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A New Examination of the Thermodynamic Properties of the Oxygen-Deficient Fluorite-Type Phase α-$PrO_{2-\delta}$

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Isoplethic (constant composition) measurements of the temperature-dependent equilibrium oxygen pressure over $PrO_{2-\delta}$ samples in the α-phase region of the Pr + O phase diagram have been made at a number of different compositions. The data show no anomalies, i.e., "kinks" or changes of slope in graphs of $\Delta G_m(O_2)$ vs T. However, isobars deduced from these isoplethic data do show anomalies, and we conclude that the deduction of M. S. Jenkins, R. P. Turcotte, and L. Eyring ["The Chemistry of Extended Defects in Non-metallic Crystals," pp. 36–53, North-Holland, Amsterdam (1970)] that there are distinguishable α-"phases" is correct.

Introduction

Improvements in the techniques of X-ray diffraction and particularly the application of electron microscopy/diffraction have allowed many phase regions, previously supposed to be homogeneous but widely nonstoichiometric, to be resolved into sequences of line phases with related, ordered structures—even at temperatures close to the melting point. Examples are manifold, ranging over the whole gamut of nonmolecular structures from oxides through sulfides and halides to metal alloys. The relationships include crystallographic shear and chemical/unit-cell twinning, etc.; see, for example, Ref. (*1*) and references therein.

On the other hand, the oxides of some transition metals and of some lanthanoids and actinoids appear to be qualitatively different: a relatively few ordered line phases existing at lower temperatures give way, at temperatures of only a few hundred degrees centigrade, to widely nonstoichiometric phases. In the iron + oxygen system, for example, Fe, Fe_3O_4, and Fe_2O_3 are augmented, above 600°C, by the nonstoichiometric wüstite phase $Fe_{1-\delta}O$ (*2*). In the lanthanoid oxide systems the low-temperature ordered phases Ln_nO_{2n-2} (Ln = Ce, Pr, or Tb), with some or all of n = 4, 7, 9, 10, 11, 12, disproportionate above about 450°C to the nonstoichiometric phases σ-$Ln_2O_{3+\delta}$

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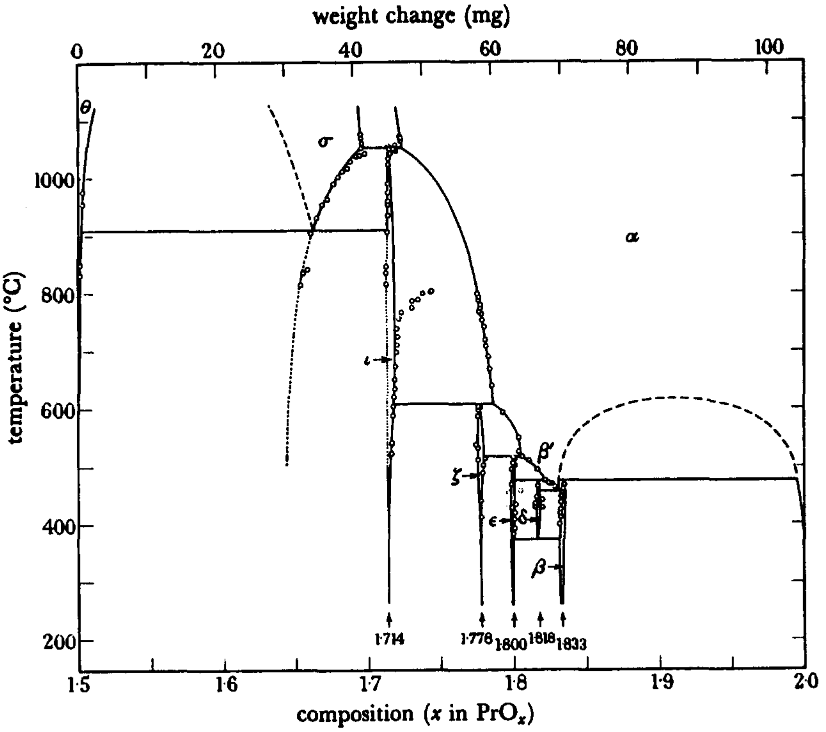

FIG. 1. The phase diagram for the system $PrO_x + O_2$, $1.5 \leq x \leq 2.0$, projected onto the T, x plane (3).

and α-$LnO_{2-\delta}$, each with a wide composition range, cf. Fig. 1 (3). Our concern here is with these nonstoichiometric phases, particularly $PrO_{2-\delta}$, the so-called α-phase.

