

FT-NMR Detection of ^{45}Sc , ^{49}Ti and ^{93}Nb in TiO_2 Single Crystal*

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Z. Naturforsch. **53a**, 549–551 (1998); received December 31, 1997

In order to determine the electric quadrupole moment of the short-lived β -emitter ^{41}Sc from the quadrupole coupling constant in TiO_2 , we measured the field gradient by detecting the Fourier-Transformed-NMR of stable isotope ^{45}Sc doped in TiO_2 . Also, in order to study the electronic structure of impurities systematically, EFGs were measured for ^{45}Sc , ^{49}Ti and ^{93}Nb in a TiO_2 single crystal.

Key words: TiO_2 ; ^{41}Sc ; Quadrupole Moment; Transition Metal Impurity; Electric Field Gradient.

1. Introduction

Nuclear electric quadrupole moments are important and indispensable clues for the investigation of nuclear shell structure and nucleon interactions. Particularly the static quadrupole moments of the LS closed shell ± 1 nucleon nuclei are of interest, because of their simple nuclear structure that make theoretical prediction easy. Previously, the quadrupole coupling constant for ^{41}Sc ($I^\pi = 7/2^-, T_{1/2} = 0.596$ sec) implanted in a TiO_2 crystal had been determined by use of modified β -NMR technique [1]. In that experiment, the TiO_2 (rutile) single crystal was used to provide an electric field gradient (EFG) and to keep the nuclear spin polarization of ^{41}Sc . It has been concluded that the implanted ^{41}Sc atoms were located at the substitutional site of Ti atoms in the TiO_2 crystal. Therefore, to know the quadrupole moment of ^{41}Sc , the knowledge on the EFG at the ^{41}Sc site is indispensable. For this purpose, high field nuclear magnetic resonance had been studied on the dilute stable isotope ^{45}Sc atoms embedded in TiO_2 , and the EFG at the Sc site was measured.

Also, in order to investigate the electronic structure of the impurities and the lattice relaxation effects caused by

the odd impurities, EFGs have been measured for ^{45}Sc , ^{49}Ti and ^{93}Nb in a TiO_2 single crystal. Concerning TiO_2 , EFGs at host Ti site had already been measured by NMR [2, 3], and EFGs at impurities ^{111}Cd and ^{181}Ta had already been studied by the PAC technique [4, 5]. These experimental results were well reproduced by *ab initio* EFG calculations in the framework of the KKR method with the local density approximation [6].

2. Crystal Structure

The rutile (TiO_2) structure (Fig. 1) is tetragonal and has two molecules in the unit cell. Metal atoms (Ti) are at $(0, 0, 0)$, $(1/2, 1/2, 1/2)$ and anions (O) at $(1 \pm u, 1 \pm u, 0)$, $(1/2 \pm u, 1/2 \mp u, 1/2)$ with the internal coordinate u

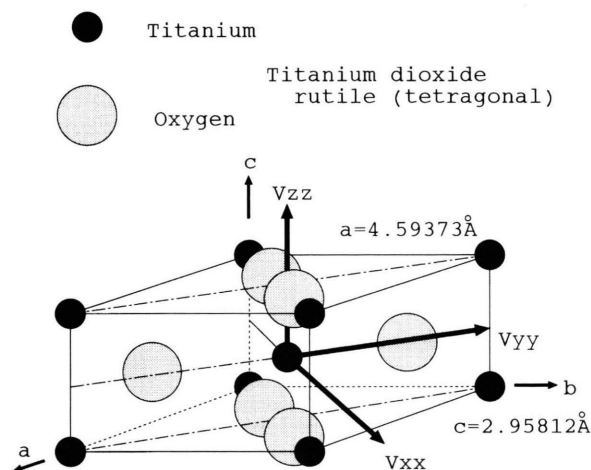


Fig. 1. Unit cell of TiO_2 (rutile). The principal coordinate system for the electric field gradient at the Ti site also shown.

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interaction, Pisa, July 20–25, 1997.

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[7]. Two metal atoms are identical crystallographically, but different geometrically, *i.e.* the metal positions are identical by a 90° rotation around the crystal c axis followed by the $(1/2, 1/2, 1/2)$ translation. This is clear when we focus on the octahedron of oxygen atoms which has different orientations for two metal ions.

