NMR Detection of Oxygen Isotopes in TiO$_2$ Single Crystal*


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Z. Naturforsch. 53a, 305–308 (1998); received December 31, 1997

We studied the electric quadrupole interactions of Oxygen isotopes in a TiO$_2$ single crystal. For $^{13}$O and $^{17}$O nuclei, quadrupole coupling constants were measured by the $\beta$-NMR technique, and for the $^{17}$O nucleus the FT-NMR technique was utilized. We synthesized a TiO$_2$ single crystal which was enriched in $^{17}$O up to 5 atom % to observe NMR signals without any perturbations from impurities. Using the known quadrupole moment of $^{17}$O, EFGs at an O site in TiO$_2$ and the quadrupole moments of $^{13}$O and $^{17}$O were determined.

1. Introduction

$\beta$-NMR is a very useful technique for the investigation of hyperfine interactions as well as nuclear moments [1]. To observe $\beta$-NMR efficiently, it is important to select a proper sample in which the polarization of the probe nuclei is well maintained. Recently, a TiO$_2$ single crystal was found to be a good implantation medium. For the case of $^{41}$Sc in a TiO$_2$ crystal, the maintained polarization reached up to 60% of the initial polarization [2], and it was reported that the TiO$_2$ crystal preserved 100% of the polarization of $^{12}$N [1]. Therefore, the systematic study of the hyperfine interactions of impurities in TiO$_2$ is of great importance for understanding the implantation mechanism and the electronic structure of impurities. In this paper we studied the electric quadrupole interactions of oxygen isotopes in TiO$_2$ single crystal (tetragonal). We detected $\beta$-NMR of short-lived $^{13}$O ($I^p = 3/2^-$, $T_{1/2} = 8.6$ msec) and $^{17}$O ($I^p = 5/2^-$, $T_{1/2} = 27.0$ sec) in TiO$_2$, the crystal structure of which is of the rutile type. The parameters of the electric quadrupole coupling constants for them in TiO$_2$ were determined.

An other aim of the present study was the determination of the electric quadrupole moment of the short-lived unstable nuclei $^{13}$O and $^{19}$O from the quadrupole coupling constants determined here. The knowledge of the electric field gradient (EFG) at the oxygen nucleus in the crystal is indispensable to extract the value of nuclear quadrupole moment of it. For this purpose, the Fourier-Transformed NMR (FT-NMR) was detected on the stable isotope of $^{17}$O in the crystal in a strong field at room temperature. In order to measure it accurately, the NMR signal was increased by using a newly synthesized TiO$_2$ crystal [3] in which the enriched isotope of $^{17}$O was doped, the concentration of which was about 5% of the oxygen atoms. In the crystal no other impurities were artificially doped. The EFG at the oxygen site had been determined for a TiO$_2$ crystal in which a certain amount of chromium was doped to make it possible to detect the NMR signal of $^{17}$O [4]. The difference of the old data from the present one is reported. These experimental values are compared with $ab$ initio calculations of the EFG at the oxygen site in TiO$_2$ [5].

2. Experimental Procedure and Results

2.1 $^{17}$O in TiO$_2$

The experimental principle and techniques were essentially similar to those of the previous $\beta$-NMR measurements [1]. The $^{17}$O was produced through the projectile fragmentation in the reaction of $^{16}$O + Be. The primary beam of $^{16}$O with the kinetic energy of 135 MeV/u was from the Ring Cyclotron ($K = 540$) at RIKEN and...
The experimental procedure was the same as that for $^{13}$O. Production of polarized $^{19}$O nuclei was carried out via the $^{18}$O (d, p) $^{19}$O reaction. An incident beam of deuterons with an energy of 3.25 MeV, extracted from the Van de Graaff accelerator at the Osaka University was used for the reaction. The deuteron beam was directed on a Ti$^{18}$O$_2$ target which was produced by oxidizing a titanium foil of 0.5 mm thickness by $^{18}$O. The recoil angle of $^{19}$O was selected to be $(40 \pm 8)^{\circ}$. A TiO$_2$ crystal was used as an implantation medium with its crystal

![Fig. 1. $\beta$-NQR spectrum of $^{13}$O in TiO$_2$.](image)

(bombarded the 481 mg/cm$^2$ thick Be target. The $^{13}$O nuclei ejected at angles of 0.5$^{\circ}$ to 2.5$^{\circ}$ relative to the incident beam were separated by RIPS (RIKEN Projectile Fragment Separator). As a result, the nuclear polarization was about $-2.3\%$. Thus obtained polarized nuclei were implanted into a disc of TiO$_2$ crystal with 0.2 mm thickness, which was placed in a magnetic field of 0.8 T. The crystal c-axis of TiO$_2$ was placed parallel to the external field. Under the EFG provided by the TiO$_2$, three transition frequencies are given for $^{13}$O. To observe the NMR efficiently, the $\beta$-NQR method was employed, and the total polarization was completely inverted by the AFP method. For this purpose, 6 RFs, whose intensity and duration time was about 7 Oe and 1 ms, respectively, were applied. The $\beta$-NQR was detected as a function of $\Delta f$, which was defined as a half of the quadrupole splitting or the deviation from the Larmor frequency. The frequency modulation width was $\pm 15$ kHz. A typical spectrum is shown in Fig. 1. From the analysis of the spectrum, $|eqQ/h|$ was obtained to be 1490 $\pm$ 75 kHz.

