Merging of the $^4F_{3/2}$ level states of Nd^{3+} ions in the photoluminescence spectra of gadolinium-gallium garnets under high pressure

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The $^4F_{3/2}$ state of Nd^{3+} dopant ions is split due to the crystal field at orthorhombic D_2 symmetry sites in several members of the garnet family of crystals. In the gadolinium-gallium garnet crystal this splitting is found to almost disappear under hydrostatic pressures between 8 and 11 GPa created in the diamond-anvil cell. This pressure is much lower than that required for the phase transition to the so called high-pressure phase. This effect is explained with help of x-ray diffraction, optical spectroscopy, and *ab initio* calculations as an effect of accidental near-degeneracy arising from a particular lattice structure of garnets.

I. INTRODUCTION

Nd^{3+} is one of the most often used rare-earth (RE) dopants in garnet hosts, mainly for laser applications. The gadolinium-gallium garnet [Gd$_3$Ga$_5$O$_{12}$ (GGG)] is also one of the most studied oxide materials. It serves as an important lasing host material for various dopants, including several kinds of rare-earth ions.[1,2] For example, GGG:Yb crystals have been shown to exhibit diode-pumped laser action at a wavelength of ∼1 μm with a certain tunability range.[3] Several other applications have been proposed for GGG; for example, it can be used as substrates for epitaxy of superconducting films.[4–7]

At ambient conditions GGG crystallizes in the $Ia3d$ space group. Previous experiments have shown that its crystallographic structure remains unchanged up to ∼80 GPa. In our recent paper we have determined the experimental equation of state (EOS) for GGG compressed in a diamond-anvil cell with use of x-ray diffraction. Moreover, density functional theory (DFT) was applied to derive the EOS based on first principles.[8] We now use the same data to explain the structural properties of the GGG:Nd crystal under pressure.

Results of the high-pressure photoluminescence experiment reported by us in Ref. 9 show that the splitting of the $^4F_{3/2}$ state of Nd^{3+} in GGG crystals, observed at ambient pressure, gradually diminishes with applied pressure and virtually disappears at ∼8–11 GPa. Above 11 GPa the splitting is restored. RE ions which are the constituents of the garnet crystals occupy eightfold-coordinated dodecahedral sites (Wyckoff position 24) with D_2 point symmetry. This symmetry is the source of the $^4F_{3/2}$ state splitting of Nd^{3+} substituting for Gd. In this symmetry the RE central ion can be viewed as located in the center of a highly distorted cube (each side of this cube is divided into two triangles, tilted slightly against each other) with eight oxygen ions located in the corners of this cube. Four out of the eight bonds between the central ion and ligands have equal length and are shorter than the other four, which have longer, equal-length bonds. Point group analysis shows that symmetry-induced degeneracy of the substates within the $^4F_{3/2}$ state occurs only in high O_h symmetry;[10] however, the symmetry of the site occupied by RE ions in garnets is always

D_2, at least up to the phase transition pressure (∼80 GPa). Hua *et al.* suggested that the splitting may disappear if the distances between the Nd^{3+} and all oxygen ligand ions became equal at a certain pressure, which presumably should not change the symmetry of the site occupied by the Nd^{3+} ion.[11]

Similar results have been reported by Hua *et al.* for Nd^{3+} ions in gadolinium scandium gallium garnet (GSGG); however, they did not observe a complete disappearance of the splitting of the $^4F_{3/2}$ level but only a certain decrease at ∼15 GPa followed by a subsequent increase.[11] The splitting of the $^4F_{3/2}$ state also decreases with pressure in YAG:Nd crystals, but the much larger bulk modulus of the latter material would require much higher pressures in order to achieve a removal of the splitting.[12]

II. EXPERIMENTAL

The high-pressure luminescence spectra of GGG:Nd^{3+} crystal, grown by the Czochralski method, were measured using a GDM-1000 double grating monochromator equipped with a cooled photomultiplier (EMI 9684B) with S1-type cathode and an SR530 lock-in amplifier. The high-pressure measurements were performed with use of a diamond-anvil cell (Diacell Products MCDAC-1) at room temperature in order to assure thermal population of the upper substate of the $^4F_{3/2}$ state. Argon was used as a pressure-transmitting medium. The polished samples of thickness ∼30 μm were loaded into the cell along with a small ruby ball. The R_1 ruby luminescence line (excited by the argon-ion laser) was used for pressure calibration. The hydrostatic conditions in the cell could be partially monitored by recording the half-width of the ruby emission. In these measurements an increase of the half-width of the ruby luminescence was observed with increasing pressure from 2.5 cm^{-1} at ambient pressure to ∼6 cm^{-1} at the highest pressure of 25 GPa. This means that the nonhydrostatic effects were rather weak.

