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# Phase Oscillations in Lead Monoxide under the X-ray Beam

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Time-resolved X-ray diffraction is used to examine phase oscillations in the lead monoxide system. The X-ray beam maintains the system far from equilibrium by producing highly disordered metastable lead monoxide. Experimentally determined logistics maps indicate that a minimum of three phases are required for the oscillations. One phase is a disordered phase, the other are commensurate and incommensurate phases in different diffraction domains. The oscillations are postulated to occur between the crystalline phases and the disordered phase. The kinetics are modeled as quasiperiodic for three or more phases, one disordered and two or more crystalline. The model predicts temperature, X-ray beam intensity, and defect dependence, but does not account for nonlinear effects.

## 1. Introduction

Although chemical oscillations in the solution and gas phases long have been under intense investigations (*1*), it is only recently that solid–solid phase oscillations have been described (*2*). The oscillations were observed during the tetragonal-to-orthorhombic phase transformation in lead monoxide (however, the role of the commensurate lead monoxide phases in the phase oscillations was uncertain). Since considerably *in situ* work is being done in solid-state reactions and phase transformations initiated and observed with X-ray and electron beams, it is important to consider quantifiable behavior that the beams may initiate. In addition, the existence and investigation of phase oscillations may provide insight into the fundamentals of solid-state reaction and transformation kinetics. In the present communication, the early data (*2*) are examined in greater detail and new results are considered in order to determine the macroscopic kinetics and mechanism of the observed solid-phase oscillations. A first approximation, quasiperiodic kinetic model is presented. The results are consistent with the phase rule and the criteria necessary for chemical oscillations; indeed, the phase rule is shown to be an important factor for the occurrence of the oscillations.

To review the early results (*2*), during the *in situ*, time-resolved powder diffraction of the lead monoxide phase transformation in an inert atmosphere, the diffraction lines of both phases are accompanied by a set of high, but variable, intensity satellite lines at $d(h, k, l) \pm n\,\delta d$, where $n$ is an integer and $\delta d$ is a $d$-spacing displacement; not all sequential values of $n$ are observed. The average position of the satellite lines is that

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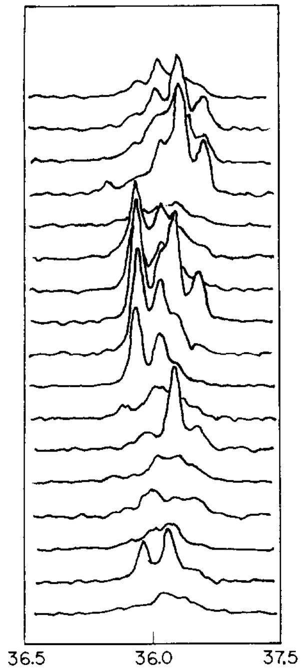

FIG. 1. Orthorhombic (020) satellite lines undergoing oscillations at 587°C in air. The lowermost scan is the initial scan and is at 45 min after temperature is reached. The scans are 5 min apart (*2*).

of the central line, but the maximum intensity is not easily related to values of $n$. The satellite lines persist after there is no apparent further tetragonal PbO ($PbO_t$) to orthorhombic PbO ($PbO_o$) transformation. No other crystalline phases are observed during or after transformation; however, only a limited two-theta region was examined at high temperature. When the transformation is quenched in liquid nitrogen, while a nitrogen atmosphere is maintained, X-ray diffraction analysis shows no other diffraction lines other then those of $PbO_o$ and $PbO_t$.

The most significant feature of the satellite and central lines is that the peak intensities are not constant, but undergo rapid oscillations in time (Fig. 1). The lines narrow and broaden as they respectively increase and decrease in intensity. The intensity of a set of lines will decrease into a very broad, nearly amorphous profile with a measured integrated intensity that is substantially lower than that for the corresponding cluster of lines when at their maximum intensities; from this the set of diffraction lines regrows.

Because the diffraction lines are narrow and have a small $2\Theta$ separation, diffraction data can only be collected and fully analyzed with confidence for lines of high intensity and at high diffraction angles. Consequently, only data from $(111)_o$, $(020)_o$, $(002)_t$, and $(101)_t$ have been discussed.

