

Cation nonstoichiometry in tin-monoxide-phase $\text{Sn}_{1-\delta}\text{O}$ with tweed microstructure

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We report a chemical, thermogravimetric, and electron-diffraction/microscopy study of a tin-monoxide phase. A large deviation from the ideal stoichiometry is observed due to metal vacancies, resulting in the formula $\text{Sn}_{1-\delta}\text{O}$. This nonstoichiometry is an intrinsic feature of this material and is accommodated through the formation of static transverse displacive modulations along the $\langle hh0 \rangle$ directions, giving a tweed microstructure without the introduction of complex arrangements of vacancy interstitials (as in wüstite). Our observation constitutes a different way of accommodating large deviations from ideal stoichiometries, especially in comparison with the well-known behavior of the transition-metal monoxides with the NaCl-type structure. The difference arises most likely from the layerlike nature of the $\alpha\text{-PbO}$ ($B-10$) structural type with average tetragonal symmetry and $P4/nmm$ space group. Metal vacancies cause a strain coupling which stabilizes the highly disordered nonstoichiometric phase. Dynamical instabilities were not observed. An origin for the thermal instability of the material is suggested. A comparison with PbO , the only isostructural compound, is outlined. SnO is shown to be a beam-sensitive material. [S0163-1829(97)07233-0]

I. INTRODUCTION

In the Sn-O system, the most frequently reported phases are SnO and SnO_2 . The latter is by far the most studied because of its considerable technological importance in applications as transparent electrodes, thin films in heat-reflecting filters, SnO_2/Si solar cells, and gas sensing devices. Efforts have been devoted partially to the study of methods of achieving monophasic SnO_2 films. Still, several basic aspects like the mechanism for the transformation $\text{SnO} \rightarrow \text{SnO}_2$ are poorly understood. For initially multiphasic thin films obtained by thermal evaporation of tin, a Mössbauer spectroscopy study¹ showed that up to 1043 K the tin atoms partially remained in the 2+ oxidation state, and monophasic films were obtained only after an additional heat treatment at 1373 K.

The SnO compound, which is isostructural to $\alpha\text{-PbO}$ at normal pressures, has hardly been investigated, perhaps because it becomes unstable above 573 K and undergoes a disproportionation reaction to metallic $\beta\text{-Sn}$ and SnO_2 . Depending on the treatment temperature, three compounds were observed in different proportions SnO_2 , $\beta\text{-Sn}$, and an intermediate oxide containing both 2+ and 4+ oxidation states. This reaction takes place both in bulk SnO and in thin films.² The actual composition,^{3,4} structure, physical properties, and reaction mechanisms leading to the intermediate oxide are still open questions.⁵ However, in a previous work we have found strong evidence that the intermediate phase could be a single phase with a narrow composition range.⁶ Thus, it is not surprising that the reported phase diagram of the Sn-O system is still incomplete.

The reasons for SnO being thermally unstable are unknown. Especially intriguing are changes that occur upon heating which involve the breaking of bonds, namely the disproportionation reaction. This reaction *a priori* requires more energy than other possible mechanisms. In contrast to PbO ,⁷ SnO does not convert to an orthorhombic form at elevated temperature or pressure. In fact, a transition to this

form has not been observed under pressure up to 7.5 GPa, although a second-order phase transition to a γ -phase at 2.5 GPa was found, similar to the isostructural tetragonal PbO .⁸ This transition as a function of pressure was associated with the collapse of an acoustic mode.⁸

It is worth noting that *in situ* studies of the disproportionation process have not been reported. Low-lying branch instabilities could be observed in electron-diffraction patterns because these low-frequency modes give rise to a highly structured and extremely characteristic diffuse intensity distribution in reciprocal space (see, for example, Ref. 9) due to soft-phonon modes. Therefore, the detection and reciprocal-space mapping of any diffuse intensity distribution is of the utmost importance.

In the framework of our work on the Sn-O system we have undertaken a careful study of SnO through compositional characterization and electron microscopy and diffraction. The results show that SnO is a nonstoichiometric phase with cation deficiency. Such nonstoichiometry giving rise to a tweed microstructure takes place in a different structural type in comparison with the well-known NaCl-type transition-metal monoxides. This is a way to accommodate large deviations from the ideal stoichiometric composition.

