

Mn²⁺ centre in corundum

To cite this article: P Mialhe *et al* 1975 *J. Phys. C: Solid State Phys.* **8** 723

View the [article online](#) for updates and enhancements.

You may also like

- [EVAPORATION AND CONDENSATION KINETICS OF CORUNDUM: THE ORIGIN OF THE 13 m FEATURE OF OXYGEN-RICH AGB STARS](#)
Aki Takigawa, Shogo Tachibana, Hiroko Nagahara *et al.*
- [HETEROGENEOUS DISTRIBUTION OF ²⁶Al AT THE BIRTH OF THE SOLAR SYSTEM](#)
Kentaro Makide, Kazuhide Nagashima, Alexander N. Krot *et al.*
- [A power device material of corundum-structured -Ga₂O₃ fabricated by MIST EPITAXY[®] technique](#)
Kentaro Kaneko, Shizuo Fujita and Toshimi Hitora

Mn²⁺ centre in corundum

P Mialhe, B Tribollet and A Erbeia

Laboratoire de Spectroscopie et Luminescence, Université Claude Bernard Lyon I, 43, Boulevard du 11 Novembre 1918, 69621 Villeurbanne, France

Received 30 April 1974, in final form 9 September 1974

Abstract. Experimental results show the deviation of the trigonal axis of the paramagnetic Mn²⁺ centre from the *c* axis of a corundum crystal. The direction is derived from forbidden line intensity and line position measurements.

1. Introduction

The investigation of the paramagnetic resonance spectrum of Mn²⁺ in corundum led Low and Suss (1960) and later Porret and Lambert (1967) to show that it was possible to incorporate divalent ions in this lattice. They derived crystalline and hyperfine spin Hamiltonian parameters from line positions in the spectrum. From the measurements of forbidden lines Folen (1962) has given an evaluation of the nuclear electric quadripolar interaction. Mialhe (1973) showed that a good description of the angular variation of the allowed and forbidden spectra is given with the approximation of the conventional spin Hamiltonian in axial symmetry. Calculations of line intensity however (Mialhe and Erbeia 1973a, b), showed that it was necessary to consider the centre itself and the modification of hyperfine interactions due to crystalline interactions.

In this lattice two types of aluminium sites are magnetically inequivalent (Geschwind and Remeika 1961) in that their cubic crystal-field axes are rotated from each other about the [111] direction by $60^\circ - 2\alpha$ ($\alpha = 4.3^\circ$). The fourth-order crystal-field parameters have been determined by Mialhe *et al* (1971) from the splitting of the lines, in the Mn²⁺ EPR spectrum, due to those two inequivalent sites in the corundum structure. All these studies showed that the Mn²⁺ centre in corundum is of axial symmetry.

This paper reports EPR experimental results that show a deviation of the trigonal axis of this Mn²⁺ centre from the crystal *c* axis.

2. Experimental procedure

The crystals used were α -Al₂O₃ single crystals, obtained from Baikowsky Co. (France) doped with approximately 0.1% by weight manganese divalent ions. They were made by a flame process and contained unwanted contaminants of Fe and Ti in concentrations in the range of 0.0001%.

Two methods may be used to obtain the static magnetic field *H* along the axis of symmetry of the paramagnetic centre; one with line position measurements and the

second with intensity measurements. Such a result is obtained when the field separation between the lines at both ends in the spectrum is a maximum (Mialhe 1973); then the intensity of forbidden lines is zero (Mialhe and Erbeia 1973a, b). The second method is a better test because of the large increase from zero of the forbidden line intensity with the angle θ that the magnetic field makes with the trigonal axis.

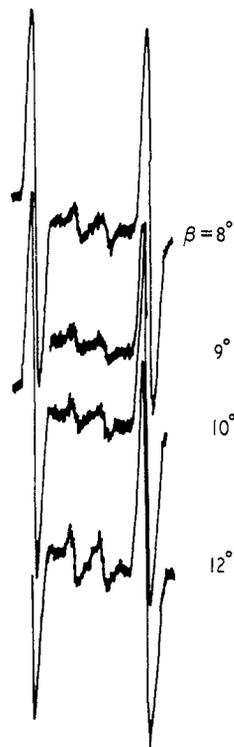


Figure 1. The intensity of forbidden lines goes through a minimum value, generally different from zero, when the magnetic field direction (given by angle β) is changed in the horizontal plane containing the crystal c axis. $\text{Mn}^{2+}\text{-Al}_2\text{O}_3$; (forbidden doublet $\frac{1}{2}, -\frac{1}{2} \rightarrow -\frac{1}{2}, -\frac{3}{2}$).

With the crystal c axis, in the horizontal plane the magnetic field lies in, it is generally not possible to obtain zero for the forbidden line intensity by rotating the magnetic field direction in this plane, as shown in figure 1, only a minimum value. We can then infer that the axis of symmetry of the paramagnetic centre is out of this horizontal plane. The EPR spectra were obtained with a Varian V4502 apparatus working in the X band. The modulation frequency of the static field was 100 kHz and the amplitude was about 0.2 G. The linewidth was 6 G at $T = 295$ K.