For oscillations in chemical systems to occur and be maintained in either solution or gas phase (heterogeneous or homogeneous), four criteria have been observed (*1*, *3*): (1) the systems are maintained far from equilibrium by energy or mass transport across the system boundaries; (2) the mechanistic equations display feedback; (3) there is component multistability; (4) the kinetics are nonlinear. There are additional considerations for solid–solid phase oscillations: (1) the phase rule cannot be violated, which supersedes microscopic reversibility; (2) growth of the system components are expected to occur at domain boundaries. The difference between chemical oscillations and the present problem, as it is now understood, is that chemical oscillations arise from the nonlinearity in the mass-action law; in solid–solid transformations and reactions, the law of mass action is not expected to apply, and nucleation and growth should be considered. Indeed, a more appropriate guide may be oscillations and chaos in dynamical systems.

## 2. Experimental

Tetragonal lead monoxide was prepared by dehydrating wet lead hydroxide in Pyrex glassware with hot 15 *N* KOH. The product was aged for 12 hr with slow cooling under the supernatant.

*In situ* transformation data were collected under flowing helium using a Rigaku DMAX-RB rotating anode diffractometer, as described earlier (*2*). The diffractometer detector was oscillated at a scan rate of 1°/min with a 0.010° sampling over a $2\Theta$ region that contained a peak of each lead monoxide phase. The X-ray beam was generated by Cu-$K\alpha$ excitation at 8000 kW power. Samples were annealed by slow temperature ramping. Temperature dependence data were collected from 540 to 710°C at temperature steps of 10°C; at each temperature step, three scans were taken after a 10- to 20-min soak.

## 3. Results and Discussion

The satellite line positions show no temperature dependence over the temperature range 560 to 710°C. The tetragonal-to-orthorhombic phase transformation was observed to be complete by 590°C, with no tetragonal phase retention. However, before the $PbO_t$ to $PbO_o$ phase transformation was complete, incidences of an increase in tetragonal phase central and satellite lines peak and integrated intensities did occur. The profiles grew from an unstructured and noisy background rise and continued with profile narrowing, giving the appearance of recrystallization.

With increasing temperatures over 610°C, the same lines persist, but are very broad and of low intensity. The satellite lines on the low $2\Theta$ side of the central line increase in relative intensity, and new, low-intensity lines may appear. The oscillations continue at high temperature, but with peak positions and relative intensities difficult to measure with confidence. The results are consistent with the lead monoxide phase transformation being incidental to the observed oscillations.

If the specimen is annealed *in situ* at temperatures above surface carbonate decomposition (340°C), but below oxide decomposition (450°C), the oscillations are partially suppressed so that reliable data is difficult to obtain. The annealing results indicate that the phase oscillations depend on defect structure and composition; they may be related to material incorporated during preparation (such as $SiO_2$).

In Fig. 2, the peak x-ray diffraction intensity for the three most intense lines in the $2\Theta$ region of $(020)_o$ and the most intense $(111)_o$ satellite line are plotted as functions of time. Five features are immediately observed: (1) there is a periodicity of approximately 20 min for all three $(020)_o$ satellite lines at 587°C and approximately 16 min for $(111)_o$ at 595°C; (2) some lines show apparent bifurcations, oscillating between two values of peak intensities; (3) the lines are in phase or nearly in phase; (4) there is a continuous increase in background intensity from the lead monoxide phase transformation—this will have minimal influence on the present discussion; (5) the transformation curve for $(111)_0$ displays pronounced asymmetry, indicating nonlinear kinetics. It can be concluded that the profile intensities are not in oscillation with one another as earlier reported, but rather grow and decay at different rates from a common parent phase.

The satellite lines do appear to be of an incommensurate phase, suggesting the possibility of an incommensurate–commensurate phase transformation. An IC phase transformation is expected to be second order, with the lattice constants serving as order parameters. If so, then the peak positions should change continuously with temperature and time. As discussed above, this is not the case, supporting that growth is from a common parent phase.