The pure (undoped) GGG samples, used for x-ray diffraction (XRD) experiments, were prepared by solid state reaction. A stoichiometric mixture of oxides Gd$_2$O$_3$ (Sigma Aldrich,

99.99%, metal basis) and Ga_2O_3 (Sigma Aldrich, nano size, 99.8% purity, metal basis) was sintered in air for 24 h at $1350\,^{\circ}\mathrm{C}$. The diffraction pattern collected at laboratory conditions proved phase purity of the studied sample.

The pressure dependent XRD experiment was performed at line B2 of CHESS synchrotron in Cornell University, Ithaca, NY, using the wavelength of 0.619921 Å and sample-to-detector distance of 384 mm. An ethanol-methanol 1:4 mixture was used as a pressure-transmitting medium. The applied pressures, calibrated by ruby luminescence, ranged up to 25 GPa, i.e., beyond the hydrostatic range of the medium. A MAR345 2D detector was used in the study. The two-dimensional diffraction patterns were converted to one-dimensional patterns using the FIT2D program.[13] The diffraction data were refined by the Rietveld method with use of the FULLPROF program.[14]

Due to the medium applied in the experiment the hydrostatic conditions were well preserved up to at least 10 GPa. At higher pressures, due to pressure-medium solidification, the effects of nonhydrostaticity involve the broadening of both the diffraction profiles and the ruby luminescence lines. The positions of the oxygen atoms were determined from the Rietveld analysis as a function of pressure. The refinements show a weak gradual variation of the oxygen position (x,y,z) with increasing pressure: The position changes, with some scatter, from (0.024, 0.060, 0.654) to (0.033, 0.060, 0.645). The bond lengths between the central Gd ion and eight oxygen atoms were calculated.

III. EXPERIMENTAL RESULTS

The luminescence of Nd^{3+} in GGG at ambient pressure consists of ten narrow lines, related to the transitions from the crystal field split excited $^4F_{3/2}$ doublet to the ground $^4I_{9/2}$ quintet. The partial energy level diagram of Nd ions in D_2 symmetry site, involving these transitions, is shown in Fig. 1.

In this point group symmetry all states are characterized by Γ_5 representations.[15] At pressures between 8.0–11.0 GPa the excited state splitting is virtually removed and the number of luminescence lines is reduced to 5. The pressure dependence of the photoluminescence at room temperature associated with
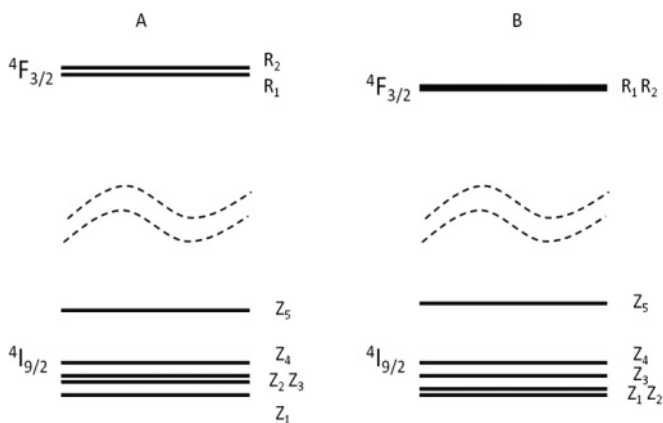
FIG. 1. (Color online) Partial energy structure of the Nd^{3+} ion in GGG crystal: (a) at ambient pressure; (b) at pressures between 8 and 11 GPa.
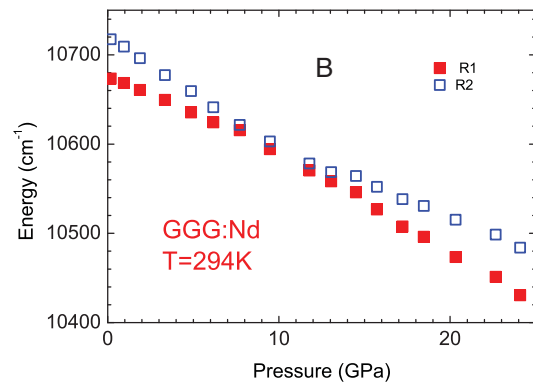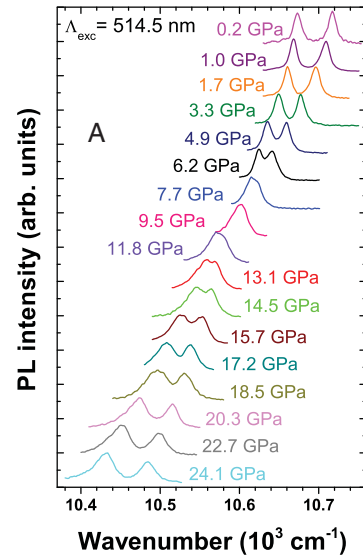
FIG. 2. (Color online) (a) Pressure dependence (the lowest energy part of the $^4F_{3/2}\rightarrow\,^4I_{9/2}$ transitions) of the luminescence spectra of Nd^{3+} ion in GGG at room temperature. (b) Spectral positions of the luminescence lines associated with the transitions from the $^4F_{3/2}$ levels (R_1 and R_2 doublet) to the most upper level of the ground $^4I_{9/2}$ state of Nd^{3+} as a function of hydrostatic pressure. R_1 and R_2 denote the lower and higher energy levels of the $^4F_{3/2}$ state, respectively, in the whole range of pressures (see also Ref. 9). Estimated errors of each point are smaller than the symbol size on the graph.

