EPR Spectroscopy

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Probing the Local Environment of Ti^{3+} Ions in TiO_2 (Rutile) by ^{17}O HYSCORE**

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Dedicated to the Fritz Haber Institute, Berlin, on the occasion of its 100th anniversary

Monitoring the state of excess electrons in oxide semiconductors is crucial for understanding and harnessing the properties of these materials for a variety of challenging applications spanning from catalysis to light harvesting, and gas sensing.[1–3] Titanium dioxide (TiO_2) is, among other semiconducting oxides, one of the most investigated systems and can be considered as a model substrate to study phenomena concerned with photoelectric charge generation and transport.[4]

Rutile, the most thermodynamically stable phase of TiO_2, has a tetragonal crystal structure and, at the stoichiometric composition, is an insulator with a bandgap of about 3 eV. The key to the applications of this oxide in different areas is excess electrons associated with intra-bandgap defective states usually induced by reductive treatment or n-type doping with aliovalent elements (e.g., Nb or F). Recently, introduction of Ti^{3+} states has been reported as an effective way to produce TiO_2-based materials capable of visible-light photosplitting of water.[5] Despite the importance of these defective states in determining the physical and chemical properties of TiO_2, however, the very nature of reduced states in TiO_2 remains poorly understood and is at the center of a lively scientific debate.[6–8]

Electron paramagnetic resonance spectroscopy is one of the most potent techniques for investigating the microscopic nature of paramagnetic defects in solids,[9] and is often employed to ascertain the presence of reduced states in TiO_2, usually associated with Ti^{3+} ions. Detailed EPR studies on oxygen-deficient TiO_2 (rutile) single crystals, based on the principal values and orientations of the g-factor splittings, have provided evidence for the existence of interstitial Ti^{3+} ions with distorted octahedral coordination.[10,11] The spatial distribution of the unpaired electron on the Ti^{3+} ion, however, cannot be determined through measuring the g factor alone, but requires measurement of the interaction between the magnetic moment of the unpaired electron and those of surrounding nuclei (hyperfine interaction), the majority of which in TiO_2 are nonmagnetic ($I = 0$).

As part of a systematic study of the nature of reduced states in TiO_2, we have now synthesized an oxygen-deficient, Ti^{3+}-rich (blue) polycrystalline TiO_2 sample enriched in ^{17}O ($I = 5/2$) and performed a hyperfine sublevel correlation (HYSCORE)[12] study to investigate the hyperfine interaction (hfi) between Ti^{3+} ions and lattice coordinated oxygen atoms.

The XRD patterns of the as-synthesized blue TiO_2 polycrystalline powders (Supporting Information, Figure 1S) indicate that the dominant phase is rutile, and only a minor contribution (ca. 3 %) of anatase phase is present. The optical absorption spectrum of the as-synthesized sample (Figure 1 A) is characterized by a broad absorption band starting at about 600 nm and extending in the near-infrared (NIR) region of the spectrum, which imparts a blue coloration to the material. This band has been interpreted[13] as due to $Ti^{3+}Ti^{4+}$ charge-transfer phenomena associated with short-lifetime electron delocalization occurring at room temperature in neighboring structural sites. We note that no shift of the bandgap edge with respect to stoichiometric rutile is observed (see Supporting Information, Figure S2). Consistent with the presence of Ti^{3+} species is the CW-EPR spectrum recorded at 4 K of the ^{17}O enriched sample shown in Figure 1 B c. The spectrum is characterized by pseudo-axial symmetry and principal g factors (Table 1) characteristic of a single unpaired electron ($S = 1/2$) in an axial crystal-field symmetry. Com-

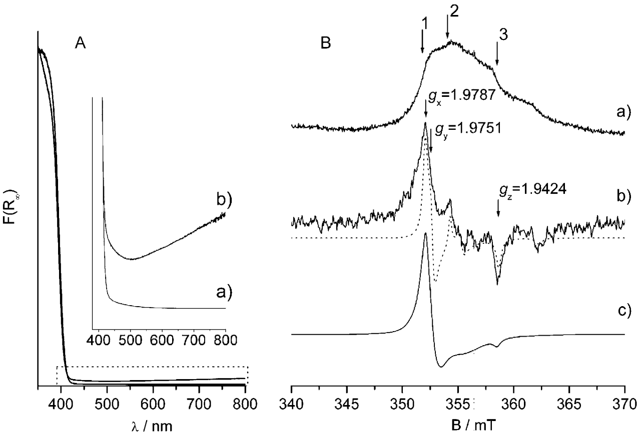

Figure 1. A) Optical absorption spectra of stoichiometric (a) and reduced (b) rutile. B) a) ESE-detected EPR spectrum of the reduced rutile sample, b) first derivative of a) and computer simulation (dotted curve), and c) CW EPR spectrum of the same sample. All spectra were recorded at 4 K. The arrows in B) a) indicate the magnetic field positions at which the HYSCORE spectra were recorded.