For lines of high intensities, logistics maps can be constructed by plotting the peak intensity $I(i + 1)$ as a function of the previous intensity $I(i)$, where $i$ represents the $i$th time slice. Such a map will represent an embedded dimension of the system and retain the properties of the system. A

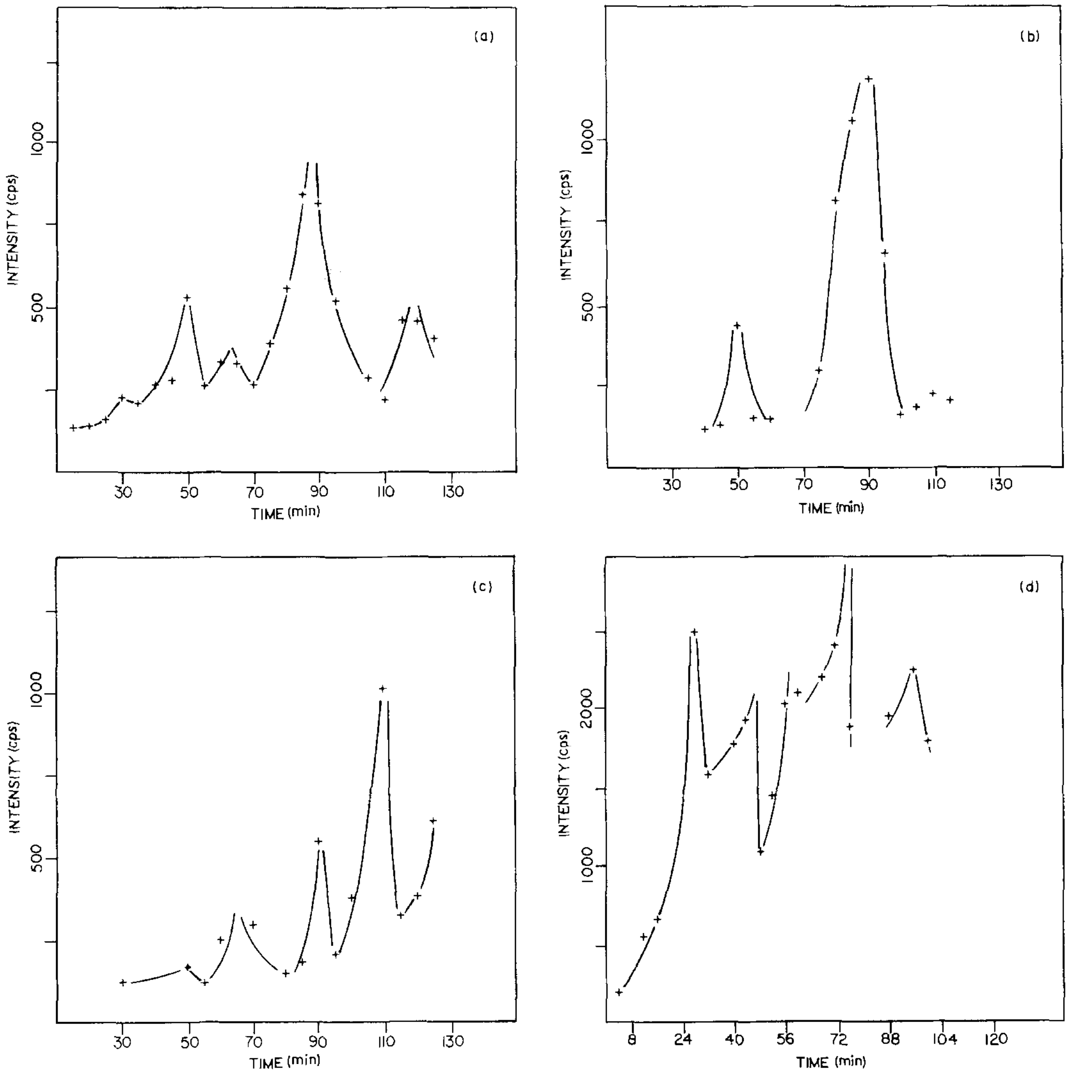

FIG. 2. Satellite line peak intensities as a function of time for orthorhombic (020) at 587°C (a, b, c) and for orthorhombic (111) at 595°C (d). For $(111)_0$ the data point at 80 min is off scale at 4500 cps. The lines are for the eye.

map constructed in this manner can be distorted by the time-dependent profile broadening, the diffraction counting statistics, and the increase in $PbO_0$ as the transformation proceeds. The integrated intensities of the profiles should be used rather than peak intensities, but profile overlap does not allow this. However, the logistics maps are still of great value. It has been shown that for chaotic systems a high noise level does not disrupt analysis of the mapping providing there is no stable point (*4*), and significant kinetic information is still present for the development of rate equations (*4*, *5*).

