

CRYSTALLINE FIELD INVESTIGATION IN $\text{CaF}_2:\text{Nd}^{3+}$

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Crystalline field investigation in CaF_2 doped with 10, 15, 20, 25 mol % of Nd^{3+} has been carried out. The absorption spectrum in the region 30,000–5,710 cm^{-1} has been measured at room and liquid nitrogen temperatures. We have compared the measured and the corresponding calculated states. According to the results we have identified the symmetry of the incorporated ion. The symmetry of the crystal field in the close vicinity of the incorporated Nd^{3+} ion is tetragonal.

ИССЛЕДОВАНИЕ СИММЕТРИИ КРИСТАЛЛИЧЕСКОГО ПОЛЯ В $\text{CaF}_2:\text{Nd}^{3+}$

В работе показаны результаты исследования симметрии кристаллического поля в CaF_2 с добавкой 10, 15, 20, 25 мол % Nd^{3+} . Для этого измеряли спектры поглощения в области 30 000–5 710 cm^{-1} при комнатной температуре а также при температуре жидкого азота.

Результаты измерений сравнивались с вычисленными данными для соответствующих состояний. Анализом этих результатов была установлена симметрия вложенного иона. Указывается что симметрия кристаллического поля в окрестности вложенного иона Nd^{3+} тетрагональная.

I. INTRODUCTION

From the viewpoint of application a very important group of materials is formed by solid solutions which appear in the systems $\text{MF}_2(\text{Y}, \text{Ln})\text{F}_3$, where $M = \text{Sr}, \text{Ba}, \text{Ca},$ and $\text{Ln} = \text{lanthanide}$. At present they are mainly used in optical light quantum generators [1], [2]. They exhibit special spectroscopic properties peculiar to both crystalline materials and glasses. CaF_2 doped by small concentrations of LnF_3 is being used as a photochromic material for optical information recording [3], [4], [5].

The electronic transitions corresponding to absorption and luminescence of Ln^{3+} in visible, UV and IR regions of the spectrum have their origin in the 4f electron sphere. The spectra of $\text{CaF}_2:\text{Ln}^{3+}$ crystals with small Ln^{3+} concentrations (below 1 mol %) have either a line structure or a narrow-band one. The number, intensity, and location of lines strongly depend on the structure of the closest vicinity of the Ln^{3+} ion in the crystalline lattice. A slight change in the distribution of coordinating ions is accompanied by a change of spectroscopic properties. Therefore, the measurement of spectroscopic properties enables to study the decomposition processes of fluoride solid solutions $\text{M}_{1-x}\text{Ln}_x\text{F}_{2+x}$ (x — molar fraction), association and dissociation of defects, and the structure of complexes from associated impurity ions.

Already at small Ln^{3+} concentrations these ions form several types of structurally excited complexes ($\text{Ln}^{3+} - \text{F})_n\text{F}_i$ is a fluorine ion in the interstitial position, n denotes the first, second, or third coordination sphere in which F_i ions are located entering the Ln^{3+} complex, with all Ln^{3+} ions located in the crystalline field of the same symmetry. By a further enlargement of complexes (e.g. by increasing the Ln^{3+} concentration) the ions are located in various fields with a lower symmetry. Therefore, the spectral lines become more complex. Furthermore, the new lines are much broader. A further increase of the Ln^{3+} concentration yields a higher intensity of lines only — the structure remains unchanged.

In the presented contribution we are concerned only with the investigation of the crystalline field of the fluoride solid solution $\text{Ca}_{1-x}\text{Nd}_x\text{F}_{2+x}$, $x = 0.1, 0.15, 0.2, 0.25$ by measuring its optical absorption.

III. EXPERIMENTAL

$\text{Ca}_{1-x}\text{Nd}_x\text{F}_{2+x}$ single crystals were prepared at the Institute of Physics Slov. Acad. Sci. by the Stockbarger method. The synthesis is performed in an atmosphere of gaseous products of Teflon pyrolysis in graphite crucibles. The products of Teflon decomposition (appearing above 800 °C) remove from the CaF_2 and NdF_3 materials absorbed water and oxygen. The incorporation of O^{2-} and OH^- ions causes among other things a change of spectroscopic properties of the crystal. The synthesized crystals were cooled to room temperature at the rate 36 °C/hour.

