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## Electric field effects in EPR of the $\text{SrTiO}_3:\text{V}^{4+}$ Jahn-Teller system

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**Abstract.** The influence of applied static electric fields on the  $\text{SrTiO}_3:\text{V}^{4+}$  Jahn-Teller system has been studied by means of EPR at liquid helium temperatures. The experimental results can be accounted for by considering a  ${}^2\text{T}_{2g}$  electronic ground state showing a strong Jahn-Teller interaction with a localized  $e_g$  mode. In the presence of electric fields, the degeneracy of the vibronic ground state is lifted appreciably by strain. This strain results from strong electrostrictive couplings in  $\text{SrTiO}_3$ .

### 1. Introduction

Illumination of  $\text{SrTiO}_3$  single crystals, doped with vanadium, with blue light ( $\lambda \approx 396$  nm) gives rise to an EPR spectrum characteristic of an  $S = \frac{1}{2}$  centre. The centre has tetragonal local symmetry, the main axes being along the  $\{100\}$  directions of the  $\text{SrTiO}_3$  host crystal [1]. On the basis of the observed hyperfine splittings, the spectrum has been attributed to  $\text{V}^{4+}$  substitutional for  $\text{Ti}^{4+}$ . In the presence of applied uniaxial stress, the induced strain produces significant changes in the relevant intensities of the (hyperfine) signals of the three  $\text{V}^{4+}$  sites in the crystal. The strain-induced effects were interpreted assuming that the  $\text{SrTiO}_3:\text{V}^{4+}$  system has a triply degenerate vibronic ground state [1]. The vibronic degeneracy is derived from a strong Jahn-Teller interaction between the electronic  ${}^2\text{T}_{2g}$  orbital state of  $\text{V}^{4+}(\text{d}^1)$  and a localized  $e_g$  mode in the linear coupling limit [2]. Strain in the crystal effectively lifts the three-fold vibronic degeneracy and effects an appreciable alignment among the tetragonal Jahn-Teller distortions.

In this paper, we present results of an EPR study of the  $\text{SrTiO}_3:\text{V}^{4+}$  impurity system in the presence of an applied electric field. In a highly polarizable host crystal such as  $\text{SrTiO}_3$ , the Stark effect of a paramagnetic ion is dominated by the local electric field strength,  $E_{\text{loc}}$ . In  $\text{SrTiO}_3$ , especially at low temperatures,  $E_{\text{loc}}$  differs by three to four orders of magnitude from the externally applied field,  $E$  [3]. Consequently, despite a relatively weak coupling of the  $\text{V}^{4+}$  metal ion to the polarized lattice, Stark shifts of the EPR lines typical of the  $\text{V}^{4+}$  can be observed even in the presence of moderate external electric field strengths. Here it will be shown that for the  $\text{SrTiO}_3:\text{V}^{4+}$  system in EPR, Stark shifts bilinear or quadratic in  $E_{\text{loc}}$  are measured, thus providing independent evidence for the centro-symmetric position of the  $\text{V}^{4+}$  ion within the octahedron of surrounding oxygen anions.

Upon the application of electric fields up to  $40 \text{ kV cm}^{-1}$ , electrostrictive interactions in the  $\text{SrTiO}_3$  crystal give rise to the concomitant occurrence of strain in the crystal [4]. Given the great sensitivity of the  $\text{SrTiO}_3:\text{V}^{4+}$  tetragonal Jahn-Teller distortions to strain, it is of no surprise that the electric field is found also to affect the intensities of the EPR lines of the tetragonal  $\text{V}^{4+}$  sites. The results are discussed in terms of an alignment of the tetragonal distortions along the electric field; the observations are analogous to those reported previously for the  $\text{SrTiO}_3:\text{Cr}^{5+}$  system [5].

