Effect of electric fields on the spectra of off-centre substitutional defects in strontium oxide

A. Edgar, I. Brunskill, N. Manson, Y. Haider

Effect of electric fields on the spectra of off-centre substitutional defects in strontium oxide

A. Edgar (*), I. H. Brunskill, N. B. Manson and Y. Haider

Department of Solid State Physics, Research School of Physical Sciences, Australian National University, Canberra ACT 2600, Australia

Résumé. — On rapporte des expériences de modulation par champ électrique de l'absorption optique et du spectre RPE d'ions Co^{2+} hors position dans SrO. Les changements dans le spectre optique induits par le champ sont attribués aux effets combinés des déplacements Stark et à la redistribution des dipôles électriques hors position dans les 8 orientations $\langle 111 \rangle$ possibles. Les mesures de vitesse de réorientation peuvent être analysées à l'aide de la loi classique d'Arrhénius avec une énergie d'activation de 0,017 eV et un facteur préexponentiel $\tau_0 = 1{,}2 \times 10^{-9}$ s.

Abstract. — Experiments involving electric-field modulation of the optical absorption and EPR spectra of off-centre Co^{2+} ions in SrO are reported. The field-induced changes in the optical spectra are assigned to the combined effects of Stark shifts and to the redistribution of off-centre electric dipoles amongst the 8 possible $\langle 111 \rangle$ orientations. Measurements of the reorientation rate may be fitted by a classical Arrhénius process with activation energy 0.017 eV and pre-exponential factor $\tau_0 = 1.2 \times 10^{-9}$ s.

1. **Introduction.** — Most studies of off-centre impurity ions in solids have been concerned with alkali halide crystals containing Li^+, Cu^+ or Ag^+ ions. Recent work by ourselves [1, 2] and others [3, 4] shows that off-centre effects also occur for some transition metal ions of the 3d series in the alkaline earth oxide lattices SrO and BaO, which are isostructural with the alkali halides. These systems are particularly convenient to study since the impurity ions have unfilled outer shells in the ground configuration and may therefore be investigated with conventional spectroscopic techniques. For SrO, we have reported Fe^{2+} and Co^{2+} ions to be off-centre along $\langle 111 \rangle$ directions using EPR and optical spectroscopy [1, 2], and in unpublished work obtain the same result for Ni^{2+} ions.

As yet, investigations into these off-centre systems in the alkaline earth oxides have not progressed far past the identification of the basic effect. Sochava *et al.* [4] have obtained a dipole moment of 1.3 Debye for Cu^{2+} ions in SrO using applied electric fields, and have observed motional averaging effects in the EPR spectra above 8 K, implying a very fast relaxation rate and thus a shallow-well off-centre system. However, this case is complicated by a Jahn-Teller interaction. The potential surfaces for Co^{2+}, Ni^{2+} and Fe^{2+} ions, which are insensitive to the Jahn-Teller effect for trigonal symmetry, have yet to be characterised.

(*) Present address : Institut für Angewandte Physik der Universität Bonn.

In this paper, we report measurements of the reorientation rate of off-centre Co^{2+} ions between equivalent $\langle 111 \rangle$ configurations using spectroscopic techniques to follow the population changes induced by time-varying electric fields.

2. **Theory.** — We consider the effect of an applied electric field upon the position and intensity of a sharp spectral absorption line arising from an off-centre ion. For simplicity, we assume that in the present case $\underline{E} /\!/ \langle 001 \rangle$, which renders the $\langle 111 \rangle$ off-centre electric dipoles equivalent in two sets of four. Generalisation to other field orientations is straight-forward. The electric field has two effects upon the absorption intensity $I(\nu)$ of a line centred at ν_0. First, it shifts the line centre for each set in opposite directions through the linear Stark effect, and second, it induces a population redistribution between the two sets of dipoles of dipole moment $\underline{\mu}$. If the instantaneous populations of the two sets are N_+ and N_- and the total population is N, then using a Taylors series expansion we obtain,

$$I(\nu, E) = NI(\nu, 0) + (N_+ - N_-)\frac{\partial I}{\partial \nu}\frac{\partial \nu_0^+}{\partial E} E + \\ + \frac{N}{2}\frac{\partial^2 I}{\partial \nu^2}\left(\frac{\partial \nu_0}{\partial E}\right)^2 E^2 . \quad (1)$$

The observed change in intensity depends upon the form of the electric field. For a step-function change, there will be a sudden step given by the third term in (1) followed by an exponential relaxation given by

the second term as the dipole population relaxes according to

$$(N_+ - N_-) = \Delta N_0 \{ 1 - \exp(-2\omega t) \} \quad (2)$$

where ω is the jump frequency, and $\Delta N_0 = (N\underline{\mu}.\underline{E})/kT$. For a sinusoidal electric field of angular frequency ω_E we have [5]

$$N_+ - N_- = \frac{N}{kT(1 + \omega_E^2 \tau^2)} \times \times \underline{\mu}.\underline{E}(\cos \omega_E t + \omega\tau \sin \omega_E t) , \quad (3)$$

where $\tau = 1/2\omega$ is the relaxation time. Thus in this case we predict a second-derivative, temperature-independent, in-phase signal given by the third term in (2), and first-derivative, temperature-dependent in-phase and quadrature signals from the second term. The quadrature component has the Debye shape of a conventional dielectric relaxation experiment.