There have been reports that some of these higher temperature, nonstoichiometric phases are also resolvable, but into contiguous nonstoichiometric "subphases" rather than line phases.

The Wüstite Phase $Fe_{1-\delta}O$

This was an early example. The classical work of Darken and Gurry (2) indicated a single phase, but Vallet and Raccah (4) reported thermogravimetric measurements that showed, within the wüstite-phase region, changes of slope at specific points on the isotherms $\delta = f\{\Delta G_m(O_2)\}_T$. These were interpreted (5) as defining subsidiary boundaries between different wüstites W_1, W_2, and W_3: "subphases" within the "single-phase" region delineated by the earlier work.

Later thermodynamic measurements (*6, 7*) failed to detect such boundaries but, later still, a careful electromotive force (emf) study by Fender and Riley (*8*) *did* confirm them. But then Giddings and Gordon (*9, 10*), after a very careful and thorough emf study, not only failed to find any subboundaries but also stated that they could explain the appearance of the anomalies found earlier.

The results of X-ray diffraction experiments on the same system show similar disagreement. Variations of the edge-length of the B1-type unit cell with composition (δ) were said by Carel (*11–13*) to confirm the existence of the subboundaries; this has been hotly contested by Cohen *et al.* (*14*), who used X-ray diffraction methods (*15*) (on samples both quenched and at equilibrium, but principally the former), and who also reexamined Carel's data (which were from quenched samples). The argument appears to be not yet settled (*16*).

Electron microscopy/diffraction studies (*17–19*), which could conceivably be a powerful aid, do not necessarily help because they also employ quenched samples, i.e., samples studied at temperatures below the eutectoid of wüstite.

The α-$PrO_{2-\delta}$ Phase

The history of the nonstoichiometric lanthanoid oxides is rather similar to that of wüstite if, so far at least, less polemic. In particular, while earlier tensimetric (*20, 21*) and isobaric thermogravimetric (*3*) measurements were interpreted as indicating a single-phase α-$PrO_{2-\delta}$ region, Jenkins *et al.* (*22*), interpolating isopleths $\Delta G_m(O_2) = f(T)_\delta$ from their isobaric data $\delta = f(T)_{p(O_2)}$, found anomalies ("kinks") in their graphs which they interpreted to be subboundaries between four contiguous nonstoichiometric regions, α_1, α_2, α_3, and α_4, within the previously reported α (single phase) domain. The anomalies were small but "believed to be outside the limits of experimental error" (*22*) and, rather surprisingly as it seemed to us but within the uncertainty of the measurements, the boundaries appeared to be isobaric. In view of the wüstite controversy it seemed desirable to check the measurements on α-$PrO_{2-\delta}$.

Because the anomalies were small it also seemed important that the data be checked *directly*, i.e., by *measuring* isopleths rather than by *deducing* them from isobars (or isotherms). We therefore set out to measure equilibrium oxygen pressures over a $PrO_{2-\delta}$ sample as its temperature was varied at a series of fixed (constant) compositions, δ. This would be achieved if, as the temperature was continuously changed, the oxygen pressure were automatically adjusted so that the sample weight stayed constant. (Such a procedure should be feasible because of the very high mobility of oxygen in the solids of the Pr + O system (*3*).) This isoplethic procedure is doubly desirable since the PrO_x system is prone to hysteresis in phase reactions (*3, 23, 24*), this being undoubtedly due to changes in structure and texture resulting from (mainly) changes in the composition of the solid. Elimination of significant composition changes might therefore be expected to minimize, if not completely avert, hysteresis, i.e., the effect of the kinetics of oxygen exchange (between gas and solid) on the measured thermodynamic properties.