the two lowest energy $^4F_{3/2}\rightarrow\,^4I_{9/2}$ transitions (R_1, $R_2\rightarrow Z_5$), is presented in Fig. 2. This dependence very well visualizes the effect since these two lines are well separated from the other ones.

With the help of Rietveld refinement analysis the crystallographic coordinates of each oxygen atom in the first coordination sphere of the Gd^{3+} ion [at the (0.125, 0, 0.25) position in lattice parameter units] as well as the distances between the central Gd ion and the surrounding oxygens have been established as a function of pressure. Due to the limited accuracy of the atomic positions obtained from Rietveld analysis of a single data set, associated with small sample size and moderate angular range available in a typical diamond anvil cell (DAC), in further considerations we use the smoothed (linearly approximated) pressure variation of each atomic coordinate. The thus-derived distances between the central Gd and the two nonequivalent surrounding oxygen ions are presented as a function of pressure in Fig. 3.
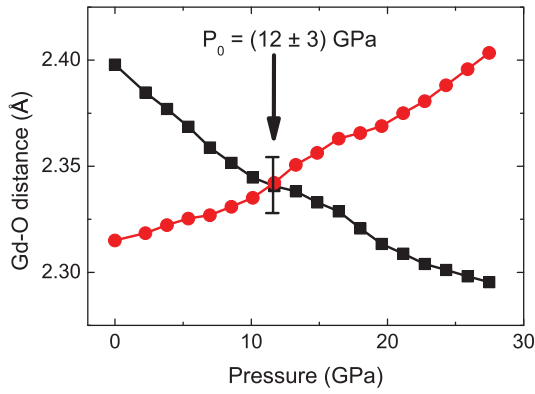
FIG. 3. (Color online) Averaged Gd-O distances in the first coordination sphere of the GGG crystal as a function of pressure. The lines serve for guiding the eyes only. The size of the error bars applies to all points.

At a pressure of ∼11.8 GPa the distances between the central Gd and all surrounding oxygen ions become approximately equal to each other. This pressure is close to that at which the splitting of the $^4F_{3/2}$ multiplet of Nd^{3+} vanishes (see Fig. 2). However, a detailed analysis of the symmetry of the central Gd^{3+} ion shows that the D_2 symmetry of the GdO_8 molecule is preserved. The approximate picture of the GdO_8 molecule at a pressure of 11.8 GPa is shown in Fig. 3. The shape of this molecule can still be viewed as a distorted cube. The two opposite slightly rectangular (not square-shaped) faces are parallel to each other but they are twisted around the vertical axis. Each of the four other faces still forms two triangles (typical for the REO_8 dodecahedron in a garnet structure).

Therefore, the equal distances between Gd-O ions at this pressure alone cannot explain the removal of the $^4F_{3/2}$ level splitting of Nd^{3+} ions substituting Gd^{3+} in the GGG host.