II. EXPERIMENTAL

To our knowledge, only the preparation of powders of SnO has been reported. Its thermal instability precludes several possible crystal-growth methods. In the case of solution methods it is difficult to control the dehydration rate. Single crystals of tin monoxide were prepared by the slow dehydration at room temperature (RT) of hydrated tin(II) oxide during periods of up to three weeks. The hydrous oxide was precipitated at $\text{pH}=9-10$ by the addition of sodium carbonate (Merck, 99.5%) to a solution of tin(II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Merck 98+%). Single crystals of the monoxide are obtained by the addition of very small amounts of NaOH to the hydrated oxide. The crystals were washed sev-

eral times with distilled water and dried at RT in vacuum. They had maximum dimensions of $150 \times 100 \times 50 \mu\text{m}$ were black or blue-black in color, with metallic luster and clean faces, as revealed by scanning electron microscopy. The presence of O-H was ruled out by infrared spectroscopy.

Powder materials prepared from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 under different conditions gave the same results as for the crystals, with the same microstructure.¹⁰ Unless noted, we report here the results for single-crystal samples.

The average Sn content was determined by using atomic emission spectroscopy by inductively coupled plasma (ICP-AES), with a model JY-70 PLUS instrument. Possible volatilization of tin has been tested by preparing the solutions under different conditions (different temperatures and open or closed to the atmosphere and time of digestion). Within the experimental error of the technique the results were the same, thus precluding tin volatilization.

Thermogravimetric analyses were performed on a thermobalance based on a Cahn D-200 electrobalance which allowed for the determination of variations of the oxygen content within $\pm 1 \times 10^{-3}$ on a sample of about 100 mg. The overall oxygen content was determined thermogravimetrically by reduction to metallic tin under an atmosphere of $0.3\text{H}_2/0.2 \text{He}$. The temperature was raised at 4 K/min up to 1073 K.

Powder x-ray-diffraction data from crushed crystals were collected with a step width of 0.02° in the range $5^\circ \leq 2\theta \leq 90^\circ$ with Cu $K\alpha$ radiation on a Philips diffractometer X'Pert-MPD with a goniometer PW 3050/00 and analyzed by the Rietveld line profile refinement method by using the FULLPROF program.¹¹

Because of the low mechanical stability of SnO, the crystals were ground gently and dispersed onto a holey carbon film, without ultrasonic dispersion. Electron-diffraction studies and qualitative x-ray energy-dispersive spectroscopy (XEDS) analyses were performed in a JEOL 2000 FX microscope, fitted with a double tilt goniometer stage ($\pm 45^\circ$) and a LINK AN 10000 analyzer system, respectively. A double tilt heating stage goniometer up to 1023 K was also used.

Tin monoxide was found to be very beam sensitive, requiring observations with low dose. The state of the material was tested after each observation by checking the reproducibility of the ED patterns, specifically those of the [001] zone axis. For this reason, diagrams shown here were exposed for long periods of time.

III. RESULTS

A. Chemical characterization

ICP was used to search for impurities from the starting materials. None were detected.

In situ analyses were carried out using XEDS. The results obtained for thin plates do not show the presence of chlorine or any additional heavy elements other than tin.

The average Sn content determined by ICP analysis for different powder and single-crystal samples was in the range of 96–99% of the total expected for a nominal composition of SnO (the quoted error corresponds to that of the technique and does not take into account errors introduced by the preparation methods).

TABLE I. Comparison of our refined structural parameters with those of Refs. 13 and 12. * indicates values for the positional parameter z of Sn, obtained by taking the isotropic thermal parameters of Refs. 13 and 12, respectively. The lattice constants refined in both cases are the same.

	Izumi ^a	Pannetier ^b	This work
a (Å)	3.7986 ₁	3.8029 ₅	3.7995 ₆
c (Å)	4.8408 ₂	4.8382 ₈	4.8395 ₈
z (Sn)	0.2369 ₃	0.2383 ₈	0.2397 ₈ * 0.2402 ₈ *
B (Sn) (Å ²)	0.66 ₄	0.57 ₇	
B (O) (Å ²)	2.6 ₄	0.99 ₉	

^aReference 13.

^bReference 12.

Thermogravimetric analyses of both single-crystal and powder samples showed an unambiguous departure to values greater than the 1:1 stoichiometric relationship for O/Sn and were consistent with a Sn content in the range of 90–96%. Although the O/Sn ratio agrees very closely with the single-crystal (next section) results, we checked for possible volatilization of tin by performing an additional experiment with metallic Sn (5N) under the same conditions as for the oxide. Cycles of reduction to metallic Sn plus subsequent oxidation to SnO₂ confirmed the value obtained for the ratio O/Sn and precluded tin volatilization, as in the ICP analysis. For all the samples, the weight-loss curves were qualitatively similar, with nearly the same onset weight-loss temperature (about 573 K). Only the total weight loss varied in the range mentioned above.

