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ABSTRACT

Titanium dioxide is a commonly used material in a wide range of applications, due to its low price, and the increasing demand for it in the food- and pharmaceutical industries, and for low- and high-tech applications. Time-differential perturbed angular correlation (TDPAC) and Mössbauer spectroscopy measurements have a local character and can provide important and new information on the hyperfine interactions in titanium dioxide. With the application of characterization techniques and radioactive beams, these methods have become very powerful, especially for the determination of temperature dependence of hyperfine parameters, even at elevated temperatures. Such measurements lead to a better understanding of lattice defects and irregularities, including local environments with low fractions of particular defect configurations that affect electric quadrupole interactions. At ISOLDE-CERN, physicists benefit from the many beams available for the investigation of new doping configurations in titanium dioxide. We report the annealing study of titanium dioxide by means of the time differential perturbed γ-γ angular correlation of 111mCd/111Cd in order to study the possible effects of vacancies in hyperfine parameters. This paper also provides an overview of TDPAC measurements and gives future perspectives.

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I. INTRODUCTION

The time-differential perturbed correlation (TDPAC) technique and Mössbauer spectroscopy are very well suited for measuring the local charge distribution and the defect configurations of materials over a wide temperature range. In parallel with the study of magnetic and electric hyperfine fields, the TDPAC method allows us to investigate the axial symmetry of electrostatic field gradients (EFGs). The perturbation of an angular correlation is due to an electric quadrupole interaction with nearby ions, bonding and conduction electrons, and the electronic shells of the TDPAC-probe ion. The Isotope mass Separator On-Line facility (ISOLDE) can produce several types of probe ions. The 1.4-GeV proton beam at CERN bombards the ISOLDE target to produce isotopes, which are transferred to the ion source where they are ionized (Fig. 1). The beam is accelerated to 60 keV and separated by mass. The resulting pure beam is delivered to the beam line, where the implantation of TDPAC probes occurs. The concentration of the radioactive probes implanted at ISOLDE-CERN is so small that they have a negligible effect on the intrinsic properties of the titanium dioxide. The structural damage caused by the implantation process can be repaired after thermal treatment for a few minutes.

During a typical TDPAC experiment, two consecutive gamma rays, emitted by the same nucleus, are detected by photon counters. The emission of the first photon is isotropic, therefore, it is important to detect it in a selected direction. By detecting the emission of the second photon, a definite angular correlation with respect to the first gamma ray is observed. Furthermore, determining the time interval between the two emissions is essential, because during the lifetime of the intermediate state between gamma-ray emissions, the nucleus can interact with its surroundings and the angular correlation becomes perturbed. This leads to a time-dependent precession
of the angular correlation. Further information about analogue or
digital TDPAC detection systems can be found in Refs. 5 and 6, and
data evaluation formalism in Refs. 7 and 8.

Considering the nuclear spin I = 5/2 of the intermediate state,
the perturbation factor for polycrystalline samples, for η ≠ 0, is given
by:

\[ G_{22}(t) = s_0 + \sum_{n=1}^{3} s_n(\eta) \cos[\omega_n(\eta)t]. \] (1)

\[ \omega_n \] are the transition frequencies between two M-states,
\[ \omega_n = \left[ E(M) - E(M') \right]/\hbar = 3|M^2 - M'^2|\omega_Q. \] However, in the case of
spin I = 1 for polycrystalline samples and η ≠ 0, the degeneracy of
the M-states is removed and the perturbation factor becomes:

\[ G_{22}(t) = \frac{2}{5} + \frac{1}{5} \cos \omega_1 t + \frac{1}{5} \cos \omega_2 t + \frac{1}{5} \cos \omega_3 t, \] (2)

with \[ \omega_1 = 2\eta\omega_Q, \omega_2 = (3 - \eta)\omega_Q, \omega_3 = (3 + \eta)\omega_Q. \]

The transition frequencies are functions of the nuclear
quadrupole frequency, which is defined by:

\[ \omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}. \] (3)

Here, Q is the nuclear quadrupole moment. Since the EFG is
represented by a symmetrical and traceless (3×3) tensor, it can be fully
characterized by the magnitude, \( V_{zz} \), and the asymmetry param-
eter, \( \eta = (V_{xx} - V_{yy})/V_{zz} \). \( \eta \) varies from 0 to 1, where 1 corresponds
to maximal asymmetry. Coefficients \( s_n \) are only slightly dependent
on \( \eta \) and are the amplitudes of the transition frequencies, \( \omega_n \). They
are determined by the angle between the detectors if the EFG is ran-
donically oriented, e.g. in a polycrystalline sample. In single crystalline
samples \( s_n \) also depends on the actual orientation of the EFG tensor
with respect to the detectors. Additionally, \( \delta \) is the relative half-width
of the EFG distribution.