The variable amount of $PbO_0$ from the lead monoxide phase transformation can be adjusted for through a multiplicative factor.

This is given by an Avrami equation fit to the kinetic data,

$$1 - f(t) = \exp[-kt^n], \qquad (1)$$

where $f(t)$ the is the fraction of the tetragonal phase transformed, and $k$ and $n$ are constants to be determined. Integrated intensities of a tetragonal phase profile with its associated satellite lines give a transformation curve for which a good fit to Eq. (1) can be made if smoothed. Since such an adjustment further increases the noise level of the data and adds an extraneous parameter, both adjusted and unadjusted mappings are considered. The results for the central line and one satellite line are shown in Fig. 3.

The mappings show that the trajectories are about two basins of attraction. There is a long-period, low-frequency cycle, interchanging with a short-period, high-frequency cycle. The effect of constant orthorhombic phase adjustment is to telescope a spiral onto the two basins of attraction. The resulting logistics maps have the form expected for strange attractors. But because of current experimental limitations on the number of cycles that can be observed and the length of the time slices, it may not be possible to appreciate transients or to exclude the existence of a limit cycle. The map does indicate that at least three phases are involved. The long-period cycle indicates an expansion of a solid-phase fraction while a second undergoes reduction. The short-period cycle indicates a contraction of the first phase through additional phases; the self-crossing of the trajectories indicates that higher dimensions must be involved.

An examination of the diffraction data for both the $PbO_t$ and $PbO_o$ regions of the diffraction patterns suggests that the crystalline phases are in oscillation with a highly disordered phase (Fig. 1). This is consistent with a comparison of diffraction data for crystalline and noncrystalline phases (*6*) when a limited region of a powder X-ray diffraction pattern is examined. Given the high vapor pressure, low melting point, and high X-ray absorbance of lead oxides, it can be hypothesized that the incident X-ray beam is transporting sufficient energy to disorder the crystalline phase near the surface. Furthermore, lead oxides are known to undergo photoreduction (*7*); this may lead to the separation of the lead oxide into oxygen-rich regions and metal clusters by lead atom migration, which may result, either directly or through recrystallization, in the formation of a compositional incommensurate phase.

Thus, a lead oxide may be disordering and then recrystallizing into an incommensurate phase, accounting for the long-period cycle of the logistics map. Additional phases may also recrystallize, accounting for the short-period cycle. But the crystalline phases are not in oscillation with one another. It remains to be shown that such a disordering and recrystallization is consistent with solid-state reaction and transformation kinetics; to examine this, first approximation kinetics is discussed below.

Experimental surfaces of section (Poincaré maps) can be constructed by plotting the peak intensity of one diffraction line against a second for the same time slice; these are just the intersection of the $n$-dimensional system trajectory with a two-dimensional slice. Points of intersection often lie along line segments that are separated by integer quantities and with maximums that differ by integer amounts. However, the results are usually not so well mannered and tend to display random intersections. Additional work is required to determine if regular and chaotic system dynamics are being displayed. Such plots may also be used to distinguish $\alpha_1/\alpha_2$ pairs: the number of satellite lines reported earlier (*2*) may actually be as few as three.

## 4. Theory

To discuss the kinetics, either the transformation volume or the transformation cell

