

Electric field effects in the EPR of tetrahedrally coordinated Cr^{5+} in SrTiO_3

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 1571

(<http://iopscience.iop.org/0953-8984/6/8/015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 17:43

Please note that [terms and conditions apply](#).

Electric field effects in the EPR of tetrahedrally coordinated Cr^{5+} in SrTiO_3

Th W Kool, H J de Jong and M Glasbeek

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands

Received 17 November 1993

Abstract. This paper reports on electron paramagnetic resonance experiments of tetrahedrally coordinated Cr^{5+} in SrTiO_3 , under the influence of applied static electric fields. At 77 K, the applied electric fields induce an alignment of the off-centre Cr^{5+} ions along the direction of the electric field. The alignment is caused by a *linear* coupling of the electric dipole moment associated with the off-centred Cr^{5+} ion within the octahedron of surrounding O^{2-} ions and the applied static electric field. From the measurements an electric dipole moment of $\mu = 2.88 \times 10^{-30}$ C m and an off-centre displacement of about 0.04 Å could be determined. Previous results of stress experiments for the $\text{Cr}^{5+}:\text{SrTiO}_3$ system, at 77 K, have also been considered; for Cr^{5+} under stress an elastic dipole model is inferred. A differential stress coupling coefficient $\beta_{1110} = 4.19 \times 10^{-24}$ cm³ has been determined.

1. Introduction

Several detailed electronic paramagnetic resonance (EPR) studies have been reported for transition metal impurity ions, characterized by a d^1 electronic configuration, in SrTiO_3 [1–11]. Most often the transition metal ions are substitutional for Ti^{4+} , the latter ion being at the centre of the octahedron formed by the oxygen anions. For Mo^{5+} and V^{4+} it was shown that the impurity ions remain on centre and that Jahn–Teller (JT) vibronic couplings, in the dynamical (Mo^{5+} [1]) and static (V^{4+} [9–11]) coupling limit, prevail. Ti^{3+} , on the other hand, replaced Sr^{2+} and it was found to be at an off-centre position (in the direction of one of the twelve surrounding oxygen ions) [2]. The situation for Cr^{5+} , at the Ti^{4+} site, is more intricate. Two different sites have been identified for Cr^{5+} ($S = \frac{1}{2}$) in SrTiO_3 : the impurity can occur at sites of either tetragonal or orthorhombic local symmetry. The concentration ratio of the tetragonal and orthorhombic Cr^{5+} species was found to depend on the rate of cooling of the crystal from temperatures above 1000 °C (after completion of the oxidation procedure for the dopant Cr^{3+} impurity ions): rapid quenching of the crystal resulted in a higher yield of the orthorhombic sites [6, 7]. Considering that octahedrally coordinated Cr^{5+} has a small ionic radius ($r(\text{Cr}^{5+}) \sim 0.54$ Å versus $r(\text{Ti}^{4+}) \sim 0.64$ Å [12]), an off-centre position for the impurity ion is conceivable. However, EPR studies of tetragonal Cr^{5+} in the presence of uniaxial stress [4] and static electric fields [5] showed that the octahedral-tetragonal reduction of the site symmetry is caused by a ${}^2T_{2g} \otimes e_g$ static JT effect. Orthorhombic Cr^{5+} in SrTiO_3 has also been studied by EPR in the presence of externally applied uniaxial stress [6, 7]. From the variation of the relative intensities of the EPR lines characteristic of the six possible orthorhombic Cr^{5+} sites (with magnetic main axes along the $[110]$, $[1\bar{1}0]$ and $[001]$ crystallographic axes), a $T_{2g} \otimes (e_g + t_{2g})$ JT interaction in the strong-coupling limit was inferred [6]. Very recently, however, Müller *et al* [8] discussed

that Cr^{5+} with orthorhombic site symmetry very likely corresponds to an off-centre case. A displacement of Cr^{5+} along one of the $\langle 110 \rangle$ crystallographic directions was proposed so that Cr^{5+} becomes quasi-tetrahedrally coordinated by four O^{2-} ions in the perovskite crystal. The similarity between the g -values of the orthorhombic Cr^{5+} sites in SrTiO_3 and the g -values of Cr^{5+} in other host crystals that are known to be tetrahedrally coordinated was used as one argument. Another argument was that at higher temperatures ($T > 105$ K), under conditions where motional averaging gives rise to a single EPR transition [6], the averaged g -value does not coincide with the average g -value of the tetragonal Cr^{5+} sites. Finally, in the temperature region $4 \text{ K} < T < 77 \text{ K}$, the rotation of the principal axes of the g -tensor away from the $\langle 110 \rangle$ directions was found to be $\alpha = \pm 2\phi$, where ϕ is the intrinsic order parameter of the structural phase transition [13, 14]. Müller *et al* [8] also pointed out the importance of a study of orthorhombic $\text{Cr}^{5+}:\text{SrTiO}_3$ under the influence of static electric fields.

