PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Hyperfine interaction between indium atoms and oxygen vacancies in stannic oxide

A. G. Bibiloni, J. Desimoni, C. P. Massolo, and M. Rentería
Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo No. 67, 1900 La Plata, Argentina

(Received 16 December 1987)

The time-differential perturbed-angular-correlation technique is applied to study the hyperfine interaction of ^{111}In atoms in stannic oxide. Two different preparation procedures were employed to obtain high-purity samples. With both of them two static quadrupole interactions are observed, characterized at room temperature by the parameters $\omega_1=31.1$ Mrad/s, $\eta_1=0.45$; $\omega_2=14.3$ Mrad/s, $\eta_2=0.65$. The temperature dependence of the hyperfine interaction is studied from 17 to 1173 K. The origin of the measured interactions is analyzed and assigned to probe atoms substitutionally replacing Sn with singly and doubly ionized oxygen vacancies as near neighbors.

I. INTRODUCTION

Many nuclear-physics methods have been used to elucidate details of solid-state systems on a microscopic level. In this context, hyperfine-interaction techniques, (NMR, nuclear orientation, Mössbauer spectroscopy, perturbed angular correlation, muon-spin rotation) have been increasingly applied to study metals, alloys, and, more recently, semiconductor compounds.[1]

The applicability of the time-differential perturbed-angular-correlation (TDPAC) method to systems with extremely low concentration of impurities (probe atoms) is important because the single-atom counting of this technique, in combination with the highly localized sensitivity, permits detailed investigations. The technique is sensitive to any static or fluctuating extranuclear field and provides information concerning crystal structure, charge density symmetry, charge exchange mechanisms, and other characteristics of the compound, at the precise site of the impurity.

Although much work has been done, there are still many open questions, such as, for example, the correlation between the magnitude of the observed electric field gradient (efg) and the charge carrier density, or dynamic effects of electronic relaxation of the probe on the measured angular correlation, which occurs if the probe decays through electron capture (EC).

In this context, we have applied the TDPAC technique to study stannic oxide which is, in its undoped form, an *n*-type, wide-gap semiconductor. Various specific and unique properties of this material make it very useful in many applications. Polycrystalline thin films and ceramics of SnO_2 have been extensively used for production of resistors. Conducting SnO_2 films are well known as transparent electrodes.[2] SnO_2 films are also used as transparent heating elements[3] for production of transistors,[4,5] for transparent antistatic coatings,[6] and other parts in electric equipment where transparency is required.

Because of its practical importance, an increasing amount of work has been done on crystals and films of SnO_2 in recent years. Although a great deal of expermental research has been carried out on the electrical and optical properties of single crystals, thin films, and sintered SnO_2, many questions concerning the basic properties of this compound still remain open.

Preliminary results of our TDPAC investigations of SnO_2 using ^{111}In as probes have been presented elsewhere.[7] Two static quadrupole interactions were found in those measurements revealing the existence of two different sites for In in the sample, but no conclusive assignments could be made for those interactions. Our investigation of the temperature dependence of the hyperfine interaction was not conclusive, either, concerning the existence of a fluctuating interaction originating in the electronic relaxation consecutive to the electron capture decay of the radiative probe (In→Cd). This interaction is usually called "after effects."

Nearly simultaneously, Wolf and co-workers[8] reported a TDPAC study of SnO_2 also using ^{111}In probes. They found a single quadrupole frequency assigned to probe atoms at substitutional Sn sites. They stated that the temperature dependence of the fraction of probes exposed to this efg reveals the presence of after effects. In a subsequent report,[9] using SnO_2 powder with higher impurity concentration, the same group found spectra similar to ours and stated that in this case the Cd atoms formed pairs with other impurities and that this caused the appearance of more than one efg.

It is the purpose of this paper to present all our further investigations consistently in a series of TDPAC measurements (17–1173 K) of three highly pure stannic oxide samples, obtained through different preparation procedures.