These results suggest that the tin monoxide is a phase with a large deviation from the ideal stoichiometry SnO which is due to cation deficiency. The approximate range of composition is given by $\text{Sn}_{1-\delta}\text{O}_{1.00}$ ($0.04 \leq \delta \leq 0.10$). Thus, we will use the term ‘‘nonstoichiometry’’ to signify only a departure from the ideal 1:1 relationship for O/Sn, without any further implication.

B. Structural characterization by powder x-ray diffraction

Nonstoichiometric materials need to be characterized at different levels of resolution as provided by different diffraction techniques (x-ray, neutron, and electrons). It is usually understood that nonstoichiometric materials have a compositional range. In this sense the results of the previous section correspond only to averaged values because they were obtained by bulk analysis.

It is worth mentioning that the nonstoichiometry of tin monoxide was not taken into account previously, especially not in the structural refinements reported by Pannetier¹² and Izumi.¹³ They considered the phase with the ideal ratio O/Sn=1.00 only. Those refinements were made from powder neutron and x-ray diffraction, respectively.

The whole measured diffractogram can be analyzed with the structure reported for SnO (structural type B10 or α -PbO). Our refinements were performed with the same profile functions, isotropic thermal parameters, and occupation factors for Sn and O as used in Refs. 12 and 13. The refined parameters are quoted in Table I which also includes previ-

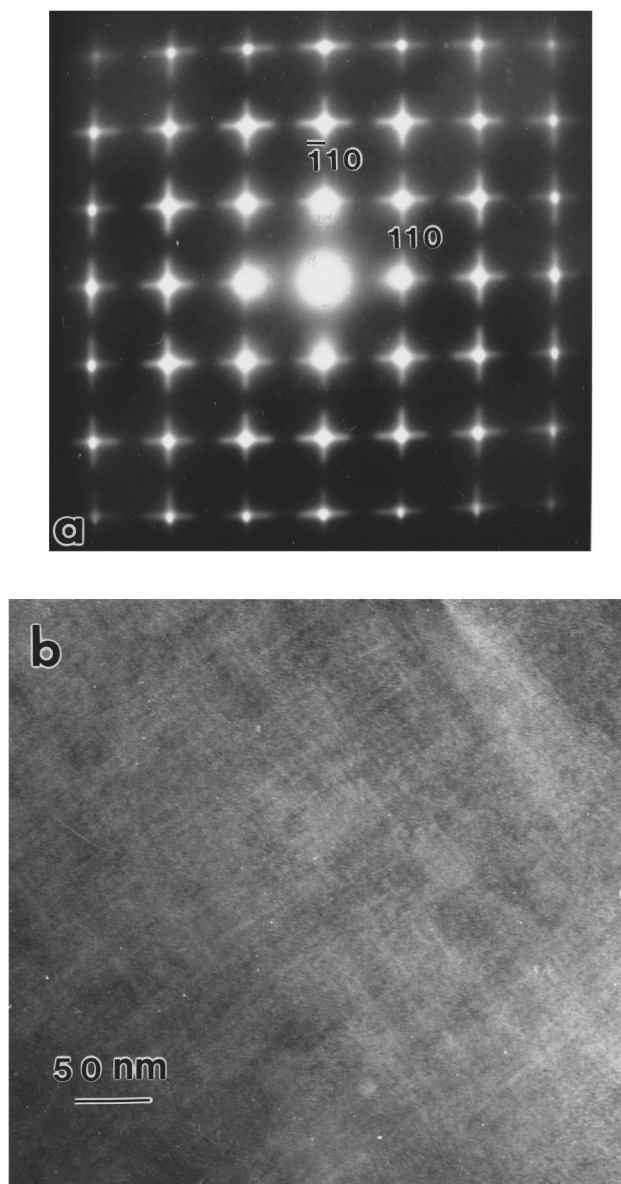


FIG. 1. (a) Typical [001] SADP zone-axis pattern taken at room temperature. (b) bright-field transmission electron micrograph of SnO showing a very finely divided tweed microstructure.

ous data for comparison. The agreement is very good, and therefore we are undoubtedly working with the same material as that which was refined and discussed in previous works.

