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Nuclear Quadrupole Effects in Spinels ($\text{Mg Al}_2 \text{O}_4$)

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The negative oxygen ions in a spinel ($\text{Mg Al}_2 \text{O}_4$) form an almost close-packed cubic structure. The positive metal ions Mg^{+2} and Al^{+3} are located at various interstices between the O^{-2} ions. There are tetrahedral and octahedral interstices with four and six O^{-2} nearest neighbours, respectively. The point symmetry of a tetrahedral site is cubic (T_d) that of an octahedral site is rhomboedric (D_{3d}).

The magnetic resonance of Al^{27} with $I = 5/2$, $\mu = + 3.6385$ n.m. and $Q = 0.149 \times 10^{-24}$ cm² was studied in a magnetic field of approximately 8000 Gauss in various naturally and artificially grown single crystals [1]. The resonance signals observed show typical electric quadrupole effects such as appearance and orientation dependence of satellites and second-order shifts of central lines [2, 3]. Carefully investigated rotation patterns and measured relative intensities of the lines yielded the following results:

a) In natural crystals the strong lines (including satellites and central lines) can be grouped into four systems of five lines each. From the angular dependence one can conclude that these systems of lines are due to Al^{27} nuclei at octahedral sites. Furthermore, the crystalline field at such a site shows rotational symmetry along one of the four body diagonals of the unit cell e.g. along the [111] direction in accordance with the point symmetry D_{3d} . Approximately 80% of all the Al^{27} in a natural spinel contribute to these signals. Besides the strong lines a weak one appears which shows neither a splitting nor a shift. It can be assigned to Al^{27} nuclei occupying tetrahedral sites with cubic symmetry. Therefore, to a great extent natural spinel approximates "normal spinel structure". The quadrupole coupling constant for Al^{27} at octahedral sites is

$$\frac{e Q V_{zz}}{h} = 3.72 \pm 0.04 \text{ Mc/sec.}$$

where V_{zz} is the field gradient along the trigonal axis. With the known quadrupole moment of Al^{27} one finds

$$V_{zz} = 10.32 \times 10^{+16} \text{ Volt/cm}^2 .$$

Under the assumption of purely ionic structure (point charge model) of spinel, V_{zz} can be calculated from the following formula given by Bersohn [4]

$$V_{zz, cal.} = (1 - \gamma_{\infty}) \sum_j e_j \sum_i \frac{3 z_{ij}^2 - r_{ij}^2}{r_{ij}^5}$$

where $\gamma_{zz} = -2.59$ is the antishielding factor for Al^{+3} . The sum is taken over all the atoms in the crystal of type j with which there is associated a charge e_j . In the case of spinel the lattice sum was carried out over approximately 11000 atoms. The value found is

$$V_{zz, cal.} = 2.15 \times 10^{+16} \text{ Volt/cm}^2 .$$

- b) Spectra taken from synthetic spinels differ appreciably from those of natural ones. No satellites can be seen. Weak central lines appear which show second-order shifts, similar to those in the above mentioned case. An unshifted line of approx. the same intensity as the shifted lines is present. The best explanation of these results follows from an assumption of a disordered cation distribution.
- c) Natural spinels when heated above 900°C and subsequently cooled yielded spectra which resemble those of synthetic spinels. From this it can be concluded that an order-disorder transition takes place in the temperature range of 800°C - 900°C which is in agreement with infrared observations [5]. Annealing a disordered crystal at a temperature of approx. 700°C over a period of two months did lead to a spectrum in agreement with what one would expect from a slightly reordered cation distribution.

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