E.P.R. study of Mn\(^{2+}\) ions in a boracite

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Abstract

The complex E.P.R. spectrum of ferroelec. Mg3B7O13Cl natural crystals at 25 Deg contains a strong hyperfine sextet ascribed to Mn2+ substituted for Mg2+ ions. By using \(S = 5/2, I = 5/2,\) and \(g = 2;\) spin Hamiltonian consts. in cm.-1 are: \(|D| = 0.30 + 0.02, |E| = 0.051 + 0.005, |Ax| = 75.5 \pm 2. * 10^{-4}, \) and \(|Ax| = 82 \pm 2. * 10^{-4}.\) The very large D value is attributed to crystal field anisotropy from 2 types of ligands in the coordination octahedron.

Reference

E.P.R. STUDY OF Mn$^{2+}$ IONS IN A BORACITE

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The E.P.R. spectrum of Mn$^{2+}$ ions, substituted for Mg$^{2+}$ ions and measured in the ferroelectric phase of the Mg$_3$B$_7$O$_{13}$Cl boracite, is essentially characteristic of a very large crystal field.

The preliminary results reported here have been obtained with natural crystals of boracite, Mg$_3$B$_7$O$_{13}$Cl, containing manganese ions as impurity. This boracite is characterized by a ferroelectric transition point at around 265°C [1], below which temperature the phase is orthorhombic [2]. In the present work, this latter phase, which can be considered as pseudo-cubic, was studied at room temperature.

From the complex E.P.R. signal, observed at a frequency of 9 070 GHz, a coherent spectrum of high intensity lines has been extracted, which is consistent with the following spin Hamiltonian:

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\[ H = g \beta B \cdot S + D S_z^2 + E (S_x^2 - S_y^2) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \]

for the following values of the constants:

- \( S = \frac{3}{2}; \quad I = \frac{1}{2}; \quad g = 2 \)
- \( |D| = (0.30 \pm 0.02) \text{ cm}^{-1}; \)
- \( |E| = (0.051 \pm 0.005) \text{ cm}^{-1}; \)
- \( |A_x| = |A_y| = (75.5 \pm 2) \times 10^{-4} \text{ cm}^{-1}; \)
- \( |A_z| = (82 \pm 2) \times 10^{-4} \text{ cm}^{-1}. \)

In fig. 1 are given the positions of the electronic spin levels calculated with this Hamiltonian for the 3 principal directions, together with the observed positions of the centres of the hyperfine sextets.

The \( z \) axis of the spin Hamiltonian is found, within the limits of accuracy of the measurements, to be the same as one of the apparent quartenary axes of the crystal. The \( x \) and \( y \) axes of the same Hamiltonian are not oriented along the 2 other quartenary axes, but make angles of 25° with them.

The observed spectra being characteristic of ions with spin \( S = \frac{3}{2} \), it is reasonable to consider substituting \( \text{Mn}^{2+} \) ions for \( \text{Mg}^{2+} \) ions. Each of these \( \text{Mg}^{2+} \) ions is surrounded, in the low boracite, by a distorted octahedron composed of 4 oxygen ions and 2 chloride ions. In this octahedron the \( \text{Cl}-\text{Cl} \) axis is approximately directed along one of the pseudo-quartenary axes; the 2 oxygen pairs axes make angles of 25° with the 2 other pseudoquartenary axes.

Those axes orientations are precisely those which are obtained for the spin Hamiltonian of the \( \text{Mn}^{2+} \) ions. Thus, the identified spectrum certainly corresponds to \( \text{Mn}^{2+} \) ions placed on one type of the magnesium sites. The chlorine pair determines the \( z \) axis orientation; the unequal distances between the \( \text{Mn}^{2+} \) ion and the two centres of gravity of the oxygen pairs, create the \( x-y \) anisotropy.

It is interesting to note that the \( D \) value, which is exceedingly high for the \( \text{Mn}^{2+} \) ion and which

† There are 2 types of such octahedrons, which slightly differ by their shape [3].

leads to a total ZFS of 1.9 cm\(^{-1}\), is probably due to the anisotropy created by the presence of two types of ligands in the coordination octahedron.

References