IV. THEORY AND DISCUSSION

Nd^{3+} ions occupy the Gd^{3+} sites, and the local site symmetry is D_2. Such a low symmetry implies nine nonzero crystal field parameters (CFP)[16] ($B_{2,0}$, $B_{2,2}$, $B_{4,0}$, $B_{4,2}$, $B_{4,4}$, $B_{6,0}$, $B_{6,2}$, $B_{6,4}$, $B_{6,6}$; we use notation equivalent to extended Stevens notation). Since we deal with the $^4F_{3/2}$ level the only equivalent operators which can cause the splitting of this level are $O_{2,0}$ and $O_{2,2}$. The solutions of the secular equation for this state are equal to

$$E_{1,2} = \mp \sqrt{3\left(3B_{2,0}^2 + B_{2,2}^2\right)}. \qquad (1)$$

In order to completely remove the splitting of the $^4F_{3/2}$ level, both $B_{2,0}$ and $B_{2,2}$ crystal field (CF) parameters have to be equal to 0 simultaneously.

In the point-charge approximation the $B_{2,0}$ and $B_{2,2}$ CF parameters can be expressed in terms of certain lattice sums of the coordinates of the surrounding ligands (oxygens), equal
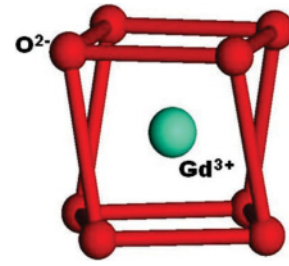

FIG. 4. (Color online) GdO_8 molecule in the GGG crystal at a pressure of 11.8 GPa.

to[17]

$$B_{2,0} \propto \sum_{i=1}^{8} \frac{3Z_i^2 - R_i^2}{R_i^5} = S_{2,0}, \qquad (2a)$$

$$B_{2,2} \propto \sum_{i=1}^{8} \frac{X_i^2 - Y_i^2}{R_i^5} = S_{2,2}. \qquad (2b)$$

The proportionality constants are not dependent on the coordinates of the ligands. In the above expressions the X_i, Y_i, and Z_i coordinates of the oxygen ions in the first coordination shell as well as the distances R_i are calculated taking the rare-earth central ion position in the dodecahedron as (0,0,0) within a Cartesian system of axes in D_2 symmetry [symmetry adapted axes system (SAAS)]. One of the C_2 axes of this SAAS coincides with the crystallographic Cartesian system of axes for the GGG garnet crystal at every considered pressure. We consider this axis as the axis z of the SAAS. The other SAAS axes (x and y) are twisted by $45°$ around the z axis with respect to the crystallographic axes.

The experimental, averaged pressure dependencies of the above lattice sums are presented in Fig. 5.

Although both values of the lattice sums (2) cross zero, it occurs at a different pressure for each sum (interestingly, the values of the lattice sums (2) equal zero simultaneously at a pressure of ∼7.0 GPa in the crystallographic system of axes). Substituting the values of the lattice sums into Eq. (1) in the form

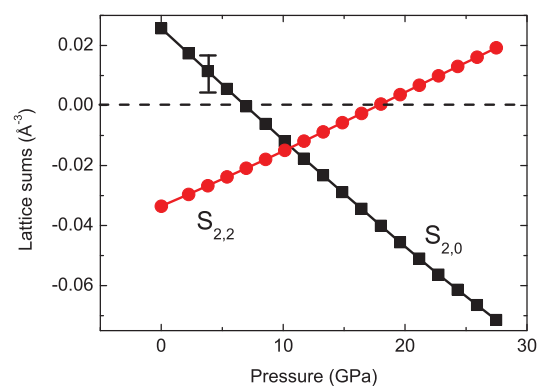$$\Delta E_{1,2} = \mp C \sqrt{\left(3S_{2,0}^2 + \lambda S_{2,2}^2\right)}, \qquad (3)$$

FIG. 5. (Color online) The experimental pressure dependencies of the lattice sums [Eqs. (1)] for the GGG crystal. The estimated size of error bars applies to all points.
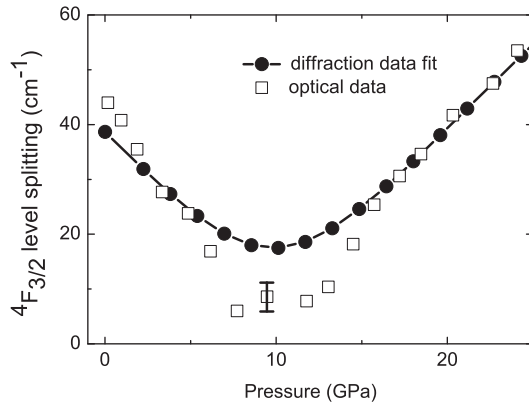
FIG. 6. The $^4F_{3/2}$ level splitting of the Nd^{3+} ions in GGG crystal obtained from the optical measurements and fitted by Eq. (3) from the XRD data. The estimated size of error bars applies to all points.