## 2. Experimental procedure

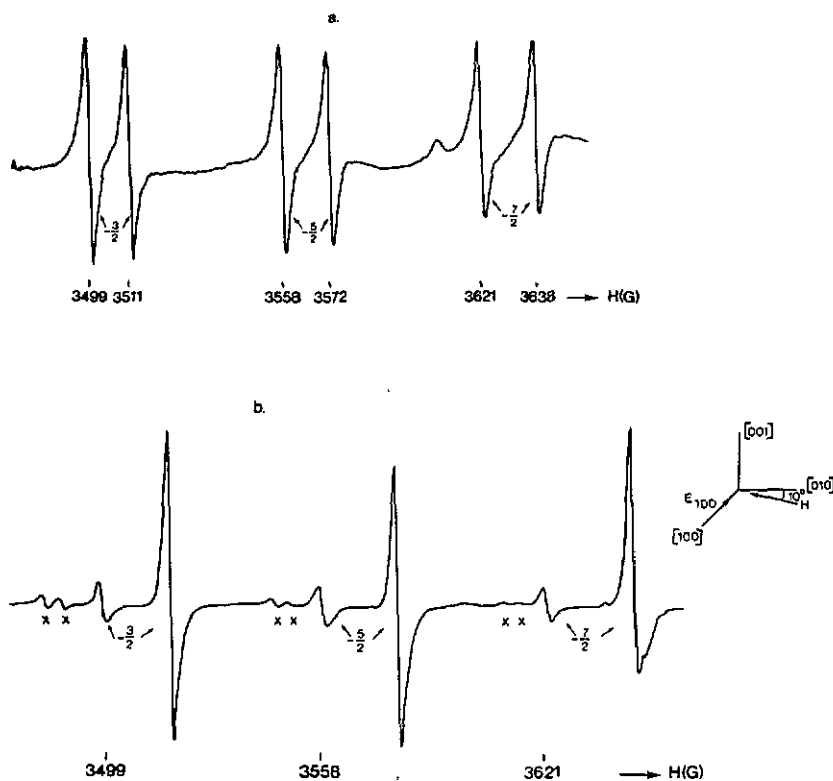
Single crystals of  $\text{SrTiO}_3$  doped with 60 ppm vanadium were purchased from Semi-Elements Inc. and National Lead Co. EPR spectra were measured at X-band (9.16 GHz) utilizing 100 kHz modulation. The samples were mounted in an optical transmission cavity. Electric fields were applied by means of a DC high-voltage power supply with copper electrodes connected to parallel gold electrodes. The gold electrodes were vapour-deposited on the polished crystal surfaces. By using the gold electrodes, hysteresis effects in the EPR resonances caused by the electric field were suppressed to a minimum. A load resistance of  $1 \text{ M}\Omega$  in the circuit prevented sparking when applying high voltages. A stainless steel liquid helium dewar with a quartz tip in the cavity was used in the experiments. By pumping on the liquid helium bath, the temperature could be lowered to 1.8 K. To obtain a maximum signal-to-noise ratio for the EPR signal of the  $\text{V}^{4+}(\text{d}^1)$  ion, the crystal was irradiated with light from a Philips high-pressure mercury arc lamp filtered by a UG-11 filter. All experiments were done at 4.2 K and 1.8 K. At higher temperatures, the EPR lines become weak and broad because of the decay of the  $\text{V}^{4+}$  ion back into the  $\text{V}^{5+}$  ion [6-8].

## 3. Results

For an arbitrary orientation of the crystal with respect to the magnetic field  $\mathbf{H}$ , the EPR spectrum of the  $\text{SrTiO}_3:\text{V}^{4+}$  system, at 4.2 K and zero electric field, consists of 24 main lines of almost equal intensity. The EPR spectrum corresponds to three tetragonal  $\text{V}^{4+}$  sites with  $g_{\parallel} = 1.942$ ,  $g_{\perp} = 1.895$ ,  $A_{\parallel} = 146.78 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp} = 44.04 \times 10^{-4} \text{ cm}^{-1}$  [1, 9].

When an electric field,  $\mathbf{E}$ , is applied along the pseudo-cubic [100] axis and  $\mathbf{H}$ , the magnetic field, is almost perpendicular to  $\mathbf{E}$  and about  $10^\circ$  from the pseudo-cubic [010] axis, we observe the following changes in the EPR spectrum (cf figure 1): (i) EPR lines corresponding to  $\text{V}^{4+}$  sites with a main  $z$ -axis parallel to  $\mathbf{E}$  exhibit a line shift. For centres with tetragonal axis perpendicular to  $\mathbf{E}$  no line shifts are measured. Figure 2 presents the shift of the EPR lines due to centres with tetragonal axes parallel to the electric field as a function of the square of the internal local field,  $E_{\text{loc}}^2$ . For electric fields larger than  $6 \text{ kV cm}^{-1}$ , the line shift is found to change linearly with  $E_{\text{loc}}^2$ . (ii) EPR lines due to sites with a main tetragonal axis parallel to  $\mathbf{E}$  are enhanced relative to the lines associated with centres with tetragonal axis perpendicular to  $\mathbf{E}$ . In figure 3, we plotted  $\ln(I_E/I)$  versus  $E_{\text{loc}}^2$ , where  $I_E$  is the EPR line intensity measured for those centres with main axes parallel to the applied electric field and  $I$  is the intensity measured for those centres with main axes perpendicular to the applied electric field. The drawn line shows the best fit to a straight line.

