Single Crystal EPR Spectrum of Cr$^{3+}$ in Lanthanum Lutecium Gallium Garnet

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Abstract. The Cr$^{3+}$ EPR spectra of YAG type crystals normally consist of four peaks whose positions are dependent on the axial zero-field splitting $D$ with axis along a (111) direction and angle $\theta$ between that direction and the applied field $H_0$. In LLGG only three principal peaks are observed with zero-field axis nearly along $x$, $y$ or $z$. This anomaly is attributed to the relatively small size of Cr$^{3+}$ compared to Lu$^{3+}$ which it displaces in an octahedral site. $D$ varies slightly for the different zero-field axes: 0.480 cm$^{-1}$ along $x$, 0.429 cm$^{-1}$ along $y$ and 0.470 cm$^{-1}$ along $z$. The spectroscopic splitting factor $g = 1.978 \pm 0.001$ is essentially isotropic and independent of axes within the experimental error.

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The Cr$^{3+}$ electron paramagnetic resonance (EPR) spectra in a number of garnet-type Cr$^{3+}$-doped laser materials have been investigated, but none have had octahedral sites with bond distances as large as in lanthanum lutecium gallium garnet (LLGG). Since Cr$^{3+}$ is widely used as a dopant to optically activate laser materials of this type, it was believed that a study of the Cr$^{3+}$ EPR spectrum in LLGG might provide some useful information on the nature of the Cr$^{3+}$ octahedral site. EPR studies on YAG [1–6], YGG [6, 7] and CGGG [8] have all shown that there are four equivalent Cr$^{3+}$ sites within the garnet unit cell, each having trigonal distortion along one of the four (111) axes as a result of point group symmetry $C_{3v}$, in complete agreement with X-ray structure analyses [9, 10]. Although the octahedral sites in the LLGG host lattice have the same $C_{3v}$ symmetry [10] as in other garnets, the Cr$^{3+}$ EPR spectra in this host reveal a much more complex environment than that in other YAG type materials that have already been investigated to date. In this paper we report an analysis of the most intense lines in terms of the axial zero-field splitting factor parameter $D$ and the spectroscopic splitting factor $g$, and locate the axes of the zero-field splitting.

1 Experimental Results

All EPR spectra were run at room temperature on a Bruker ER-200 spectrometer with the LLGG crystal mounted on a quartz rod suspended from a goniometer head into the microwave cavity. The crystal was oriented by means of back-reflection Laue diffraction patterns. A small specimen of a 0.5% Cr$^{3+}$-doped LLGG laser rod was obtained from M. Kokta of the Electronic Division, Materials Group, Union Carbide Corporation. Since it was expected that the zero-field splitting axes would be aligned parallel to the (111), etc., directions of the crystal, the crystal was oriented with the (111) axis perpendicular to the rotation axis of the crystal mount, which in turn was defined as the $y'$ axis of the laboratory coordinates. The $z'$ axis was defined as the fixed direction of the magnetic field and with the goniometer set to zero, the (111) direction was also parallel to $z'$. The second three-fold axis was oriented in the $y'z'$ plane so that the other two three-fold axes made equal angles of 54.7356° with the $y'z'$ plane.

The laboratory coordinates are then defined in terms of the crystal coordinates $x$, $y$, $z$ by

\[
x' = x \cos \theta + z \sin \theta, \\
y' = y, \\
z' = -x \sin \theta + z \cos \theta,
\]

(1)

where $\theta$ is the angle of rotation about $y'$ between the (111) crystal direction and $H_0$. The spin operators $S_x$, $S_y$, $S_z$ are related to $S_{x'}$, $S_{y'}$, $S_{z'}$ in the same manner as the two sets of Cartesian coordinates.
The energy levels of Cr\textsuperscript{3+} in LLGG in the crystal coordinate system \(x, y, z\) are described by the well known Hamiltonian
\[
\mathcal{H} = g_\parallel \beta H_0 S_z + g_\perp \beta (H_x S_x + H_y S_y) \\
+ D(S_z^2 - 1/4S(S + 1)). \tag{2}
\]

In terms of the fixed laboratory coordinates \(x', y', z'\) the Hamiltonian (2) can be rewritten [11]
\[
\mathcal{H} = \beta (g_\parallel \cos^2 \theta + g_\perp \sin^2 \theta)H_0 S_z' \\
+ \beta (g_\parallel - g_\perp) \sin \theta \cos \theta H_0 S_y' \\
+ \frac{1}{2} D(3 \cos^2 \theta - 1)(S_z'^2 - \frac{1}{2}S(S + 1)) \\
+ D \sin \theta \cos \theta (S_x S_x' + S_y S_y') \\
+ \frac{1}{2} D \sin^2 \theta (S_z'^2 - S_x'^2). \tag{3}
\]

With this Hamiltonian one can obtain energy levels as solutions of the eigenvalue equation \(\mathcal{H}\Psi_n = E_n\Psi_n\), where the \(E_n\) are the energy eigenvalues and \(\Psi_n\) are the eigenvectors of the four spin states of Cr\textsuperscript{3+} for \(S = 3/2\) in a magnetic field, i.e., \(S_n' = \pm 3/2, \pm 1/2\).