On the other hand, we have undertaken a single-crystal x-ray-diffraction study for this material. Results from analyses of several single crystals indicate that the oxygen sublattice is complete and the metal vacancy concentration is about 10%. The complete structure refinement will be published elsewhere.

C. Microstructural characterization

The results of transmission electron microscopy were the same for all the crystals examined. The tweedlike structure is the only microstructural feature observed. This is illustrated in Fig. 1 which shows a typical [001] zone-axis selected area

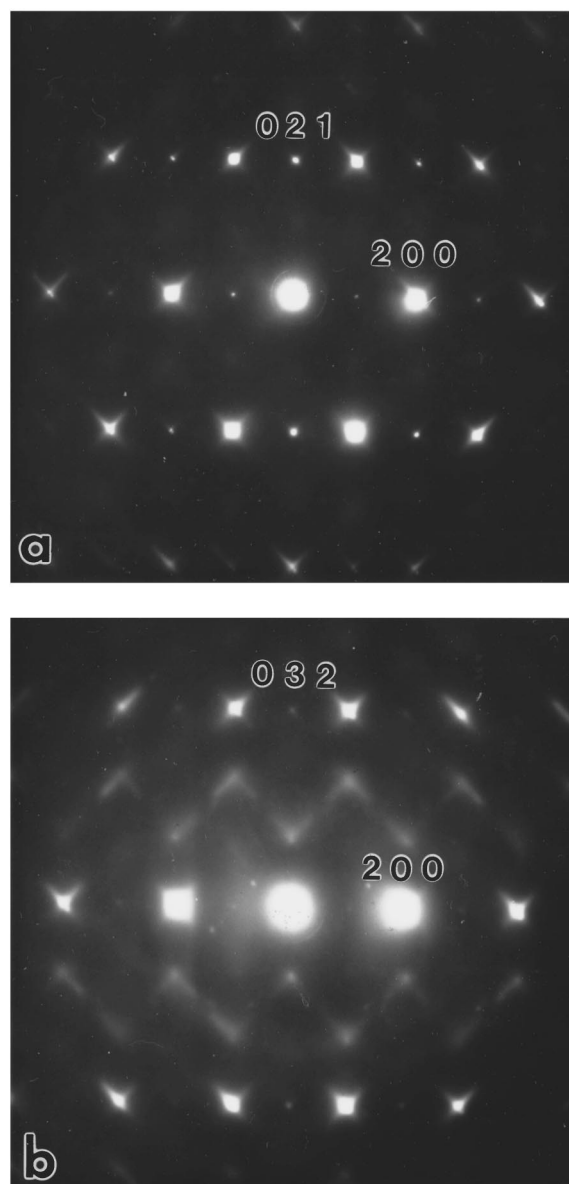


FIG. 2. Room temperature (a) [012] and (b) [023] zone axes SADP's. Note the cross-shaped diffuse streaking.

electron diffraction pattern (SADP) and the corresponding bright-field image showing the characteristic cross-hatched contrast, both taken at room temperature. The presence of a narrow star-shaped diffuse intensity distribution in the diffraction pattern is observed. Its magnitude is not so strong as in the diagram which was exposed for a longer time to enhance the weak diffuse intensity. Tilting experiments (see Fig. 2) indicate that the diffuse intensity perpendicular to the $\langle hh0 \rangle^*$ directions (centered on each of the Bragg reflections of the parent $P4/nmm$ average structure) exists in the form of discs or rods. Because of the platelike morphology of the grains, we cannot obtain complete information on the reciprocal space. Therefore, we have been unable to obtain zone axes with the (001) reflections excited, and thus, we cannot evaluate the diffuse distribution intensity along this direction. However, this should not be critical for the characterization of the microstructure, as will be discussed below. From Figs. 1 and 2 we note the absence of any additional

