

PARAMAGNETIC OXYGEN CENTRES IN SrTiO<sub>3</sub> INDUCED BY LIGHT

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The ESR spectra of two light-induced defect centres in annealed SrTiO<sub>3</sub> single crystals are reported and ascribed to O<sub>2</sub><sup>3-</sup>. In crystals treated in a water vapour at high temperature a third light-induced centre was found, assigned to O<sup>-</sup>.

### 1. Introduction

Several investigations concerning defect-centres generated by heat treatment and/or irradiation of SrTiO<sub>3</sub> single crystals have been reported [1-5]. Various types of heat treatment are currently used, notably heating in vacuum, heating in a hydrogen atmosphere and heating in an oxygen atmosphere. For nominally pure crystals the effect of heating in a particular atmosphere is mainly a change in the concentration of oxygen vacancies, while heat treatment of transition metal ion doped crystals can alter the valence state of the impurities [1-6]. Light induced changes of impurity ions were also reported [5, 7].

In this paper we communicate the observation of the ESR spectra of three light-induced defect centres, arbitrarily labeled V<sub>I</sub>, V<sub>II</sub> and V<sub>III</sub>, in undoped SrTiO<sub>3</sub> single crystals. Although conclusive evidence regarding the nature of these centres could not be obtained, we will argue that the V<sub>I</sub> and V<sub>II</sub> centres can be assigned to O<sub>2</sub><sup>3-</sup>-hole centres. Centre V<sub>III</sub> formed only after irradiation of crystals which were subjected to a "water treatment" [8, 9], is assigned to O<sup>-</sup>.

### 2. Experimental

SrTiO<sub>3</sub> single crystals were purchased from Semi-Elements Inc. Iron was present as a trace impurity as was revealed by the ESR spectra. The crystals were transparent.

Measurements were carried out on:

(a) a crystal vacuum heated for several hours at 1000°C,

(b) a crystal treated in an oxygen atmosphere for several hours at 1000°K,

(c) a crystal heated at 1000°K in water vapour for 48 hours.

Irradiation was performed with a focused Philips 500 W high-pressure Hg arc. Filters were used to select the required excitation ranges. ESR measurements were made at X-band using a conventional Varian E-6 spectrometer with the samples mounted in an optical transmission cavity.

### 3. Results

When at 77°K a vacuum- or oxygen-treated crystal is irradiated with unfiltered light of the Hg arc, a complex ESR spectrum due to the V<sub>I</sub> centres is obtained. Rotation of the crystal with respect to the magnetic field in the (100) plane results in a variation of the line positions as shown in fig. 1. The same angular variations are found when the crystal is rotated in either the (010) plane or the (001) plane.

The ESR spectra can be described in terms of  $S = \frac{1}{2}$ . Diagonalization of the  $g$ -tensor yielded the principal  $g$ -values for one site to be:  $g_1 = 2.009 \pm 0.001$ ,  $g_2 = 2.016 \pm 0.001$  and  $g_3 = 2.021 \pm 0.001$  along [110], [111] and [112] respectively. The magnetic axes of the other equivalent sites can be obtained by applica-

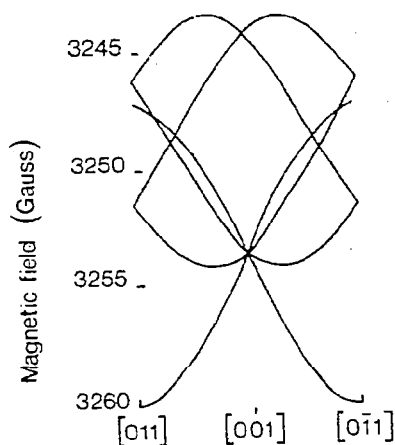


Fig. 1. Angular variation of the ESR spectrum of  $V_I$  on rotation of the crystal about a  $[100]$  axis.

tion of the cubic symmetry operations.

After the light was switched off the ESR absorption decayed exponentially with a characteristic time of about 25 sec.

Only when the light was filtered with a Schott UG-11 band-filter, which has a maximum transmission at 3300 Å, the ESR spectrum due to  $V_{II}$  centres appeared superimposed upon the spectrum of the  $V_I$  centre. Obviously the  $V_{II}$  spectrum is bleached in the visible. The observation of the anisotropy of this spectrum is largely obscured by the presence of the more intense  $V_I$  spectrum, the intensity ratio being 1:5 approximately. However, sufficient experimental points of the angular variation curves could be collected in order to establish the spin-hamiltonian parameters. It turned out that the  $g$ -tensor is diagonal for the magnetic axes parallel to those of the  $V_I$  centre; only the  $g$ -values differ slightly:  $g_1 = 2.00(7)$ ,  $g_2 = 2.01(1)$  and  $g_3 = 2.01(8)$ .

The intensity of the lines in the ESR spectra of the  $V_I$  and  $V_{II}$  centres decreased gradually as the temperature was raised from 77°K up to 125°K, when no signals could be observed anymore. No specific effects due to the phase transition at 105°K [10] could be observed.

After irradiation of a vacuum treated crystal and subsequent decay of the  $V_I$  centre an isotropic line with  $g = 2.014$  appears, which was identified by Müller et al. [11] as due to  $Fe^{5+}$ . The existence of

the  $V_I$  centre in relation to observed changes in the ESR signals of the  $Fe^{5+}$ , cubic and axial  $Fe^{3+}$  centres [12, 13], will be reported in a separate paper.