In this paper we report on an EPR study of Cr^{5+} in SrTiO_3 in externally applied electric fields. From our EPR data it is confirmed that the Cr^{5+} ion is displaced off centre in the $[110]$ direction. The electric dipole moment, μ , and the off-centre displacement of the Cr^{5+} ion could be determined. The results led us to reconsider our former stress experiments on the $\text{Cr}^{5+}:\text{SrTiO}_3$ system [7]. The behaviour of the intensities of the EPR lines of the six orthorhombic Cr^{5+} sites under the influence of uniaxial stress is now discussed in terms of an elastic dipole model.

2. Experimental details

Single crystals of SrTiO_3 with Cr (50 ppm) were purchased from Semi-Elements Inc. and National Lead Co. Cr^{5+} ions of orthorhombic local symmetry were obtained by oxidation of Cr^{3+} (by placing the crystal in a flow of oxygen at 1100°C for 4 h), followed by rapidly cooling the sample to room temperature [5–8]. Slower cooling enhanced the yield of Cr^{5+} ions of tetragonal local symmetry [4–8].

The EPR spectra were recorded with the samples mounted in a cavity of a Varian E-6 spectrometer operating at 9.1 GHz. The measurements were performed at 77 K. Electric fields up to 64 kV cm^{-1} could be applied across the crystal by using Cu foils attached to two parallel (polished) crystal surfaces as electrodes, the latter being connected to a DC high-voltage power supply.

3. Results and discussion

Figure 1 shows the angular dependence of the EPR lines of the orthorhombic Cr^{5+} in SrTiO_3 with \mathbf{H} rotated in the $\langle 110 \rangle$ plane at 77 K [7]. The angular dependence of the EPR lines is characteristic of an $S = \frac{1}{2}$ -system and can be described by the spin Hamiltonian $H = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}$, with $g_x = 1.956$, $g_y = 1.981$ and $g_z = 1.944$. The principal axes of the g -tensor are along the $[110]$, $[1\bar{1}0]$ and $[001]$ crystallographic axes, respectively. The orientations of the main axes of the six orthorhombic sites are as labelled in figure 2. The intensity ratios of the EPR lines are as indicated by the numbers in parentheses in figure 1. In figure 3(a), the EPR spectrum of the $\text{SrTiO}_3:\text{Cr}^{5+}$ system, for \mathbf{H} in the $\langle 110 \rangle$ plane and rotated by about 25° from the $[001]$ axis, is shown. Upon the application of a static electric field \mathbf{E} ($\approx 64 \text{ kV cm}^{-1}$), directed along a $[1\bar{1}0]$ axis, the following changes in the EPR spectrum were observed. The amplitude of the EPR signal due to site 1 (corresponding with

the EPR line at 3333 G) is enhanced relative to the amplitude of the EPR signal associated with site 2 (corresponding with the EPR line at 3341 G). The electric field had no effect on the linewidths, nor were g -shifts observed (cf figure 3(b)). The ratio of the line intensities of sites 1 and 2 has been measured as a function of the electric field strength and the results are represented by the dots in figure 4.