Considering this crystal symmetry, the principal axes of the EFG tensor are like the one shown in Fig. 1 for pure TiO_2 . For the body centered Ti atom, the Z axis points along the crystallographic c axis, the Y axis along $\langle 110 \rangle$ (towards the oxygen) and the X axis along $\langle 110 \rangle$. In this conventional notation the coordinate axes are chosen such that

$$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|,$$

$$V_{ZZ} + V_{YY} + V_{XX} = 0,$$

and the EFGs are described with the parameters q (the largest component of the absolute value of the diagonalized EFG tensor) and η (the asymmetry parameter), which are defined as

$$q = V_{ZZ},$$

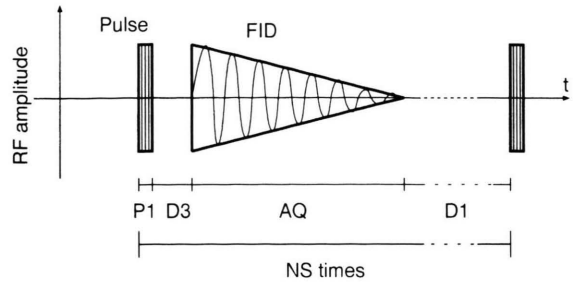
$$\eta = (V_{XX} - V_{YY})/V_{ZZ}.$$

At the Sc site in the TiO_2 , however, it was shown by the present experiment that the absolute value of V_{YY} becomes the largest component of the coordinate system in Fig. 1, resulting the inequality $|V_{YY}| > |V_{ZZ}| > |V_{XX}|$. So the Z and Y axes have to be interchanged in calculating the asymmetry parameter η .

3. Experimental Procedure

The electric quadrupole interactions were investigated with the Pulsed-Fourier-Transformed-NMR method, which is well established for stable nuclei. The sample was prepared by mixing a proper amount of $^{45}\text{Sc}_2\text{O}_3$ powder and TiO_2 material before TiO_2 single crystal was synthesized [8]. The concentration of ^{45}Sc and ^{93}Nb in TiO_2 were 0.5 atom% and 0.05 atom%, respectively. The signals from ^{49}Ti , the natural abundance of which was 5.5% were detected without enrichment of the isotope.

The $m = \pm 1/2 \leftrightarrow \mp 1/2$ transition frequencies were observed for ^{45}Sc ($I = 7/2$), ^{49}Ti ($I = 7/2$) and ^{93}Nb ($I = 9/2$) as a functions of the rotation angle of the crystal around the axis vertical to the external field. For the pure and Nb doped TiO_2 crystal the $\langle 110 \rangle$ axis was placed close to the rotation axis, and for the Sc doped TiO_2 crystal the crystallographic a -axis was set so. FT-NMR



	P1(μsec)	D3(μsec)	AQ(msec)	D1(sec)	NS(times)
^{45}Sc	1	18	12	5	360
^{49}Ti	2.5	30	16	1	600
^{93}Nb	1	30	5	2	1800

Fig. 2. Summary of parameters of the pulse sequence for FT-NMR measurements.

measurements were performed by a simple one pulse sequence. The parameters of the pulse sequence are summarized in Fig. 2. From the analyses, we extracted the quadrupole coupling constant eqQ/h and the asymmetry parameter η , as well as the exact direction of the crystal axes.

4. Results

For Sc in the TiO_2 , the experiments were performed under external magnetic fields of 7.0 and 9.4 T to separate out the effect of the anisotropic chemical shift. The observed transition frequencies are shown in Fig. 3 as a functions of crystal orientation. Two signals were observed because the unit cell had two geometrically different positions for the metal. The shapes of the rotation patterns at the two different external magnetic field differ slightly. This is because of the anisotropic chemical shift. The solid curves are the theoretical ones best fitted to the data in which the anisotropic chemical shift was taken into account.

For ^{93}Nb , the NMR was detected only under the external field of 7 T. However, we can separate out the anisotropic chemical shift effects from the angular dependence of the frequency shift.

For ^{49}Ti , the NMR was detected only under the external field of 9.4 T. Because of the low Larmor frequency, the perturbation due to the anisotropy of the chemical shift was negligible.