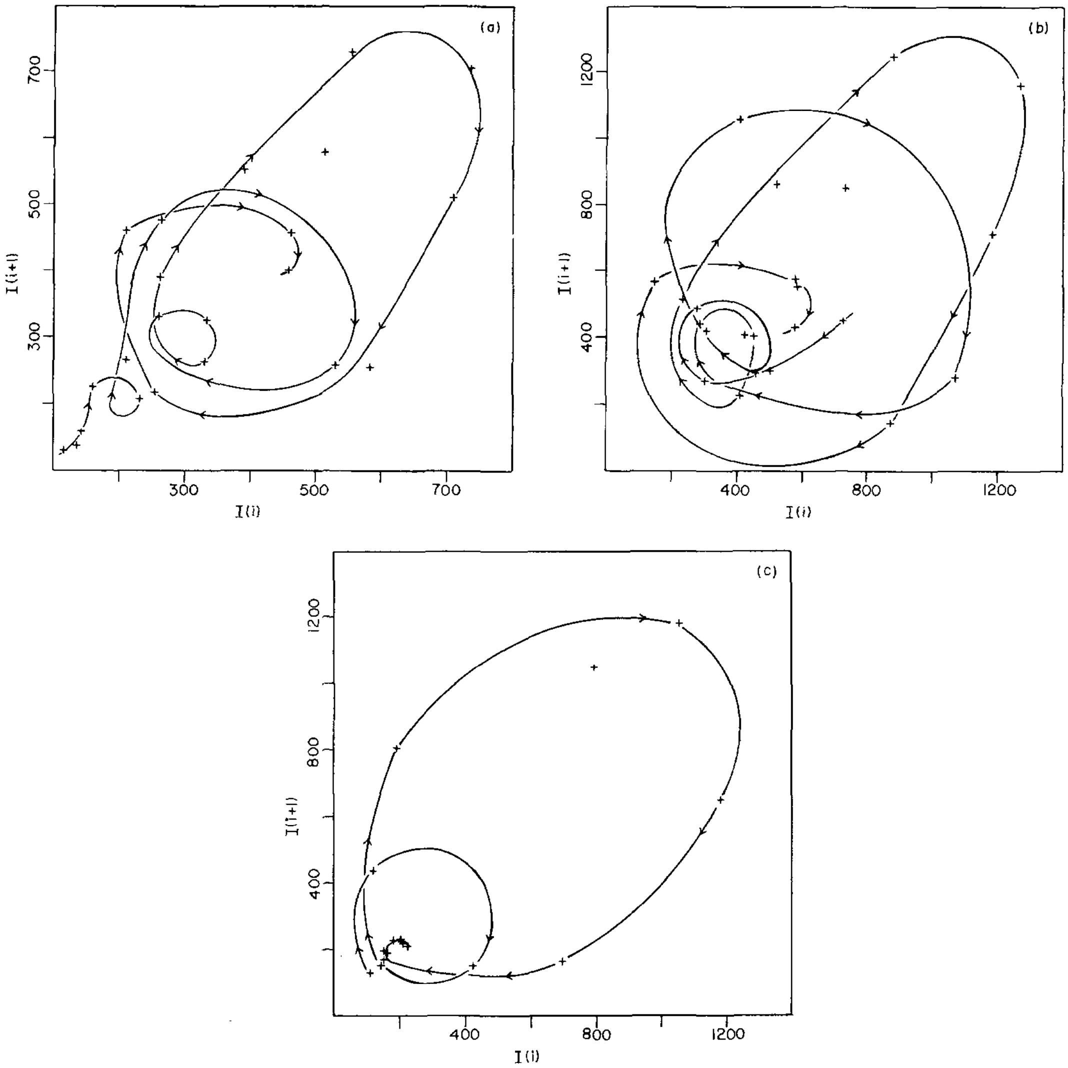

FIG. 3. Logistics maps for orthorhombic (020) satellite lines: (a) adjusted for constant amount of $PbO_0$ (see Fig. 2a); (b) not adjusted; (c) the central line, not adjusted (see Fig. 2b). The lines are for the eye. Arrows represent the trajectory direction.

can be used. Here the latter is used. The transformation cell is defined as a region of the crystal with an order parameter invariant to translation through ($\delta x, \delta y, \delta z, \delta t$) and for which $\Sigma n_i$ is constant, where $n_i$ is the number of atoms of type $i$ in the cell. For a transformation, $i$ may include all types of atoms present, and for a chemical reaction $i$ will include atom types present in one initial phase and the final phase. The volume of the cell is constant only for a second-order phase transformation; the size of the cell depends on the observation time interval and is self-similar.

