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V²⁺ in SrTiO₃: an extreme double acceptor

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Abstract. Vanadium-doped SrTiO₃ reduced above 1200 °C and then quenched is shown to contain a V²⁺ *double acceptor level* about 40 meV below the conduction band from resistivity measurements. Electron spin resonance (ESR) central hyperfine and *g*-shift values both indicate a 40% delocalisation of the spin density onto Ti conduction band levels. Upon cooling below 130 K, the ESR intensity freezes out. An exponential linewidth narrowing is observed with an activation energy E_D of 200 meV, which can be accounted for by the thermally activated hopping between V²⁺ and V³⁺ single acceptors. All data are compatible with the tight-binding calculations of Selme, Pecheur and Toussaint for the vanadium-impurity in SrTiO₃.

1. Introduction

Group-V substitutional impurities in elemental semiconductors form *shallow* donor levels, which in Si are of the order of 40 meV below the conduction band [1]. Electron spin resonance (ESR) experiments by Feher and co-workers first revealed the electronic structure and delocalisation of these impurities [2]. In contrast, 3d substitutional transition-metal impurities could be considered to be deep centres and relatively well localised [3], as also shown by ESR experiments for a number of them [4]. This certainly applies to the large-gap oxides such as MgO, Al₂O₃ and the titanates. A model substance for the latter class is SrTiO₃, where magnetic resonance results have been reviewed more recently [5]. Here we report combined electron spin resonance and relaxation with optical absorption and resistivity experiments in reduced and quenched SrTiO₃ doped with vanadium that indicate a V²⁺ d level first reported by Müller and Aguilar [6]. This d level lies just as far below the conduction band as the group-V donor elements are in silicon, but behaves as a very deep double-acceptor level. Both the V²⁺ level localisation and its energy difference from the single acceptor V³⁺, as well as its delocalisation, are in good agreement with the recently published tight-binding calculations of Selme *et al* for the same centre [7].

2. Creation and identification of the centre

The present experiments were carried out on vanadium-doped SrTiO₃ single crystals grown by the Verneuil technique. The V is substitutional for Ti. In well oxidised SrTiO₃,

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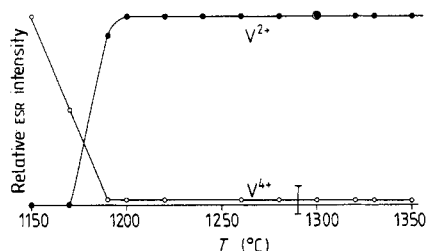


Figure 1. Intensity of the EPR V^{4+} and V^{2+} signals in $SrTiO_3$ at 80 K as a function of reducing temperature T before quenching the samples to room temperature.

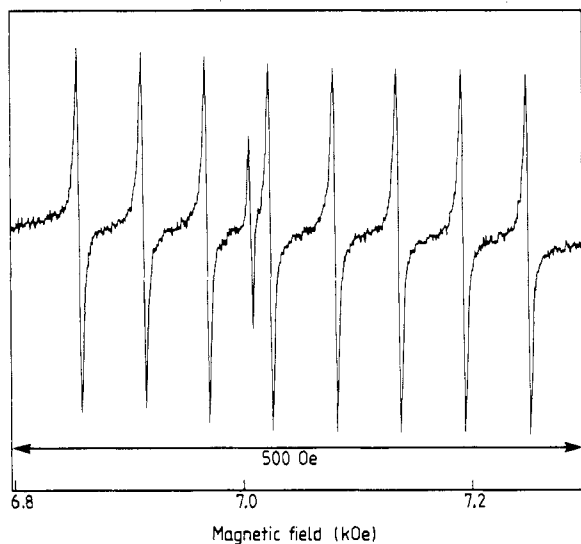


Figure 2. V^{2+} EPR signal at 80 K of reduced $SrTiO_3$. The line between the V^{2+} hyperfine split lines 3 and 4 is due to Cr^{3+} of oxidised parts of the sample. No other lines were recorded. The microwave frequency was 19.4 GHz.

