

BRITISH ACOUSTICAL SOCIETY

69/34

Microwave Ultrasonics

Symposium

November 7th 1969

Acoustic Paramagnetic Resonance of V^{3+} in MgO
and Cr^{2+} in Al_2O_3 .
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Introduction.

The technique of acoustic paramagnetic resonance (a.p.r.) is especially useful for studying the low lying energy levels of paramagnetic ions which are strongly coupled to the host crystal lattice. Among such ions we have studied by a.p.r. are Cr^{2+} and V^{3+} . An extensive investigation of Cr^{2+} in MgO is described by Fletcher et al. (1966) and Marshall and Rampton (1968). We have extended this work by using Cr^{2+} in Al_2O_3 . I shall describe some results of a.p.r. studies on V^{3+} in MgO . (Brabin-Smith and Rampton 1969). These two ions in these host crystals give strong a.p.r. absorptions but cannot be observed by conventional electron paramagnetic resonance (e.p.r.) because of the different selection rules for a.p.r. and e.p.r. absorptions.

Experiments

The experiments were made using a pulse-echo method with longitudinal ultrasonic waves at about 9.4 GHz. The pulses were 0.5 μ sec long and at a repetition rate of 1000 sec^{-1} . Quartz transducers were used bonded to the paramagnetic specimens by Araldite. The experiments were made in the temperature range 1.5°K to 20°K.

Results

(i) V^{3+} in MgO .

Specimens have been used in which the ultrasonic waves travelled along a $\langle 100 \rangle$ direction and another specimen in which the waves travelled along a $\langle 110 \rangle$ direction. The results can be fitted by an effective spin Hamiltonian

$$\mathcal{H} = g_{11} \beta H_z S_z + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + A I_z S_z$$

where the z-axis is taken along a $\langle 100 \rangle$ direction and the total effective spin $S = 1$, total nuclear spin $I = \frac{1}{2}$. The experiment gives

$$\begin{aligned} g_{11} &= 0.69 \pm 0.01 \\ D &= 10.2 \text{ cm}^{-1} \pm 1.0 \text{ cm}^{-1} \\ |A| &= 0.0042 \text{ cm}^{-1} \pm 0.0001 \text{ cm}^{-1} \end{aligned}$$

The magnitude of the resonance absorptions enables the spin-lattice coupling to be estimated. Using the definition of Dobrov (1964) we find

$$\begin{aligned} |G_{11} - G_{12}| &\geq 1000 \text{ cm}^{-1} \\ |G_{11}| &< 30 \text{ cm}^{-1} \end{aligned}$$

(ii) Cr²⁺ in Al₂O₃.

Cr²⁺ ions are formed in chromium doped corundum from Cr³⁺ ions during x-irradiation.

Specimens have been cut of irradiated chromium doped Al₂O₃ in which the ultrasonic waves could propagate along the c-axis and specimens for which the ultrasound travelled at right angles to the c-axis, along the b axis at right angles to the diad axis of the lattice.

For propagation along the c-axis no resonance absorptions are observed. For propagation at right angles to the c-axis strong resonance absorptions are found. These have not been accounted for in detail yet as their behaviour is complex as the orientation of the applied magnetic field is varied. In the figures shown we plot the magnetic field at the peak of an absorption line as a function of its direction. Figure 1 shows the resonances as the field is rotated through an angle θ away from the c-axis towards the direction of ultrasonic propagation. Figure 2 shows the resonances as the field is rotated through an angle ϕ away from the c-axis and always perpendicular to the direction of ultrasonic propagation. Figure 3 shows the resonances if we maintain the field at an angle of 15° to the c-axis and rotate about the c-axis.

Discussion

V³⁺ in MgO.

The a.p.r. spectrum shows axial symmetry showing that the V³⁺ ions must be at tetragonally distorted sites, this is presumably because they are associated with another defect required to neutralise the excess positive charge of the V³⁺ ion. It may be necessary to invoke the Jahn-Teller effect to explain the large difference in magnitude between $|G_{11} - G_{12}|$ and $|G_{66}|$.

Cr²⁺ in Al₂O₃.

Cr²⁺ in Al₂O₃ is subject to a dynamic Jahn-Teller effect and the energy level scheme is complex. We have not yet been able to definitely assign the observed resonances to transitions of the ion. It is likely that Cr²⁺ is very sensitive to small local strains in the specimen crystal and these may have to be taken into account.

References

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Dobrov W.I. Phys. Rev. 134 A734 - 742 (1964)
Fletcher J. R., F. G. Marshall, V. W. Rampton, P. M. Powell and K. W. H. Stevens. Proc. Phys. Soc. 88, 127 - 130 (1966)
Marshall F. G. and Rampton V. W. J. Phys. C. (Solid State Physics) 1, 594-598, (1968)

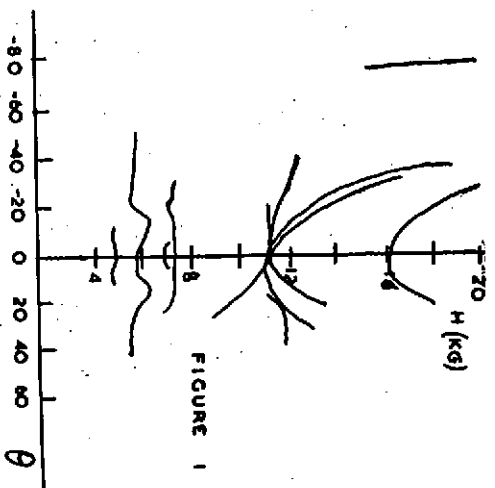


FIGURE 1

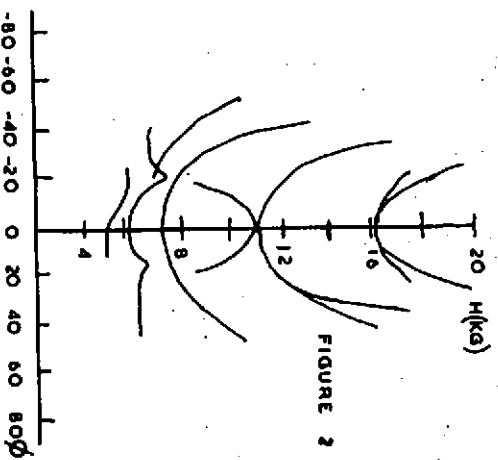


FIGURE 2

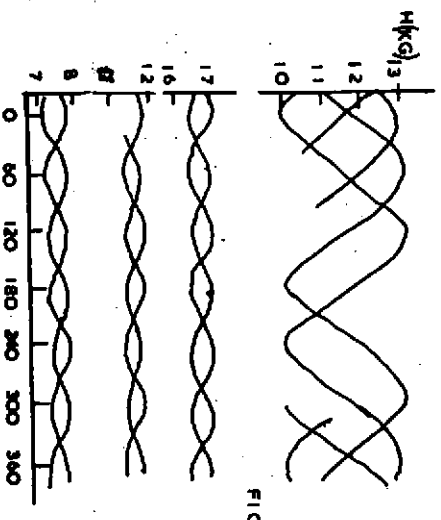


FIGURE 3