A simple transformation scheme consistent with the above data interpretation can be constructed. The kinetics will be modeled for a three-phase system consisting of two stable crystalline phases and one thermodynamically metastable phase induced by the incident X-ray beam; this last phase may be the disordered phase discussed above, and is referred to as such in the discussion, although it need not be. If $A$ represents the metastable phase with $a(t)$ cells and if $P$ represents the two crystalline phases with $n(t)$ and $m(t)$ cells, then the equations for phase growth are

$$P_n + A_a \xrightarrow{k_a(h\nu)} P_{n-1} + A_{a+1}$$

$$P_n + A_a \xrightarrow{k_n} P_{n+1} + A_{a-1}, \qquad (2)$$

where $k_a(\mathrm{h}\nu)$ and $k_n$ are the disordering and growth rate constants for phase $P_n$ and have the corresponding nucleation rate constants $k_{\eta a}$ and $k_\eta$. There are equivalent equations and rate constants for the phase $P_m$ and will be designated with a prime. In addition, for a closed system, it must hold for all times t that

$$N = a(t) + n(t) + m(t), \qquad (3)$$

where $N$ is the number of cells observed through the X-ray beam and is constant. The set of transformations (2) holds for the oscillations in both the tetragonal and orthorhombic phases, although they are taken as being independent of the lead monoxide phase transformation. In the following discussion, the relative amounts of tetragonal and orthorhombic phase present if the oscillating system is experimentally quenched is set constant.

Once growth of a crystalline phase begins, by the phase rule, it must proceed. However, the probability of nucleation of a daughter phase anywhere in the specimen is proportional to the fraction of parent phase. Therefore, with increasing amount of a crystalline parent phase, the probability of nucleation and growth of the disordered, metastable daughter phase in the specimen must increase. The metastable phase is subject to the same conditions. This places the system in a physical dilemma, resulting in bistability; the system switches from one state to the other, driven by the incident beam.

To determine rate equations for the proposed scheme, the kinetics for the appearance of activated nuclei $\eta_{p'}$ of phase $P'$ from phase $P''$ can be taken as

$$\frac{d\eta_{p'}}{dt} = k_\eta \beta P'', \qquad (4)$$

where $\beta$ is the number of nucleation sites per reaction cell and $k_\eta$ is the nucleation rate constant for $P'$ from $P''$. Note that $\beta P''$ is just the number of nucleation sites in the specimen and Eq. (4) reduces to first-order nucleation kinetics. Growth kinetics for the appearance of a phase $P'$ can be expressed in the simple form

$$\frac{dP'}{dt} = \eta_{p'}(t)\, G(t), \qquad (5)$$

where $G(t)$ is the rate of growth of a nucleus, which will be taken as constant and one-dimensional and given by $k_g$. This is a simple model for growth by a single advancing boundary. It will be taken that the activated nuclei are widely spaced and particle impingement is not significant.

By Eqs. (4) and (5), the rate equations for the appearance of each phase in Eqs. (2) are given by

$$\frac{da}{dt} = k_a k_{a\eta} \beta_a \int n(t)dt + k'_a k'_{a\eta} \beta'_a \int m(t)dt - k_\eta k_\eta \beta_\eta \int a(t)dt - k'_m k'_\eta \beta'_m \int a(t)dt \qquad (6a)$$

$$\frac{dn}{dt} = k_n k_\eta \beta_{\mathrm{n}} \int a(t)dt - k_a k_{a\eta} \beta_a \int n(t)dt \qquad (6b)$$

$$\frac{dm}{dt} = k'_m k'_\eta \beta'_m \int a(t)dt - k'_a k'_{a\eta} \beta'_a \int m(t)dt. \qquad (6c)$$

To make Eqs. (6) more tractable to analysis, it is reasonable to take

$$k_a k_{a\eta}\beta_a = k'_a k'_{a\eta}\beta'_a = k_1, \tag{7}$$

that is, the kinetics of disordering are the same for both crystalline phases.

