

AN INTUITIVE METHOD FOR THE DETERMINATION OF CRYSTAL-FIELD PARAMETERS IN LASER CRYSTALS

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ABSTRACT

Expanding the crystal field in terms of operators that transform as the irreducible representations of the T_d group leads to an intuitive interpretation of the crystal-field parameters. We apply this method to the crystal field experienced by Nd^{3+} dopants in the laser crystals $YLiF_4$, YVO_4 , and $KLiYF_5$.

INTRODUCTION

Crystal-field calculations are an integral part of modelling the luminescence from dopants in laser crystals. Traditionally, the crystal field has been described in terms of operators that transform as the spherical harmonics. This makes the calculation of the matrix elements very easy to perform, and before high speed computers were readily available this was the most important consideration. Unfortunately, such a description of the crystal field does not easily lend itself to a useful physical interpretation. As such, crystal-field parameters are often tabulated in the literature, but are rarely applied to any extent. We present here a different approach towards the calculation of crystal-field parameters for dopants in laser crystals. We expand the field in terms of operators that transform as the irreducible representations of the tetrahedral group, T_d . Since we are using a basis set that more closely represents the symmetry of the crystal field, the number of off-diagonal matrix elements is reduced. This leads to a definite advantage in interpreting the fitting parameters. Ultimately, we can apply this information towards other applications such as understanding how the dopant couples to stress or to vibrations.

In the next section, we describe the expansion of the crystal field in terms of operators transforming as the irreducible representations of the T_d group. We then investigate the crystal field felt by Nd^{3+} dopants in several laser crystal materials: $YLiF_4$, YVO_4 , and $KLiYF_5$. Finally, we demonstrate that the crystal-field parameters have an intuitive interpretation in terms of the crystal structure of the host material.

METHOD

We have chosen to expand the crystal field in terms of operators transforming as the irreducible representations of the group T_d because in each of the host crystals we are investigating, the nearest neighbors to the Nd^{3+} dopant are eight F ions that form a cage about the Nd that can be best described as two distorted tetrahedra inverted from one another. Hence, our expansion of the crystal field in these terms is quite natural.

The valence shell of the Nd^{3+} ion consists of three f electrons. In the T_d group, the seven f states span the irreducible representations a_1 (a singlet), and t_2 and t_1 (both triplets). The combinations of the $l = 3$ spherical harmonics that make up the states of these representations are:

$$\begin{aligned}
 |a_1\rangle &= -\frac{i}{\sqrt{2}}|3,-2\rangle + \frac{i}{\sqrt{2}}|3,2\rangle \sim xyz \\
 |t_{2z}\rangle &= \frac{\sqrt{5}}{4}|3,-3\rangle - \frac{\sqrt{3}}{4}|3,-1\rangle + \frac{\sqrt{3}}{4}|3,1\rangle - \frac{\sqrt{5}}{4}|3,3\rangle \sim (5x^2 - 3r^2)x \\
 |t_{2y}\rangle &= -\frac{i\sqrt{5}}{4}|3,-3\rangle - \frac{i\sqrt{3}}{4}|3,-1\rangle - \frac{i\sqrt{3}}{4}|3,1\rangle - \frac{i\sqrt{5}}{4}|3,3\rangle \sim (5y^2 - 3r^2)y \\
 |t_{2x}\rangle &= |3,0\rangle \sim (5z^2 - 3r^2)z \\
 |t_{1x}\rangle &= -\frac{\sqrt{3}}{4}|3,-3\rangle - \frac{\sqrt{5}}{4}|3,-1\rangle + \frac{\sqrt{5}}{4}|3,1\rangle + \frac{\sqrt{3}}{4}|3,3\rangle \sim (y^2 - z^2)x \\
 |t_{1y}\rangle &= -\frac{i\sqrt{3}}{4}|3,-3\rangle + \frac{i\sqrt{5}}{4}|3,-1\rangle + \frac{i\sqrt{5}}{4}|3,1\rangle - \frac{i\sqrt{3}}{4}|3,3\rangle \sim (z^2 - x^2)y \\
 |t_{1z}\rangle &= \frac{1}{\sqrt{2}}|3,-2\rangle + \frac{1}{\sqrt{2}}|3,2\rangle \sim (x^2 - y^2)z
 \end{aligned} \tag{1}$$