(iii) Small satellite lines denoted by  $\times$  in figure 1(b) appear when an electric field is applied. These lines represent the 'forbidden'  $\Delta M = \pm 2$  quadrupole transitions. They appear when the magnetic field is perpendicular to the tetragonal centre axis. From the position of the weak lines, the magnitude of the quadrupole interaction,  $|P|$ , is determined as  $|P| = (-2.142 \pm 0.005) \times 10^{-4} \text{ cm}^{-1}$ . This value is of the same order of magnitude as the quadrupole couplings found for  $\text{V}^{4+}$  in  $\text{GeO}_2$  [10] and  $\text{TiO}_2$  [11]. For the  $\text{SrTiO}_3:\text{V}^{4+}$  system the same results were obtained when the temperature was lowered to 1.8 K.



**Figure 1.** (a) EPR spectrum of the  $\text{SrTiO}_3:\text{V}^{4+}$  system for  $H$  in the (001) plane, about  $10^\circ$  away from the [010] axis,  $T = 4.2 \text{ K}$ . (b) The same spectrum, but with an applied electric field  $E \parallel [100]$ ,  $E = 21 \text{ kV cm}^{-1}$ . The lines marked  $\times$  are 'forbidden' quadrupole transitions.

Upon the application of an external electric field along the pseudo-cubic [110] axis and choosing the magnetic field along the [110] direction, the following effects are observed (cf figure 4): (i) EPR lines due to sites with tetragonal axes along the [100] and [010] directions undergo the same shift, while those with their main axis along the [001] direction show no shift. The electric field does not affect the separation of the hyperfine lines indicating that the hyperfine interactions of the  $\text{SrTiO}_3:\text{V}^{4+}$  system are not influenced by the applied electric field. (ii) EPR lines due to sites with tetragonal axes along the [100] or [010] direction are enhanced in intensity, while the intensity corresponding to centres with main axes along the [001] direction is decreased.

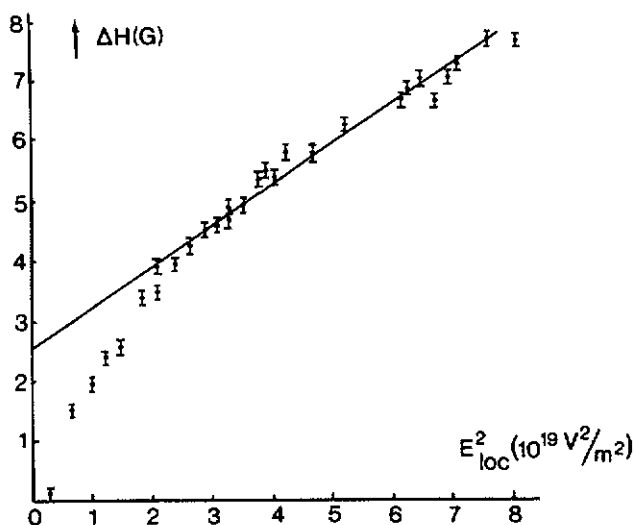


Figure 2. Plot of the EPR line shift versus  $E_{loc}^2$  ( $E \parallel [100]$ ) for  $V^{4+}$  sites with the tetragonal axis parallel to  $E$ . The solid line is a least square fit to a straight line.

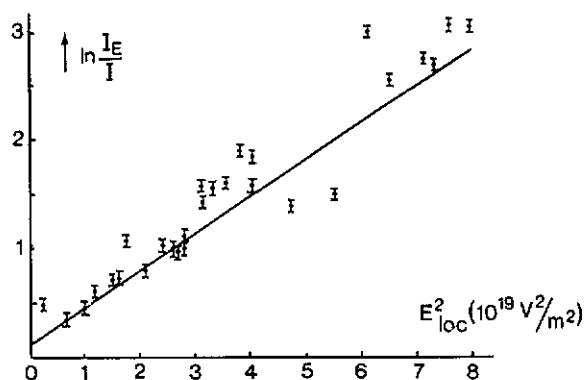


Figure 3. Plot of the intensity ratio  $\ln(I_E/I)$  versus  $E_{loc}^2$  ( $E \parallel [100]$ ) for the  $SrTiO_3:V^{4+}$  system. The solid line is a least square fit to a straight line.