The integrals in Eqs. (6) can be eliminated by taking the time derivatives; using relation (7) and Eq. (3), this yields

$$\frac{d^2a}{dt^2} + ka(t) - k_1 N = 0 \tag{8a}$$

$$\frac{d^2n}{dt^2} + k_1 n(t) - k_2 a(t) = 0 \tag{8b}$$

$$\frac{d^2m}{dt^2} + k_1 m(t) - k'_2 a(t) = 0 \tag{8c}$$

where

$$\begin{aligned} k_n k_\eta \beta_n &= k_2 \\ k'_n k'_\eta \beta'_m &= k'_2 \\ k_1 + k_2 + k'_2 &= k. \end{aligned} \tag{9}$$

Equations (8) are a set differential equations of motion for three coupled linear oscillators. A quasiperiodic solution is expected; elsewhere, nonlinear coupling, which may give rise to complex behavior, will be considered.

Equations (8) can be solved by the method of the Laplace Transform. If the initial conditions are taken to be initial rates zero and

$$a(0) = m(0) = 0,\ n(0) = N \tag{10}$$

the Laplace Transform method yields

$$f_a(t) = \frac{2}{\lambda^2}\sin^2\left(\frac{\lambda z}{2}\right) \tag{11a}$$

$$f_n(t) = \left(1 - \frac{\sigma}{\lambda^2} - \frac{\sigma}{\lambda^2(\lambda^2-1)}\right)\cos(z) + \frac{\sigma}{\lambda^2(\lambda^2-1)}\cos(\lambda z) + \frac{\sigma}{\lambda^2} \tag{11b}$$

$$f_m(t) = -\left(\frac{\sigma'}{\lambda^2} + \frac{\sigma'}{\lambda^2(\lambda^2-1)}\right)\cos(z) + \frac{\sigma'}{\lambda^2(\lambda^2-1)}\cos(\lambda z) + \frac{\sigma'}{\lambda^2} \tag{11c}$$

where the reduced variables and phase fractions are defined as

$$\begin{aligned} \sqrt{k_1}\,t &= z \\ \sqrt{k}\,t &= \lambda z \\ k_2/k_1 &= \sigma \\ k'_2/k_1 &= \sigma' \\ \lambda^2 &= \sigma + \sigma' + 1 \\ f_a(t) &= a(t)/N \\ f_n(t) &= n(t)/N \\ f_m(t) &= m(t)/N. \end{aligned} \tag{12}$$

Since observation indicates that more than two crystalline phases may be involved, the case for *i*-crystalline phases is also considered; this can be determined in the same way as Eqs. (11) to yield for the *i*th crystalline phase

$$f_i(t) = \left(\frac{\sigma_i}{(\lambda^2-1)}f_{a0} + f_{i0} - \frac{\sigma_i}{\lambda^2} - \frac{\sigma_i}{\lambda^2(\lambda^2-1)}\right)\cos(z) + \left(\frac{\sigma_i}{\lambda^2(\lambda^2-1)} - \frac{\sigma_i}{(\lambda^2-1)}f_{a0}\right)\cos(\lambda z) + \frac{\sigma_i}{\lambda^2} \tag{13a}$$

where $f_{a0}$ and $f_{i0}$ refer to the initial amounts of the metastable phase and the *i*th stable phase, respectively; the initial rates of transformation are taken as zero. Note that there are no new periodic terms, although the frequency and amplitude of the oscillations for a given stable phase are affected. The accompanying expression for the amount of photo produced phase is

$$f_a(t) = \frac{2}{\lambda^2}\sin^2\left(\frac{\lambda z}{2}\right) + a_o\cos(\lambda z). \tag{13b}$$

To numerically evaluate Eqs. (11) or (13) the value of $\lambda$ can be taken as 2 since no more than two basins of attraction have been observed; for higher rational values of $\lambda$ the oscillatory behavior becomes consid-

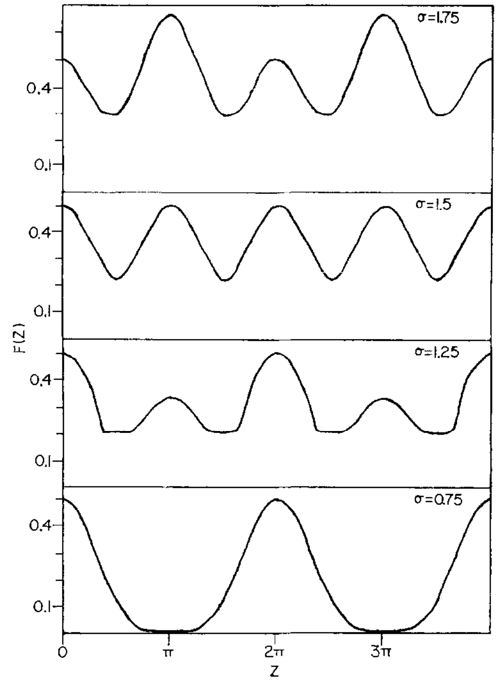

FIG. 4. Theoretical phase fractions for oscillations as a function of reduced time $z$ for $\lambda = 2$ and increasing values of $\sigma$.