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Table 1: Spin Hamiltonian parameters for the dominant EPR signal. The ^{17}O hfi and nuclear quadrupole coupling constants are given in units of MHz.

g_x	g_y	g_z	A_x	A_y	A_z	β [°]	$\lvert e^2qQ/h \rvert$	Ref.
1.9787	1.9751	1.9424	5.5 ± 0.5 0.5 ± 0.3	8.5 ± 0.5 0.5 ± 0.3	10.0 ± 0.5 1.4 ± 0.1	80 ± 10 –[a]	1.5 ± 0.2 1.9 ± 0.3	this work
1.9780	1.9746	1.9414						[11]

[a] Unresolved.

puter simulation of the CW and electron spin echo (ESE) detected EPR spectra of normal (Supporting Information) and ^{17}O-enriched (Figure 1B) samples allows the principal g values of the dominant signal to be extracted (Table 1). The presence of additional lines in the range $g = 1.97$–1.92, clearly revealed by the ESE spectra, points to the presence of other Ti^{3+} centers with approximate axial symmetry. The relative abundance of these other Ti^{3+} species is about 10–20% as estimated from spectral simulation.

The principal g factors of the dominant species (Table 1, Figure 1B) agree quantitatively with values observed by Hasiguti and Aono[11] for Ti^{3+} interstitial ions in rutile single crystals which underwent the same thermal treatment as in this work. This agreement strongly suggests identity of the two defects. However, another recent single-crystal study[14] on Ti^{3+} ions in fluorine-doped rutile gave an almost identical **g** tensor which is assigned to lattice ions and not to interstitials, in contradiction to Hasiguti and Aono.

To probe the spatial extent of the unpaired electron wave function of these Ti^{3+} ions and their local environment, HYSCORE spectra were recorded at different field positions corresponding to the principal g values of the dominant EPR signal. A typical spectrum (Figure 2) shows the presence of ^{17}O correlation peaks in both $(+,+)$ and $(-,+)$ quadrants, which are absent in the non-enriched sample.

The two off-diagonal cross-peaks at about (−2, 6) and (−6, 2) MHz in the $(-,+)$ quadrant (^{17}O-1 in Figure 2) are separated by approximately $2\nu_O$ (where $\nu_O = 2.021$ MHz is the ^{17}O Larmor frequency) and relate the m_I $1/2 \rightarrow -1/2$ transitions of the two m_S manifolds. The narrow shape of the ridges and the absence of multiple quantum transitions in the spectrum indicate a low value of the quadrupole interaction consistent with ^{17}O NMR measurements of $e^2qQ/h = 1.4$ MHz.[15] Under these circumstances the frequencies of the observed transitions are given to first order (neglecting the quadrupole interaction) by $\nu_{\alpha(\beta)} = (A/2 \pm \nu_O)$, where A is the hyperfine coupling for the given orientation of the paramagnetic species. The values of A extracted from the HYSCORE spectra recorded at the observer positions indicated in Figure 1Ba and refined by computer simulation[16] (Supporting Information) are reported in Table 1. From these values a Fermi contact (a_{iso}) term of about 8 MHz and an anisotropic coupling tensor $\mathbf{T} = [-2.5 \pm 0.5 + 0.5 \pm 0.5 + 2.0 \pm 0.5]$ MHz are extracted. The orientation of the tensor relative to the **g**-tensor principal frame, given by the Euler angle β, shows that ^{17}O is situated in a plane perpendicular to g_z. A maximum quadrupole interaction (e^2qQ/h) of about 1.5 MHz is found.