#### 4. Discussion

The electric field-induced shifts in the positions of the EPR lines of the  $SrTiO_3:V^{4+}(d^1)$  system can be described by including in the spin Hamiltonian the following terms [3, 12]:

$$\mathcal{H} = \mu_B T_{ijkl} E_i E_j H_k S_l \quad (1)$$

where

$$T_{ijkl} = \frac{\partial^2 g_{kl}}{\partial E_i \partial E_j}$$

In equation (1) the Einstein notation is used, i.e. summations have to be taken over suffixes occurring twice in the same term. With  $E_{loc} = P/\epsilon_0$  [3], expression (1) is

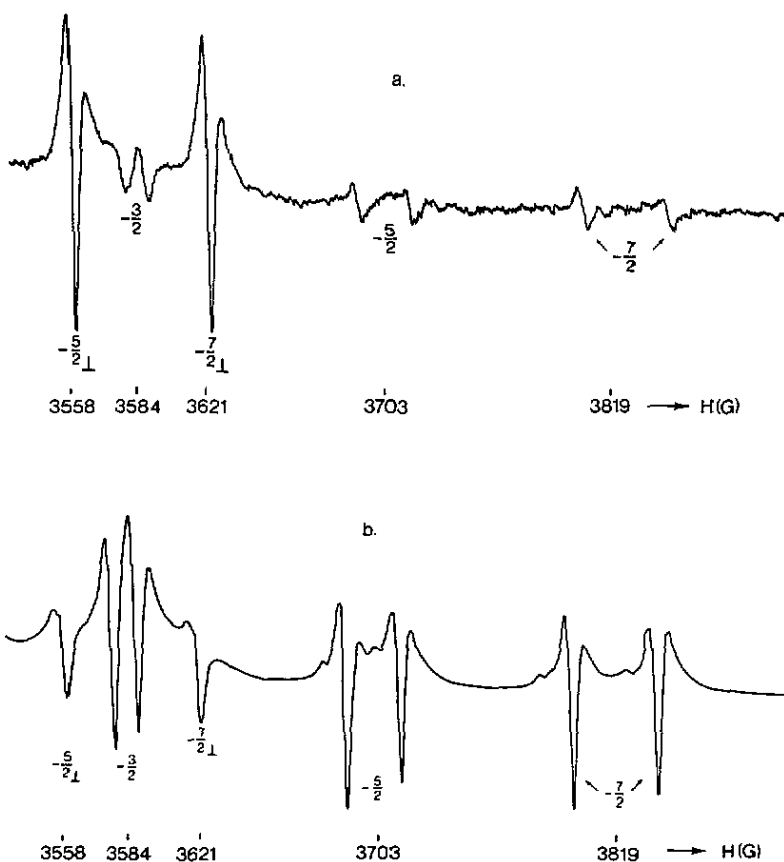


Figure 4. (a) EPR spectrum of the  $\text{SrTiO}_3:\text{V}^{4+}$  system for  $H$  a few degrees from the  $[110]$  direction at 4.2 K. (b) The same spectrum, but with an applied electric field  $E \parallel [100]$ ,  $E = 18 \text{ kV cm}^{-1}$ .

rewritten as,

$$\mathcal{H} = \mu_B T_{ijkl} P_i P_j H_k S_l \quad (2)$$

where

$$T_{ijkl} = \frac{\partial^2 g_{kl}}{\partial P_i \partial P_j}$$

and the polarization,  $P$ , as a function of the applied external field at 4.2 K, has been given by Itschner [13] for electric values up to  $1.5 \text{ MV m}^{-1}$ . We extrapolated these values for the polarization to those obtained by Unoki *et al* [14].  $T_{ijkl}$  in equation (1) is a fourth-rank symmetric tensor. For the point symmetry of class  $C_{4h}$  ( $4/m$ ) the

relevant fourth-rank tensor takes the form [15]