It is possible however to position the crystal so that the c axis and the magnetic field, in the same horizontal plane, make a defined angle. (The H direction may be determined by values of an arbitrary angle β , in the horizontal plane.) Thus, with a given value of angle β , the crystal may be rotated around the c axis (position defined by angle φ).

For each φ value between 0° and 360° we have determined the values of β that give the minimum value for forbidden line intensities and then measured this minimum value. Values of angle φ were controlled by the measurements of the splitting of hyperfine lines due to the two magnetically inequivalent sites (Mialhe *et al* 1971). These minimum values are plotted in figure 2. The results indicate that, through a complete rotation of the crystal

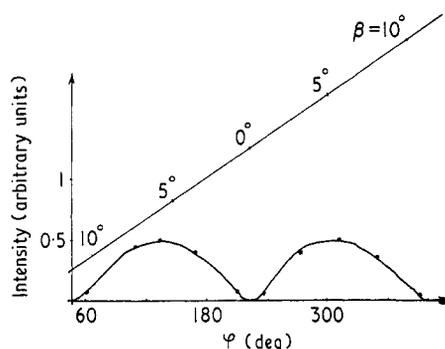


Figure 2. β values indicate the magnetic field direction that gives the minimum value of the forbidden doublet $\frac{1}{2}, -\frac{1}{2} \rightarrow -\frac{1}{2}, -\frac{3}{2}$ line intensity along a complete rotation of the crystal (angle φ) around the c axis. The points show measured values for $\text{Mn}^{2+}\text{-Al}_2\text{O}_3$.

around the c axis, it is possible to obtain zero for forbidden line intensities (that is, to get the magnetic field direction along the Mn^{2+} centre axis) for two φ values different by 180° . For such magnetic field directions, $\beta_1 = 0^\circ$ and $\beta_2 = 11.5^\circ$.

3. Discussion

Figure 3 shows the magnetic field direction, the crystal c axis and the centre trigonal t axis in an horizontal plane. It clearly shows that the trigonal axis t may be put along H (forbidden line intensities being equal to zero), by rotating the crystal around the c axis, for only two symmetrical positions of the c axis in the horizontal plane relative to the H direction. Angle γ between the crystal c axis and the trigonal axis of the centre is then

$$\gamma = \frac{1}{2}(\beta_2 - \beta_1) = 5.75^\circ.$$

This differentiation of c and t axes must induce a variation of line positions in the spectrum when rotating the crystal around the c axis. Comparisons with the angular variation of the whole spectrum, that Mialhe (1973) derived from the consideration of the complete spin Hamiltonian operator, lead to a second evaluation of γ , namely, $\gamma = 6^\circ$. This verification is good and considers the displacements of the lines (as pointed out by Lupei *et al* 1968), as an effect of the two magnetically inequivalent sites in this lattice.

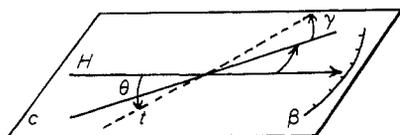


Figure 3. Crystal c axis, Mn^{2+} centre trigonal axis t and magnetic field direction H in a horizontal plane.

Angular variation of the whole spectrum with measurements of both line positions and line intensities has shown the axial symmetry of the Mn^{2+} centre in corundum. The splitting of hyperfine lines (Mialhe *et al* 1971) shows that trigonal symmetry is preserved although the ionic radius of Mn^{2+} is larger than that of the Al^{3+} ions. Our results show a small deviation of the centre trigonal axis from the crystal c axis. This local distortion of the lattice may be due to the charged compensating defect probably with interstitial trivalent ions Al^{3+} (or Mn^{3+}). These results show that local distortions do not lower the

symmetry (because there are no axial subgroups of C_3). But a charge compensation with trivalent ions requires only one, interstitial Al^{3+} ion say, for three divalent impurities. Not in the near vicinity of the paramagnetic centre, the charge compensating ions give only a small contribution to the crystal potential that influence to a small extent the centre point symmetry. In other words the Mn^{2+} centre in corundum may be considered as being 'approximately axial' with a tilted axis making an angle of 5.7° with the crystal c axis.

References

- Folen V J 1962 *Phys. Rev.* **125** 1581–3
Geschwing S and Remeika J P 1961 *Phys. Rev.* **122** 757–61
Low W and Suss J T 1960 *Phys. Rev.* **119** 132–3
Lupei V, Lupei A and Ursu I 1968 *Revue Roum. Chim.* **13** 327–36
Mialhe P 1973 *J. Phys. Chem. Solids* **34** 217–22
Mialhe P, Briguet A and Erbeia A 1971 *Solid St. Commun.* **9** 755–7
Mialhe P and Erbeia A 1973a *J. Phys. C: Solid St. Phys.* **6** 1965–70
———1973b *Phys. Rev. B* **7** 4061–4
Porret F and Lambert E 1967 *Helv. Phys. Acta* **40** 264–70