Experimental Procedure

The main apparatus was similar to that used previously (*3, 22*): an automatic, recording, semimicro Ainsworth balance operating in a closed system. The PrO_x sample, contained in a platinum bucket, was suspended from the balance beam into a silica-glass tube (part of the closed system) which was surrounded by a tube furnace. Oxygen (99.9%) was continuously bled into the system *via* a Granville–Phillips automatic-control valve, and continuously removed by pumping *via* a manually adjusted needle valve. The automatic-control valve was actuated by the signal from an auxiliary potentiometer (with its own ancillary stabilized power supply) which was "ganged" to an identical potentiometer in the control and record system of the balance, which itself defined the weight indication. Any tendency toward (say) a loss in weight of the sample caused the control valve to open wider, thus increasing the rate of ingress of oxygen to the system and hence also the ambient oxygen pressure. This in turn caused the sample to oxidize and increase in weight, thus correcting the tendency for the sample weight to fall. (The manual needle valve through which oxygen was pumped from the system simply enabled the control of the gas pressure to be "tuned," between "hunting" and "lagging," differently at different oxygen pressures. It needed to be reset only once or twice during each experiment.)

The arrangement was sufficiently sensitive, and the speed of response of the phase system $PrO_x(s) + O_2(g)$ sufficiently high, that it was not difficult to control the indicated weight of the sample to within the ultimate resolution of the balance controller and recorder system, viz. ±20 μg. Since the sample weight was ~1.5 g, the apparent control of composition was $\Delta x \simeq \pm 0.0001_4$. However, the variation with temperature of buoyancy and thermal transpiration effects limited the *accuracy* of composition control to $\Delta x \simeq \pm 0.001$. (These latter effects were measured in blank runs using neodymium sesquioxide instead of PrO_x. Its composition is independent of ambient conditions, within the range employed in the PrO_x experiments.)

High-purity praseodymium oxide [from Koch-Light, nominal purity 99.999%, traces of Mg, Fe, and Si (<20 ppm) detected spectrographically] was weighed and loaded onto the thermo-balance. The sample was then heated to approx 1250 K in vacuum, in order to reduce it to the sesquioxide. This gave one (composition) calibration point: PrO_x, with $x = 1.500$. After admitting dry air the sample was once again heated and then cooled to room temperature to produce Pr_6O_{11}, $x = 1.833$: a second calibration point which also defined the composition scale on the thermo-balance recorder chart. The balance chart readings corresponding to these two reference points were checked several times during the course of the experiments and varied by no more than the balance precision, i.e., $\pm 0.0001_4$ in x.

Jenkins *et al.* (*22*) had found it necessary to "pretreat" the sample in order to achieve reversibility in the α-phase region during isobaric runs. In the present experiments this was accomplished by traversing the whole accessible composition interval with a series of isobars using the earlier procedure (*3*). In this way the sample was "conditioned," and the compositions of the phase boundaries were checked. (They agreed with the earlier values within the experimental uncertainty of approx. ±0.001.)

The sample temperature was measured with a Pt/Pt + 10% Rh thermocouple situated inside the closed system and close to the sample bucket. Its emf was monitored by recording it on the thermo-balance chart, but accurately measured manually (using a Pye precision vernier potentiometer) and entered, at the appropriate time marker "pip," on the chart of a separate recorder connected to the output of a Granville–Phillips capacitance (pressure) gauge. This last measured the oxygen pressure over the PrO_x sample utilizing a thermostated, 1000 Torr head (sensitivity 0.05%) which had been calibrated over its entire range against a precision, wide-bore mercury manometer (with all the necessary corrections for T, g, etc.). "Hunting" in the oxygen-pressure control system was reduced to a negligible level by connecting the whole system to a large ballast volume (0.23 m^3) and by adjusting the vacuum bleed valve as already described. The furnace temperature was programmed to rise at approx 14 K per hour up to a maximum [at $p(O_2) \simeq 720$ Torr] and then to fall at the same rate. [The rate, 0.23 K min^{-1}, may be compared with that of Jenkins *et al.* (*22*), which was 0.1 K min^{-1}. According to their analysis this difference would have little effect on the degree of reversibility and, we emphasize, since there was virtually no composition change during our (isoplethic) runs the reversibility in the present experiments was expected to be much better than in their isobaric runs.]