Additional details of the formalism and the TDPAC tech-
technique can be found in Refs. 9–11. Different lattice effects, such as
small thermal expansions and anisotropic thermal vibrations, con-
tribute to variations in the asymmetry parameter. The data can
be interpreted using \textit{ab initio} codes,12–14 including temperature
dependence.25

A short literature review of previous TDPAC measurements
for TiO2 in the anatase and rutile phases, for investigations using
\(^{181}\text{Hf}\) and \(^{111}\text{In}\) as probes, is described in Ref. 16. In addition to con-
ventional isotopes, other works have successfully employed \(^{44}\text{Ti}\),26
\(^{111}\text{Ag}\),27,28 or, more recently, \(^{111}\text{mCd}\).29 Here we present an overview
of TDPAC measurements, including \(^{111}\text{In}\) experiments,16,30 and
new experimental results of single crystals after the implantation of
\(^{111}\text{mCd}\) at ISOLDE-CERN. To our knowledge, measurements have
never before been performed on annealing in an O\(_2\) atmosphere and
vacuum at 10\(^{-4}\) mbar.

II. AXIAL SYMMETRY OF THE ELECTRIC FIELD

Not only is the EFG different for the same probe, \(^{111}\text{Cd}\), if it
originates from different parents \(^{111}\text{In}, \(^{111}\text{Ag}, \text{ or }^{111}\text{mCd}\)), but the
axial symmetry of the EFG also differs. Minor distortions of the
angles from those of a pure TiO\(_2\) lattice geometry can produce dif-
ferent \( \eta \) values. During the time window of the measurement, the
nuclear quadrupole interaction takes place with either: (i) a Cd\(^{2+}\)
ion that has a filled 4d\(^{10}\) electron configuration; (ii) a Ta\(^{5+}\) ion that
has a filled 4f\(^{14}\) and an empty 5d\(^{9}\) electron configuration; or (iii) a
\(\text{Sc}^{3+}\) ion with \(3p^6\) and an empty \(3d^0\) electron configuration. Using \(^{111}\text{In}\), previous studies obtained the value \(\eta \approx 0.18\) for rutile, whereas \(\eta = 0.23\) was observed with \(^{111}\text{Ag}\). Studies profiting from the possibility of simultaneous \(^{111}\text{In}\) and \(^{111m}\text{Cd}\) implantation, which is currently possible only at ISOLDE, observed \(\eta = 0.175\). \(^{111}\text{In}\) and \(^{111m}\text{Cd}\) were implanted, three sites were reported with \(\eta = 0.22\), \(\eta = 0.79\), and \(\eta = 0\). Axial symmetry (\(\eta = 0\)) is expected in anatase due to its \(4m2\) crystal symmetry. However, \(\eta = 0.22(1)\) was reported for \(^{181}\text{Hf}\) after low-temperature annealing, which has been correlated with poor crystallinity. Figure 2 compares \(\eta\) and EFG values reported in previous work.

By considering \(^{44}\text{Ti}\) in the rutile phase, Ryu et al. reported the strong dependence of \(\eta\) on the internal O position, \(u\).\(^{17}\) However, the large asymmetry parameter appears not to be affected by small variations in the internal lattice parameter. In addition, they observed discrepancies in the temperature dependence of the asymmetry parameters for Ti and Hf.