the V is pentavalent with empty d orbitals, d^0 , i.e. it is a donor. An optical absorption band at 2.24 eV is observed due to charge transfer from the valence band, split by 0.42 eV, to the $d^0(t_{2g})$ level of V^{5+} [8]. Theoretical *ab initio* calculations by Weyrich [9] independently verified this splitting as being a feature of the valence band. Upon reducing such crystals containing 0.2% V in an atmosphere of 6% H_2/N_2 between 800 °C and 1200 °C and subsequent quenching to room temperature, the known ESR spectrum of V^{4+} is observed [10], i.e. the reduction process has populated the $d(t_{2g})$ level with one electron. The V^{4+} is a neutral centre as it replaces the intrinsic Ti^{4+} ion. In figure 1, the intensity of the V^{4+} ESR spectrum measured at 80 K is plotted versus reducing temperature. It is seen that the V^{4+} state is prevalent up to 1150 °C and then drops to a very low value for reducing temperatures of 1200 °C and above.

After reduction at just below 1200 °C, a new ESR signal is observed, as shown in figure 2, which is attributed in section 3 to $V^{2+}(3d^3)$, $S = \frac{3}{2}$, which, being doubly negatively charged with respect to Ti^{4+} , is a double acceptor. From the intensity curve in figure 1, it is evident that near 1170 °C the vanadium can be neither in the V^{4+} nor in the new V^{2+} state. $V^{3+}(3d^2)$ has an even number of electrons with $S = 1$ not observed by ESR in cubic symmetry. Thus we attribute the missing ESR signals to this intermediate state. Charge transfer bands at 1.8 eV, which correlate neither with V^{4+} nor V^{5+} and are attributed to the V^{3+} single acceptor, corroborate this conclusion [11]. Since the vanadium exists as V^{5+} donors, neutral V^{4+} , and V^{3+} single and V^{2+} double acceptors in $SrTiO_3$, it is amphoteric in character. In figure 3 we reproduce the levels for the four vanadium nominal charges as computed by Selme *et al* [7] for clarification.

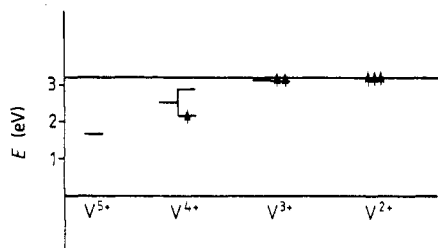


Figure 3. Energy levels of V⁵⁺, V⁴⁺, V³⁺ and V²⁺ from unrestricted tight-binding calculations of Selme *et al* [7].

The new ESR spectrum is observed below 130 K. Figure 2 shows it has an eight-line hyperfine splitting as expected for a vanadium centre and is very slightly tetragonal below 105 K, mirroring the tetragonal symmetry of SrTiO₃ below its structural phase transition at this temperature. Its hyperfine splitting is less than half that of V⁴⁺. The spectrum can be accounted for, to a first approximation, with half-integral spin S , and g -values and hyperfine splitting parameters of $\bar{g} = 1.965(2)$ and $A = 48.5(3) \times 10^{-4} \text{ cm}^{-1}$ using an isotropic Hamiltonian $\mathcal{H} = g\beta S \cdot H + AS \cdot I$. The linewidth $\Delta H(4.2 \text{ K}) = 2.25 \text{ G}$. An integral spin would yield a considerably larger linewidth due to the increased spin–lattice coupling [12]. Whereas V⁴⁺ exhibits a large anisotropic ESR spectrum due to the static Jahn–Teller effect [10], the nearly cubic symmetry of the new spectrum suggests a half-filled t_{2g} subshell, or the presence of a dynamic Jahn–Teller effect. It appears from figures 1 and 3 that V²⁺ with $S = \frac{3}{2}$ is the most likely possibility. As SrTiO₃ is tetragonal below 105 K, the $S = \frac{3}{2}$ state of V²⁺ should show the split $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ fine-structure lines. These have not been observed. The same was actually the case for the isospin Fe⁵⁺ centre with $S = \frac{3}{2}$ [13]. Small fine-structure splittings of a few gauss with large linewidths have been found for Cr³⁺ and Mn⁴⁺ with $S = \frac{3}{2}$ [5]. The ionic radii of the latter two ions match that of the substituted Ti⁴⁺ in contrast to Fe⁵⁺ or V²⁺. Thus for the latter species, strain due to this mismatch may be a cause for excessive linewidth broadening. For V²⁺, there is also a large spin density delocalisation to be discussed next.