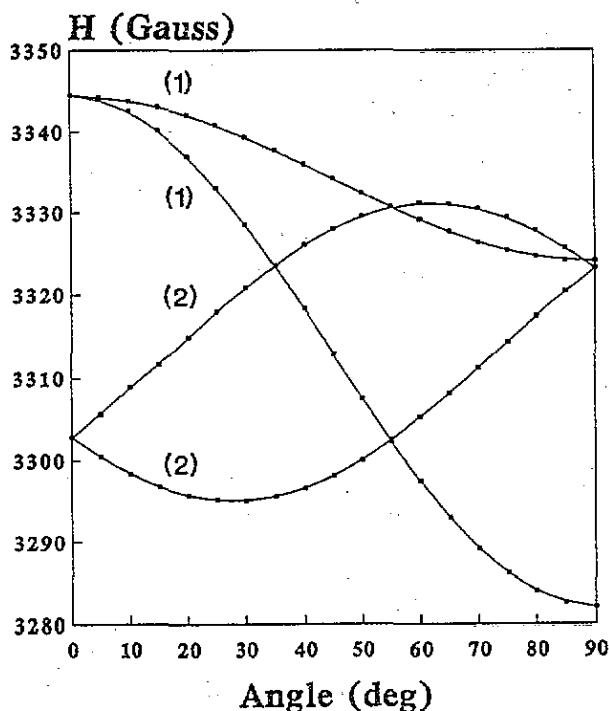


Figure 1. The angular dependence of the EPR lines of the orthorhombic $\text{Cr}^{5+}:\text{SrTiO}_3$ system for H in the (110) plane at 9.1 GHz; $T = 77$ K. Dots represent experimental data; drawn curves represent computer-simulated fits.

To discuss the results we consider an electric dipole, associated with an off-centre impurity cation. This impurity ion is surrounded by the six face-centring O^{2-} ions in the SrTiO_3 unit cell. Upon the application of an electric field, the sixfold orientational degeneracy of the electric dipole is lifted. For off-centre cations displaced parallel or anti-parallel to the electric field, the energy in the field will be shifted by $\pm eEd$, while the energies of the off-centres ions perpendicular to the electric field remain unaffected [2]. Thermal equilibrium being maintained, it follows that site 1 (which is considered to correspond to an off-centre displacement parallel to the electric field) becomes preferentially populated at the expense of the occupancy of the other sites. An essential feature of this electric dipole approach is that one anticipates that the ratio, I_e/I , where I_e is the peak-to-peak height of the EPR line due to sites 1 and I is the peak-to-peak height of the EPR line due to sites 2, is given by

$$I_e/I = \cosh(\mu E_{\text{loc}} \cos \theta / kT) \quad (1)$$

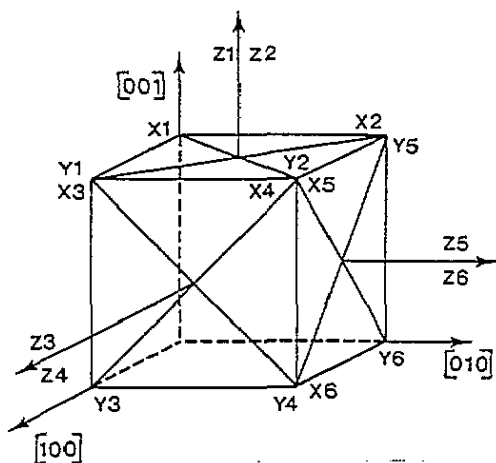


Figure 2. Labelling of the orthorhombic Cr^{5+} centres and directions of the principal centre axes.

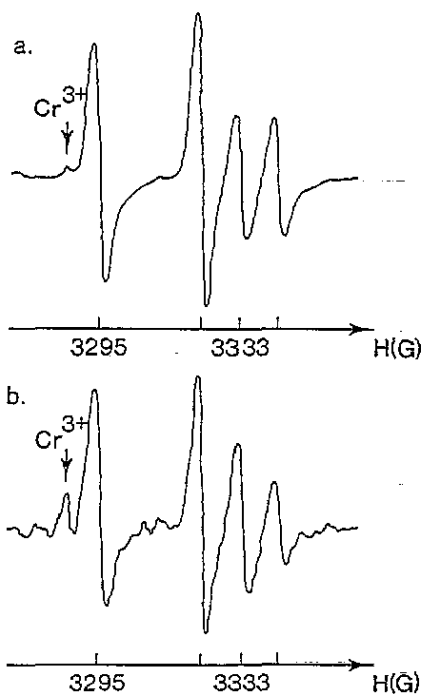


Figure 3. (a) EPR spectrum of orthorhombic Cr^{5+} in SrTiO_3 . H is oriented in the (110) plane, and about 25° away from the $[001]$ axis; $T = 77$ K. (b) As in (a), but now a static electric field has been applied; $E \parallel [1\bar{1}0]$, $E = 64$ kV cm^{-1} .