III. THE ELECTRIC FIELD GRADIENT

Only a single local environment was reported with the titanium/scandium probe\(^{17,18}\) for rutile, although different fractions were observed after simultaneous \(^{111}\text{In}\) and \(^{111m}\text{Cd}\) implantations.\(^{20}\)

Several reports used \(^{181}\text{Hf}\) as probe nucleus.\(^{16,19,22-24}\) Phase transitions from anatase to rutile have been studied with \(^{181}\text{Hf}\)\(^{24}\) and three different nuclear quadrupole interactions have been reported, one of which was not assigned to rutile or anatase, which assumes \(V_{zz} \approx 9 \times 10^{21} \text{ V/m}^2\). Its origin was associated with the static inhomogeneity of the surface due to an uneven arrangement of oxygen bridging sites.\(^{24}\) The same unknown local environment was observed in two other works, with \(V_{zz} \approx 8.5 \times 10^{21} \text{ V/m}^2\)\(^{20}\) and \(V_{zz} \approx 8.7 \times 10^{21} \text{ V/m}^2\).\(^{22}\) Ab initio calculations are, therefore, required to interpret the data. For the anatase phase, \(V_{zz} \approx 4.6 \times 10^{21} \text{ V/m}^2\) was reported, while \(V_{zz} \approx 14 \times 10^{21} \text{ V/m}^2\) was the average value assigned to the rutile structure. The values reported with \(^{111}\text{In}\) can be found in Ref. \(^{16}\). For instance, for room temperature the values for site 1 and 2 were \(V_{zz} \approx 5.6 \times 10^{21} \text{ V/m}^2\) and \(V_{zz} \approx 9.6 \times 10^{21} \text{ V/m}^2\), respectively.

A peculiar aspect of the nuclear quadrupole interactions observed for titanium dioxide is the increase of the quadrupole frequencies with temperature. This was clearly observed with the \(^{181}\text{Hf}\)\(^{22,24}\) and \(^{44}\text{Ti}\) probes. Since titanium is a very active getter,\(^{26}\) this behavior offers strong evidence for oxygen diffusion from the surface. The diffusion effect has been previously studied for different temperature ranges in single crystals\(^{27}\) and thin films.\(^{28}\) However, the same effect has not been observed uniquely for \(^{111}\text{In}\).\(^{22}\) Theoretical works show that Cd impurity induces anisotropic structural relaxations\(^{14,15}\) on the nearest oxygen neighbors. The diffusion of oxygen into the host Ti\(^{4+}\)O\(_2^-\) is affected by distortions and lattice imperfections caused by the probes. With Sc incorporation, the cell volume tends to increase due to the ionic radius; however, this is an anisotropic process influenced by the number of O vacancies created by the heterovalent character of this probe.\(^{14}\) It is expected that after Ta doping, the formation of Ti vacancies or Ti\(^{3+}\) is enhanced, whereas the formation of anionic vacancies, such as O vacancies, is suppressed. Therefore, competition between two diffusion processes must be considered. Thermal reduction is important from \(875\) °C\(^{27}\) for the out-diffusion mechanism while the in-diffusion process takes place below that temperature and depends on the annealing atmosphere. Furthermore, re-oxidation and reduction effects are influenced by interstitial Ti, which becomes mobile from about \(200\) °C.\(^{31}\) If the TDPAC probes are in the migration pathways, both diffusion processes will influence the perturbed angular correlation.

IV. PRE-DOPED SAMPLES

It is well known that doping can significantly alter the properties of titanium oxide, making it suitable for many applications.\(^{32}\) To our knowledge, few works have reported on pre-doped titanium oxide samples measured by the TDPAC technique. For instance, doping with iron enhances its photocatalytic activity, allowing it
to absorb higher wavelengths of light.\textsuperscript{31} Measurements carried out using $^{111}$In in Fe-doped thin films\textsuperscript{32} show only the paramagnetic state of the hyperfine interaction. These results agree with Mössbauer emission experiments\textsuperscript{33} performed at ISOLDE-CERN, which also showed Fe$^{3+}$ in the paramagnetic state.

Doping with an optimal concentration of Zr can lead to a higher photoactivity.\textsuperscript{33} The reported mean values of the nuclear quadrupole interaction frequency and the asymmetry parameter measured using $^{181}$Hf probes on Zr-doped rutile in Ref.\textsuperscript{37} did not change significantly. However, the authors noted that the frequency distribution depends on the amount of Zr.

V. EXPERIMENTAL

TiO$_2$ (100) single crystals, of 99.6% purity, were obtained commercially from Goodfellow. The molten Sn target was installed at the General Purpose Separator (GPS) at ISOLDE-CERN for the production of a pure $^{111}$mCd beam. Room temperature $^{111}$mCd implantation at low dose, $\sim$5x10$^{13}$ atoms/cm$^2$, was performed at 30 kV. Following implantation, rapid thermal annealing (RTA) was performed at 873 K for 10 minutes in vacuum (10$^{-4}$ mbar) or in a flux of O$_2$. Measurements were carried out at room temperature in air using an analogue TDPAC setup equipped with four detectors with conical BaF$_2$ scintillators. The time resolution was 0.96 ns (FWHM). Theoretical perturbation functions were fitted to spectra using \textit{Nightmare} software to extract the hyperfine parameters.