Included here are the real-valued third-order polynomials that serve as basis functions for these representations. From these polynomials, we can determine the shapes of the various wave functions. The a_1 state has eight lobes pointing in the [111] directions. The t_2 states on the other hand have large lobes along the coordinate axes, e.g. t_{2z} has its lobes along the z axis. Finally, the t_1 states have eight lobes like the a_1 state, but these lobes are located in the planes formed by the coordinate axes. For example, the t_{1z} state has four lobes in the xz plane and four lobes in the yz plane, and each of these lobes is tilted away from the xy plane by $\pm 35^\circ$. Our work demonstrates how we can interpret the crystal-field parameters in terms of the shapes of these wave functions and simple point-ion models.

As stated previously, the crystal field at the site of the Nd dopant results primarily from two distorted tetrahedra of F ions. The distortions we consider in this work are a tetragonal distortion (stretching/compression) along what we define as the z axis, and a trigonal distortion (shearing) having the same axis as its axis of symmetry.

The effect of the tetrahedral component of the crystal field is to split the f states into an a_1 singlet, and t_2 and t_1 triplets. The energy of the t_2 triplet we label by β , and the energy of the

t_1 triplet by γ . In order that the center of mass remain constant, the energy of the a_1 state is then $-3(\beta+\gamma)$. The tetragonal distortion splits each of the triplets into a singlet (the "z component" of the triplet) and a doublet (the x and y components). The parameter B(C) describes this splitting within the $t_2(t_1)$ triplet. In addition, the tetragonal field mixes the x(y) components between the two triplets (parameter Y). The trigonal distortion mixes the x and y components *within* each triplet (parameter P(Q) for the $t_2(t_1)$ triplet), and mixes the x and y components between the two triplets (parameter R). Finally, the trigonal distortion mixes the a_1 state and the t_{2z} state (parameter T). The existence of these various parameters is determined from group theory.

The crystal-field Hamiltonian, using a basis set $\{a_1, t_{2z}, t_{2y}, t_{2x}, t_{1z}, t_{1y}, t_{1x}\}$, is thus given by the matrix

$$\mathcal{H}_{cf} = \begin{pmatrix} -(3\beta+3\gamma) & 0 & 0 & T & 0 & 0 & 0 \\ 0 & \beta - \frac{B}{2} & P & 0 & -Y & R & 0 \\ 0 & P & \beta - \frac{B}{2} & 0 & -R & Y & 0 \\ T & 0 & 0 & \beta+B & 0 & 0 & 0 \\ 0 & -Y & -R & 0 & \gamma - \frac{C}{2} & Q & 0 \\ 0 & R & Y & 0 & Q & \gamma - \frac{C}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma+C \end{pmatrix} \quad (2)$$

Absorption and luminescence spectra were collected for each crystal using a high resolution Fourier spectrometer and sample temperatures of 1.7K and 80K. From these data, we determine accurate Stark levels for the 4I_J ($J = 9/2, 11/2, 13/2,$ and $15/2$) and the ${}^4F_{3/2}$ multiplets. We then performed a best-fit calculation to determine the crystal-field parameters. In addition to these crystal-field parameters, our fit includes an adjustment of the energies of the excited J manifolds relative to the $J = 9/2$ manifold (parameters E(J)).

RESULTS AND DISCUSSION

The resulting crystal-field parameters for the Nd^{3+} dopant in the different host crystals are given in Table I. In each case, the root-mean-square deviation of our fit is better than 7 cm^{-1} . For the case of $KLiYF_5$, two separate dopant sites are observed.[1] These sites are resolved using site-selective photoluminescence. However, the photoluminescence to the ${}^4I_{15/2}$ multiplets is extremely weak and not fully resolved, so our fit does not include the ${}^4I_{15/2}$ Stark levels for $KLiYF_5$. We interpret these parameters in terms of the structure of the cage of F ions surrounding the Nd.