The results of analysis are summarized in Table 1.

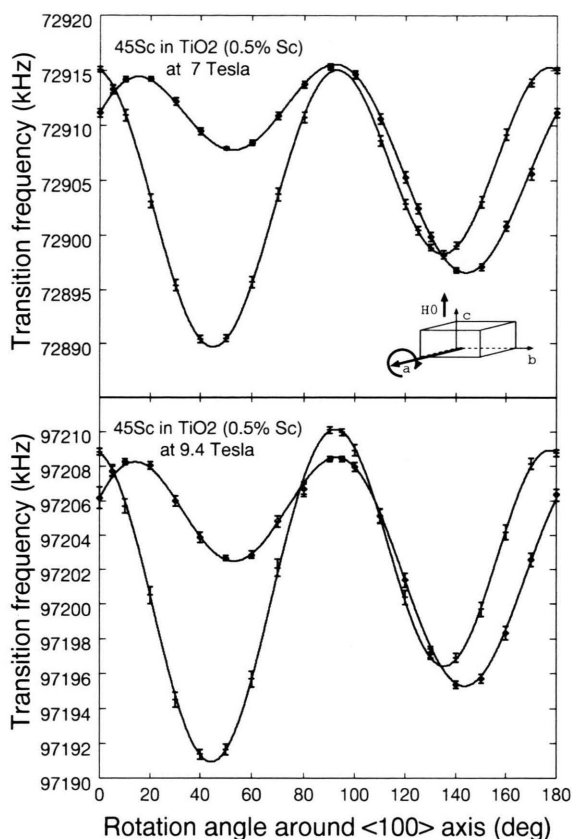


Fig. 3. Resonance frequency as a function of crystal orientation. The $m = \pm 1/2 \leftrightarrow \mp 1/2$ transition frequencies are shown. The crystal was rotated about the axis near $\langle 100 \rangle$.

5. Discussion

Since the electric quadrupole moments of ^{45}Sc , ^{49}Ti and ^{93}Nb were known, the EFG's at their sites were derived from the experimental values of eqQ/h . In Table 1, it is shown that the maximum principal components q and the asymmetry parameters of them differ from each other. In order to explain the observed EFGs, *ab initio* calculations of the EFGs at Sc, Ti, Nb, Cd, and Ta site

Table 1. Experimental results of electric field gradients ($\times 10^{15} \text{ V/cm}^2$) at the Sc, Ti and Nb sites in TiO_2 (rutile).

	^{45}Sc	^{49}Ti	^{93}Nb
Nuclear spin	7/2	7/2	9/2
$Q (\text{fm}^2)$	$-23.6(2)$ [9]	$+24(1)$ [10]	$-32(2)$ [10]
sample shape (mm)	$5 \times 7 \times 20$	$10 \times 10 \times 2$	$8 \times 8 \times 12$
rotation axis	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$
external field (T)	7, 9.4	9.4	7
$leqQ/hl$ (MHz)	11.02 (1)	14.00 (3)	49.83 (13)
η	0.983 (3)	0.192 (8)	0.463 (7)
$ q $	193 (2)	241 (11)	644 (40)
\hat{q}	$\langle 110 \rangle$	$\langle 001 \rangle$	$\langle 001 \rangle$

were performed. The calculated EFGs at the impurity site by the KKR method successfully predicted the systematic variation of the experimental results. The computational details are explained in [6].

The quadrupole coupling constant of ^{41}Sc in TiO_2 had been determined by T. Minamisono to be $eqQ(^{41}\text{Sc})/h = 7.31(7)$ MHz [1]. Using the presently measured field gradient, $Q(^{41}\text{Sc}) = -15.6(3) \text{ fm}^2$ was determined.

6. Summary

Both at the host Ti atom and at the impurity Sc and Nb atom, the EFGs were determined experimentally. It was shown that their principal components and asymmetry parameters of the EFG differ significantly from each other. Using the obtained EFG value at Sc in TiO_2 , $Q(^{41}\text{Sc}) = -15.6(3) \text{ fm}^2$ was determined. *Ab initio* calculations of the EFGs by the KKR method with the supercell reproduced there experimental results well.

Acknowledgement

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

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