Electron Spin Resonance of V⁴⁺(VO²⁺) in Beryl

D. R. Hutton, F. A. Darmann and G. J. Troup

Department of Physics, Monash University, Clayton, Vic. 3168, Australia.

Abstract

Synthetic Australian Biron beryl coloured green by vanadium was irradiated with a dose of 10 kGy of ¹³⁷Cs γ rays. The resulting ESR spectrum has been modelled as being due to 12 equivalent VO²⁺ centres, each arising from a complex formed from the substitution of V³⁺ in the beryl aluminium octahedral site, together with electron loss and motion towards a nearest neighbour oxygen. Each centre can be fitted to an axial spin Hamiltonian

$$H = \beta H \cdot g \cdot S + I \cdot A \cdot S,$$

with parameters $S = \frac{1}{2}$, $I = \frac{7}{2}$ and

 $g_{||} = 1 \cdot 93 \pm 0 \cdot 01, \qquad g_{\perp} = 1 \cdot 97 \pm 0 \cdot 01,$ $A_{||} = (170 \pm 2) \times 10^{-4} \text{ cm}^{-1}, \qquad A_{\perp} = (55 \pm 2) \times 10^{-4} \text{ cm}^{-1},$

and with the z axis at 64° to the crystal c(0001) axis and at 74° to a crystal a axis.

1. Introduction

The silicate mineral beryl has long been of importance to the gem industry and is increasing in importance to the laser industry. Gem varieties coloured by ~1% transition metal impurities are emerald (bright green—chromium and vanadium), aquamarine (clear sky blue–ferrous iron) and of lesser importance yellow heliodor (ferric iron) and pink morganite (manganese). Synthetic pink Biron 'morganite' is coloured by titanium (Troup *et al.* 1990).

The structure of beryl $Be_3Al_2Si_6O_{18}$, space group P6/mcc, was determined by Bragg and West (1926), and has been illustrated in many publications since, for example Deer *et al.* (1986). It contains large open rings of composition Si_6O_{18} made up of SiO₄ tetrahedra and arranged in layers in the basal plane and linked laterally and vertically by Be^{2+} and Al^{3+} ions in fourfold tetrahedral and sixfold octahedral coordination respectively. The stacking of the rings gives large honeycomb-like, open channels parallel to the hexagonal *c* axis of the crystal. Large impurities such as water molecules, alkali metal ions and carbonate ions may be accommodated interstitially at various positions within the channels (Deer *et al.* 1986). However, transition metal ions are generally considered to substitute for Al^{3+} and Be^{2+} ions, with both Cr^{3+} in emerald (Geusic *et al.* 1959) and V^{3+} in beryl (Beckwith and Troup 1973) substituting into the Al³⁺ site, trigonially distorted along the *c* axis of the crystal.

ESR has provided a very useful probe of transition metal impurity sites in beryl, giving valuable information on single ion site symmetry, pair arrangements, and the effects of radiation and heat treatment. The commonly present ions $Cr^{3+}(3d^3)$ and $Fe^{3+}(3d^5)$ give valuable orientation data for crystals containing other atoms or ions such as hydrogen, CO_3^- and Mn^{2+} . Vanadium



Fig. 1. ESR spectra from γ irradiated vanadium doped beryl, illustrated for the magnetic field along the *c* axis, and the perpendicular twofold rotation axes. For the later two, the spectra have collapsed into three sets of four equivalent spectra, labelled according to the centre allocation shown in Fig. 2.

has been previously measured as $V^{3+}(3d^2)$ by optical means (Beckwith and Troup 1973), with its detection by ESR requiring radiation treatment to $V^{4+}(3d^1)$ or $V^{2+}(3d^3)$.

2. Experimental

All measurements were carried out at X band and at room temperatures. Initial data were collected from a 4 mm a side cube of sample, mounted on a horizontal axis rotator (Hutton and Seed 1966) installed in a purpose built single crystal spectrometer. Precision data were collected from a Varian E12 X band spectrometer, using a 1 mm a side crystal mounted on a two-axis goniometer (Morton *et al.* 1981). This machine yielded accurate measurements from an EIP548A microwave frequency counter and a precision magnetic field Hall probe calibrated by proton NMR.

Initial experiments on V^{3+} doped beryl showed only a spectrum from a trace of Cr^{3+} present in the crystal growth feedstock. However, the angular dependence of this spectrum was very useful in identification of the *c*-axis direction (Geusic *et al.* 1959) of the beryl crystal.

The samples were then irradiated with a 10 kGy dose of γ radiation from an Isomedix Gammacell 1000 ¹³⁷Cs source. This left the chromium line unaffected, but created an ESR spectrum of nearly 100 lines close to g = 2.

Along the *c* axis the spectrum collapsed to eight lines (see Fig. 1), which indicated that all vanadium centres present were equivalent along the *c* axis. This also indicated that this axis was not a principal axis of the centres, and hence the site was neither cubic nor trigonal, as are most other transition metal substitutional sites in beryl. Rotation of the crystal to the (0001) plane reduced the spectrum to 48 lines and further rotation to twofold symmetry rotation axes, to 24 lines (see Fig. 1). An orthogonal set of axes A, B, C was then chosen for the ESR data collection, A being the *c* axis and B and C the orthogonal twofold symmetry axes of the crystal. The axes B and C were identified relative to the structure of beryl by carrying out X-ray 2θ scans and rocking curves, with final verification of axis directions being by Laue back reflection photographs.