$$\mathbf{T} = (T_{ijkl}) = \begin{bmatrix} T_{11} & T_{12} & T_{13} & & & T_{16} \\ T_{12} & T_{11} & T_{13} & & & -T_{16} \\ T_{13} & T_{13} & T_{33} & & & \\ & & & T_{44} & T_{45} & \\ & & & -T_{45} & T_{44} & \\ T_{16} & -T_{16} & & & & T_{66} \end{bmatrix} \quad (3)$$

where the indices refer to the Voigt notation, i.e. 1 =  $xx$ ; 2 =  $yy$ ; 3 =  $zz$ ; 4 =  $yz$ ,  $zy$ ; 5 =  $xz$ ,  $zx$ ; 6 =  $xy$ ,  $yx$  and where  $x$ ,  $y$  and  $z$  denote the centre axes, the  $x$ -axis being the tetragonal axis. With the electric field applied parallel to the centre  $z$ -axis we obtain,

$$\mathcal{H}_P = \mu_B P_z^2 (T_{33} H_z S_z + T_{13} H_x S_x + T_{13} H_y S_y). \quad (4)$$

On the other hand, the EPR line shifts are obtained from

$$\mathcal{H}_P = \mu_B [\Delta g_{\parallel} H_z S_z + \Delta g_{\perp} (H_x S_x + H_y S_y)]. \quad (5)$$

It follows that

$$T_{33} = \frac{\Delta g_{\parallel}}{P_z^2} = \frac{\Delta g_{\parallel}}{\epsilon_0^2 E_{loc}^2} \quad (6)$$

and

$$T_{13} = \frac{\Delta g_{\perp}}{P_z^2} = \frac{\Delta g_{\perp}}{\epsilon_0^2 E_{loc}^2}. \quad (7)$$

Experimentally, we find that  $\Delta g_{\parallel} = -0.0030$  for  $E_z = 2.4 \text{ kV cm}^{-1}$  and  $\Delta g_{\perp} = -0.0039$  for  $E_z = 3.6 \text{ kV cm}^{-1}$ . From equations (6) and (7) and the extrapolated values for the local electric field strength (*vide supra*) it follows that  $T_{33} = -0.55 \text{ m}^4 \text{ A}^{-2} \text{ s}^{-2}$  and  $T_{13} = -0.51 \text{ m}^4 \text{ A}^{-2} \text{ s}^{-2}$ .

Experimentally, EPR lines due to centres with tetragonal axes along the [010] and [001] directions and perpendicular to the applied electric field ( $\mathbf{E} \parallel [100]$ ) are not shifted and thus  $T_{11} = T_{12} = T_{13} = T_{16} = 0$ . Since the centre main axes remain untilted upon the application of an electric field we also find  $T_{44} = T_{45} = T_{66} = 0$ . The same values for the  $T$ -tensor elements are obtained when analysing the EPR results for  $\mathbf{E} \parallel [110]$ .

The linear relationship between the Stark shift and the square of the local electric field strength is good evidence that the  $V^{4+}$  ion in  $\text{SrTiO}_3$  is at a centro-symmetric position. A similar behaviour in an electric field has previously been reported for  $\text{Cr}^{5+}$  in  $\text{SrTiO}_3$  [5], which is also at a centro-symmetric site. Likewise, a quadratic electric field dependence has been found for  $\text{Fe}^{3+}:\text{SrTiO}_3$  [16] and for  $\text{Fe}^{3+}$  and  $\text{Gd}^{3+}$  impurity ions in  $\text{KTaO}_3$  [17, 18].

We now turn to the effect of  $\mathbf{E}$  on the EPR line intensity. As mentioned in section 3, an increase in the EPR intensity of the centres with tetragonal axes parallel to the applied external electric field and a decrease of the signals due to those centres with tetragonal axis perpendicular to the applied electric field was observed. From figure 3

it is seen that the logarithm of the intensity ratio of the EPR signals due to centres with a tetragonal axis parallel to the applied electric field and centres with a tetragonal axis perpendicular to the electric field depends on the square of the internal field. Previously it has been mentioned that SrTiO<sub>3</sub>:V<sup>4+</sup> can be treated as a <sup>2</sup>T<sub>2g</sub> ⊗ e<sub>g</sub> vibronic system in the strong coupling limit [1, 9]. This system has a triply degenerate vibronic ground state which is very sensitive to crystal strain. When an electric field is applied such a strain can be produced by electrostrictive couplings. The strain perturbation for the vibronic system is written as [2]