VI. RESULTS AND DISCUSSION

The TDPAC spectra in Fig. 3 display a superposition of two quadrupole interaction signals. To aid discussion, the hyperfine parameters obtained will be quoted as A and B, corresponding to local environment 1 and 2, respectively, for measurements taken after annealing in vacuum.

The interaction (A) presents a well-defined electric quadrupole interaction frequency $\delta = 8(3)$% and an asymmetry parameter $\eta = 0.22(1)$, corresponding to $\omega_0 = 101(3)$ Mrad/s. The fraction, f, of the crystalline site occupied by the TDPAC probe was $82(7)$%. Similar frequency and asymmetry parameters have been reported previously\textsuperscript{30} and attributed to Cd at the Ti-site. However, the reported fraction value was much lower (12$\%$) than that reported in this work ($82(7)$%). This means that rapid thermal annealing at lower vacuum, ($\sim$10$^{-4}$ mbar), could induce a much higher fraction for Cd at substitutional Ti-sites than the result reported for $10^{-2}$ mbar.

The second local environment (B) presents the frequency $\omega_0 = 294(7)$ Mrad/s with $\eta = 0.17(1)$ for $\delta = 2(4)$% and $f = 18(5)$%. The existence of an oxygen vacancy, in the oxygen octahedron surrounding the impurity, can cause an increase in $\omega_0$, in contrast with the result without vacancy.\textsuperscript{30} By comparing our results with those from previous work,\textsuperscript{20} on $^{111}$mCd $\omega_0 = 235(8)$ Mrad/s with $\sigma = 117(10)$ Mrad/s or on $^{111}$mCd for $\omega_0 = 257(14)$ Mrad/s with $\sigma = 68(16)$ Mrad/s, we were able to associate the observed hyperfine parameters with defects. Therefore, we expect that this local environment is related to non-stoichiometric titanium dioxide and/or Magnéli phases\textsuperscript{38} resulting from the thermal treatment in vacuum and implantation processes.

We now discuss the results obtained after RTA in an O$_2$ atmosphere. The nuclear quadrupole interaction for the main local environment presents a fraction $f = 92(8)$% for $\omega_0 = 100(2)$ Mrad/s with $\eta = 0.20(1)$ and $\delta = 4(2)$%. The frequency and asymmetry parameters are very close to the local environment (A). In contrast with the other spectrum, the data show a lower damping in modulations of the R(t) function and higher fraction value. This indicates the ease with which Cd occupies regular substitutional Ti-sites upon thermal treatment in O$_2$.

The second local environment presents a higher frequency, $\omega_0 = 295(5)$ Mrad/s, to that of Cd at the substitutional Ti-site associated with a defect, and assumes a lower frequency distribution $\delta = 1(4)$%. In comparison with the local environment (B), its fraction decreased to $f = 8(6)$%, and the asymmetry parameter $\eta = 0.15(1)$ assumed similar value. There are two types of effects that should be considered: the non-stoichiometry of the system and the lattice distortions caused by Cd as an impurity. Both interfere in the mechanism of oxygen diffusion.\textsuperscript{27}

VII. NEW PERSPECTIVES

This paper briefly describes perturbed angular correlation measurements in titanium dioxide, and we conclude that our investigations address several challenging topics. Results obtained using perturbed angular correlation measurements have generated much interest over the past few decades. Innovative experimental methods, such as those of Banerjee et al.\textsuperscript{23} who measured TDPAC spectra after exposing titanium dioxide to gamma radiation, highlights important potential applications, such as an immobilizing matrix for nuclear waste. Here we have reported on $^{111}$mCd measurements carried out at ISOLDE-CERN in different annealing atmospheres. The hyperfine parameters were very sensitive to local changes in the non-stoichiometry of rutile, as can be observed in the behavior of the second local environment. Currently, we are investigating local defects in nanostructured TiO$_2$:H thin films to improve their inherent photocatalytic efficiency.\textsuperscript{31}

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