II. EXPERIMENTAL

A. Experimental technique and data reduction

The TDPAC measurements were made using the well-known 173–247 keV γ-γ cascade in ^{111}Cd created via electron capture by ^{111}In with a 2.8-d half-life. A conventional automatic two-detector apparatus with one INa(Tl) and one CsF scintillator was employed.

Details of the experimental technique can be found in Ref. 10. The $R(t)$ ratios were determined from the experimental data by

$$R(t)=2\frac{N(180°,t)-N(90°,t)}{N(180°,t)+2N(90°,t)}\simeq A_2G_2(t) \ . \qquad (1)$$

Theoretical perturbation factors of the form $A_2G_2(t)$, folded with the measured time-resolution curve (full width at half maximum 2.4 ns) were fitted to the experimental $R(t)$ ratio.

The proposed perturbation factors, corresponding to static quadrupole interaction, were of the form

$$G_2(t)=\sum_i f_i \sum_{n_i=0}^{3} S_{n_i} e^{-\delta_i \omega_{n_i} t}\cos(\omega_{n_i} t) \ , \qquad (2)$$

where f_i are the relative fractions of nuclei that experience a given perturbation. The frequencies ω_n are related by $\omega_n = F_n(\eta)\omega_Q$ to the quadrupole frequency $\omega_Q = eQV_{zz}2\pi/40h$. The F_n and S_n are known functions[11] of the axial asymmetry parameter η defined by $\eta=(V_{xx}-V_{yy})/V_{zz}$, where V_{ij} are the principal components of the efg tensor. The exponential function accounts for a Lorentzian frequency distribution of relative width δ around ω_n.

B. Sample preparation

Two different kinds of samples were prepared.

Sample 1. Commercially obtained carrier-free $^{111}InCl_3$ was dropped onto 99.999% pure Sn foils. The active Sn foil was melted at 290 °C in Ar, then the resulting pellet was rolled down to 20 μm and oxidized at 210 °C for 20 h in air. Finally, it was reoxidized at 830 °C for 2 h in air. A Mössbauer measurement was performed on the white-yellow powder resulting. The spectrum obtained shows the SnO_2 characteristic hyperfine interaction.

Sample 2. Commercially obtained $^{111}InCl_3$ was dropped onto high purity SnO_2 powder, kindly provided by Renn and co-workers. It was dried using an infrared lamp and finally was heated in order to diffuse the activity at 1000 °C during 1.5 h in air, sample 2a. An additional TDPAC sample was prepared in the same way but heated at 1000 °C during 1.5 h in Ar (120 Torr), sample 2b.

C. Stannic oxide: general remarks

SnO_2 crystallizes with the tetragonal rutile structure, space group D_{4h}^{14} $(P4_2/mnm)$.[12] The unit cell contains six atoms, two tin and four oxygen as illustrated in Fig. 1. Each tin atom is at the center of six oxygen atoms approximately at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms approximately at the corners of an equilateral triangle. The lattice parameters[12] are $a=b=4.737$ Å and $c=3.186$ Å. The ionic radii for O^{2-} and Sn^{4+} are 1.40 Å and 0.71 Å, respectively.

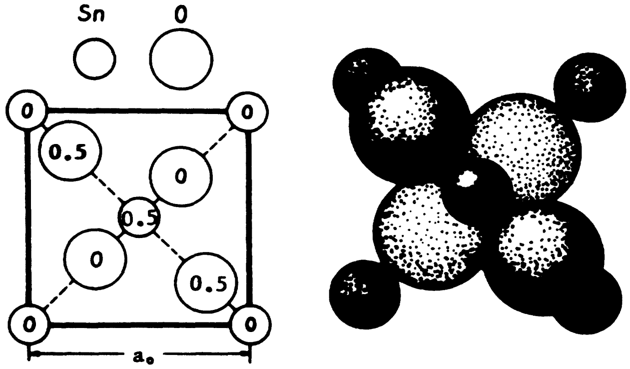

FIG. 1. Left: The atomic arrangement in the tetragonal unit of SnO_2 projected on the basal plane, *c*; the small circles represent tin atoms. Right: A drawing to show the way the atoms of SnO_2 pack together if they are given their expected ionic sizes. The large spheres are the oxygen ions. Numbers inside the circles mean distance to the basal plane in percent of the *c* parameter.