3. **Experimental techniques.** — EPR spectra were recorded with a Varian E-12 35 GHz spectrometer using a cavity and electrode structure similar to that described earlier [5]. Optical absorption spectra were measured with a Spex 3/4 meter monochromator and EMI 9659B photomultiplier. Two different arrangements were used to obtain sample temperatures between 4.2 K and 295 K. In the first system, used solely for the optical measurements, the sample was clamped to the cold finger of an Air Products continuous flow cryostat. Electric fields up to 40 kV/cm could be obtained before breakdown occurred. In the second arrangement, used for both optical and EPR measurements, the sample was attached to a variable temperature insert immersed in helium exchange gas within an Oxford Instruments superconducting magnet cryostat. Breakdown of the exchange gas limited the maximum field strength in this case to $\lesssim$ 10 kV/cm. For the optical experiments, the electric field was always applied perpendicular to the direction of the light beam.

Sinusoidal voltages of up to 10 kV at 115 Hz were provided from a conventional oscillator and step-up transformer arrangement, and pulsed voltages up to 1.5 kV were obtained by chopping a high voltage DC supply. The pulse rise time was $\sim$ 20 μs.

4. **Experimental results.** — Strong electromodulated signals were observed in the EPR spectrum of $SrO:Co^{2+}$ using simultaneous sinusoidal electric-field and magnetic-field modulation [5], and these signals were at first assigned to the re-orientation and Stark effects described earlier. However, the use of pulsed electric fields clearly showed that the effects were in fact due to an electric-field-induced modulation of the saturation factor in the EPR lines, and that the relaxation observed when the field was switched both on and off was due to electronic spin-lattice relaxation rather than to ionic relaxation. The use of very low microwave powers eliminated these saturation effects but the Stark shift and re-orientation signals could not then be detected with the maximum electric field strengths available.

However, the optical experiments for $SrO:Co^{2+}$ clearly showed the behaviour predicted in section 2. Figure 1 shows the optical absorption in the band

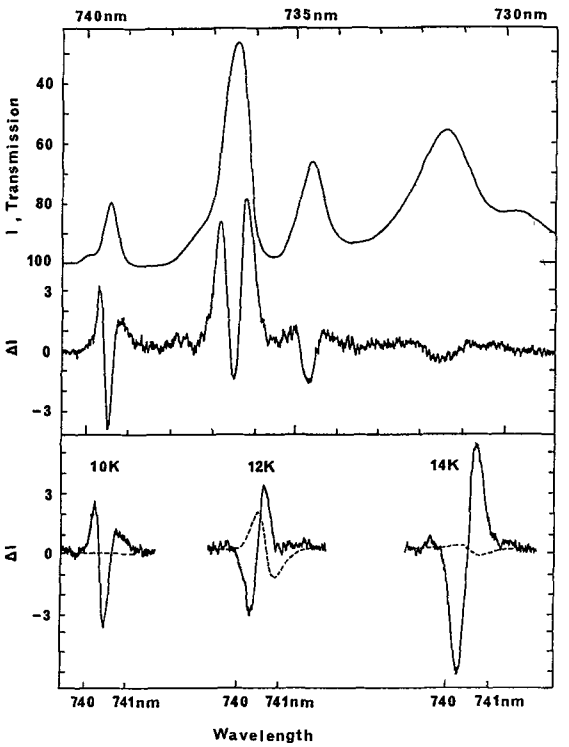

Fig. 1. — Optical absorption spectrum and electric-field-modulated absorption signals for the 735 nm band in $SrO:Co^{2+}$. The lower traces give in-phase (solid line) and quadrature (dashed line) electric-field-modulated signals at various temperatures for the zero-phonon line at 739.5 nm.

at 735 nm [1]. The modulated absorption signal, induced by an alternating electric field with $E /\!/ \langle 111 \rangle$, and detected using a two channel lock-in amplifier operating at $2\omega_E$, is also shown for various sample temperatures. Below about 10 K, the in-phase detected signal has the temperature independent second-derivative shape expected for a pure Stark effect, and there is no quadrature signal. As the temperature is raised above about 14 K the shape of the in-phase signal changes and it eventually takes on almost a first derivative shape. At the same time, a quadrature, first-derivative signal appears, reaches a maximum at $\approx$ 12 K, and then diminishes for higher temperatures. These effects also occur for $SrO:Ni^{2+}$, except that the temperature at which the quadrature signal reaches a maximum is considerably higher at $\sim$ 55 K. These lineshapes and their temperature dependences are exactly as predicted in section 2, and can in principle be used to measure the characteristics of

the dipole re-orientation as was done for $CaF_2:Gd^{3+}$ using EPR [5]. However, having established the origin of the electromodulated signals, it is more convenient to use pulsed electric fields and to measure the relaxation processes directly, with the aid of signal averaging techniques. Figure 2 shows the time