erably more complex, and for irrational values will be aperiodic. The results for no initial disordered phase and $f_{i0} = 0.5$ are shown in Fig. 4 for increasing values of $\sigma$. Note that with increasing values of $\sigma$ (that is the ordering rate constant) there will be a greater amount of background crystalline phase; a small amount of remaining crystalline phase is indeed observed experimentally, although the diffraction lines show considerable broadening. Small values of $\sigma$ (less than 1.5) describe the observed kinetics, and are consistent with the definition of $\lambda$ (Eq. (12)). A theoretical logistics map can be constructed demonstrating the two basins of attraction; it follows that if only one crystalline phase is present, no attraction basin exists.

Equations (11b) and (11c) for the growth of two crystalline phases are $\pi/2$ out of phase, which is not consistent with the experimental results; however they can be brought into phase if the initial quantities of both crystalline phases are identical. This suggests that either the incommensurate phase formation may occur independently from the disordered phase, perhaps through reduction, or that it begins forming early from small fractions of disordered phase material; the latter possibility can be accounted for by treating the initial commensurate phase PbO as transient and allowing it to redistribute over new commensurate and incommensurate phase material.

The theory is not adequate in that it cannot account for the sharpness of the transformation curves, the possibility of a strange attractor, or the asymmetry of the transformation curves. The first point requires finer data. The last two points may be amended by the inclusion of nonlinear terms.

By definitions (12), $\lambda^2$ must be greater than one. The limit $\lambda^2 \rightarrow 1$ corresponds to the case of a large disordering rate constant and/or small ordering rate constants; this is just the resonance condition, for which the rate constant for disordering approaches that of the system. Such cases may include high temperatures, high rate of energy transport across the system boundaries, or high defect concentration. To consider the limit $\lambda^2 \rightarrow 1$, Eq. (11b) may be recast as

$$f_n(t) = \frac{2\sigma}{\lambda^2}\sin^2\left(\frac{z}{2}\right) - \frac{\sigma}{\lambda^2(\lambda^2 - 1)}[\cos(z) - \cos(\lambda z)] + \cos(z) \quad (14)$$

Then using L'Hospital's rule,

$$f_n(z) = 2\sigma \sin^2\left(\frac{z}{2}\right) + \cos(z) - \frac{\sigma z}{2}\sin(z), \quad (15)$$

$f_n(t)$ quickly approaches zero, then blows up to aphysical values. This can be interpreted as widespread disruption of the crystalline phase. Similar results are obtained if the rate constants for recrystallization are taken as zero; for first-order nucleation controlled kinetics, by Eq. (5) the crystalline phase fraction will decay exponentially.

## 5. Conclusion

Both experiment and theory support that the phase oscillations in the lead monoxide system involve a minimum of three phases. It is postulated that one of the phases results from the interaction of the X-ray beam with the lead oxide, producing a metastable, highly disordered phase. This metastable phase is oscillating with a minimum of two crystalline phases. The X-ray beam is driving the oscillations through energy transport across the system boundaries. It should be noted that it is not required that the phase produced by the incident X-ray beam be disordered, only that it is metastable.

Experiment indicates that there is a temperature dependence, which is predicted by theory through the rate constants. It is implied by experiment that the role of impurities and crystal defects must be an important consideration in future work.

The proposed model is linear, quasiperiodic kinetics; however, for chemical systems, periodic behavior is related to the coupling of rate equations through nonlinear terms. For both chemical and dynamical systems, the nonlinear terms may give rise to complex behavior such as limit cycles and chaos. Asymmetry in the transformation curves and data analysis by logistics maps indicate the existence of complex, possibly chaotic, behavior. Because of this, future considerations will involve nonlinear terms.

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