Stannic oxide is a broadband semiconductor with an energy gap of around 4 eV and an *s*-character conducting band.[13]

The nature of the defect structure of pure SnO_2 is not completely elucidated yet. Although both doubly ionized oxygen vacancies and interstitial tin ions have been proposed, and either one is possible, it is generally accepted that oxygen vacancies predominate as native disorder.[14,15]

The electrical properties of single crystals are well understood, and the properties of SnO_2 powder are similar to those of single crystals.

The results of conductivity measurements, performed on samples of purity comparable to those used in the present work, show three different regions,[16] namely: region I in a temperature range 130–300 K; region II from 10 to 130 K, and region III from 4.2 to 10 K. In the first region the resistivity increases with increasing temperature, while in the last two regions the resistivity decreases with increasing temperature. Above 300 K the conductivity changes by the equation $\sigma=(\text{const})\,T^{-1}$. The investigation of the electrical properties of stannic oxide reported in the literature reveals that the complicated temperature dependence of conductivity in pure SnO_2 crystals is mainly due to the different temperature dependence of the conduction electron concentration and the charge carrier mobility, both related to the native defects of the semiconductor (oxygen vacancies and interstitial tin atoms). It is interesting that in the temperature range from 4.2 to about 130 K the conductivity varies by 9 orders of magnitude. Thus, pure SnO_2 crystals can be either a good insulator at very low temperatures or a good conductor at a temperature of about 130 K.

III. RESULTS AND DISCUSSION

The TDPAC measurements performed with sample 1 in the temperature range 17–1073 K are shown in Fig. 2. A strong damping is the main feature of the spectra taken at temperatures from 17 to 773 K. At higher tempera-

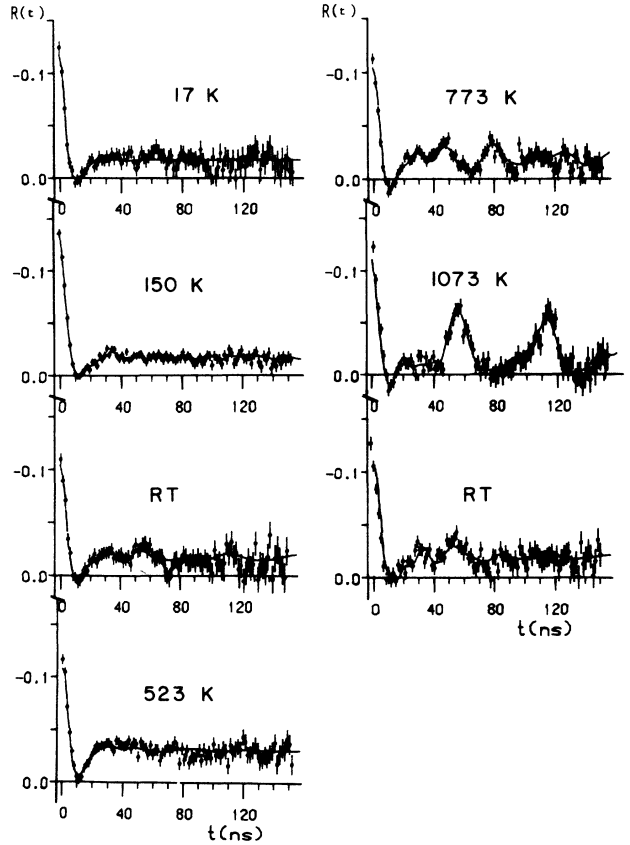

FIG. 2. TDPAC spectra of ^{111}In in sample 1 of SnO_2 taken at the indicated measuring temperatures. Full lines show the results of least-square fits of Eq. (2) to the data with the hyperfine parameters quoted in Table I.

tures, a well-defined oscillatory pattern is noticeable. We also show a second room temperature spectrum [see (a) in Table I], taken at the end of the sequence of measurements, which indicates the reversibility of the processes responsible for the temperature evolution of the spectra. No change in the experimental anisotropy was observed in the studied temperature range.