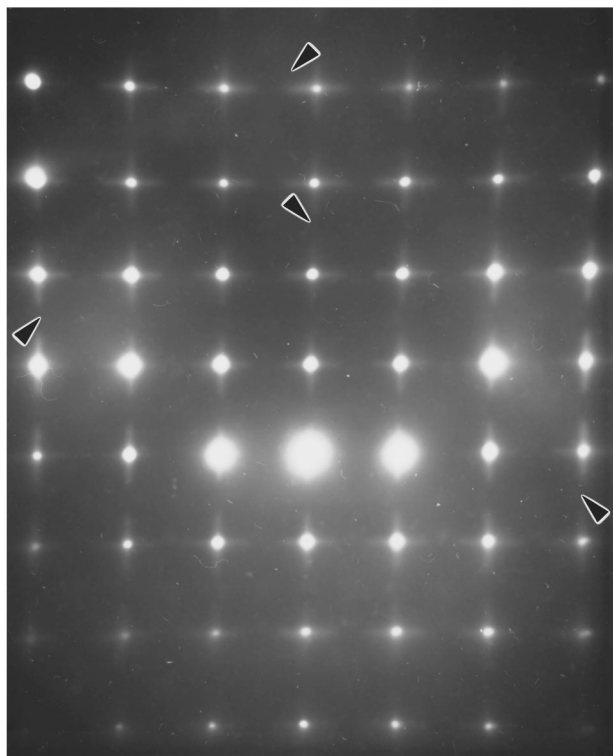


FIG. 3. SADP of the [001] zone-axis orientation taken slightly tilted away. Note the partial extinction of diffuse intensity along the $\langle hh0 \rangle^*$ direction. With further tilting it was complete. Note also the bands of absence of diffuse intensity along the $\langle h00 \rangle^*$ directions as indicated with arrows.

features that would reveal an ordering of defects in any superstructure and no other diffuse scattering.

The diffuse intensity depends strongly on the scattering angle. The relative variation compared to the main spots of the $P4/nmm$ average structure increases with the scattering angle. This is true even in the near-zone-axis diffraction pattern shown in Fig. 3. This intensity distribution is more characteristic of scattering from atomic displacements than compositional variations as will be discussed later. Kinematically the intensity of the diffuse scattering arising from displacement disorder increases approximately with the square of the scattering vector \mathbf{s} , while that due to substitutional (compositional) disorder is periodic with the period of the lattice.¹⁴

Such modulations have a static character because we can observe the typical tweed contrast. Because the characteristic times for taking an image are on the order of seconds, we obtain a time average result;¹⁵ if the modulations were time dependent, then we would not observe any specific contrast in the corresponding image.

The diffraction pattern shown in Fig. 3 was taken nearly at the [001] zone axis to minimize the multiple-scattering paths. The dominance of the nonradial streaks for the $(hh0)$ reflections can be seen clearly. With further tilting, the extinction of the radial streaks was complete. Similar extinction was observed for equivalent diffuse intensity distributions in high-temperature superconductors and attributed to multiple scattering by Zhu, Suenaga, and Tafto.¹⁶ We conclude that the actual direction for the diffuse streaks is the nonradial

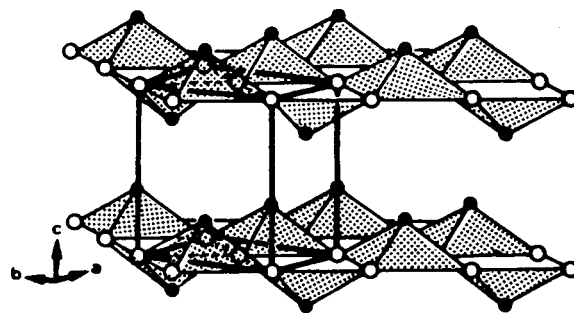


FIG. 4. Schematic polyhedral representation of the idealized average tetragonal structure of SnO with space group $P4/nmm$. Black circles represent tin atoms and hollow circles oxygen atoms.

component which indicates the direction \mathbf{q} along which the atomic displacements are correlated in the reciprocal space.

The extent of the diffuse streaking of the diffraction spots along the $\langle hh0 \rangle^*$ directions corresponds to a minimum distance in real space of 8–9 Å ($\approx 3 \times d_{110}$). This value is nearly constant in all crystals measured, and it could represent the minimum distance for the location of atoms displaced from their position in the ideal structure (Fig. 4). Another important feature is that the length of the streak does not increase as the order of the diffraction spots increases (this feature was verified even in diagrams with exposures lower than that of Fig. 1). The narrowness of the diffuse streaks allows us to estimate a coherence length of 60–70 Å along this direction for the domains that constitute the tweed microstructure. In addition Fig. 5 shows a SADP from a crystal with the incident beam parallel to the [001] zone axis taken at 923 K.