Whereas the experimental results for the vacuum and for the oxygen-treated samples are indistinguishable, the water-treated crystals behaved quite differently. In the latter a rather stable  $S = \frac{1}{2}$  centre was formed at 77°K upon irradiation with light filtered by an UG-11 filter. This centre was labeled  $V_{III}$ . The ESR spectrum shows the following characteristics:

(i) three lines arising from defect centres having mutually perpendicular tetragonal axes with  $g_{II} = 2.012 \pm 0.001$  and  $g_{\perp} = 2.017 \pm 0.001$ ,

(ii) the principal axes coincide with the crystal axes.  $V_I$  and  $V_{II}$  centres are absent. Red light bleaches the  $V_{III}$  centre instantaneously.

#### 4. Discussion

##### 4.1. $V_I$ and $V_{II}$ centres

Defect centres on either a titanium or a strontium site are expected to have at least one of the principal axes of their  $g$ -tensor along a crystal axis [4, 13–15], centres at a titanium site being furthermore characterized by axial symmetry. The  $V_I$  and  $V_{II}$  centres, however, do not possess any of these symmetry properties.

Not only the direction of the principal magnetic axes of the centres but also the  $g$ -values favour a model in which oxygen ions are involved as hole centres.

An extensive treatment of the  $SrTiO_3$  crystals with an inert gas at high temperature did not alter the intensity of the ESR lines. Therefore it is assumed in the following that the  $V_I$  and  $V_{II}$  centres do not involve interstitial oxygen.

In the literature four types of paramagnetic oxygen centres are reported, namely  $O_3^-$  [16],  $O_2^-$  [17, 18],  $O_2^{3-}$  [19, 20] and  $O^-$  [7, 21, 22] where the latter may be delocalized.

For an  $O_3^-$  ion the smallest  $g$ -value is to be measured along an axis perpendicular to the molecular plane [23, p. 145]. For any combination of three neighbouring oxygen atoms in the lattice having a bond angle of about 110°, this axis should be parallel to a  $[111]$  axis or equivalent axes. Experimentally, however, the smallest  $g$ -value is found along  $[110]$  and equivalent axes.

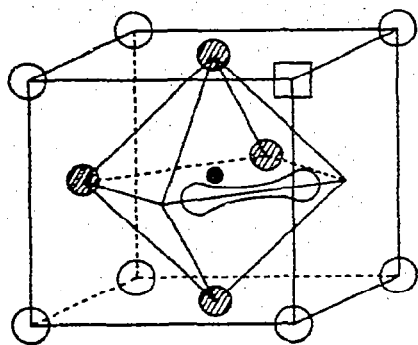


Fig. 2. Location of  $O_2^{3-}$  with respect to the  $Sr^{2+}$  vacancy.  
 $\bullet$   $Ti^{4+}$ ,  $\circ$   $Sr^{2+}$ ,  $\bullet$   $O^{2-}$ ,  $\square$   $Sr^{2+}$  vacancy.

In the case that the  $V_I$  and  $V_{II}$  centres would be diatomic oxygen hole centres,  $O_2^-$  or  $O_2^{3-}$ , only those combinations of two oxygen ions are meaningful which have their principal magnetic axes parallel to those determined experimentally. Since a diatomic oxygen hole centre, for which the molecular axis is along an O–Sr–O (strontium being absent), would hardly be stabilized on account of the large oxygen–oxygen distance, one has to consider in the following only hole centres consisting of two adjacent oxygen atoms in an octahedron around a titanium site.

The smallest  $g$ -values of  $V_I$  and  $V_{II}$  are found along O–O axes of the octahedrons. For  $O_2^-$  the highest and for  $O_2^{3-}$  the smallest  $g$ -value is expected along the molecular O–O axis [23, p. 247]. Therefore we have to assign the centres to  $O_2^{3-}$ .

In order to obtain charge compensation, oxygen anions easily trap holes if cation vacancies are in the neighbourhood. Therefore it is likely that  $O_2^{3-}$  centres are created near an  $Sr^{2+}$  vacancy. This view is supported by the fact that the axis connecting the middle of an O–O axis with the nearest strontium site is of the type  $[\bar{1}\bar{1}\bar{2}]$  (fig. 2).

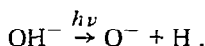
On the basis of the observed  $g$ -values one still has to consider the creation of  $O^-$  centres as an alternative. However, only  $O^-$  centres with an  $Sr^{2+}$  vacancy on a next nearest site would have principal axes compatible with those observed for the  $V_I$  and  $V_{II}$  centres. Although we cannot rigorously exclude this possibility, we like to disregard this type of defect centres because it is hard to see why  $O^-$  centres with a vacancy on a nearest  $Sr^{2+}$  site are absent.

The slight difference between  $V_I$  and  $V_{II}$  points to a minor variance in the distant environment.

#### 4.2. $V_{III}$ centre

The  $V_{III}$  centre can be created by light in crystals which have been subjected to a water treatment. From infra-red absorption measurements [8, 9] it is known that  $OH^-$  exists in water-treated  $SrTiO_3$  crystals.

Hydroxyl impurities in alkali halides have been investigated amongst others by Kerkhoff [24] who found the following reaction to occur on illumination:



This reaction may also be relevant to our case; the  $V_{III}$  centre, which exhibits a positive  $g$ -shift with respect to the free-electron  $g$ -value, can then be assigned to  $O^-$ .

In  $SrTiO_3$  an  $O^-$  centre with a relatively small  $g$ -shift has been reported before by Ensign and Stokowski [7]. These authors proposed a hole shared by the six oxygen ions at the corner points of the octahedron around an  $Al^{3+}$  ion at the  $Ti^{4+}$  site. In our case, however, the nature of the central ion is unknown.

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