Although from crystalline structure considerations (see Sec. II C) only one static electric quadrupole hyperfine interaction should be expected for In atoms substitutionally replacing Sn in the lattice, our best fits, which reproduce the experimental data quite well (see full lines in Fig. 2), reveal the existence of two different sites for In probes in the sample. The hyperfine parameters obtained in this fit are quoted in Table I and displayed in Fig. 3.

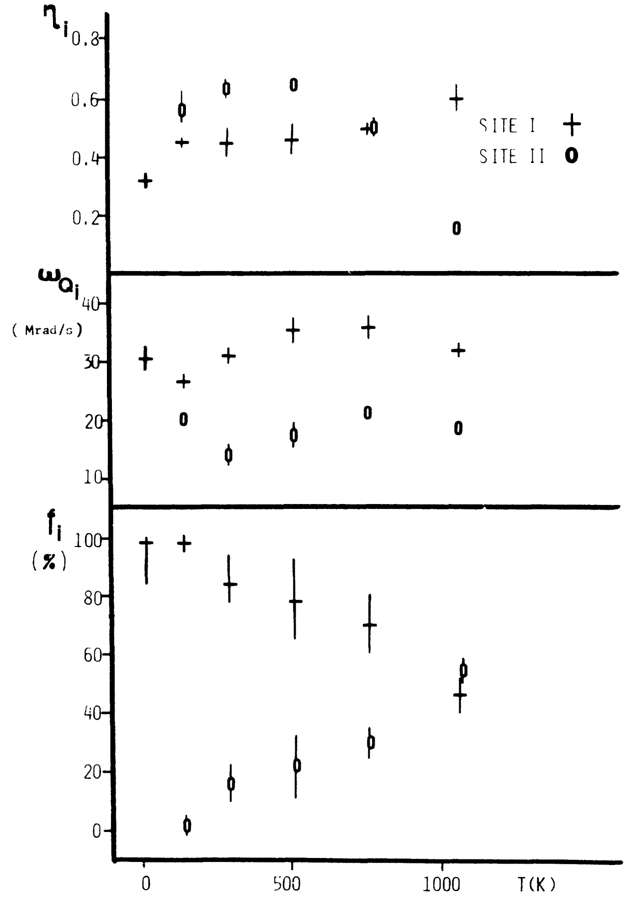

FIG. 3. Temperature dependence of the hyperfine parameters measured in SnO_2, sample 1. Vertical bars take into account statistical and fitting-procedure errors.

A different temperature dependence of the parameters characterizing the two interactions is observed.

Site I. At low temperatures, the highest fraction of probes (f_1) is exposed to a hyperfine interaction characterized by a quadrupole frequency $\omega_1 = 30$ Mrad/s and an asymmetry parameter $\eta_1 = 0.45$. There is a strong depen-

TABLE I. Fitted hyperfine parameters of the TDPAC spectra taken with sample 1. The results of a second RT measurement (a), performed at the end of the sequence are also shown, demonstrating the reversibility of the processes. When no errors are given, this means that the parameter was kept fixed.

	Site I				Site II			
T (K)	f_1 (%)	ω_{Q_1} (Mrad/s)	η_1	δ_1 (%)	f_2 (%)	ω_{Q_2} (Mrad/s)	η_2	δ_2 (%)
17	100±29	31.0±4.7	0.33±0.14	48±13				
150	98±3	26.5±0.6	0.41	46±4	2±2	20.4±0.6	0.57±0.06	0±6
300	84±6	31.1±0.9	0.45±0.04	15±2	16±6	14.3±0.6	0.65	7±6
523	78±13	35.4±2.0	0.46±0.06	23±5	22±11	17.6±1.1	0.65	16±10
773	70±10	36.1±1.7	0.50	22±6	30±5	21.0±0.2	0.50±0.02	4±1
1073	46±7	32.3±1.1	0.60±0.04	12±3	54±4	18.4±0.1	0.16±0.02	2±1
300(a)	75±7	32.5±0.8	0.40±0.04	12±2	25±9	14.3	0.66±0.05	10±6

dence on the temperature as observed for the fraction f_1. It decreases from around 100% at low temperatures to less than 50% at 1073 K.