IV. DISCUSSION

A. Nonstoichiometry and defect structure

The results given above indicate that SnO contains cation deficiencies. These vacancies are independent of the prepa-

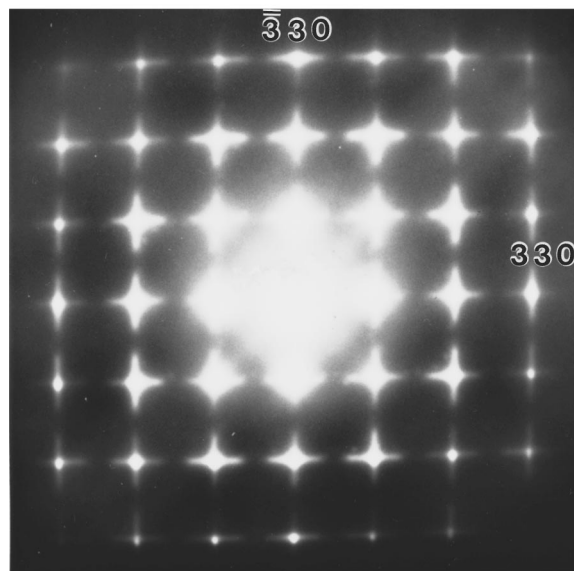


FIG. 5. High-temperature (923 K) SADP [001] pattern. Note the absence of additional diffuse features.

ration method, i.e., they are an intrinsic feature, and SnO is a nonstoichiometric phase. This hypothesis is supported by the crystallographic density obtained from our refinements, which agrees closely with the thermogravimetric results. As we discussed above, the previous structural refinements arose from powder materials, and nonstoichiometry was not taken into account in the previous studies.^{12,13} A possible explanation is that there was no previous study about the (non)stoichiometry. Also, the grain morphology *always* induces preferred orientation on powder samples, which must be corrected in the line profile refinement. It is well known that this is one of the problems that can affect the accuracy of the derived crystals parameters, especially the occupation factors.¹⁷

Although several grossly nonstoichiometric monoxides (e.g., TiO, VO, FeO) have been reported, all of them have the NaCl-type substructure. In these materials the strong departure from the ideal composition is accommodated in more or less “well” defined ways:^{18–22} in a disordered structure (i.e., random vacancies), or by formation of modulated structures of the basic substructure due to clusters that contain the *interstitial* cations required for charge compensation. The structure of the clusters resembles structural units of higher intermediate oxides. Much effort has been dedicated to the theoretical understanding of such vacancy-interstitial clusters (see, for example, Ref. 23). To our knowledge there have not been similar reports for monoxides with a very open layer-like structure, as is the SnO-PbO type. Here, we provide empirical bounds which are needed for future theoretical calculations aimed at elucidating the stabilization of phases with such large deviations from ideal stoichiometry by mechanisms such as strain coupling (see next section) and by the delicate equilibrium between the metal vacancy concentration and thermal disproportionation.

The ideal 1:1 stoichiometric structure is shown in Fig. 4.²⁴ It can be described as a fluorite-type structure with alternate oxygen layers missing, resulting in an array of square pyramids with the Sn atoms at their apexes and with the oxygen atoms at the bottom corners. In the *ab* plane, the pyramids share edges along the $\langle 110 \rangle$ directions and alternate up and down along those directions.

In contrast to other systems, like, e.g., some compositions in the TiO system, in our case an ordering of the vacancies is not observed, *even* as a function of temperature, above RT (see Fig. 5) or at 90 K. Our results show good agreement with previous x-ray diffraction²⁵ and Mössbauer spectroscopy studies.²⁶ Multiple factors could contribute to this result such as the fact that the synthesis of the material was at RT and that the structure type is a peculiar one, whose structural possibilities to accommodate different compositions are unknown up to date. Our evidence suggests that the compound with stoichiometry SnO does not exist (see next section).

On the other hand, because of the platelike morphology our knowledge of the reciprocal space of SnO is incomplete. However, from Figs. 1 and 2 the “nonstoichiometry” of SnO seems to be reflected *only* in the cross-shape diffuse streaking. The displacive nature for the diffuse streaking suggests strongly that the material does not contain interstitial cations which act to achieve the electrical neutrality as in Fe_{1-x}O . The single-crystal x-ray-diffraction study confirms this hypothesis.

