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# Study of Electron Paramagnetic Resonance in Titanium Sesquioxide*

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Single crystals of $Ti_2O_3$, pure and doped with various impurities, have been studied by Electron paramagnetic resonance (EPR). In most samples two different paramagnetic centers were observed. One of them produces a resonance corresponding to spin density of approximately $10^{19}$ spins/cm$^3$. The $g$-tensor is axially symmetric about the $c$-axis with $g_\parallel = 2.0029(2)$ and $g_\perp = 1.9040(2)$, line width = 4 G. The other center is relatively weaker with $10^{17}$ spins/cm$^3$. Its $g$-tensor is completely anisotropic and can be described by the following parameters.

$$g_{x'} = 1.9497(2), g_{y'} = 1.9638(2), g_{z'} = 1.9365(2)$$

where $x', y', z'$ are related to the $x(\|a), y, z(\|c)$ axes of the crystal by a coordinate transformation defined by Euler angles:

$$\varphi_z = 16.3° \pm 0.2°, \theta_{x''} = 77.2 \pm 0.1°, \psi_{z'} = 29.3° \pm 0.2°.$$

## Introduction

Titanium sesquioxide $Ti_2O_3$ has recently been studied extensively in an effort to understand its electronic properties. It exhibits a smooth semiconductor to metal transition above room temperature. Most of the results have been explained satisfactorily by a model of band structure given by Goodenough (*1*). The magnetoresistance experiments (*2*, *3*) show some anomalous behavior, which has been explained in terms of scattering of charge carriers by magnetic centers assumed to be present in these samples. We have performed EPR experiments in an effort to observe and understand the behavior of any localized paramagnetic centers.

## Experimental Results

Single crystals of near stoichiometric $Ti_2O_3$, pure and doped with small amounts (0.01–0.1%) of various impurities (Sc, Fe, N, V) were grown by the Central Crystal Growth facility at Purdue University. Details of growth are described in Ref. (*3*). The experiments were performed primarily at X-band frequencies; some results were also obtained at 34 GHz for comparison purposes. No signals were observed at 77 K or at higher temperatures. At liquid He temperature two paramagnetic centers were observed (Fig. 1). No resolved hyperfine structure was observed.

One of the centers exhibits a strong, single-line resonance corresponding to approximately $10^{19}$ spins/cm$^3$. The line is anisotropic and the $g$-tensor is axially symmetric about the $c$-axis with $g_\parallel = 2.0029(2)$ and $g_\perp = 1.9040(2)$. The width of the line changed from around 4 G, with the magnetic field parallel to the $c$-axis, to 10 G in a perpendicular direction. At 34 GHz the $g$-values are the same within experimental error ($\sim 5 \times 10^{-4}$), but the line width is larger, being roughly proportional to the frequency. The corresponding values are 12 and 30 G. When the temperature was raised, the (X-band) signal showed a noticeable broadening at 30 K; and the width ($H \| c$) increased to 15 G at 40 K. The effect may be due to a decrease in the relaxation time.

The low (below 0.1%) doping with elements other than vanadium had very little effect on

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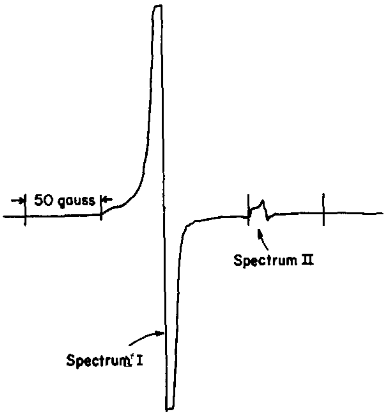

FIG. 1. Electron paramagnetic resonance spectrum with magnetic field parallel to $c$-axis taken at low gain. Spectrum I is at very near the free electron $g$ value ($g_{\parallel} = 2.0029$). $\nu = 8.97$ GHz.

the signal. In V-doped crystals, no signals were observed at concentrations above 0.01 %. At this concentration a line with intensity about two orders of magnitude weaker than that in pure $Ti_2O_3$, but having essentially the same line width and $g$ values, was obtained. The number of V atoms required to quench the signal is about equal to the number of spins observed in pure samples.