The absorption spectrum in the region 30,000–12,500 cm^{-1} was recorded by the double-ray recording spectrophotometer Speedord UV-VIS, Carl Zeiss Jena, with a resolution lower than 30 cm^{-1} and a frequency within $\pm 50 \text{ cm}^{-1}$. The measurements were performed with all four samples at both room (RT) and liquid nitrogen temperatures (LNT). During measurements the sample was inserted into a nitrogen cryostat. In the near-infrared region 15,500–5,710 cm^{-1} a single ray

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recording spectrophotometer constructed from Carl Zeiss Jena devices was used. It consists of the following parts: lighting by a tungsten bulb, a compensating GIT1 recorder, a specular monochromator SPM 2 with a quartz prism, and a PbS photoresistor with an amplifier, detector, and a short-stop equipment. The measurement was performed with two samples of the highest concentration.

IV. RESULTS

In the analysis of spectra, recorded at LNT, the quantum states and the corresponding energy values were related to the absorption lines. In the region 30,000–24,500 cm^{-1} two levels of the ${}^2P_{3/2}$ state were observed; the other six states were not resolvable and, therefore, they were entirely related to the states ${}^2L_{15/2}$, ${}^4D_{1/2}$, ${}^2I_{11/2}$, ${}^4D_{5/2}$, ${}^4D_{3/2}$.

In the region 24,500–19,000 cm^{-1} three lines were related to the $\beta^2D_{5/2}$ state, one line to the ${}^2P_{1/2}$ one, eight lines entirely to the states ${}^4G_{11/2}$, $\beta^2D_{3/2}$, ${}^2K_{15/2}$, ${}^4G_{9/2}$ and $\beta^2G_{9/2}$. Nine lines between 19,680 and 19,030 cm^{-1} were related to the states ${}^2K_{13/2}$ and ${}^4G_{7/2}$. In the region 19,000–12,500 cm^{-1} four lines were related to the $\beta^2G_{7/2}$ and ${}^4G_{5/2}$ states, three lines to $\beta^2H_{11/2}$, three lines to ${}^4F_{9/2}$, three lines to ${}^4F_{7/2}$ and two lines to $\beta^2H_{9/2}$ and ${}^4F_{5/2}$.

In the last region, 15,500–5,710 cm^{-1} , two lines were related to the ${}^4F_{9/2}$ state, another two lines were related to ${}^4F_{7/2}$ and ${}^4S_{3/2}$. Three lines were related to $\beta^2H_{9/2}$ and ${}^4F_{5/2}$ and, two lines were related to the ${}^4F_{3/2}$ state. The last eight lines were related, in agreement with theoretical calculations, to the ${}^4I_{15/2}$ state.

In the analysis of absorption spectra we have tried to employ the fact that four samples of various concentrations were prepared simultaneously by the same method. Voronyko et al. [6] measured such concentration series. They came to the conclusion that with an increasing concentration the number of absorption peaks increases and their intensity becomes stronger. Although our sample series was smaller and the samples were not prepared from the same ingot (a condition to prepare concentration series) we observed most absorption peaks also in the sample with the highest concentration.

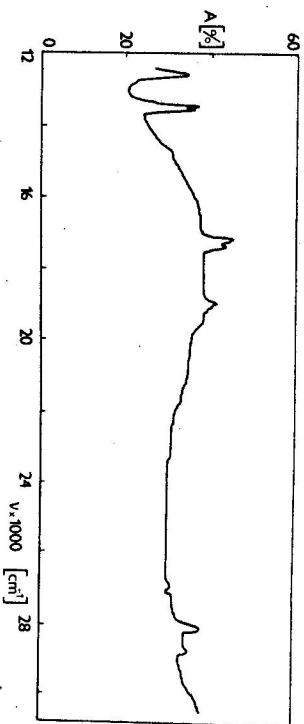
The calculation of the crystalline field splitting for the ${}^4F_{3/2}$, ${}^4F_{5/2}$, ${}^4F_{7/2}$, ${}^4F_{9/2}$, and ${}^4I_{15/2}$ states was performed with the help of an optimization program (Gašparík [7]). This program enables an iterative optimization of a given theoretical function with several theoretical parameters in order to fit the course of the experimentally exposed curve. The calculation starts from estimated values of $\text{CaF}_2:\text{Nd}^{3+}$ crystalline field parameters.

The optimization program is applied for solving a secular equation by the Jacobi diagonalization of the real symmetric matrix [7]. All calculations were performed with the Siemens 4004/150 computer in UVTV VŠ UK.

The calculated values of the crystalline field parameters for the 4F term and for the state ${}^4I_{15/2}$ are $A_2^0 = 170$, $A_4^0 = -200$, $A_4^4 = -1000$, $A_6^0 = 33$, $A_6^4 = -1000$.

