t^0 \sim 10^{10}$ s$^2 \sim 1$ day. Since the time scale $t_0$ for vacancy generation under external conditions [cf. Eqns (1) and (4)] must be much less than the characteristic relaxation time $t^0$ of mesoscopic LSRORs, it can be concluded that $t_0 \ll 1$ day, and $t^0 \gg 1$ day. More accurate estimates require a knowledge of the microscopic mechanisms involved.

As already noted, a characteristic feature of the oscillations is that they collapse in a sudden jump rather than damping out. This behaviour is readily understood by assuming that the system has more than one self-organisa-

tion mechanism. It suffices to assume, for example, that the 'predator–prey' system is attained not only for LSRORs, vacancies, and $\beta$ phase regions, but also for the dislocation loops that result from vacancy clustering. The dependence of Fig. 1 then arises from beats due to the superposition of oscillations whose frequencies $\omega$ and $\omega'$ correspond to the above mechanisms. As seen from the data in Section 2, their ratio is determined by the condition $(\omega' - \omega)/\omega = 7/28$ giving $\omega'/\omega = 5/4$.

The explanation given above is formal in character. It seems therefore appropriate to elucidate the essence of the oscillation collapse mechanism as it appears at the microscopic level. The phase portrait in Fig. 3b suggests that the change in the vacancy concentration $n(t)$ in the matrix is one quarter of the period ahead of the corresponding change in the intensity $I(t)$ of the diffraction maximum (400). So before the dependence $I(t)$ arrives at the third oscillation maximum $(t_c = 23$ days) the matrix vacancy concentration has reached its maximum value. Apparently it becomes so large as to satisfy the condition $n(t) > n_c$, where $n_c$ is the critical value beyond which the vacancies cluster into prismatic dislocation loops. In other words at the time $t_c$ given by the condition $n(t) = n_c$, a second self-organisation mechanism sets in, the 'devouring' of vacancies by dislocation loops. With respect to the first mechanism, in which predators are represented by LSRORs and $\beta$ phase inclusions, the above reduction in vacancy concentration may be reflected by a sudden decrease in the annihilation parameter $n_0$ in Eqns (1) and (4). On the phase plane $\rho n$ (Fig. 3b) this will lead to the bifurcation-induced rearrangement of a stable centre (surrounded by closed trajectories) into an attracting focus, i.e. the oscillations will transform into a relaxation process. It is this latter which corresponds to the dip in   Fig. 1.

As time goes on, some of the prismatic dislocation loops—whose density exceeds the stationary value—disintegrate into isolated vacancies. As a result, the parameter $n_0$ grows again, so that the vacancy concentration regains the value $n$ necessary to keep the oscillation process going by the first mechanism. Since, however, not all of the vacancies escape their traps, the oscillations will now be less regular in character. As the process evolves further, the supply of catalysing vacancies is reduced rendering the oscillations stochastic. From the synergy viewpoint this means that the average vacancy concentration acts as a control parameter whose value determines the behaviour of the system. In particular, this explains the need for multiple hydrogen saturation: its role is to secure the required initial value of the control parameter $n$.

In addition, necessary conditions for the existence of the predator themselves, i.e. of the LSRORs, must be met. The fact that oscillations fail to occur for the Pd–7 at.% W composition indicates that the tungsten concentration is another control parameter. However, in contrast to the vacancies, the role of the tungsten concentration is quite trivial: whereas the vacancy concentration secures the self-organisation oscillatory regime by participating actively in the process, the tungsten concentration just specifies the point on the phase diagram of the Pd–W alloy which corresponds to the region of existence of LSRORs [3] and secures the formation of an (LSROR-related) mesoscopic hydrogen-affinity heterogeneity.

# 4. Conclusion

Thus, the methodology outlined in the Introduction — an x-ray-kinetic study of microheterogeneous samples preliminarily saturated by hydrogen — gives evidence for an oscillatory regime in the structural changes in a solid solution with a complex heterophase and defect structure. A characteristic feature is a large oscillation period, due to the mesoscopic size of the LSRORs and $\beta$ phase regions whose volume fraction varies as a result of vacancy diffusion. This means that the approach we adopted has enabled us to discover an unusual type of structural transition exhibiting the auto-oscillatory behaviour of the system.

It may be conjectured that the present data reflect some features of the structural transitions occurring in open systems with dissipative structures. Among these may be listed various types of solid-state systems containing gas atoms (H, O, etc), as well as systems relaxing after powerful external disturbances (radiation, etc.).

Although the synergetic scenarios of Section 3 are of course not the only ones possible for the oscillatory behaviour of the alloy studied, we believe them to be the most probable. In particular, we did not take into account the presence of the dislocation ensemble, which is known [16, 17] to play a major role in the process of degassing of a hydrogen saturated metal; nor did we include the diffusion of hydrogen atoms from the system, the displacement of tungsten atoms, etc. Therefore the review of results and the data generalisation and analysis we present here should rather be considered as a report on nontrivial experimental phenomena, complemented by theoretical explanations which we believe are quite plausible ones. Further experimental and theoretical work will show whether our belief is correct.

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