$$\mathcal{H}' = V_2(\epsilon_\theta e_\theta + \epsilon_\epsilon e_\epsilon) \quad (8)$$

where  $V_2$  is the strain coupling coefficient,  $e_\theta$  and  $e_\epsilon$  are the strain parameters defined by

$$e_\theta = e_{zz} - \frac{1}{2}(e_{xx} + e_{yy})$$

and

$$e_\epsilon = \frac{1}{2}\sqrt{3}(e_{xx} - e_{yy}).$$

Taking  $\psi_\xi$ ,  $\psi_\eta$  and  $\psi_\zeta$  as the degenerate basis set for the T-state, the electronic orbital operators in matrix notation become [2]

$$\epsilon_\theta = \begin{bmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \epsilon_\epsilon = \begin{bmatrix} -\sqrt{3}/2 & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

In the SrTiO<sub>3</sub>:V<sup>4+</sup> system, the degeneracy among the  $\psi_\xi$ ,  $\psi_\eta$  and  $\psi_\zeta$  states is lifted in the different domains on account of the residual spontaneous local strain  $e$  [1]. Previously it was found that  $e = 8 \times 10^{-5}$  at 4.2 K [1]. In zero-electric field, the energy difference between the ground-state and upper-lying Jahn-Teller states is equal to  $\Delta E = \frac{3}{2}V_2e$  [1] (see figure 5). When  $E \neq 0$ , the electric field-induced electrostrictive strain,  $e_E$ , for an electric field directed along the [100]-axis is given by  $\Delta E = \frac{3}{2}V_2e_E$ , where  $e_E = e_{zz} - \frac{1}{2}(e_{xx} + e_{yy}) = e_\theta$  and  $e_\epsilon = 0$ , as shown below.

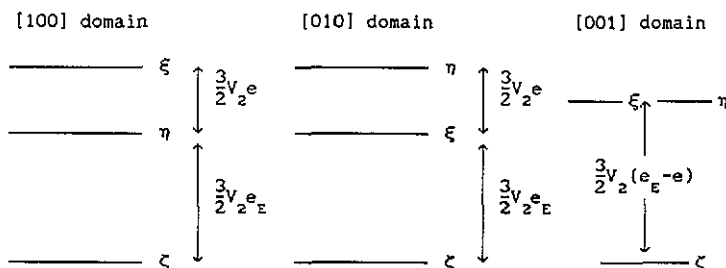


Figure 5. Splitting of the  $\psi_\xi$ ,  $\psi_\eta$  and  $\psi_\zeta$  states in the [100], [010] and [001] domain, respectively, in the presence of the residual spontaneous local strain,  $e$ , and the electric field-induced electrostrictive strain,  $e_E$ , when  $E \parallel [100]$ .



The electric field-induced strain components are given as  $e_{jk} = g_{ijkl} E_i E_l$ , where  $g_{ijkl}$  is a fourth rank tensor of the same symmetry as  $T$  in equation (3) [15]. For centres with tetragonal axes along the [100] crystallographic axis we have

$$\begin{aligned} e_{xx} &= g_{11} E_x^2 + g_{12} E_y^2 + g_{13} E_z^2 + g_{16} (E_x E_y + E_y E_x) \\ e_{yy} &= g_{12} E_x^2 + g_{11} E_y^2 + g_{13} E_z^2 - g_{16} (E_x E_y + E_y E_x) \\ e_{zz} &= g_{13} E_x^2 + g_{13} E_y^2 + g_{33} E_z^2. \end{aligned}$$

Since  $E = E_z$  and  $E_x = E_y = 0$ , we obtain  $e_{xx} = g_{13} E_{\text{loc}}^2$ ,  $e_{yy} = g_{13} E_{\text{loc}}^2$  and  $e_{zz} = g_{33} E_{\text{loc}}^2$ . We thus find that  $e_{\theta} = e_{zz} - \frac{1}{2}(e_{xx} + e_{yy}) \neq 0$  and  $e_{\epsilon} = e_{xx} - e_{yy} = 0$ . The electric field-induced strain,  $e_E$ , can be expressed as  $e_E = g_E E_{\text{loc}}^2$ , where  $g_E = g_{33} - g_{13}$ . Figure 5 illustrates the resulting splittings of the Jahn-Teller states.