It should be noted that the magnetic states representing the energy levels obtained from the Hamiltonian in (3) are linear combinations of all four spin states defined by \(S_n'\) except in the special case where \(\theta = 0^\circ\) and the eigenvalue equation is diagonal. In YAG, where the zero-field axis direction of \(D\) can be along the four different \(\langle 111\rangle\) axes, each direction has to be assigned a different vector and each of these vectors is rotated in turn by a 2-dimensional rotation matrix involving \(\theta\) in order to find all possible resonances for the unit cell. Depending upon the values of \(D\) and \(\theta\), up to 6 resonances may exist for each zero-field axis and \(\theta\), or up to 24 for the entire unit cell. About half or more of these will either be too weak to observe, or will be eliminated by \(D\) values being too large, so that in the case of YAG a typical spectrum may show only 4 resonances for most values of \(\theta\).

Since the energy matrix and eigenvectors are only of dimension \(n = 4\), advances in microcomputer hardware in the past decade have made it possible to not only calculate energy levels for the above Hamiltonian exactly, but to search for all the allowed transitions for a given frequency \(v\) within the magnetic field range of the spectrometer. A program was written, initially in interpreter Basic, taking advantage of second order perturbation theory and the Feynman-Hellmann theorem [12, 13], to search for the allowed transitions using an IBM-PC microcomputer. Later the program was upgraded to Turbo Basic and run on a Zenith Z-386 microcomputer. The program also calculates intensities for each transition (see discussion by Kahn [11]). While requiring about 15-20 s for the calculations for a given set of \(\theta, v, D, g_\parallel\), and \(g_\perp\), most of the time was used for printer input/output, only about 6 s being needed for the actual calculations and half of that time occurring during output.

The program was tested against the tables for ruby in [11] and found to agree within 0.5 G with \(H_0\) as well as with the intensities. The iterated convergence of the resonant field values was estimated to be typically within 0.1 G of exact diagonalization values. In addition, actual EPR spectra on ruby were fitted with the program.

Since the spectrometer magnet was not provided with a rotating base, it was necessary to rotate the crystal within the resonant microwave cavity of the spectrometer in order to obtain spectra as a function of crystal orientation. Due to the large size of the crystal relative to the cavity width and to its asymmetric mount within the cavity, the microwave frequency varied over the range 9.518-9.597 GHz as the crystal was rotated. The stable free radical DPPH (\(g = 2.0037\)) mounted next to the crystal in a sealed capillary provided a \(g\)-value marker for the spectrum and an indirect measure of the cavity frequency.

A surprising discovery was that the strongest peaks in the spectra collected for \(\theta = -10^\circ\) - 190\(^\circ\) at 5\(^\circ\) intervals, could not be fit by any set of values of \(D\) and \(g\). At most only three strong peaks are observed, never the four expected with the axis of \(D\) along \(\langle 111\rangle\), etc. It was suspected, however, that the large diameter of the octahedral sites normally occupied by Lu\textsuperscript{3+} might permit the Cr\textsuperscript{3+} ions to move off-center to positions with axial symmetry axes oriented in directions other than along the three-fold axes. By simply replacing the four sets of direction cosines of the \(\langle 111\rangle\), etc., axes in the computer program by three sets directed along \(\langle 100\rangle\), \(\langle 010\rangle\), and \(\langle 001\rangle\), and recalculating the resonances for all \(\theta\), it was confirmed that there were indeed three zero-field axes very nearly directed along the three principal cubic axes. Additional proof that the observed strong resonances in Fig. 1 could not be attributed to Cr\textsuperscript{3+} at sites with point-group symmetry \(C_3\) characteristic of the \(\langle 111\rangle\) axes in LLGG was found when it was realized that the calculated resonances on the \(\langle 111\rangle\) axis labelled 3 in Fig. 1 reach a maximum field at \(\theta = 69.5^\circ\) independent of \(D\) or \(g\). On