Site II. The complement of site I constitutes In probes in site II. It is characterized by a temperature-independent frequency of $\omega_2 = 18$ Mrad/s and an asymmetry parameter η_2 which remains constant around 0.65 from 17 up to 523 K and strongly decreases for higher temperatures down to 0.16 at 1073 K. The fraction of probes f_2 exposed to this interaction, which is nearly zero at low temperatures, increases up to more than 50% at the highest measured temperature.

The small frequency distribution δ_2 remains always lower than the corresponding δ_1 of site I which varies from 40% to 15%.

The characteristics of the two quadrupole interactions described above do not allow a direct assignment of either of them to a particular site in the perfect stannic oxide lattice. In fact, a point charge calculation predicts an asymmetry parameter of 0.17 for the efg in the substitutional cation site. We find such an asymmetry parameter at high temperatures for site II. One could then be tempted to assign site II to probes substitutionally replacing Sn in the lattice, supposing that the misalignment of the ionic radii produces a distortion which is released only with the lattice thermal expansion at high temperatures. But this hypothesis cannot explain the temperature dependence of the fraction f_2 which should remain constant.

A low quadrupole frequency in the range 15–20 Mrad/s, with an asymmetry parameter between 0.6 and 0.7 (as we find in site II up to 523 K) has been observed in the internal oxidation of very small concentration of indium in a silver matrix[17,18] arising from the oxidation of indium atoms, and in perturbed-angular-correlation studies of several oxides.[19–23] In all cases this interaction was assigned to In-O_x clusters, where the number of In and O atoms, the details of coordination between them, and the size of the clusters could not be determined. But in none of these previous studies was a change in the η value of this interaction detected, in contrast to the decrease we observe for η_2 (from 0.6 to 0.16 at $T > 500$ K).

Furthermore, the reversible variation with temperature of the fraction of site II cannot be explained in this picture. Hence, we do not believe that the interaction in site II can be assigned to the existence of In-O_x clusters.

Another important fact can be the cause of the measured hyperfine interactions; this is the native disorder. As we mentioned in Sec. II C, oxygen vacancies are generally considered to be predominant in SnO_2. The donor levels related to these defects have been measured by several authors (see the review article of Ref. 16), and they range between 0.03 eV for the shallow level and 0.15 eV for the second donor level. Due to the shallow energy level, the first donor level should be ionized in the studied temperature region while the second level should ionize with increasing temperature.

Since the charge imbalance introduced by the presence of In^{3+} probes may relieved by the creation of oxygen vacancies, it is possible that during oxidation, oxygen vacancies will be created as In near neighbors. A similar effect has been found in Zn-doped sintered stannic oxide.[24] Also, from ionic radii considerations (0.81 Å for In^{3+} and 0.71 Å for Sn^{4+}) it is apparent that indium atoms will have lower energies on Sn sites with an oxygen vacancy as near neighbor. Thus, the two measured hyperfine frequencies could arise from the interaction of the probe atoms with singly-ionized and doubly-ionized oxygen vacancies as near neighbors. At low temperatures, most of these vacancies are singly ionized giving rise to the interaction in site I. With increasing temperature, the ionization of the second donor level would correspond to the interaction of probes with doubly ionized oxygen vacancies. Since the intensity of both interactions ought to be related to the native defect thermal equilibrium, the reversibility observed in our measurements favors the above-mentioned hypothesis.

Unfortunately, it is not possible to check this assignment since there are no previous measurements nor theoretical predictions of hyperfine interactions with such point defects in this compound to compare with our results. The point charge model cannot be used in this case since the atomic coordinates, modified by the presence of oxygen vacancies, are not known.