The crystal structure of $YLiF_4$ has recently been established using x-ray techniques by

Table I. Crystal field parameters for the Nd dopant in various crystals. The parameters are described in the text. The values are in cm^{-1} .

Parameter	YLiF ₄	YVO ₄	KLiYF ₄ (A)	KLiYF ₄ (B)
β	-126.6	190.6	-50.1	-48.0
γ	-125.5	-59.6	-121.2	-126.4
B	68.3	-386.2	333.1	316.4
C	-219.0	30.4	-53.8	-41.4
Y	-147.8	-99.0	-245.7	-219.8
P	---	---	-90.5	-122.9
Q	---	---	0.6	8.2
R	---	---	183.8	150.7
T	---	---	17.2	5.4
E(11/2)	1864	1866	1863	1863
E(13/2)	3838	3836	3838	3838
E(15/2)	5890	5872	5895	5895

Goryunov and Popov.[2] This structure is shown in Figure 1, though the distortions have been exaggerated for clarity. The two tetrahedrons of F ions are both tetragonally distorted along the symmetry axis of the crystal. The tetragonal distortions are in opposite senses however. One tetrahedron is stretched and the other is compressed. These distortions result in a site symmetry at the position of the Nd of D_{2d} . The site symmetry is further reduced by a twisting of the tetrahedrons by a few degrees

from one another. That is, the angle between the line segments AE and GC is not 90° , but is about 4° off. Thus, the final site symmetry is S_4 , though this latter reduction in symmetry is slight and has only a small contribution to the crystal field. We find that a crystal field based on the D_{2d} symmetry yields a good fit to the spectra, and that the inclusion of the extra parameters describing the reduction in symmetry to S_4 does not significantly improve the fit.

The parameters in Table I can be interpreted in terms of the structural model in Fig. 1. The lobes of the a_1 state are pointed towards the negatively charged F ions, making this a high energy state. In contrast to this, the three t_2 states have their large lobes pointed along the associated cubic axes, between the negative F ions, making the t_2 states energetically favorable. In between these two extremes are the t_1 states, whose eight lobes are tilted away from the cubic axes making them closer to the negative F ions, and thereby increasing the energy of the t_1 states relative to the t_2 states. These simple arguments explain the signs and relative sizes of β and γ . Consider now the state t_{2z} , which has its lobes along the z axis. In the presence of a stretching tetragonal distortion, the F ions are now closer to the z axis than to the x or y axis. Hence the energy

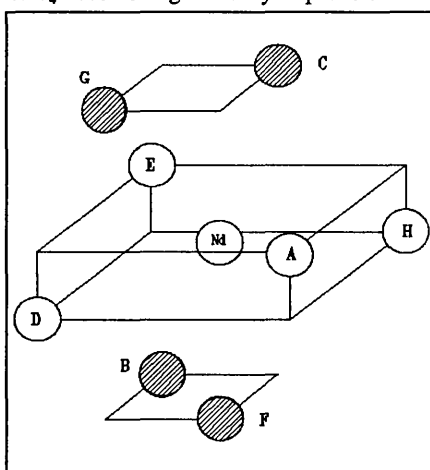


Fig. 1 -- Cage of eight F ions surrounding the Nd ion in YLiF₄. The cage forms two tetragonally distorted tetrahedra. The distortions are exaggerated for clarity.

of the t_{2z} state is going to be increased, i.e. B is positive. By the same token, the energy of the t_{1z} state, whose lobes are slightly tilted from the x and y axes, is going to be reduced, i.e., C is negative. It is more difficult to interpret off-diagonal matrix elements, particularly those between different manifolds, e.g. between t_2 and t_1 . As such, we will make no attempt here to interpret the parameter Y. Our results are fully consistent with a crystal field of D_{2d} symmetry resulting from a tetragonally distorted (stretched) tetrahedron of negative charges. This is exactly the case for the BCFG set of F ions shown in Fig. 1. We note that while this set is slightly more distant from the Nd than the ADEH set, the tetragonal distortion associated with this farther set is more pronounced. We argue that the greater distortion overcomes the effects of being slightly more distant. Hence, the dominant crystal field is that due to the neighbors labeled BCFG in Fig. 1.

