FT-NMR Detection of $^{45}$Sc, $^{49}$Ti and $^{93}$Nb in TiO$_2$ Single Crystal*


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In order to determine the electric quadrupole moment of the short-lived $^{41}$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 ($I^* = 7/2^+$, $T_{1/2} = 0.596$ sec) implanted in a TiO$_2$ crystal had been determined by use of modified $\beta$-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 ± $u$, 1 ± $u$, 0), (1/2 ± $u$, 1/2 ± $u$, 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.](image-url)

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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 〈110〉 (towards the oxygen) and the X axis along 〈110〉. 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 $\eta$ (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 $\eta$.

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 $^{45}$Sc$_2$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 〈110〉 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 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 $\eta$, 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.


5. Discussion

Since the electric quadrupole moments of $^{45}\text{Sc}$, $^{49}\text{Ti}$ and $^{93}\text{Nb}$ 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, \textit{ab initio} calculations of the EFGs at Sc, Ti, Nb, Cd, and Ta site 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 $^{41}\text{Sc}$ 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, $Q(^{41}\text{Sc}) = -15.6 (3)$ 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$_2$, $Q(^{41}\text{Sc}) = -15.6 (3)$ fm$^2$ was determined. \textit{Ab initio} calculations of the EFGs by the KKR method with the supercell reproduced their experimental results well.

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\begin{table}[h]
\centering
\caption{Experimental results of electric field gradients $(\times 10^{15}$ V/cm$^2$) at the Sc, Ti and Nb sites in TiO$_2$ (rutile).}
\begin{tabular}{|c|c|c|c|}
\hline
 & $^{45}\text{Sc}$ & $^{49}\text{Ti}$ & $^{93}\text{Nb}$ \\
\hline
Nuclear spin & 7/2 & 7/2 & 9/2 \\
$Q$(fm$^2$) & $-23.6(2)$ & $+24(1)$ & $-32(2)$ \\
\hline
sample shape (mm) & $5 \times 7 \times 20$ & $10 \times 10 \times 2$ & $8 \times 8 \times 12$ \\
rotation axis & (100) & (110) & (110) \\
\hline
external field (T) & 7, 9.4 & 9.4 & 7 \\
$eqQ/h$ (MHz) & $11.02(1)$ & $14.00(3)$ & $49.83(13)$ \\
$\eta$ & $0.983(3)$ & $0.192(8)$ & $0.463(7)$ \\
$ql$ & $193(2)$ & $241(11)$ & $644(40)$ \\
$q$ & $q(110)$ & $q(001)$ & $q(001)$ \\
\hline
\end{tabular}
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