Ideally, for δ cation vacancies there will be 2δ electrons to redistribute. Depending on the existence or nonexistence of localization, δSn^{4+} cations should appear. However, in SnO covalence effects are very important. Clearly we will have a redistributed electron density, but the extent of the modification for the oxidation state is subtle. It is worth noting that by using Mössbauer spectroscopy on another sample, a signal corresponding to the $4+$ oxidation state for tin was not observed down to 16 K.²⁶ However, it is typical to observe the $4+$ oxidation states as a function of time, but this is attributable to atmospheric oxidation.²⁷ We also observe this oxidation by thermogravimetric experiments on samples exposed to the atmosphere. The work reported in Ref. 26 was performed on a commercial sample. It could be interesting to know what would happen on samples with a well-known history like the ones reported here.

If localization occurs, ideally this should leave atoms with very different ionic radii in the same sublattice and the interaction between short-range ordering on this sublattice and the associated displacive structural relaxation could lead to the characteristic diffraction effects of the so-called *atomic size effect* (ASE).²⁸ The diffraction effects are asymmetric in the diffuse intensity across integer reciprocal-space positions because intensity from regions on one (e.g., the high-angle) side of the Bragg peaks is transferred to regions on the other (e.g., the low-angle) side. This “normal” Warren size effect is greatly enhanced when there is a large difference in the scattering power of the atomic species. The size effect displacement of the diffuse short-range order peak is considerable for x-ray diffraction but absent for in-zone electron-diffraction patterns. However, if observations are made on a crystal tilted in such a way as to avoid strong dynamical interactions, then the size effect displacement of these peaks is visible.²⁹ Recently a different feature in the diffraction patterns due to the ASE was reported.³⁰ It consists of planar “bands” of diffuse intensity absence. This effect is weaker than the one mentioned previously. The smaller the difference in the scattering factors, the bigger this effect will be.³¹ In Fig. 3 dynamical effects are still considerable, but we can observe “bands” of diffuse intensity along the $\langle h00 \rangle$ and $\langle 0h0 \rangle$ directions of reciprocal space. Tilting experiments reveal that these are planar bands, suggesting definitively a certain degree of localization. It is not evident if these features are related to the fine structure observed around the Bragg positions in the in-zone diagram of Fig. 1. The definitive assessment for charge localization and distinguishable oxidation states will require further investigation, by other techniques, and this is beyond the scope of the present work.

B. The tweed microstructure. Comparison with PbO

Tweed microstructures are known to develop in materials which exhibit statistical fluctuation in their compositions or in an order parameter.³² The fluctuation has been associated with high-low symmetry structural phase transitions.³³ Such structural instabilities generated by strain lead to the loss of point-group symmetry elements and a change in the crystal class. In recent years, there have been several reports of computer simulations of the microstructure in non-martensitic materials which have emphasized the highly anisotropic character of the elastic interactions that give rise to tweed structures.^{34,35}

In our case, the symmetry seems to be tetragonal, but the presence of the diffuse streaks indicates that the refined $P4/nmm$ structure described above is only an average one. As a result of the modulations along the $\langle hh0 \rangle$ directions the short-range ordering has a two-dimensional character (uncorrelated along c) and the microstructure consists of mutually orthogonal lenticular and elongated domains in the $\langle 001 \rangle$ directions for tetragonal materials.^{36,37} Such modulations lead to domains with minimum dimensions of $8 \times 60 - 70 \text{ \AA}$, resulting in a finely divided microstructure. The relaxation that accommodates the disorder leads to the ill-defined character typical of these structures and precludes the use of techniques such as convergent beam electron diffraction to elucidate properly the actual symmetry of the domains. Because of the greater coherence length along the c direction the diffuse intensity is well projected in the $[001]$ zone axis and an incomplete knowledge of the reciprocal space is not a critical issue.

We mentioned above that the diffuse intensity can be attributed essentially to a static transverse displacive modulation. However, we must bear in mind that this is only an approximate description because the origin of such modulations lies in the disorder introduced into the lattice by the metal vacancies and subsequent relaxation, with the minimum wavelength of the modulations responsible for the diffuse streaking of about $8 - 9 \text{ \AA}$.

We suggest that the strains that arise as a consequence of the "self-organization" of the lattice to accommodate the nonstoichiometry of the SnO (metal vacancies and different ionic radii of Sn^{2+} and the Sn^{4+}) are the microscopic mechanism responsible for the microstructure, or the modulations. In fact, cationic defects create an effective local field that tends to order the crystal around that site. The directions for the diffuse streaking suggest that these are elastically softer directions in the structure involving the least strain energy. The relaxation process is propagated elastically to other unit cells by the knock-on effect, i.e., by pushing or pulling neighboring atoms or polyhedra.^{34,35} If we consider the average crystal structure of SnO, with tetragonal symmetry and with edge-sharing pyramids along the $\langle 110 \rangle$ directions, it is not surprising that the resulting microstructure is a tweed structure. This is because such a structure allows for the introduction of a high degree of disorder without the introduction of vacancy-interstitial clusters. This is in agreement with the assumption that tweed structures are metastable,³³ i.e., usually an intermediate ordering mechanism between ordered phases without macroscopic strain.