### 2.2 $^{19}$O in TiO$_2$

$^{19}$O is the only stable oxygen isotope which has a finite electric quadrupole moment. Since the natural abundance of $^{17}$O is 0.04%, the NMR signal of $^{19}$O in a TiO$_2$ crystal is almost undetectable. Gabathuler et al. succeeded to enhance the signal of $^{17}$O by doping a certain amount of Cr, and determined the coupling constant and the asymmetry parameter to be $1497 \pm 4$ kHz and $0.868 \pm 0.005$, respectively [4]. To get a reliable coupling constant, we synthesized a TiO$_2$ single crystal which was enriched in $^{17}$O up to about 5 atom % and detected the FT-NMR of $^{17}$O without any perturbations from artificially doped impurities. The c-axis of the TiO$_2$ single crystal was set perpendicular to the external field. The transition frequencies between $m = \pm 1/2 \leftrightarrow \mp 1/2$ and $m = \pm 1/2 \leftrightarrow \pm 3/2$ were measured as a function of the rotation angle for the determination of the quadrupole coupling constant and the asymmetry parameter of the EFG. The NMR was detected under an external field of 7.0 Tesla and 9.4 Tesla for separating the quadrupole effects from the anisotropic chemical shifts. The results are shown in Figure 2. The lines are the theoretical ones best fitted to the data. The quadrupole coupling constant was obtained to be $1512 \pm 4$ kHz and the asymmetry parameter was determined to be $0.831 \pm 0.007$.

| Experiment  | $|eqQ/h|$ (kHz) | $V_{zz}$ ($\times 10^{15}$ V/cm$^2$) | $\eta$ |
|-------------|---------------|----------------------------------|-------|
| present result | 1512 $\pm$ 4 | 240 $\pm$ 30 | 0.831 $\pm$ 0.007 |
| Gabathuler et al. [4] | 1497 $\pm$ 4 | 240 $\pm$ 30 | 0.868 $\pm$ 0.005 |
| Theory | FLAPW method [7] | $-196$ | 0.84 |

Table 1. Experimental and theoretical EFGs for the O site in TiO$_2$. $Q(\text{O}) = 26 \pm 3$ mb is used.
3. Discussion

Using the known quadrupole moment of $^{17}\text{O}$ [6] we extracted the EFG from the coupling constant. In Table 1, the experimental values of EFGs are summarized with Gabathuler's data. The difference of the asymmetry parameter between them suggests that a certain disturbance from the Cr might exist. The theoretical prediction by the KKR method in the framework of the local density approximation and the prediction by the FLAPW method [7] are also shown in Table 1.

Now, we obtained the EFG at the O site in TiO$_2$ with a high precision. Therefore, the quadrupole moment of $^{13}\text{O}$ and $^{19}\text{O}$ can be derived from the quadrupole coupling constant. Two independent sites with similar populations of implanted nuclei were observed for $^{13}\text{O}$ as shown in Figure 1. This means that half of them was located at the substitutional site of oxygen in the crystal, which was expected to be most likely in the present implantation, and that the other half was located in a site different from the substitutional site. Assuming that the peak at the higher frequency is from the $^{13}\text{O}$ nuclei implanted at the substitutional site of oxygen, the quadrupole moment of $^{13}\text{O}$ was determined to the $26 \pm 3$ mb. This is comparable with the theoretical value of $16$ mb by OXBASH with Cohen-Kurath wave functions. On the contrary, if we assume a substitutional location for the smaller coupling frequency of $\Delta f \sim 15$ kHz obtained from the second peak in Fig. 1, we have $|Q| \sim 6$ mb which is much smaller than the prediction. Therefore the second site cannot be sub-
stitutional. By a similar consideration, the quadrupole moment of $^{19}\text{O}$ is determined to be $3.8 \pm 0.5$ mb.

In the measurements of the stable isotope, only one definite field gradient was observed, as expected. Therefore, the one extra site found in the $\beta$-NMR of $^{13}\text{O}$ and $^{19}\text{O}$, suggests a site with shallow potential, an isometric state, produced through the implantation of the ions in the crystal.

4. Summary

We determined the quadrupole coupling constants of $^{13}\text{O}$, $^{19}\text{O}$ and $^{17}\text{O}$ in a TiO$_2$ single crystal. Using the known quadrupole moment of $^{17}\text{O}$, the EFG at the O site was extracted. The agreement with the theoretical predictions is fairly good. The quadrupole moments of $^{13}\text{O}$ and $^{19}\text{O}$ were determined from their coupling constants in TiO$_2$ by using the obtained EFG value. The spectrum of $^{13}\text{O}$ and $^{19}\text{O}$ suggests that there are two implantation sites in TiO$_2$. It is supposed that one of the extra sites is a site with shallow potential produced through the ion implantation.

Acknowledgement

The present work was supported in part by the Grant in Aid for Scientific Research and the Special Project for Isotope-Beam Science from the Ministry of Education, Culture and Science, Japan.