3. d spin and charge delocalisation

The central hyperfine parameter \bar{A} observed for V²⁺ in the present case is anomalously low, only 68% that of $\bar{A} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$ of V⁴⁺ [10]. For the transition-metal ions Me^{*n+*}, \bar{A} is known to be due to the negative core polarisations (CP) of the 1s, 2s and 3s filled shells by the 3d electrons reduced by the positive CP of the 4s [14]. The latter is larger for the Me⁴⁺ than for the Me²⁺ as well as for the more covalently bonded semiconductors [14]. The 4s orbitals of the magnetic ion hybridise with the sp-like conduction band states. In SrTiO₃, the empty bands derived from Ti 4s lie well above the conduction band which has Ti(3d)–O(2p) character and therefore cannot be the origin of the large reduction in \bar{A} . It is also important to bear in mind that the V²⁺ hyperfine constant in the standard cubic oxide MgO is entirely normal. Table 1 compares the hyperfine constants A of V²⁺ in the two oxides with those of Mn²⁺. As is well known and can be seen in the table, they are nearly the same for the deep-lying localised V²⁺ and Mn²⁺ in MgO. Therefore we have to attribute the reduction of $(38 \pm 2)\%$ of $\bar{A}(\text{V}^{2+})$ in SrTiO₃ to the delocalisation of the V(t_{2g}) electrons onto t_{2g} orbitals of the Ti–O (t_{2g}) conduction band states. This conjecture is confirmed by the observed V²⁺ g -values. In MgO, $g(\text{MgO}) = 1.991$ which is mainly due to the admixture of higher V²⁺ states by spin–

Table 1. Absolute hyperfine splitting parameters A in 10^{-4} cm^{-1} of Mn^{2+} and V^{2+} in MgO and SrTiO_3 from [5], [15] and this work.

	MgO [15]	SrTiO ₃
Mn^{2+}	81.2	82.6†
V^{2+}	75.1	48.5‡

† From [5].

‡ From this work.

orbit interaction. Here $g(\text{SrTiO}_3) = 1.966$ which is considerably larger. Assuming the difference to be due to delocalisation onto Ti t_{2g} orbitals only, and knowing that the \bar{g} -value of Ti^{3+} in oxides ranges from 1.926 to 1.953 [15] in the absence of the Jahn–Teller effect, a Ti^{3+} percentage of 33 to 53% is obtained from $(g(\text{MgO}) - g(\text{SrTiO}_3))/\Delta g(\text{Ti}^{3+})$. The average is a $(45 \pm 10)\%$ delocalisation. This value is less precise than the value $(38 \pm 2)\%$ derived from the reduced central hyperfine interaction, but still quite similar. The unrestricted Green function calculation by Selme *et al* [7] yielded a 47% density on the V^{2+} , i.e. a total delocalisation of 53%, of which 2% are on the oxygen and 51% on the Ti 3d orbitals. This justifies our approach in using only the g -shifts of Ti^{3+} to estimate the delocalisation of these d orbitals. All in all, we can regard the agreement between our estimates from the reduced hyperfine interaction and g -shifts with the theoretical calculation to be quite satisfactory with a large delocalisation of between 35 and 51%.

4. The V^{2+} and V^{3+} energy levels near the SrTiO_3 conduction band

V^{2+} ions in oxides have long spin–lattice relaxation times due to their small coupling coefficient to the lattice, and their spectra are easily detected at and above room temperature [12, 15]. The present spectrum is anomalous in this respect also, because it disappears above 130 K owing to an exponential linewidth broadening. Figure 4 shows a plot of $\log \Delta H$ versus $1/T$, where $\Delta H = \Delta H(T) - \Delta(H)$ (4.2 K). The activation energy is $E_{\Delta H} \approx 200 \text{ meV}$. Such exponential linewidth broadening is either due to Orbach relaxation via an excited state [16] in insulators, or to carrier hopping between different charged states of an impurity in a semiconductor [17].