We have analyzed the temperature dependence of the fraction f_2 supposing that it is directly related to the number of doubly ionized defects. A function of the form

$$f \propto \exp -(E_g/2kT) \tag{3}$$

fitted to our f_2 data (see full line in Fig. 4) leads to an energy of the second donor level of 0.10±0.02 eV, which is consistent with previous measurements.[15,25]

Considering the temperature dependence of the hyperfine parameters, the small variation of the quadrupole frequencies can be due to thermal expansion of the crystalline lattice. This would also cause the more im-

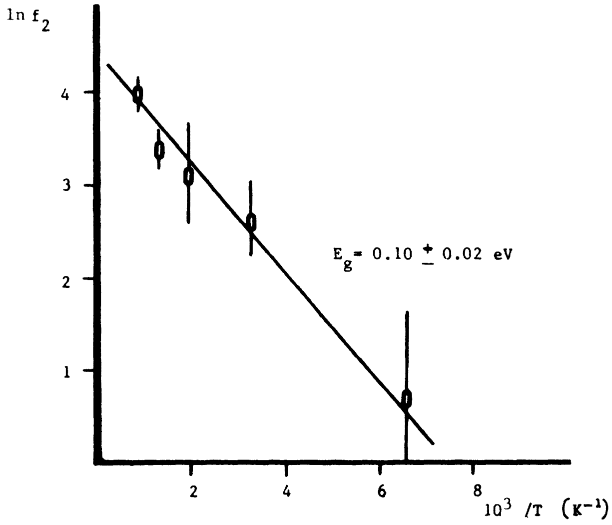

FIG. 4. Relative intensity of the fraction of probes located in site II as a function of temperature. Vertical bars take into account statistical and fitting-procedure errors. The full line shows the fit of Eq. (3) to the data.

portant change observed in the asymmetry parameters which are much more sensitive to symmetry distortions. As we said before, no exact calculation can be done in order to prove this statement. Nevertheless, due to the low oxygen vacancies concentration, the effect of the crystal thermal expansion on the hyperfine parameters can be qualitatively checked using the point charge model assuming the expansion of the perfect crystal lattice. We performed a series of calculations separately expanding the principal axis of the unit cell. This shows that even a slight expansion of 1% in any of these leads to a 75% variation of the η value; meanwhile the calculated efg only varies 15%. The calculations also show that a continuous expansion in the a_0 axis leads to a nonmonotonous variation of the asymmetry parameters.

Although an important increase in the conductivity is known to take place in the studied temperature range, this is not supposed to produce an important change in the measured efg due to the s character of the conduction band.[13]

We have performed measurements at room temperature and high temperatures using sample 2 (a and b), where the indium activity was diffused in air and an argon atmosphere, respectively. We have not found any difference in the hyperfine interaction originated in the sample preparation. The same two static quadrupole interactions discussed above are present in the whole temperature range. We show in Fig. 5 a typical spectrum at high temperatures where the oscillatory pattern is best defined.

The similarity of results obtained with sample 2a and b shows that the measured interactions cannot originate in the diffusing process of the activity. In particular, the possibility of the formation of In-O_x clusters in the surface may be discarded.

On the other hand, although a change in the defect concentration is to be expected in both samples due to the different annealing atmospheres,[16] our results indicate that in both cases the number of oxygen vacancies is larger than the probe concentration. If not, a third interaction should appear in the TDPAC spectra, corresponding to probes substitutionally replacing tin in perfect lattice sites.