where λ expresses the $(S_{2,0}/S_{2,2})^2$ ratio, and treating λ and C as adjustable parameters, a fit of Eq. (3) to the experimental dependence of the splitting of the $^4F_{3/2}$ level is obtained. Both dependencies are shown in Fig. 6. The fitted values of the parameters are equal to $C = 480$ and $\lambda = 4$.

The fit of Eq. (3) based on the XRD data exhibits a minimum value at a pressure of $\sim$10 GPa, which coincides very well with the minimum of the splitting obtained from the optical data. Since at any pressure the lattice sums (2) do not vanish simultaneously, the removal of the splitting of the $^4F_{3/2}$ level is not complete, in accordance with Eq. (1), although the transitions from both sublevels of $^4F_{3/2}$ level overlap strongly due to the inhomogeneous broadening (see Fig. 2). Although the minimum of the splitting obtained from the XRD data measured for Gd^{3+} coincides very well with the optical experiment, the values of the splitting observed in the luminescence are lower than those obtained from the fit. This may be associated with the substitution of the Nd^{3+} ions in place of Gd^{3+} and a possible small deviation of the surrounding oxygen dodecahedron due to slightly larger ionic size of Nd^{3+} than Gd^{3+} (1.109 and 1.053 Å, respectively).[18] Due to the relatively small concentration of Nd^{3+} (0.5%) it would be impossible to obtain reliable XRD results for this ion. The very small value of the splitting observed in the luminescence suggests that the minimum of the lattice sums (3) for Nd^{3+} ions must occur at closer to zero value simultaneously for both sums. Group theory analysis shows that even if both $B_{2,0}$ and $B_{2,2}$ are equal to zero simultaneously at a certain pressure but the symmetry is still D_2, the ground $^4I_{9/2}$ state of the Nd^{3+} remains split into five sublevels due to the influence of the higher-order equivalent operators which are dominant in this case. This is in perfect agreement with the optical data showing the five luminescence lines in the luminescence spectra at a pressure of $\sim$12 GPa, presented in Fig. 7.

Theoretical calculations with use of the DFT method, under assumption that one Nd ion replaces one Gd in an 80-atom supercell, are only in partial agreement with the experimental results. For these calculations the VASP code[19,20] was used with pseudopotentials obtained by the projector augmented wave (PAW) method and plane-wave basis set with a 26-Ry cutoff energy. The k points were generated with the $3 \times 3 \times 3$ mesh. The exchange correlation energy was calculated
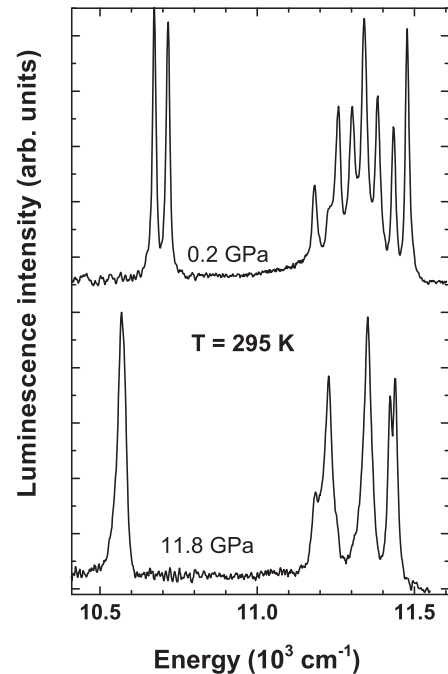

FIG. 7. The spectra of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ optical transitions of the Nd^{3+} ions in GGG crystal excited by the 514.5-nm argon-ion laser line at pressures 0.2 and 11.8 GPa.

using the generalized gradient approximation and the atomic coordinates were relaxed with a conjugate gradient technique. To determine the equilibrium configurations for each unit cell with size adequate for the studied pressure, the criterion that the maximum force is <0.01 eV/Å was used.