V. DISCUSSION

According to the above results it is clear that our case corresponds to the tetragonal symmetry of the incorporated ion, confirmed by very good agreement with the calculated ${}^4F_{3/2}$ splitting.



Figs. 1, 2, 3, 4 show an absorption spectrum of CaF_2 doped with 10, 15, 20, 25 mol % NdF_3 measured at 77 K.

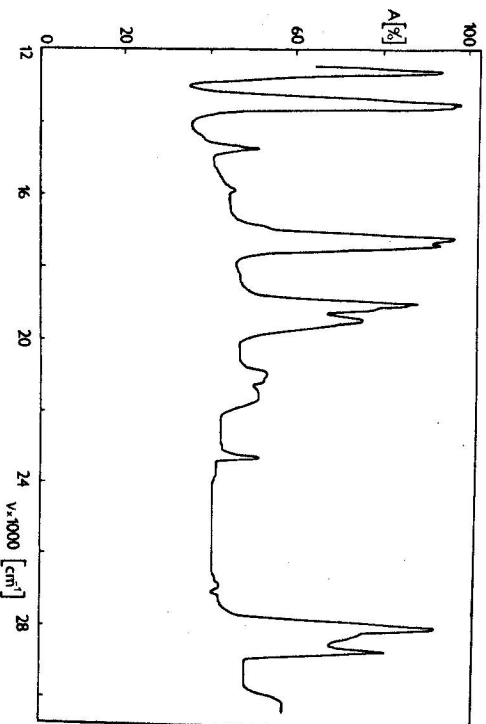


Fig. 2.

When calculating the splitting of the 4F term, seven measured values (out of the 14 possible ones) of absorption maxima were available. Three lines only were related to the ${}^4F_{9/2}$ state, but using the above crystalline field parameters all the five lines were calculated. The agreement between the three measured and the corresponding calculated values is very good. Therefore we may assume that the

remaining two calculated lines have a position corresponding to reality. Three absorption lines were related to the ${}^4F_{7/2}$ and ${}^4S_{3/2}$ states. Excluding one of them - which according to a comparison with free ion levels belongs more probably to the ${}^4S_{3/2}$ state - instead of the proposed four absorption peaks only two are present. Using the introduced parameters of the crystalline field, four related splitting values were calculated.

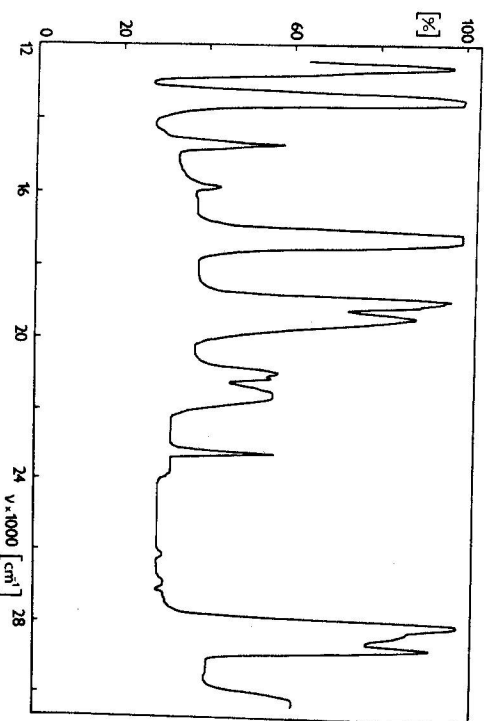


Fig. 3.

It was most difficult to ascribe lines to the ${}^4F_{5/2}$ state. In this case there was no reason - with regard to the calculated values of the free ion - to ascribe to this state even a single line. A comparison with the calculated values also shows that the lines considered for ${}^4F_{5/2}$ and ${}^2H_{9/2}$ probably correspond to the state ${}^2H_{9/2}$.

We were much more successful in identifying two lines of the ${}^4F_{3/2}$ state with the measured values corresponding to the calculated ones. This fact is to be considered as an important factor when deciding about the tetragonal symmetry in our case.

In our original treatment the parameters corresponding to the cubic symmetry were also taken into account; however, a great disagreement between the measured and the calculated values was found.

The splitting of the ${}^4I_{13/2}$ state was first calculated with the same parameters as for the 4F term but no good results were obtained. By changing the crystal field parameters a better agreement with the measured values was obtained though not so good as for the 4F term. In the case of the ${}^4I_{13/2}$ state we succeeded to record all the eight proposed absorption peaks.