In order to distinguish between these two possibilities, four-point probe resistivity measurements were carried out on a sample of reduced $\text{SrTiO}_3:\text{V}$. The contacts consisted of silver paint. Figure 5 shows $1/R(T)$, the temperature dependence of the conductivity, plotted against $10^3/T$. In the range between 100 and 300 K, a line is observed corresponding to an activation energy of approximately $\Delta E_R = 40 \text{ meV}$. This value is five times smaller than that obtained from the line broadening, $\Delta E_{\Delta H} = 200 \text{ meV}$. Assuming that the V^{2+} relaxes via an Orbach process to the conduction band states, i.e.

$$\Delta H_{\text{pp}} - \Delta H_{\text{pp}}(0) \propto 1/T = (1/T_0) \int_0^{100 \text{ meV}} \exp(-(E_D + E)/kT) D(E) dE \quad (1)$$

with $D(E) = \alpha(E - E_c)^2$ or $D(E) = \alpha'(E - E'_c)^3$ from photoemission experiments [18], the observed linewidth broadening gives $E_D \approx 96 \text{ meV}$, which is still a factor of 2.5 larger than the observed E_R . Thus band Orbach relaxation of the shallow V^{2+} is highly unlikely.

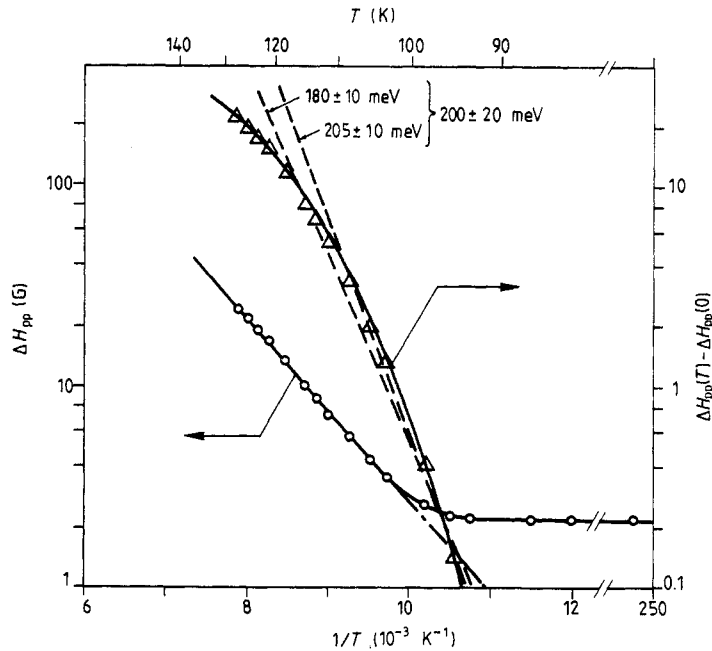


Figure 4. The peak-to-peak linewidth of ΔH_{pp} of V^{2+} hyperfine line plotted logarithmically versus $1/T$.

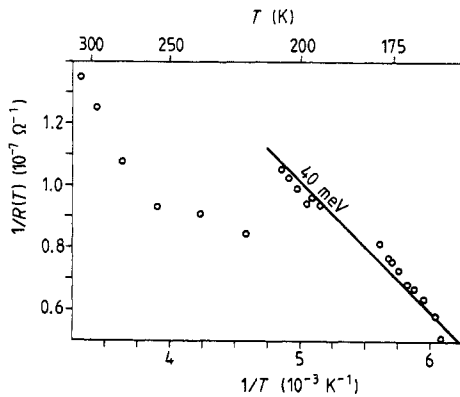


Figure 5. $1/R(T)$ of $SrTiO_3:V$ reduced at $1200^\circ C$ plotted versus $1/T$. $R(T)$ was measured by the four-point method.

This conclusion is further strengthened by the large energy $\Delta E \geq 96$ meV, where according to equation (1) the relaxation would peak at 170 meV (or about three times the highest phonon energy in $SrTiO_3$).

Considerable progress in understanding was achieved as a result of subsequent theoretical calculations of V impurity levels in $SrTiO_3$ [7]. As there is agreement between observed spins and calculated charge delocalisation, one may also assume, to begin with, that the calculated locations of the energy level of V^{2+} are correct. The theoretical result is that V^{2+} is very shallow with respect to the conduction band. Thus we can conclude from the resistivity experiment that $\Delta E_R \approx 40$ meV is that distance, although this is idealised since the $SrTiO_3$ conduction band is not spherical [19].