The calculations reveal that Nd^{3+} ions are located exactly in the crystallographic positions of Gd^{3+} ions at each applied pressure; however, there is a very small rearrangement of surrounding oxygen ions around the central Nd^{3+}. There is no shift of the Nd^{3+} dopant outside of the lattice position, such as found in $LiNbO_3$:Nd. In the latter system the Nd^{3+} ions are shifted along the ferroelectric c axis in respect to

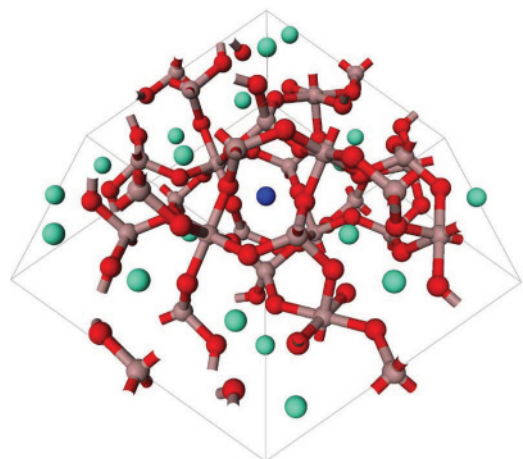

FIG. 8. (Color online) The schematic view of the atom arrangement (calculated by DFT method) of GGG:Nd crystal in 80-atom supercell at pressure of $\sim$12 GPa. Nd: blue (single, in center); Gd: green (unattached); Ga: grey; O: red.
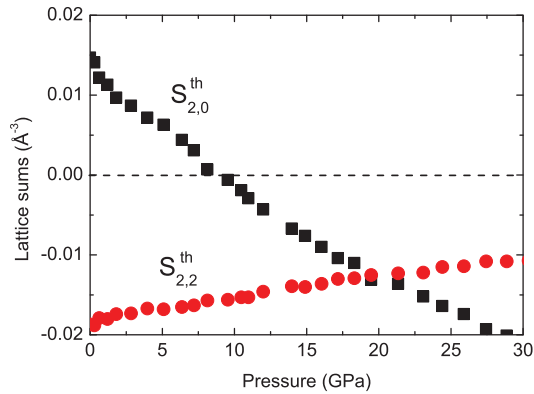
FIG. 9. (Color online) The theoretical pressure dependencies of the lattice sums [Eqs. (2)] for the GGG crystal.

the Li$^+$ octahedrons as a result of lattice rearrangement after the domain inversion processes.[21] The schematic picture of the atom arrangement of the calculated supercell at a pressure of ~12 GPa is presented in Fig. 8.

The DFT results predict that the lattice parameter of the GGG crystal at ambient pressure is equal to ~12.51 Å, as compared with the experimental value of 12.375 Å. Theory also shows that the distances between the central Gd^{3+} ions and surrounding oxygens eventually become equal, but at a larger pressure of ~33.0 GPa. The theoretical pressure dependencies of the lattice sums $S\mathrm{th}_{2,n}$ [Eqs. (2)] are presented in Fig. 9. The theory predicts a weaker variation of the lattice sums with applied pressure than found in the XRD experiment. According to the calculations there is no crossing of the zero value for the $S\mathrm{th}_{2,2}$ lattice sum in the examined range of pressure. Using theoretical values of the lattice sums (2) it is possible to find a minimum of the splitting of the $^4F_{3/2}$ levels with Eq. (3); however, with a different set of fitting parameters. The origin of the discrepancy between the theoretical and experimental results is unknown; however, theoretical dependencies are in qualitative agreement with the experimentally observed dependencies (compare Figs. 5 and 9).

V. CONCLUSIONS

The pressure-induced decrease of the splitting and eventual merging of the $^4F_{3/2}$ sublevels of the Nd^{3+} in GGG crystals at 8–11 GPa observed in photoluminescence is most probably not complete and is partially a result of the inhomogeneous broadening of the optical transitions. The effect is accidental and is associated with the particular lattice structure of garnets, since no rise of symmetry occurs at this pressure. The levels are characterized by the same group theory representations (Γ_5) as in the nondegenerate case. This is confirmed by the total number of the luminescence lines in the $^4F_{3/2} \to {}^4I_{9/2}$ luminescence spectrum at pressures at which the accidental degeneracy occurs, which is equal to 5, i.e., equal to the number of sublevels for the $^4I_{9/2}$ ground state of Nd^{3+} ion in D_2 symmetry. In cubic crystal field symmetry the $^4I_{9/2}$ ground state should be split into only three levels.[19] This explanation is supported by the theoretical calculations with the use of DFT and experimental results obtained by XRD.

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