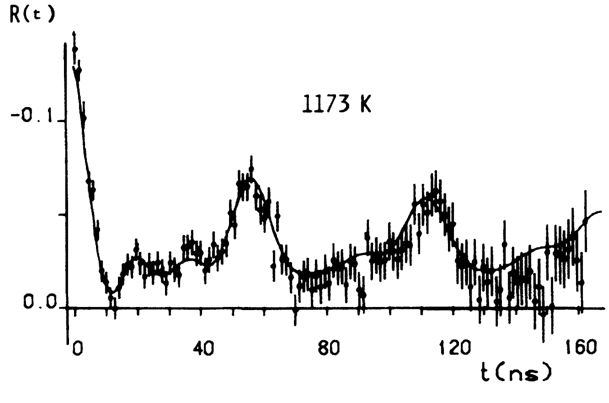

FIG. 5. Typical TDPAC spectrum of ^{111}In in sample 2 of SnO_2 taken at 1173 K. Full line shows the result of a least-square fit of Eq. (2) to the data with the following parameters; $f_1=56\pm8\,\%$, $\omega_1=30.6\pm2.0$ Mrad/s, $\eta_1=0.93$ (fixed in this fit), $\delta_1=34\pm8\,\%$; $f_2=44\pm4\,\%$, $\omega_2=18.7\pm0.1$ Mrad/s, $\eta_2=0.16\pm0.03$, $\delta_2=3\pm1\,\%$.

The fact that the same two interactions have been observed using sample 1, sample 2, and one prepared with a less pure tin metal (99.95%, see Ref. 7), indicates that the measured hyperfine interaction can be associated neither with the nature nor with the concentration of impurities in the sample.

As we mentioned in the Introduction, nearly simultaneously with the publication of the preliminary results of this investigation,[7] Wolf *et al.* reported a TDPAC measurement on ZnO and SnO_2.[8] They find only one quadrupole frequency of 19 Mrad/s with $\eta=0.1$ in the whole temperature range (4–1170 K). However, the fraction of probe atoms f_1 which are exposed to this efg depends on temperature, increasing from 25% at 4 K to 70% at temperatures above 1000 K. They assign this interaction to In probes located at substitutional Sn sites and do not give any explanation for the rest of the probes that seem to be unperturbed. They claim that the temperature dependence of the fraction f reveals the decay aftereffects. The fact that in a hydrogen-doped sample they find a faster increase of the fraction f with temperature seems to confirm their hypothesis.

In a further investigation[9] using SnO_2 powder with an impurity concentration a factor of 100 higher than in the sample referred to above, the same authors find spectra very similar to ours and state that in this case the Cd atoms form pairs with other impurities and that this causes the appearance of more than one efg. Nevertheless, our results are in disagreement with this explanation. In fact, using the high-purity powder provided by these authors, we have also found the same two interactions which are not related to the impurity concentration.

In order to check the existence of a fluctuating interaction arising from the decay aftereffects, we have fitted all our spectra with a theoretical perturbation factor including an exponential term. In none of our spectra did we observe an improvement of the fits using this theoretical function; therefore we find that there is no evidence of the presence of any time-dependent interaction in our samples.

We do not find any explanation for the discrepancy between our results and the ones reported by Wolf *et al.* Probably a combination of native defects and the presence of contaminants is at the origin of this discrepancy.

IV. SUMMARY AND CONCLUSIONS

The TDPAC technique has been applied to study the hyperfine interaction of ^{111}In probes in stannic oxide. High-purity samples have been used, obtained by two different preparation procedures: sample 1, introducing the activity in a 99.999% tin metal foil subsequently oxidized and sample 2, diffusing the In activity in 99.999% SnO_2 powder.

With both types of samples we have found two static quadrupole interactions which we assign to In probes substitutionally replacing Sn with an oxygen vacancy as near neighbor. Site I: The interaction of probes with singly ionized oxygen vacancies as near neighbors is characterized by a quadrupole frequency of around 30 Mrad/s and η varying from 0.4 to 0.6. Site II: The interaction characterized by a quadrupole frequency around 19 Mrad/s and η varying from 0.65 to 0.16 is related to a doubly ionized oxygen vacancy.

Both frequencies remain nearly constant in the studied temperature range (17–1173 K) as expected taking into account the s character of the conduction band of this semiconductor.

The variation of the asymmetry parameter of both sites is attributed to the thermal expansion of the crystalline lattice.