The procedure for each experiment was as follows. The sample was first brought manually to the required composition/weight, with the temperature steady at about 700 to 900 K, and the system isolated so that the oxygen pressure was also constant at the appropriate equilibrium value. The large ballast volume was then filled with oxygen to a total pressure of just over 1 atm, and the oxide system was brought under automatic control by switching on the auxiliary potentiometer and opening the bleed valve to the vacuum pumps (to a previously determined setting). The (automatic) oxygen-ingress control valve then started to function; small oscillations ($\not>$ ± 100 μg, corresponding to $\Delta x < 0.0007$) occurred in the sample weight. These quickly died out (within less than 10 min). When the weight was quite steady the run was started by switching on the temperature programmer. The starting point for each run was close to the boundary of the α-phase, usually just outside it. Thus, as the temperature rose, so at first the oxygen pressure fell [cf. (*3*)]: then, when (if) the boundary was reached (and, as one might presume, any ordered phase(s)—β, δ, ε, ζ, and/or ι, coexisting as minor component(s) with α-disappeared) the equilibrium pressure of oxygen rose again. It fell once more as the temperature was lowered (to traverse the α—region in the opposite direction). After each run (which lasted several hours) the sample was allowed to cool to room temperature.

Pressure and simultaneous temperature readings were taken from the chart record and plotted as graphs of partial molar free energy of oxygen, $\Delta G_m(O_2) = RT \ln p(O_2)$, versus temperature, T.

The Results and Their Interpretation

The experimental data for the α-phase only are shown in Fig. 2. In addition to the experimental points we also show the previously determined (*3*) phase boundaries (as broken lines) and the approximate positions of the subboundaries, $\alpha_1 \rightleftharpoons \alpha_2$, $\alpha_2 \rightleftharpoons \alpha_3$, and $\alpha_3 \rightleftharpoons \alpha_4$ of Jenkins *et al.* (*22*), idealized to isobars (as the light, full, near-horizontal lines.[1] The inset shows a run at a higher composition: it was restricted to the (ordered) β-phase because oxygen pressures were limited to not more than 1 atm.

Note that the irreversibility in the α-phase is very small: less than $\Delta T = 3$ K, or $\Delta\{G_m(O_2)\} = 0.5$ kJ mol^{-1}, or $\Delta x = 0.0005$—usually much less. [Compare the gross hysteresis in the β-region, Fig. 2, inset, and the larger hysteresis in the α-phase region in Fig. 1 of Ref. (*3*).]

There is no indication or suggestion of any anomaly or "kink" in our experimental curves—either at the subboundaries of Jenkins *et al.* (*22*) or elsewhere—and so it would be reasonable to conclude that our results contradict the notion that there are several distinct subphases in the α-region of $PrO_{2-\delta}$. This indeed was our conclusion when the experiments were completed some years ago. But we have now reconsidered the data.

In particular [and reversing the procedure of Jenkins *et al.* (*22*)] we have interpolated isobaric data from the isopleths shown in Fig. 2. The resulting isobars are shown in Fig. 3. These isobars seem to us to support the deduction by Jenkins *et al.* (*22*) that there are several thermodynamically distinct regions in the α-phase space. There are anomalous changes of slope in any curves fitted to these data. However, they do *not* correspond to the regions α_1, α_2, α_3, and α_4 identified previously (*22*). In the plane $\Delta G_m(O_2)$ vs T the two sets of boundaries are almost orthogonal but, in light of the earlier work (*22*), the available results are worthy of some discussion.

The best fit to each deduced isobar appears to be a sequence of four rectilinear

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[1] NB, it is to be expected that all these boundaries will be in slightly different positions for different samples, and we emphasize that the data in Fig. 2 come from three different samples—the present one (experimental points), that of Jenkins *et al.* (*22*), and that of Hyde *et al.* (*3*).