where μ is the electric dipole moment, θ is the angle between the off-centre dipole and the applied electric field, and E_{loc} , the local electric field, is given by $\frac{1}{3}(\epsilon + 2)E$, where the Lorentz factor $\frac{1}{3}(\epsilon + 2) \simeq 530$ [2, 15]. The full curve in figure 4 is a cosh function and represents the least-squares fit to the experimental behaviour represented by the dots. From the satisfactory agreement between the fit and the experimental results it is concluded that orthorhombic Cr^{5+} in SrTiO_3 at the Ti^{4+} site gives rise to a linear electric field effect on the orientational degeneracy that exists in zero field and thus the recently proposed off-centre assignment is confirmed by our experiments. The fit of figure 4 was obtained for $\mu = 2.88 \times 10^{-30}$ C m ($= 0.18e \text{ \AA}$). From $ed = 0.18e \text{ \AA}$ we infer an off-centre displacement of about 0.04 \AA (e is taken as five elementary charges). When the EPR experiments were

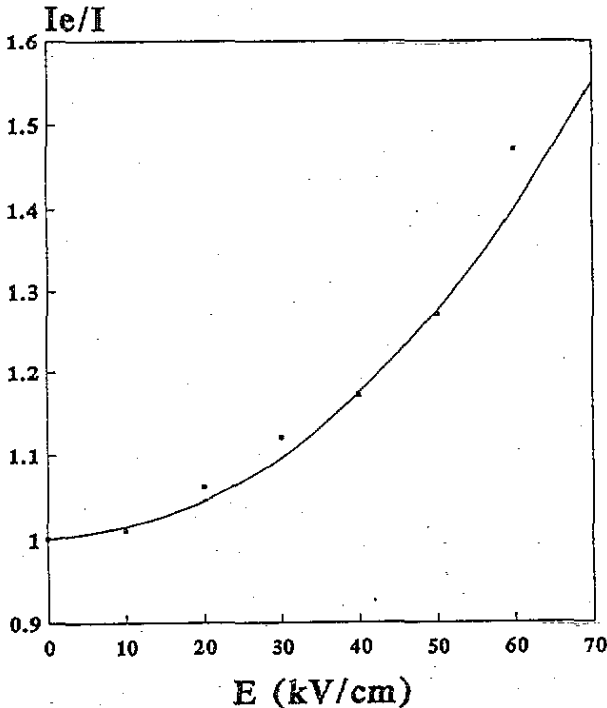


Figure 4. Plot of the intensity ratio I_c/I versus the strength, E of the applied electric field. I_c is the integrated line intensity due to site 1 and I is the integrated line intensity due to site 2; $E \parallel [110]$. The ratio was normalized to unity for $E = 0$. The full curve is a least-squares fit to a coth function.

repeated but now with H in the (100) plane and $E \parallel [110]$, the same values were obtained.

Previously, uniaxial stress experiments were performed for the orthorhombic $\text{SrTiO}_3:\text{Cr}^{5+}$ system [6, 7]. The results were interpreted in terms of a $T_{2g} \otimes (e_g + t_{2g})$ JT coupling. However, in the light of the new results reported here and elsewhere [8], the orthorhombic Cr^{5+} ion in SrTiO_3 is considered to be displaced off-centre in one of the $\langle 110 \rangle$ crystallographic directions. Therefore we reconsidered the results of our previous uniaxial stress experiments, now within the framework of an 'elastic' dipole model [15, 16].

As reported in more detail elsewhere [6, 7], when uniaxial stress is applied to the $\text{Cr}^{5+}:\text{SrTiO}_3$ single crystal, with the stress direction along the $[110]$ direction, the effect on the EPR spectrum of figure 3(a) is that the relative intensity of the EPR lines due to sites 1 and 2, is changed in favour of site 1 (having the resonance field at 3333 G) at the expense of site 2 (with its resonance field at 3341 G). No g -shifts or linewidth changes were observed when applying stress. More generally, regardless of the stress direction, we always found that the alignment was in favour of sites having an off-centre displacement perpendicular to the stress direction whereas the centres along the stress direction were suppressed. In this respect the stress behaviour of the Cr^{5+} centres is quite analogous to that of the $\text{Fe}^{2+}-\text{O}^-$ hole centre in SrTiO_3 [16]. Within the elastic dipole concept, the sixfold orientational degeneracy of the elastic dipole becomes lifted upon the application of uniaxial stress. One expects the off-centre position perpendicular to the stress direction to be lowest in energy. Thus, at thermal equilibrium, such centres are preferentially populated.