In this interpretation, the ionization of the second donor level introduced by the defects is responsible for the evolution with temperature of the measured relative intensities. The temperature dependence of the fraction of probes interacting with ionized oxygen vacancies leads to an energy level of 0.10 ± 0.02 eV consistent with previous measurements.

We have not found in our investigation any evidence of the existence of a time-dependent interaction arising from the decay after effects.

ACKNOWLEDGMENTS

M. Renn kindly provided the high-purity SnO_2 powder used as sample 2 and communicated results of a previous publication. We wish to thank L. Terminiello for the Mössbauer characterization of sample 1. This work was partially supported by the Consejo National de Investigaciones Científicas y Técnicas (CONICET) and Comisión de Investigaciones de la Provincia de Buenos Aires (CIC-BA), Argentina. A. G. Bibiloni was partially supported by CONICET. J. Desimoni, C. P. Massolo, and M. Rentería were fully supported by CONICET.

---

[1] See, for example, the Proceedings of the last International Conference on Hyperfine Interactions [Hyp. Int. **34**, 1 (1987)].

[2] R. E. Aitchison, Aust. J. Appl. Sci. **5**, 10 (1954).

[3] J. W. Ward, Appl. Ind. **16**, 408 (1955).

[4] H. A. Klasens and H. Koelmans, Solid State Electron. **7**, 701 (1964).

[5] A. Aoki and H. Sasakura, Jpn. J. Appl. Phys. **9**, 582 (1970).

[6] L. Holland and G. Siddal, Vacuum **3**, 375 (1953).

[7] J. Desimoni, A. G. Bibiloni, L. A. Mendoza Zélis, L. Damonte, F. H. Sánchez, and A. R. López García, Hyp. Int. **34**, 271 (1987).

[8] H. Wolf, S. Deubler, D. Forkel, H. Foettinger, M. Iwastschenko-Borho, F. Meyer, M. Renn, and W. Witthum (unpublished).

[9] M. Renn, private communication.

[10] See, for example, H. Frauenfelder and R. M. Steffen, in *Alpha, Beta and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland, Amsterdam, 1966), pp. 997 and 1182.

[11] L. A. Mendoza Zélis, A. G. Bibiloni, M. C. Caracoche, A. R. López García, J. A. Martinez, R. C. Mercader, and A. F. Pasquevich, Hyp. Int. **3**, 315 (1977).

[12] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1968), Vol. 1, p. 250.

[13] R. Summitt, J. A. Marley, and N. F. Borrelli, J. Phys. Chem. Solids **25**, 1465 (1964).

[14] C. G. Fonstad and R. H. Rediker, J. Appl. Phys. **42**, 2911 (1971).

[15] S. Samson and C. G. Fonstad, J. Appl. Phys. **44**, 4618 (1973).

[16] Z. M. Jarzebski and J. P. Marton, J. Electrochem. Soc. **123**, 199C (1976); 123, 299C (1976).

[17] A. F. Pasquevich, F. H. Sánchez, A. G. Bibiloni, J. Desimoni, and A. R. López García, Phys. Rev. B **17**, 963 (1983).

[18] J. Desimoni, A. G. Gibiloni, L. A. Mendoza Zélis, A. F. Pasquevich, and A. R. López García, Phys. Rev. B **28**, 5739 (1983).

[19] P. Wodniecki and B. Wodniecka, Hyp. Int. **12**, 95 (1982).

[20] M. Uhrmacher and W. Bolse, Hyp. Int. 15/16, 445 (1983).

[21] W. Bolse, M. Uhrmacher, and K. P. Lieb, Mater. Sci. Eng. **69**, 375 (1985).

[22] W. Bolse, M. Uhrmacher, and K. P. Lieb, Phys. Rev. B **36**, 1818 (1987).

[23] C. P. Massolo, M. Rentería, J. Desimoni, and A. G. Bibiloni, Phys. Rev. B **37**, 4743 (1988).

[24] E. Mattheus and E. E. Kohnke, J. Phys. Chem. Solids **29**, 653 (1968).

[25] A. Marley and R. C. Dockerty, Phys. Rev. **140**, A304 (1965).