We consider now the case of YVO_4 . The relevant structure here is given in Fig. 2, and is much simpler than that of $YLiF_4$. We need only consider the nearest neighbor tetrahedron of F ions, the second tetrahedron is significantly farther away.[3] The four F ions are very nearly on the x and y axes. Therefore, the lobes of the a_1 state are pointing away from the F ions, so $\beta + \gamma$ is positive. The lobes of the t_{2z} and t_{2y} states are more nearly directed towards the F ions, so these are the highest energy states. Hence, β is positive and B is negative. As before, the t_1 manifold is split in exactly the opposite sense making the energy of the t_{1z} state higher than the energy of the t_{1x} and t_{1y} states, i.e. C is positive. Again, we find that the results of our fit is entirely consistent with what we predict from the crystal structure.

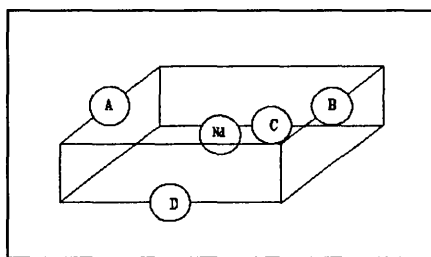


Fig. 2 -- Cage of the nearest neighbor F ions in YVO_4 . The next nearest neighbor cage is sufficiently far away to be neglected.

$KLiYF_5$ has a monoclinic crystal structure, which has been detailed through x-ray techniques by Goryunov *et al.*[4] Many distortions of the perfect tetrahedra of F ions surrounding the Nd ion are needed in order to achieve the final structure. However, we find that this structure closely resembles that of Fig. 1, though there are shears that need to be added. In addition, the centers of the two tetrahedrons do *not* coincide, though they are within 0.13 Å of each other. This result may be responsible for the presence of two stable positions for the Nd ion with very similar crystal fields. While many shears are needed to transform the structure of Fig. 1 into the actual structure found in $KLiYF_5$, we find that only one shear contributes significantly to the overall crystal field. The symmetry axis of this shear coincides with the axis of the tetragonal distortion, which is nearly perpendicular to the b axis of the crystal, resulting in a C_{2v} site symmetry. This shear makes the distance between the F ions along the segment BF(DH) in Fig. 1 different than the distance between the F ions along the segment GC(AE). Inclusion of other shears improves the root-mean-square deviation of our fit by only a few tenths of a wavenumber. Hence, we find a reasonably good fit assuming a C_{2v} site symmetry.

The signs of B and C imply that the stretched tetrahedron is again the one that contributes

most significantly to the overall crystal field. Which tetrahedron contributes more significantly depends upon the details of the distances from the Nd ion and the radial extents of the wave functions. Even though $\beta > \gamma$, because B is such a large number, the average energy of the t_{2g} and t_{2n} states is less than the average energy of the t_{1x} and t_{1y} states. This is consistent with the results for YLiF₄ in which the crystal field is also dominated by the contribution from the stretched tetrahedron. Like the parameter Y, the parameters R and T couple different manifolds together, so we will not attempt here to interpret these parameters. We can however offer an interpretation for the off-diagonal parameters P and Q, which operate in an identical fashion within the triplets t_2 and t_1 , respectively. We concentrate on the parameter P. The effect of this parameter is to rotate the t_{2g} and t_{2n} states by 45° about the z axis and to remove their degeneracy. The shear distortion giving rise to the parameter P makes the F ions closer to the lobes of one these two rotated states than to the lobes of the other state. Hence, we can readily see how this shear removes the degeneracy of these two t_2 states.

CONCLUSIONS

The expansion of the crystal field in terms of operators transforming as the irreducible representations of the T_d group leads to an easy and intuitive interpretation of the crystal-field parameters in terms of the shapes of the f wave functions and point-ion structural models. This interpretation is likely to help explain other effects important in solid state laser crystals such as the response of the levels to pressure and line broadening. It will also elucidate the coupling of the dopant to various phonons, which will help in modelling non-radiative decay, lattice relaxation, and phonon assisted energy transfer. The potential to employ the information gained from the crystal-field parameters we are proposing here serves as justification for the methods we have discussed in this work.

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