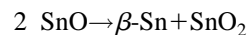
The apparent constancy of $8 - 9 \text{ \AA}$ for the extension of the tweed microstructure and the beam sensitivity overshadow a possible coarsening of the microstructure at scales within the illuminated area, and we cannot preclude this. However, in this model, if the compositional range should include the stoichiometric composition, the tweed must not be observed. This fact was not observed by us and suggests that possibly SnO does not exist.

In the case of the isostructural compound, PbO, a similar tweed microstructure was found.³⁸ Although the structural details of the modulations were the same as those reported here for SnO, the tweed microstructure was interpreted as a precursor effect of the ferroelastic low-temperature improper phase transition. This hypothesis is plausible, but we want to

point out that there is no study, like the present one on SnO, on the correct stoichiometry for PbO. In addition, the authors did not rule out completely that the origin of the tweed lies in the synthesis of the material.³⁸ Considering these facts, we postulate that the tweed microstructure in PbO could have a similar origin as in SnO. The absence of both a lock-in phase and a thermal evolution of the modulation vector for the low-temperature incommensurate phase was suggested as due to the presence of defects, without further explanation.³⁹ Moreover, the extent of the tweed microstructure in real space of about $15 - 20 \text{ \AA}$ (Ref. 33) is greater than in SnO. This difference cannot be attributed only to variations in the elastic constants.⁸ At low temperature an evidence similar to Fig. 3 for the atomic size effect was observed.³⁷ We can rationalize these results with our model. We postulate that PbO is also a nonstoichiometric phase, with cation deficiency similar to that observed in SnO, but with a narrower concentration range, i.e., only a minor concentration of cation vacancies. This should result in larger spacings (compared with SnO) for vacancies, i.e., a minor extent of the diffuse streaking.

C. Thermal instability

Concerning the instability of SnO, in a previous work⁴⁰ calculations from first principles by using the full potential-linear muffin-tin orbital method failed to predict the process



both numerically, and also in sign. Those calculations were carried out for an ideal phase, i.e., a fully ordered and stoichiometric SnO compound. Strain coupling is now recognized as playing a very important role in a variety of order-disorder structural phase transitions in crystals.⁴¹ We believe that the tweed microstructure is responsible for the stabilization of the nonstoichiometric phase $\text{Sn}_{1-\delta}\text{O}$. Furthermore, Fig. 5 suggests that the elastic correlations are stable up to 923 K , but visual inspection in the microscope showed the tweed contrast up to the temperature of thermal decomposition. On the other hand, at room temperature we have not observed any diffuse scattering of dynamical origin due to low-lying branch instabilities in the phonon-dispersion curves. These results suggest that very possibly the structure of SnO becomes unstable and decomposes when elastic correlations are not sufficiently strong to stabilize it. In addition, we note that in the absence of dynamical instabilities the mechanism that drives the decomposition probably lies in the strains arising from a reordering of the polyhedra.

V. CONCLUSIONS

A chemical, thermogravimetric, and electron-diffraction study of tin monoxide is reported. A large deviation from the ideal stoichiometry by metal vacancies is observed, with $\text{Sn}_{1-\delta}\text{O}$ ($0.04 \leq \delta \leq 0.10$). This is an intrinsic feature of this material and seems to be accommodated, without the introduction of complex vacancy interstitials (like in wüstite), through the formation of static transverse displacive modulations along the $\langle hh0 \rangle$ directions, which give rise to a tweed microstructure. This constitutes a different way of accommo-

dating large nonstoichiometries, compared with the well-known behavior of the transition-metal monoxides with NaCl-type structure. The difference lies in the layer-like average tetragonal structure. Metal vacancies cause the strain coupling which stabilizes a highly disordered nonstoichiometric phase. Dynamical instabilities were not observed. An origin for the thermal instability of the material was suggested. A comparison with PbO, the single isostructural compound, is outlined, and similar behavior is suggested for this phase. SnO was found to be a beam-sensitive material.

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