In a three-domain crystal the Jahn-Teller sites in the different domains ( $E \parallel [100]$ ) give rise to the following intensity ratios of the corresponding EPR signals,

$$\ln \left( \frac{I_z}{I_y} \right) = \ln \left( \frac{I_z}{I_x} \right) = \frac{3V_2 e_E}{2kT}. \quad (9)$$

From a least-square fit to a straight line (cf figure 3) we obtain a slope equal to  $4.04 \times 10^{-20}$ . This yields a value for the electrostrictive constant of  $g_E = 3.93 \times 10^{-24} \text{ m}^2 \text{ V}^{-2}$ . This value is compatible with the electrostrictive value of  $g_{13} = 6.7 \times 10^{-24} \text{ m}^2 \text{ V}^{-2}$  found by Rupprecht *et al* [4].

For  $\text{SrTiO}_3$  it is known that when an electric field  $E$  is applied parallel to the [100] axis, the domain axis tends to re-orient itself perpendicular to the applied electric field [14, 16, 19]. The alignment of the domain axis illustrates that the applied electric field induces through electrostrictive couplings a tensile strain perpendicular to the electric field and a compressive strain parallel to  $E$ . As shown above, at the same time the  $z$ -axis of the oxygen octahedron surrounding  $V^{4+}$  likes to re-orient itself parallel to  $E$ . It is thus found that for the  $\text{SrTiO}_3:V^{4+}$  system, the Jahn-Teller distortion corresponds to a flattening of the oxygen octahedron along the tetragonal main axis.

Finally, we briefly comment on the non-linear behaviour of the EPR line shifts as a function of  $E_{\text{loc}}^2$  in figure 2, when  $E < 6 \text{ kV cm}^{-1}$ . A similar non-linear behaviour has also been reported for a few other impurity ions at centrosymmetric positions in  $\text{SrTiO}_3$ , namely for  $\text{Gd}^{3+}$  substitutional for  $\text{Sr}^{2+}$  [14] and the cubic  $\text{Fe}^{3+}$  impurity ion substitutional for  $\text{Ti}^{4+}$  [16]. It is added that no such non-linear behaviour was observed for the intensity ratio,  $\ln(I_E/I)$ , versus  $E_{\text{loc}}^2$  (cf figure 3). The reason is that the line shifts directly result from the electric field-induced polarization in the crystal, whereas the EPR intensity changes are related to electrostrictive interactions. This is seen as follows. Previously, the effects of uniaxial stress on the EPR spectrum of  $\text{SrTiO}_3:V^{4+}$  were reported [1, 9]. At a stress of  $9.5 \times 10^8 \text{ dyn cm}^{-2}$  along the [100] direction, the strain components are  $e_{xx} = 4.0 \times 10^{-4}$  and  $-e_{yy} = -e_{zz} = 1.1 \times 10^{-4}$ , and no EPR line shifts are observed. In this work, electric fields up to  $36 \text{ kV cm}^{-1}$  were applied; at the latter field value the strain,  $e_E$ , would be  $3.8 \times 10^{-4}$ , and, as already noted, at this strain magnitude EPR shifts cannot be observed. It remains that the observed EPR line shift when an electric field is applied, is due to induced electronic polarization. On the other hand, intensity changes are induced by electrostrictive couplings.

## 5. Conclusion

The electric field-induced quadratic shifts of the EPR lines of the  $\text{SrTiO}_3:\text{V}^{4+}$  system reported in this paper confirm that  $\text{V}^{4+}$  in  $\text{SrTiO}_3$  is at a centro-symmetric position. Electric-field induced intensity changes in the EPR spectrum of  $\text{V}^{4+}$  are also reported. The results are consistent with the idea that  $\text{SrTiO}_3:\text{V}^{4+}$  is a static  $T_{2g} \otimes e_g$  Jahn-Teller system. The tetragonal Jahn-Teller distortion corresponds to a flattening of the oxygen octahedron surrounding the  $\text{V}^{4+}$  site. The EPR observations for the  $\text{SrTiO}_3:\text{V}^{4+}$  system in the presence of an externally applied electric field are similar to those reported previously for the  $\text{SrTiO}_3:\text{Cr}^{5+}$  Jahn-Teller system.

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