In reanalysing the experimental data of the stress experiments we write for the elastic

dipole energy [17]

$$\Delta U = V_0 \lambda \cdot \sigma \equiv \beta \cdot \sigma \quad (2)$$

Where β is the linear stress coupling tensor, with the dimension of a volume, and the stress tensor is given by σ . The λ tensor contains isotropic and anisotropic parts. The anisotropic part λ' , has zero trace [18]. For a uniaxial stress along the $[1\bar{1}0]$ direction, the differential stress coupling coefficient $\beta_{[1\bar{1}0]}$ of an orthorhombic defect in a solid of cubic symmetry is given as [17]

$$\beta_{[1\bar{1}0]} = V_0[\lambda'_2 - \lambda'_1] \quad (3)$$

where λ'_1 , λ'_2 and λ'_3 are the principal values of the λ' tensor. At thermal equilibrium, the EPR line intensity ratio becomes

$$I_\sigma/I = \exp(\beta_{[1\bar{1}0]}\sigma/kT) \quad (4)$$

where I_σ is the peak-to-peak height of the EPR line due to centre 1 (corresponding to the EPR line at 3333 G) and I is the peak-to-peak height of the EPR line due to centre 2 (corresponding to the EPR line at 3341 G). From our stress data [7] we find $\beta_{[1\bar{1}0]} = 4.19 \times 10^{-24} \text{ cm}^3$. This value is of the same order as the value ($3.48 \times 10^{-24} \text{ cm}^3$) found for the Fe^{2+} -O⁻ hole centre in SrTiO_3 [16].

In conclusion, we report on electric field experiments performed for the orthorhombic Cr^{5+} off-centre ion in SrTiO_3 . The data yield a linear electric field effect on the relative intensities of the EPR lines of the six orthorhombic Cr^{5+} sites. The results are additional evidence for the off-centre displacement of the Cr^{5+} impurity ion. As a consequence, we have also reconsidered our previous observations of changes of the relative intensities of the EPR lines of the orthorhombic sites when uniaxial stress is applied. Orthorhombic Cr^{5+} , besides being an off-centre ion, is also associated with an elastic dipole, and the results are interpreted in terms of the alignment of the elastic dipole in the presence of stress.

References

- [1] Faughnan B W 1972 *Phys. Rev. B* **5** 4925
- [2] Schürmer O F and Müller K A 1973 *Phys. Rev. B* **7** 2986
- [3] Müller K A 1971 *Magnetic Resonance and Related Phenomena, Proc 16th Congress Ampere* ed I Ursu (Bucharest: Rumanian Academy of Science) p 173
- Legendijk A, Morel R J, Glasbeek M and van Voorst J D W 1972 *Chem. Phys. Lett.* **12** 518
- [4] de Jong H J and Glasbeek M 1976 *Solid State Commun.* **19** 1197
- [5] de Jong H J and Glasbeek M 1978 *Solid State Commun.* **28** 683
- [6] Glasbeek M, de Jong H J and Koopmans W 1979 *Chem. Phys. Lett.* **66** 203
- [7] Koopmans W E 1985 *PhD Thesis* University of Amsterdam
- [8] Müller K A, Blazey K W and Kool Th W 1993 *Solid State Commun.* **85** 381
- [9] Kool Th. W and Glasbeek M 1979 *Solid State Commun.* **32** 1099
- [10] Kool Th. W. 1991 *PhD Thesis* University of Amsterdam
- [11] Kool Th. W. and Glasbeek M 1991 *J. Phys.: Condens. Matter* **3** 9747
- [12] Megaw H D 1973 *Crystal Structures: A Working Approach* (London: Saunders)
- [13] Unoki H and Sakudo T 1967 *J. Phys. Soc. Japan* **23** 546
- [14] von Waldkirch Th, Müller K A and Berlinger W 1972 *Phys. Rev. B* **5** 4324
- [15] Sakudo T and Unoki H 1971 *Phys. Rev. Lett.* **26** 851
- [16] Kool Th. W. and Glasbeek M 1993 *J. Phys.: Condens. Matter* **5** 361
- [17] Nowick A S and Heller W R 1963 *Adv. Phys.* **12** 251
- [18] Schoemaker D and Legendijk A 1977 *Phys. Rev. B* **15** 115