NUCLEAR QUADRUPOLE HOLEBURNING IN PREPARATION-DEPENDENT EuVO₄


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Abstract. – This paper reports on the study of EuVO₄ samples grown from different fluxes. It is the first application of optical holeburning to investigate preparation-dependency between defect lines in samples of nominally the same compound. Analysis suggests that very few of the defect lines are common to the different growths.

1. Introduction.

Previous workers have utilized the existing techniques of holeburning for the study of hyperfine splittings of Eu³⁺. The work reported here investigates a range of perturbed sites in samples of nominally identical stoichiometric EuVO₄, and has arisen directly out of earlier studies [1].

New samples have been grown using conventional techniques [2] from a variety of fluxes, some of which were doped with low levels of other rare-earth ions. Many different batches were grown but only the most interesting growths will be discussed further. All growths produced crystals of high optical quality.

EuVO₄ has a tetragonal zircon structure with D₄d point group symmetry at the rare-earth site. This forbids the ⁷F₀ – ⁵D₀ transition in the absence of an applied magnetic field. The existence of other zero field lines shows that the site symmetry has been lowered – indicating a Eu³⁺ defect site in the stoichiometric compound.

2. Experiments and discussion.

The crystals used were all flux-grown in the Clarendon Laboratory. Conventional cryogenic techniques were used to cool the samples by immersion in liquid ⁴He pumped down to 1.5 K. A Coherent 599/21 dye laser, working in R6G, was used to provide some 20 mW of tunable output to scan the region around the intrinsic ⁷F₀ – ⁵D₀ transition (515543 GHz). Optical absorption was detected by monitoring the integrated fluorescent emission ⁹D₀ – ⁷F₂, ⁷F₁. This fluorescence was conveyed out of the cryostat to a detecting photomultiplier by a fibre-optic bundle. For experiments requiring magnetic fields a 9T superconducting magnet was used.

Figure 1 shows the absorption spectra of six different growths of stoichiometric EuVO₄. Growth A was grown with excess V₂O₅ and corresponds to the most pure growth. Growth B was produced with a flux of excess K₂O and V₂O₅; C with excess PbO and PbF₂; and D with excess KF and V₂O₅. Growth E and F were grown like D but with an additional 1 % of Dy³⁺ and Ho³⁺ respectively.

The broad features are similar, but in detail it is clear that the spectra differ markedly. Samples of the different growths revealed up to fifty different absorption lines in their spectra. Each one of these must correspond to a distinct crystallographic site. This is a surprisingly large number for such a simple crystal structure as the vanadate. The lines spread from approximately 300 GHz (10 cm⁻¹) below the energy of the intrinsic transition to about 1200 GHz (40 cm⁻¹) above it. Between different growths there is a wide...
range of linewidth, intensity and energy of the lines. Even samples grown with exceptional regard to purity (growth A) display numerous lines. Different samples from the same growth are, however, remarkably consistent so the uniqueness of the spectra for each growth must indicate a high degree of preparation-dependency.

Few of the defect lines are common to the different growths. This is a surprising result if one considers that the mechanisms producing the defect sites should be common to all growths. However, the notable exceptions are two of the high energy lines – at about 516389 GHz and 516635 GHz. These lines appear to be strong in all growths where fluorine was present in the growth process.

Optical holeburning has been applied to the defect lines in these growths. This is a useful optical technique for establishing the hyperfine structure in both the ground and the excited states. The $^{5}D_{0}$ nuclear structure is determined is determined by the following Hamiltonian:

$$H = P \left\{ I_x^2 - I (I + 1) / 3 + \eta \left( I_x^2 - I_y^2 \right) / 3 \right\} - g \mu_B B \cdot I$$

where the last term is the nuclear Zeeman effect. $P$ is the quadrupole coupling constant which determines the magnitude of the overall splitting. The different contributions to $P$ have been discussed by Blok and Shirley [3]. The asymmetry parameter, $\eta$, characterizes the departure from axial symmetry.

Figure 2 shows the zero field holeburning structure of the 516635 GHz line in sample D. This observation is evidence of admixing of the nuclear eigenstates, consistent with a departure from axial symmetry. Values of $P$ and $\eta$ were obtained for the two equally abundant isotopes of Eu$^{3+}$ by analysis of the holeburning pattern. These were then compared for near-coincident lines ($< 3$ GHz apart) in different growths. The analysis of zero-field data for $^{5}D_{0}$ splittings revealed that the parameters $P$ and $\eta$ (see Tab. I for values) were, to within experimental error, the same for the 516389 GHz line between growths C, D, E and F. Similarly the line at 516635 GHz was also common to these growths. On the other hand, many lines that appeared near-coincident had widely differing nuclear structure in the different growths.

Application of a magnetic field greatly complicates the holeburning pattern as the Kramers degeneracy of the nuclear $I = 5/2$ states is removed. However, Zeeman studies of the high energy defect lines at 516389 and 516635 GHz have been successfully carried out. The analysis of these spectra involves the iterative diagonalization of the Hamiltonian for the spherical polar angles ($\theta$, $\phi$) of the nuclear quadrupole axis to the crystallographic $c$-axis. This uniquely defines the direction of the nuclear quadrupole axis. For the line 516389 GHz in both growths C and D, $\theta = 69.5^\circ$ and $\phi = 63.2^\circ$. Similarly the line at 516635 GHz had equal angles of $\theta = 14.1^\circ$ and $\phi = 53.1^\circ$ in the two growths. These angles suggest a nuclear quadrupole axis direction corresponding approximately to that expected for an interstitial site.

3. Conclusion.

It is clear from figure 1 and the detailed analysis of the holeburning spectra that very few of the defect lines are common to the different growths. The highest energy lines at 516389 and 516635 GHz appear to be the most common.

It is possible to infer from the orientation of the quadrupole axis that the origin of these two defect lines might be an interstitial ion located in the direction of an otherwise empty part of the unit cell. This is consistent with the observation that fluorine is present whenever these lines are seen.

Table I. – Nuclear parameters for $^{5}D_{0}$ state of EuVO$_4$ ($P$ in MHz).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line at 516389 GHz</th>
<th>Line at 516635 GHz</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$^{151}$Eu</td>
<td>$^{152}$Eu</td>
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<tr>
<td></td>
<td>$P = 11.2 \pm 0.2$</td>
<td>$P = 11.3 \pm 0.2$</td>
</tr>
<tr>
<td></td>
<td>$\eta = 0.65 \pm 0.02$</td>
<td>$\eta = 0.65 \pm 0.02$</td>
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<tr>
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<td>$P = 11.5 \pm 0.2$</td>
<td>$P = 11.5 \pm 0.2$</td>
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<td></td>
<td>$\eta = 0.40 \pm 0.02$</td>
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