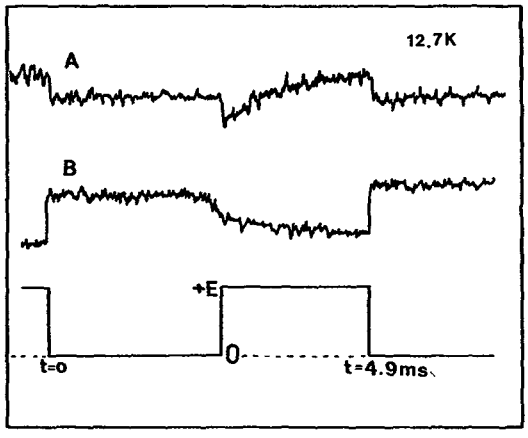

Fig. 2. — Response of the optical absorption at 736,2 nm (A) and 736.7 nm (B) to a pulsed electric field for a sample temperature of 12.7 K.

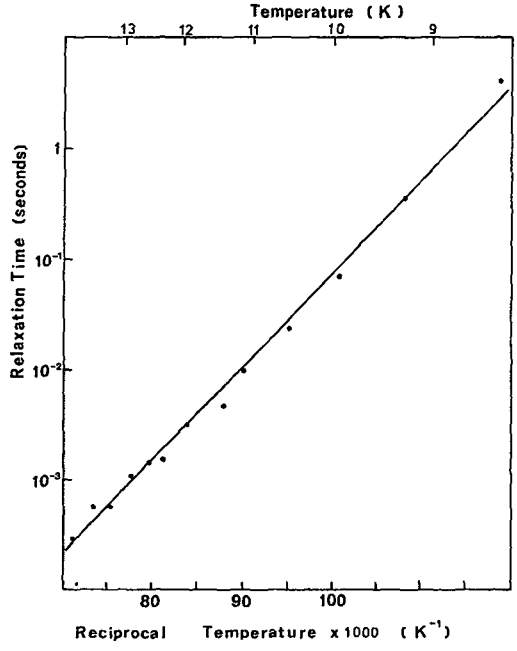

Fig. 3. — Relaxation time for off-centre Co^{2+} ions as a function of temperature.

dependence of the photomultiplier signal at 736.2 nm and 736.7 nm as an electric field of 5 kV/cm along $\langle 110 \rangle$ is switched on and off. At 736.2 nm there is first a very fast response as the field is switched on, corresponding to the Stark splitting of the line, followed by an exponential decay due to dipolar re-orientation. At 736.7 nm the second derivative of the lineshape is zero and so only the decay is observed. The time constant τ of the decay was determined over the temperature range $\sim$ 8 K-14 K by least squares fitting to the averaged signals. Figure 3 shows the observed temperature dependence of τ, which may be described by a classical thermally activated process of the form $\tau = \tau_0 \exp(-u/kT)$, with $u = 0.017$ eV and $\tau_0 = 1.2 \times 10^{-9}$ s.

5. **Conclusions.** — The measurements reported here provide further support for the off-centre character of Co^{2+} ions in strontium oxide. The very low energy barrier for re-orientation is incompatible with other models involving nearby lattice defects which might otherwise account for the observed trigonally symmetric EPR spectra. No evidence for quantum-mechanical tunneling in the ground state has been obtained, but the comparatively large value of τ_0 obtained suggests that re-orientation may occur *via* tunnelling in an excited vibrational state.

DISCUSSION

Question. — S. KAPPHAN.

What is the order of magnitude of the dipole moment ? Can at low temperatures the dipoles be aligned to separate the dipole alignment and the Stark-effect part ?

Reply. — A. EDGAR.

Our theoretical investigations suggest a value of $\sim$ 0.5 Debye and we intend to obtain an experimental value through the field dependence of the relaxation time. In the step function experiments, the Stark and dipolar reorientation signals are, in effect, time-resolved, and so separation is no problem.

Question. — O. KANERT.

Is it possible, to extend your measurements to lower temperatures in order to observe deviations from the Arrhenius-behaviour (given for instance by phonon-assisted tunnelling effects) ?

Reply. — A. EDGAR.

We plan to follow the relaxation behaviour down to our lower temperature limit of 4.2 K in order to check for such effects.

References

[1] MANSON, N. B. and EDGAR, A., *J. Semiconductors and Insulators* **3** (1978) 209.
[2] EDGAR, A. and HAIDER, Y., *J. Phys. C* **11** (1978) 2595.
[3] TOLPAROV, Yu. N., BIR, G. L., SOCHAVA, L. S. and KOVALEV, N. N., *Soviet Phys. Solid State* **16** (1974) 573.
[4] SOCHAVA, L. S., TOLPAROV, Yu. N. and KOVALEV, N. N., *Soviet Phys. Solid State* **17** (1975) 127.
[5] EDGAR, A., *J. Phys. E* **10** (1977) 1261.