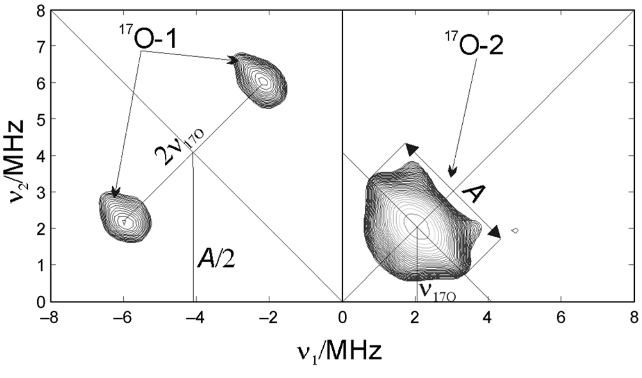

Figure 2. ^{17}O HYSCORE spectrum recorded at field position 3 of Figure 1Ba (358.7 mT). The two sets of peaks corresponding to the two inequivalent sets of ^{17}O hfi are indicated. HYSCORE spectra at the other field positions together with the corresponding simulations and the experimental details are given in the Supporting Information.

The second signal appearing in the $(+,+)$ quadrant and centered at (ν_O,ν_O) (^{17}O-2 in Figure 2) indicates the presence of weakly coupled ^{17}O (i.e., $A < 2\nu_O$) with maximum coupling of about 1.5 MHz. The two observed couplings can be ascribed to hyperfine interactions between the unpaired electron in the d_{xy} orbitals of Ti^{3+} and two distinct types of coordinated oxygen atoms.

The ^{17}O hfi of about 8 MHz observed in the HYSCORE spectrum (^{17}O-1) can be rationalized by considering the π overlap between the metal d and oxygen p orbitals in the equatorial plane, where the unpaired electron dwells.[17] This bonding interaction will induce a negative spin density on oxygen as a result of a spin polarization mechanism, and the positive sign of a_{iso} is due to the negative ^{17}O nuclear g factor ($g_n = -0.757516$). Remarkably, a ^{17}O a_{iso} value of the same order was recently observed by some of us[18] for molecular complex $[Ti(H_2{}^{17}O)_6]^{3+}$, in which the same type of Ti-O π bonding occurs. This small (positive) ^{17}O hfi appears to indeed be a distinctive feature of d^1 metal–oxygen π-bonding mechanisms as observed in other molecular cations such as $[VO(H_2{}^{17}O)_6]^{4+}$.[19] This comparison strongly suggests that excess electrons in the blue rutile sample are (at 4 K) largely localized over a single Ti ion, which bears strong similarities to a genuine Ti^{3+} molecular cation.

The smaller ^{17}O hfi responsible for the signal in the $(+,+)$ quadrant of the HYSCORE spectrum (^{17}O-2) can be interpreted as arising from the interaction between the unpaired electron in the Ti $3d_{xy}$ orbitals and the axially coordinated oxygen atoms. The ^{17}O hfi parameters are expected to be highly dependent on the coordination position of the O ligand and in the case of molecular aqua vanadyl cations values of about 2 MHz have been predicted for axially coordinated water.[19]

In summary, this initial study on the nature of reduced states in TiO_2 has shown that stable Ti^{3+} ions can be generated in the bulk of TiO_2 by a direct and simple synthetic method. The ^{17}O HYSCORE spectra of such Ti^{3+} ions allowed the spin density delocalization over the first shell of oxygen ligands to be monitored for the first time. It is comparable to that observed for genuine molecular Ti^{3+} aqua complex cations, that is, a molecular system characterized by the same type of metal–oxygen bonding interaction, for which localization of the unpaired electron in the metal 3d orbitals is obvious. This observation points to the important conclusion that in this type of defective rutile the excess electron wave function is largely localized over single Ti ions associated with TiO_6^{9-} "molecular" fragments. Remarkably, preliminary experiments performed on a ^{17}O-enriched TiO_2 having anatase phase show that no such ^{17}O coupling is present in this case, that is, the nature of the Ti^{3+} unpaired electron wave function in anatase is much more delocalized.

We believe that these results will be of importance in understanding and controlling the properties of reduced TiO_2 and that the reported experimental approach may be of relevance to addressing the open question of the degree of charge localization in n-type doped semiconducting oxides.

Experimental Section

Blue TiO_2 polycrystalline powders enriched in ^{17}O were synthesized by a new and simple method based on hydrolysis of $TiCl_4$ in $H_2{}^{17}O$. Details on the synthesis and spectroscopic measurements are given as Supporting Information.

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