In the papers published so far there have been only values of crystal field parameters of a cubic symmetry. Kumar, Dass and Chandra [8] published the

values for $\text{CaF}_2:\text{Nd}^{3+}$: $A_6^0(r^4) = -419.0 \text{ cm}^{-1}$; $\text{CaF}_2:\text{Nd}^{3+}$: $A_6^0(r^6) = 33.0 \text{ cm}^{-1}$. The work does not mention clearly states for which this parameters have been calculated.

Voronko et al. [9] assume also a cubic symmetry of the crystal field and their calculated values are: $A_6^0(r^4) = -214 \text{ cm}^{-1}$, $A_6^0(r^6) = 29 \text{ cm}^{-1}$. The comparison of the measured and the calculated splittings is transferred to the states ${}^4I_{15/2}$, ${}^4I_{13/2}$,

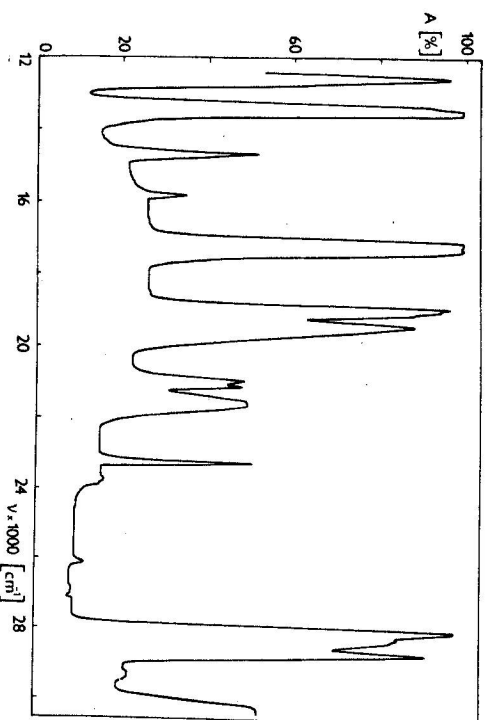


Fig. 4.

${}^4I_{11/2}$, ${}^4F_{9/2}$, $\beta^2H_{11/2}$, ${}^4F_{7/2}$ and ${}^4G_{11/2}$. It shows that the assumed model (except the state ${}^4F_{9/2}$) is in accordance with the total splitting. However, it is not clear how it is in the case of other states of the term 4F and 4I of this model.

Further information about the measurements and about relating energetic levels to single quantum states can be found in papers [10] and [11]. In [11] it is considered that the symmetry of the crystal field in the close vicinity of the incorporated Nd^{3+} ion is trigonal but values of the crystal field parameters are missing.

A characteristic of the solid solutions $\text{Ca}_{1-x}\text{Ln}_x\text{F}_{2+x}$, with Ln as an element from the left part of the lanthanide row, is a large value of dissociation of the tetragonal complex $(\text{Ln}^{3+} - \text{F}^-)_1$ (the F^- ions being in the closest vicinity of the Ln^{3+} ion). In the case of Nd^{3+} this type of complex remains up to the melting point of the solid solution. The mentioned complex is thus the simplest structural unit, and all the other complexes are products of the $(\text{Nd}^{3+} - \text{F}^-)_1$ association.

In order to obtain an exact picture of the presence and concentration of the particular associates, it is necessary to reach a thermodynamic equilibrium at a given temperature. For this purpose one has to anneal samples at a certain

temperature and quench them. Since in our case no such experiments were performed, it is to be assumed that our result-tetragonal symmetry of the incorporated Nd^{3+} ion- corresponds to equilibrium at high temperatures.

Further knowledge about the vicinity of the incorporated ion could be obtained by luminescent measurements and measurements at liquid helium temperature.

Finally, we can say that the symmetry of the crystal field in close vicinity of the incorporated Nd^{3+} ion is tetragonal. The states ${}^4F_{9/2}$, ${}^4F_{7/2}$, ${}^4F_{5/2}$, ${}^4F_{3/2}$ satisfy the following crystal field parameters: $A_2^0 = 170$, $A_4^0 = -200$, $A_4^4 = -1000$, $A_6^0 = 33$, $A_6^4 = -1000$ with the root means square $\delta = 0.3$ and the state ${}^4I_{15/2}$ the same parameters with the root means square $\delta = 563.4$.

Hence we can suppose that for the term 4I J -mixing must be taken into account.

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