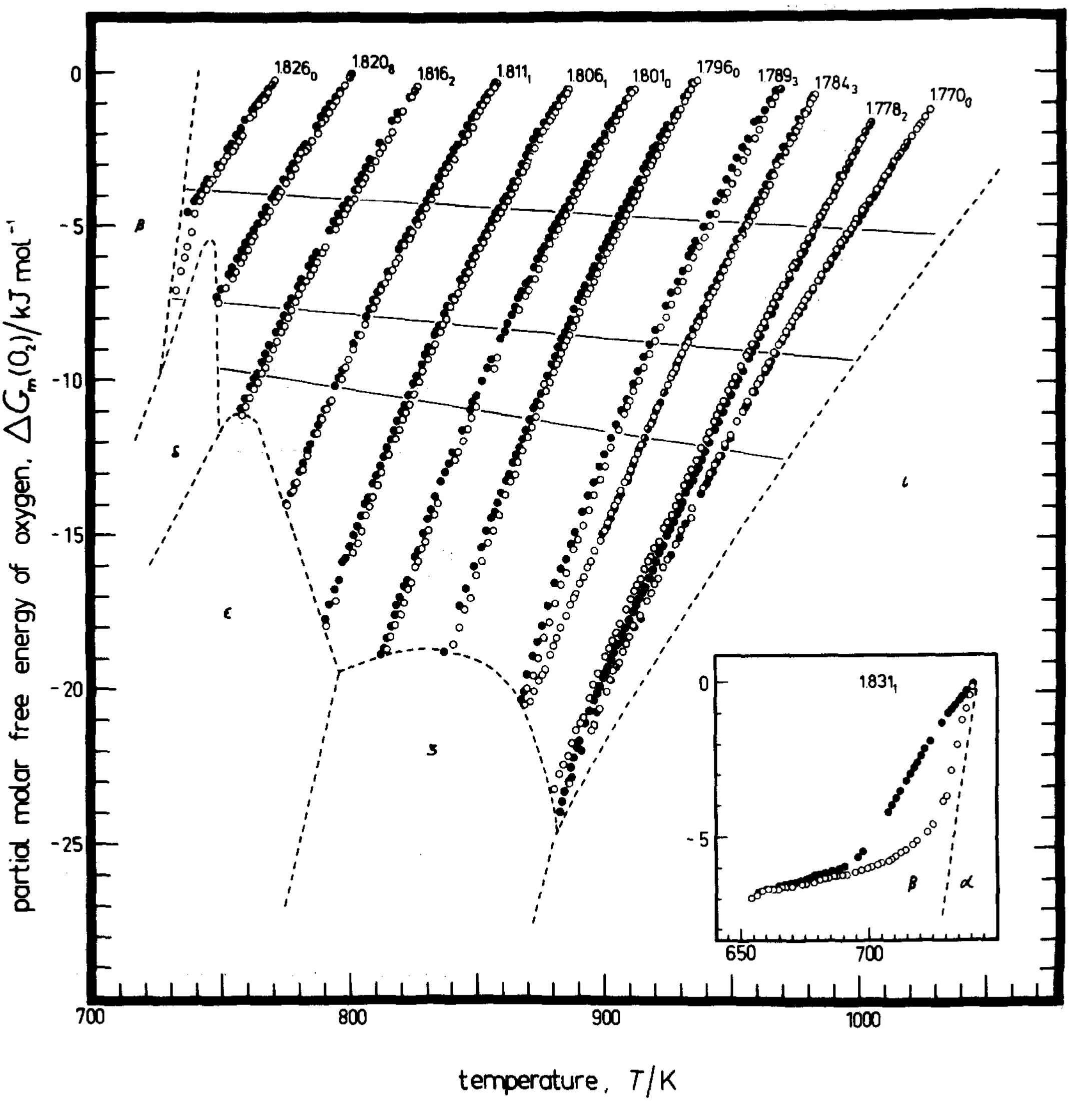

FIG. 2. Experimental isopleths, $\Delta G_m(O_2) = f(T)_x$, in the α-$PrO_{2-\delta}$ phase region. Open circles are points obtained during heating, filled circles during cooling. The number at the top of each isopleth is the composition, x in PrO_x. The small degree of irreversibility is to be contrasted with that in the β-phase region, shown in the inset. The broken lines are the boundaries of the various phases adjacent to the α-phase region, determined previously (*3*). While they were not redetermined in the present study it is clear that their positions are now slightly different—for the present sample, and for that of Jenkins *et al.* (*22*). The fine, almost horizontal lines indicate isobaric boundaries approximately equivalent to those between α_1, α_2, α_3, and α_4 according to Fig. 8 of Ref. (*22*). [For the sample used in that work it appears that they coincide with the maximum $\Delta G_m(O_2)$ values of δ, $(\beta + \delta)$, and ε; so that $\beta \rightarrow \alpha_1$, $\beta \rightarrow \alpha \rightarrow \delta \rightarrow \alpha_2$, $\beta \rightarrow \delta \rightarrow \alpha_3$, and $\varepsilon \rightarrow \alpha_4$.]