Using the ESR two-circle goniometers, data were then collected in the three mutually orthogonal planes *AB*, *AC* and *BC*. From these data sets the eight lines arising from one centre were identified and then carefully and with much difficulty traced throughout the three planes. First and second order perturbation theory was then applied to calculate the Zeeman and hyperfine parameters g and A for every 5° of rotation, and then these data were fitted to curves of the form

 g^2 , $g^2 A^2 = A_i + B_i \cos 2\theta + C_i \sin 2\theta$,

with θ measured for each axis in turn over the planes. From the parameters A_i, B_i, C_i so calculated, the matrices for $g^2, g^2 A^2, A^2$ are generated, whereupon diagonalisation gives the principal values and directions of the tensors for the ESR centre.

3. Results and Discussion

The X-ray methods detected a strong Bragg reflection at $2\theta = 11^{\circ}$ with a wavelength of 1.54 Å. This arises from beryl (0110) planes 8 Å apart, and shows that the *C* axis is a crystal '*a*' axis. This orientation was then confirmed with a Laue back reflection photograph.

The ESR data gathered were fitted to the spin Hamiltonian appropriate to V⁴⁺ ($S = \frac{1}{2}$, $I = \frac{7}{2}$ for ⁵¹V 99.5% abundant)

 $H = \beta H.g.S + I.A.S,$

and a good fit was obtained from the diagonalisation procedure for the following parameters:

 $g_{zz} = g_{||} = 1 \cdot 93 \pm 0 \cdot 01, \qquad g_{yy} = g_{xx} = g_{\perp} = 1 \cdot 97 \pm 0 \cdot 01,$

 $A_{zz} = A_{||} = (170 \pm 2) \times 10^{-4} \text{ cm}^{-1}$, $A_{xx} = A_{yy} = A_{\perp} = (55 \pm 2) \times 10^{-4} \text{ cm}^{-1}$.



Fig.2. Stereographic projection illustrating the data collection planes, the angular direction of a principal axis Z_1 of one VO²⁺ centre, and the direction of the other 11 centres (2–12) related by the symmetry elements 6/*mmm* of beryl. Also illustrated are the AlO₆ bond directions *P*, *Q*, *R* for the Al₁O₆ octahedron and *L*, *M*, *N* for the Al₂O₆ octahedron.

Thus the calculations revealed that the Zeeman and hyperfine tensors are very nearly (if not) axial, to within the uncertainties indicated, and their directions are coincident to within $\pm 2^{\circ}$. Fig. 2 shows the orientation of the principal axis of one of the ESR centres, and indicates the orientation of the other 11 centres generated by the symmetry elements 6/mmm of the crystal.

Note that the magnetic axes nearly coincide with the Al–O bond directions for the AlO_6 units in beryl (Fig. 2), six for Al_1 and six for Al_2 , the two Al atoms in the unit cell.

The more complex spectra of Fig. 1 can now be explained as being the sum of the spectra from 12 centres, all equivalent for spectrum A, and for spectra B and C, the sum of three sets of four directly equivalent centres as illustrated in Fig. 1, in terms of the centre numbering of Fig. 2.

Since V^{3+} in beryl substitutes into the aluminium site with a trigonal distortion along the *c* axis, we would like to postulate that, on irradiation which produces the loss of one further d electron, the vanadium ion moves towards one of the oxygens of the AlO₆ unit forming the vanadyl VO²⁺ complex, with a centre of essentially tetragonal symmetry. Irradiation does not obviously affect the colour of this material and there are only marginal changes in the optical–UV spectrum (a band at $2 \cdot 64 \times 10^{-4}$ cm⁻¹ is replaced by one at $2 \cdot 86 \times 10^{-4}$ cm⁻¹). The deviation of *g* values from 2 is consistent with the optical–UV absorption spectrum, a spin–orbit coupling parameter of 250 cm⁻¹ (Kohin 1979) and a tetragonally distorted octahedral crystal field.

To maintain charge balance and compensate for the electron loss the VO²⁺ site may be charge compensated by an associated monovalent alkali ion, which often are included in the channels of beryl (Deer *et al.* 1986). However, we are unable to detect any associated super-hyperfine structure due to such a charge compensator. So perhaps the remaining small angular deviation remains the only evidence of its presence. Detection of lower symmetry in the **A** tensor, or non-coincidence of **g** and **A** tensors would require more precise measurements and fitting using direct computer diagonalisation. There is some evidence that higher doses of radiation produce other centres, either VO²⁺ or V²⁺ (see e.g. Fig. 2) which illustrates a centre with $g \approx 1.97$ and $A(c axis) \approx 69 \times 10^{-4}$ cm⁻¹. Laborious computer simulation and subtraction techniques would be required to fit these centres. The VO²⁺ lines have also been detected in a natural emerald crystal from Poona, Western Australia (Hutton and Barrington 1977). A search for further natural crystals of known origin, which may have been subjected to in situ irradiation, is being undertaken.

4. Conclusions

The complex multi-line spectrum formed in some natural emeralds and in recently manufactured γ irradiated Biron emerald is shown to be due to multiple VO²⁺ centres, of tetragonal symmetry substituted into the octahedrally coordinated Al³⁺ sites. Other centres may be generated by higher doses of radiation.

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