The other observed spectrum is somewhat more complicated and of weaker intensity with about $10^{17}$ spins/cm$^3$. Since $Ti_2O_3$ has a threefold symmetry about the $c$-axis ($z$) and twofold symmetry about the $a$-axis ($x$), an impurity located at any arbitrary point in the space will have six crystallographically equivalent positions. In an EPR experiment with the magnetic field in an arbitrary direction, the anticipated six-line spectrum was observed but not further analyzed. However, a simpler three-line pattern was obtained by choosing the twofold axis to be the axis of rotation, so that the magnetic field is confined in the $z$–$y$ plane. The observed angular dependence is shown in Fig. 2. The $g$-tensor parameters were obtained by varying all six of them and obtaining a least-square fit to the data. The following values have been assigned: $g_{x'} = 1.9497(2)$, $g_{y'} = 1.9638(2)$, $g_{z'} = 1.9365(2)$, where $x'$, $y'$, $z'$ axes are related to the $x$, $y$, $z$ axes system of the crystal by a coordinate transformation defined by Euler Angles: $\varphi_z = 16.3° \pm 0.2°$, $\theta_{x''} = 77.2° \pm 0.1°$, $\psi_{z'} = 29.3 \pm 0.2°$; the subscripts refer to the direction about which indicated rotations are performed while double primes refer to an intermediate set of axes. Alternatively, one can also represent the three axes $x'$, $y'$, $z'$ in polar coordinates in the $x$, $y$, $z$ system. One obtains $\varphi_{x'} = 23.3°$, $\theta_{x'} = 61.5°$; $\varphi_{y'} = 174.7°$, $\theta_{y'} = 31.7°$; $\varphi_{z'} = -73.7°$, $\theta_{z'} = 77.2°$. It may be remarked that the coordinate system as defined above is not unique in that any one of the six systems obtained by performing the symmetry operations indicated above would adequately describe the results. Raising the temperature and doping had very similar effects on this centre; in particular, V doping suppressed these lines as well.

## Discussion

Electron paramagnetic resonance spectra in several different oxides of titanium have been reported previously (*5*). No information about the $g$-value in $Ti_2O_3$ is given, and con-

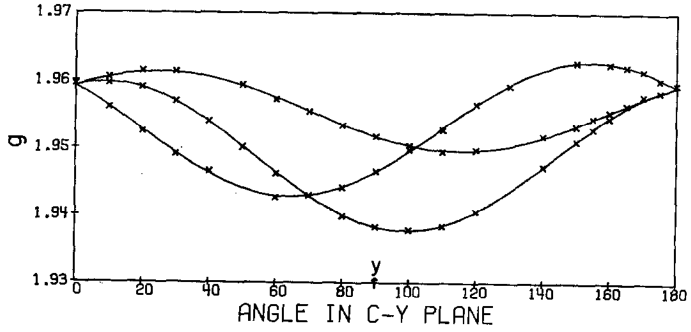

FIG. 2. Angular dependence of spectrum II. The angles are measured from $c$-axis in the $c$–$y$ plane.

trary to our observations, their spectrum was obtained at 77 K. One other observation was reported recently (*6*) with similar *g*-values as the spectrum with axial *g*-tensor reported here. However, for the magnetic field along the *c*-axis, the line width was reported to be from 11 to 31.5 G for samples of different stoichiometry. In one of our samples grown earlier (at M.I.T. containing 0.01–0.1% of N, C, Mn, Mg, Fe) a 35 G-wide line was observed. Since our *c*-axis line widths are 4 G at 9 GHz and 12 G at 34 GHz, this implies that our line widths are due to variations in *g*-values, presumably due to lattice strains. Therefore, even though our samples are probably better than those reported in Ref. (*6*), they are still not good enough to determine the "perfect" lattice EPR line widths.

One may assign the axial spectrum to a $3d^1$ electron in an $a_{1g}$ type orbital localized on a $Ti^{3+}$ ion. According to the accepted band model (*1*) this electron forms a paired off bond with a neighboring electron on a nearby titanium ion along the *c*-axis. One would, therefore, not expect to see any paramagnetic resonance in the pure material. The concentration of impurities in our pure samples is small enough (50 ppmw of Si, C, other impurities 10 ppmw or less) to rule the possibility of the axially symmetric center (with $\sim 2 \times 10^{-4}$ spins per Ti atom) being an impurity resonance.

On the other hand, slight nonstoichiometry towards excess oxygen is known to be present in these samples. Presumably, the nonstoichiometry is due to $Ti^{3+}$ vacancies. Each $Ti^{3+}$ vacancy will introduce three holes in the crystal for reasons of charge compensation. These holes are not mobile at low temperatures; the estimated number of charge carriers at liquid He temperature is $10^{10}/cm^3$ (*7*). If these holes are singly trapped by bonded pairs of $Ti^{3+}$ along the *c*-axis near the vacancy, a spectrum similar to an isolated $Ti^{3+}$ could be obtained. Only about one part per ten thousand of oxygen excess would be needed to explain the results. Lack of any dependence of signal intensity on relatively large oxygen excess observed in Ref. (*6*) may be due to the presence of other possible trapping mechanisms in which no unpaired spins are produced: for example, when the holes are trapped in pairs. The presence of V in this material creates holes at the top of the valence band and may favor the creation of centers of the latter type. Given our linewidths and the fact that titanium has two isotopes, $^{47}Ti$ (7.75% abundance, spin 5/2), and $^{49}Ti$ (5.51% abundance, spin 7/2) having magnetic moment, one expects to see resolved hyperfine structure. Absence of any such structure suggests that the unpaired spin is shared by several Ti nuclei: for example, by a pair of Ti atoms along the *c*-axis adjacent to the vacancy or by three Ti pairs surrounding the vacancy. A planned ENDOR experiment should provide conclusive proof for one of these models. The other low symmetry center could be due to any of the several impurities present in ppm quantities and not having abundant isotopes with magnetic moment.

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