The theoretical energy separation between the V^{3+} single and V^{2+} double acceptors is of the order of 130 meV [7]. This energy is comparable to the 200 meV measured via

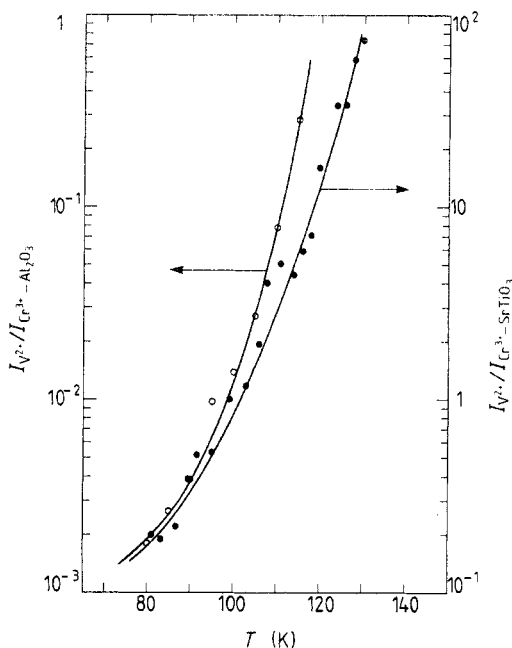


Figure 6. Intensity (amplitude $\times \Delta H(T)^2$) of the V^{2+} ESR signal as a function of temperature: relative to an $Al_2O_3:Cr^{3+}$ sample, and relative to the Cr^{3+} signal in the V-doped $SrTiO_3$; see figure 2. The lines are guides to the eye.

the linewidth broadening. Thus carrier hopping between the V^{2+} and V^{3+} levels is a possible broadening mechanism, as has been identified for the neutral Fe^{3+} ESR linewidth in GaAs where $\Delta E_{\Delta H} \approx 58$ meV. If this is the case, then carrier freeze-out to the V^{3+} should occur upon cooling and reducing the V^{2+} signal. In order to investigate this possibility, we have tried to measure the intensity of the V^{2+} EPR spectrum as a function of temperature.

The V^{2+} intensity measurements were quite difficult to carry out since the high temperature-dependent dielectric constant of $SrTiO_3$ caused changes of the mode in the cavity and therefore in spectrometer sensitivity. Furthermore, the samples were partially conducting. It was therefore decided to measure the intensity of the V^{2+} signal relative to a standard. A first series of data were taken with a small piece of ruby, $Al_2O_3:Cr^{3+}$, glued to the $SrTiO_3:V$ reduced sample. The result of these measurements is shown in figure 6. Upon cooling, the V^{2+} intensity first decreases almost linearly below 120 K, then more quadratically.

Since the possibility exists that the microwave mode in the low-dielectric-constant Al_2O_3 is not the same as in $SrTiO_3$, a second type of relative measurements was performed. The V^{2+} signal was measured against the Cr^{3+} impurity which was unintentionally present in the same $SrTiO_3$ crystal, as seen in the spectrum of figure 2. The result of this second measurement is also plotted in figure 6. The decrease is even more nearly linear than that for Al_2O_3 . However, the Cr^{3+} signal is due to better oxidised parts of the single crystal, as its level lies about mid-band. Thus this curve is again not entirely reliable. However, both curves indicate that a substantial freeze-out occurs below 130 K. We do not expect an exponential freeze-out to the V^{3+} level because the V^{2+} level lies so close to the conduction band, which in addition has minima along $\langle 100 \rangle$ cubic directions [19]. Be this as it may, our intensity measurements show that a V^{2+} intensity freeze-out is compatible with the theoretical $V^{2+}-V^{3+}$ level separation.

5. Conclusion

The spin density of the double acceptor V²⁺ in SrTiO₃ is delocalised by 35 to 51% to the conduction-band titanium wave function as inferred from its core polarisation and ESR g-shift. This is in agreement with theoretical tight-binding calculations of Selme *et al* [7]. From resistivity measurements, the V²⁺ is located ≈ 40 meV below the conduction band; hopping relaxation data indicate that V²⁺ (t_{2g}³) is 200 meV above the V³⁺ (t_{2g}) level, near the theoretical value $E(V^{2+}) - E(V^{3+}) \approx 130$ meV. An intensity freeze-out of the V²⁺ to V³⁺ is also observed. Thus the agreement between experiment and theory is found to be quite satisfactory for these extremely deep acceptors with energies nearly equal to the band gap of 3.2 eV in SrTiO₃.

Acknowledgments

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