lines. (The boundary of α precludes low-temperature points for some isobars: the upper segment or two of those on the left of Fig. 3 is therefore absent.) The boundaries between the segments are at compositions O/Pr = x of about (i) 1.816–1.820, (ii) 1.808,

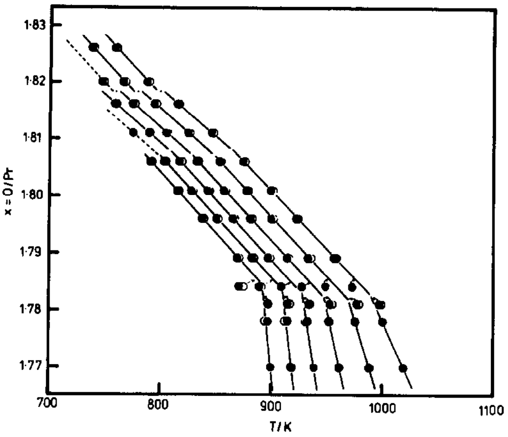

FIG. 3. Isobars, $x = f(T)_{p(O_2)}$, interpolated from the isopleths in Fig. 2: from right to left 0.786_9, 0.487_3, 0.301_7, 0.186_9, 0.115_7, and 0.071_6 atm pressure of oxygen. Filled circles are during cooling, open circles (largely obscured) during heating. Note the four linear segments corresponding to (from top to bottom) $\delta \rightarrow \alpha$, $\varepsilon \rightarrow \alpha$, $\zeta \rightarrow \alpha$, and $\iota \rightarrow \alpha$.

and (iii) 1.783. These are close to the compositions of the α boundary at the peritectoids (i) $\delta \rightleftharpoons \varepsilon + \alpha$, (ii) $\varepsilon \rightleftharpoons \zeta + \alpha$, (iii) $\zeta \rightleftharpoons \iota + \alpha$ (Fig. 1), which is consistent with the upper segment corresponding to α derived from δ, the next to α derived from ε, the next to α derived from ζ, and the lowest to α derived from ι; i.e., the four regions correspond to entering the α domain from four different ordered phases. This is exactly the hypothesis that was proposed by Jenkins *et al.* (*22*), but now it occurs along isoplethic instead of isobaric paths. *The same general conclusion may therefore be drawn from both sets of experiments.*[2]

In the experiments of Jenkins *et al.* the observed anomalies ("kinks," "boundaries") are isobaric because the experiments were also isobaric; in the present experiments they are isoplethic because the experiments were also isoplethic. In both cases, the α-phase behavior depends on a "memory" of the ordered phase (e.g., δ, ε, ζ) from which (in a given run) the α-phase was produced.

It has been argued (by a referee) that "If experimentally determined isobars show no kinks, but the derived isopleths do and if the experimentally determined isopleths show no kinks but the derived isopleths do, then the derived results are misleading and should be dismissed." This assertion we believe to be logically unsound, while the explanation given in the previous paragraph is at least logical. The referee's conclusion seems to us to rest on an implicit assumption that equilibrium obtains. If this premise were correct then his conclusion would be correct also. But we believe that the assumption is usually not justified in the case of solid–gas interaction [thus, for example, the hysteresis in the experimental data from $PrO_x + O_2$ (*3*) and $TiO_x + O_2$ (*25*)].

Discussion

In the classical terms previously used to describe the behavior of the system $PrO_x + O_2$ (*3*), this conclusion could be interpreted as some sort of memory effect: Jenkins *et al.* (*22*) suggested that microdomains with structures related to those of the ordered phases persist metastably and coherently into the α region—different ones in different regions—α_1, α_2, α_3, and α_4. But (a) the persistence of the "memory"; i.e., the absence of any discontinuities in the *experimental* isobars of Jenkins *et al.* [at which such domains of ordered structure might be expected to decompose (also metastably) from one type to another, as the ordered structure do at lower temperatures/oxygen pressures[3]], (b) the near orthogonality of the two sets of subboundaries on the $\Delta G_m(O_2) = f(\delta, T)$ "surface," and (c) the

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[2] The data in Fig. 3 at $x = 1.782$ (not shown in Fig. 2) and at $x = 1.784$ are somewhat anomalous due, we suspect, to their being close to boundary (iii).

[3] Cf. the *metastable* extensions of some equilibrium boundaries in (*3*).

lack of *perfect* reversibility in our isopleths (Fig. 2) all lead us to suspect the operation of a quite distinct phenomenon, not previously alluded to in discussions of "homogeneous solid solutions" such as α-$PrO_{2-\delta}$, wüstite $Fe_{1-\delta}O$, etc.

In the last few years many other systems, such as plagioclase feldspars, pyrrhotites, "Yb_3S_4," etc. [(*26*) and references therein], and Sr_2SiO_4 (*27*), have been shown, on more careful examination especially by electron diffraction, to exhibit modulated, frequently incommensurate, structures where simple, homogeneous, nonstoichiometric phases had previously been assumed to exist. While we are not at present in a position to provide an explanation for the "subphases" which appear to inhabit the α-$PrO_{2-\delta}$ phase space, the observed behavior—consistent with the simultaneous presence of memory effects, the (experimentally) continuous variation of the free energy, but the absence of a single, continuous surface $\Delta G_m(O_2) = f(T, \delta)$—suggests the possible presence of some form of "Devil's Staircase." Theoretical treatments of this topic have recently been developed (*28, 29*) based on spin or epitaxial models, the latter being especially relevant to α-$PrO_{2-\delta}$, given the diffuse phase transitions in fluorite-based ionic conductors (*30*).

As a function of change in external experimental parameters like $p(O_2)$ or T, a series of discrete phases appears in the complete Devil's Staircase so that the superlattice diffraction wavevector (which commonly serves as the order parameter) "locks in" to all rational values of the commensurability ratio. Each commensurate locked-in phase occupies the whole of the parameter interval between rational values, and they are separated by second-order phase transitions. The effect of reducing the temperature can be to reduce drastically the number of locked-in phases, and a series of these may then be interspersed with incommensurate phases, which display a continuous wavevector variation. Such a situation, corresponding to an incomplete Devil's Staircase, would account for the observed behavior of PrO_x, the low-temperature phases being the Pr_nO_{2n-2} superstructures.

The implication is that, for the oxygen array at least, the ergodic hypothesis may not be valid; resulting in the breakdown of the usual canonical prescription of thermodynamics and the possibility of pronounced memory effects.

Corresponding diffraction effects should then be observable, most readily by electron (rather than X-ray) diffraction. Unfortunately, experiments with $PrO_{2-\delta}$ at equilibrium (at relatively high $p(O_2)$ and T) in an electron microscope are impossible. It is possible that success in this regard is more likely to be achieved by examining an appropriate analog ternary system, such as $Y_2O_3 + CeO_2$, in which connection it may well be relevant that "diffuse b.c.c. diffraction lines" have already been observed in the (f.c.c.) X-ray powder-diffraction patterns from the α-phase in that and other, related systems (*31*).

We conclude by emphasizing that whether or not the discontinuities are observed depends upon the way in which the experimental data are presented. It is therefore possible that the disagreement as to whether or not, for example, the wüstite domain consists of several contiguous subphase regions, may be sterile: as with α-$PrO_{2-\delta}$, the *obvious* deduction depends on the standpoint from which the data (any data) are viewed. (In the published papers on wüstite it is not always clear exactly how the presented data were derived from the experimental measurements.) Finally, it is worth noting that modulated, incommensurate structures have already been observed in wüstite: Koch and Cohen (*15*) state that they attempted to analyze the (incommensurate) "superstructure peaks" (from a single crystal of $Fe_{0.902}O$) "in terms of a modulation of atomic displacements and scattering factor," but that this approach was unsuccessful. However, this was a quenched sample, with strong, sharp "superstructure peaks": it is not clear whether or not they attempted a similar interpretation of the similar, but broader and much weaker, peaks observed under *equilibrium* conditions. Such an interpretation is exactly what would be expected if modulated structures occur in that system, and so it is interesting that, *using the same data* (*15*), Yamamoto (*32*) has successfully solved the structure in these terms, using a six-dimensional space group.

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