CRYSTAL-FIELD ANALYSIS OF SPLITTINGS OF THE ENERGY LEVELS FOR THE Nd^{3+} CENTRE IN THE GASE CRYSTAL

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The splittings of the $4f^3$ energy levels of trivalent neodymium ions in the GaSe crystal are investigated by means of the crystal-field approach. The crystal-field parameters for the system GaSe:Nd^{3+} are determined. The comparison of the calculated energy levels with the experimental data is made.

GaSe layer crystal is a material of great importance in fields of both fundamental research and technical applications because of its structural, optical, electronic and photoelectronic properties. It is very useful to get detailed information on energetic parameters of impurity centres in this semiconductor in order to obtain high-quality devices [1]. The impurity levels of different ions in GaSe have been extensively studied recently [1-7].

In the papers [2,8] intrashell photo- and electroluminescence of trivalent neodymium ions in the GaSe and GaS single crystals have been observed and the scheme of splittings of the Nd^{3+} energy levels in these crystals experimentally have been established . The theoretical investigation of the splittings of the Nd^{3+} energy levels in GaS crystal is carried out and the values of crystal-field parameters for the GaS:Nd^{3+} system are calculated, what we have already reported [9]. The same theoretical problem for the GaSe:Nd^{3+} system is considered here.

The properties of rare-earth ions in the crystals, such as the splittings of energy levels in the crystalline electric field, its luminescence etc. strongly depend on the site of rare-earth ion in the crystal, on its site symmetry and on the nature of neighbouring ions. The sites of stabilization of rare-earth ions in the crystal GaSe are studied in the papers [10,11]. It is established that the complex, consisted of the trivalent rare-earth ion and the alkaline metal ion (such as Li^+ or Na^+, which are employed for the charge compensation) substitutes the $(2Ga)^{4+}$ covalently bounded pair in the GaSe lattice. In this case the rare-earth ion is situated in the centre of layer, while the alkaline metal ion is placed in the interlayer space.

The analysis of excitation and emission spectra [2,8] shows that the charge compensation has the weak influence on spectra of rare-earth ion. Therefore, the effect of the charge compensation on the crystalline electric field may be neglected. Then, the point symmetry at the site of the Nd^{3+} ion, as well as the symmetry of the crystalline electric field, which has effect on the Nd^{3+} ion can be treated as a hexagonal symmetry D_{3h}, and the corresponding crystalline electric potential V is taken as [12]

$$V=B_{20}(3z^2-r^2)+B_{40}(35z^4-30z^2r^2+3r^4)+B_{60}(231z^6-315z^4r^2+105z^2r^4-5r^6)+ +B_{66}(x^6-15x^4y^2+15x^2y^4-y^6) \quad , \qquad (1)$$

where B_{nm} are the crystal-field parameters, the centre of the Nd^{3+} ion is taken as the centre of the coordinate system and the z axis is directed along the C_3 symmetry axis of crystal.

Under the influence of crystal-field potential (1) the free-ion energy levels of Nd^{3+} are split into several components. In this work the crystal-field splittings of Nd^{3+} levels in a first-order approximation of perturbation theory and the matrix elements of potential (1) by means of Steven's operator equivalents method are calculated [12,13]. Within this framework the energy of Stark components are expressed by four parameters:

$$b_{20}=B_{20}\langle r^2\rangle, \quad b_{40}=B_{40}\langle r^4\rangle, \quad b_{60}=B_{60}\langle r^6\rangle, \quad b_{66}=B_{66}\langle r^6\rangle . \qquad (2)$$

Here

$$\langle r^n\rangle=\int R_{4f}^2(r)\, r^{n+2}dr \quad , \qquad (3)$$

where $R_{4f}(r)$ is the radial wave-function of the $4f$ electron.

The simple calculation method for the B_{nm} parameters is the point-charge approximation [13]. In this approximation, using the values of $\langle r^n\rangle$, which are given in the work [12], for the Nd^{3+} situated in the centre of the GaSe layer we have:

$$b_{20}= 4160\ cm^{-1}, \quad b_{40}= -43{,}6\ cm^{-1}, \quad b_{60}= -1{,}94\ cm^{-1}, \quad b_{66}= -11{,}5\ cm^{-1} \quad , \qquad (4)$$

The point-charge model used to calculate the potential (1) has several weaknesses[13]. It neglects the finite extent of charges on the ions, the overlap of the Nd^{3+} ion's wave functions with those of neighbouring ions, and the screening of the $4f$ electrons by the outer electron shells of the Nd^{3+} ion. Therefore, the point-charge model can't give the right quantitative results for b_{nm} ; the results were mostly too large for the n=2 terms, of the right order of magnitude for the n=4 terms, and an order of magnitude too small for the n=6 terms [14]. However, this approximation may be used to determine the signs of the b_{nm} , as well as to calculate ratios of terms of the same degree in the potential (1), since these ratios are

independent of the model used and are determined solely by the symmetry [13].

In this work the b_{nm} parameters are determined by means of the comparison of the theoretical results for the splittings of the $4f^3$ levels under the influence of crystal-field potential (1) with the experimental data [8]. For the signs of b_{nm} , as well as for the ratio of b_{66}/b_{60} we have taken the results, which obtained on the base of the point-charge approximation (4), that gives b_{66}=5,9b_{60}. Thus, the fitting is made by means of the three independent parameters $|b_{20}|$, $|b_{40}|$ and $|b_{60}|$. The absolute magnitude of b_{20}, b_{40} and b_{60} are determined from the analysis of splittings of the free ion ground term $^4I_{9/2}$,as well as the higher term $^4I_{11/2}$ by the method of least squares.

Since the quantum numbers of crystal-field energy levels is not established in the experiments [2,8], we must examine the different variants of order of the crystal-field energy levels of $^4I_{9/2}$ and $^4I_{11/2}$ terms and within the every variants we must determine the set of the b_{nm} parameters. The best set of b_{nm} parameters is that, for which one can obtain the satisfactory agreement in the description of crystal-field splittings not only for $^4I_{9/2}$ and $^4I_{11/2}$ levels, but also for the higher $^4I_{13/2}$ and $^4F_{3/2}$ levels. It is necessary to note that the order of Stark components of the Nd^{3+} terms in GaSe obtained in this manner is found similar to that in GaS.

The values of b_{nm} parameters obtained in this manner for the system GaSe:Nd^{3+} are:

$$b_{20}= 710\ cm^{-1},\ b_{40}= -63\ cm^{-1},\ b_{60}= -32\ cm^{-1},\ b_{66}= -189\ cm^{-1}\ . \qquad (5)$$

These values of crystal-field parameters have the small differences from the corresponding values of b_{nm} parameters [9] for the system GaS:Nd^{3+} (b_{20}= 790 cm^{-1},b_{40}=-64 cm^{-1},b_{60}=-34 cm^{-1},b_{66}=-183 cm^{-1}). The likeness of the Nd^{3+} spectra in GaSe and GaS [2,8], as well as the small differences between the obtained values of crystal-field parameters in these crystals show the similar types of luminescence centres for Nd^{3+} in GaSe and GaS.

We note, that the values of parameters b_{n0} in GaSe:Nd^{3+} are found somewhat smaller than the values of corresponding parameters in GaS:Nd^{3+} (excepting the value of b_{66} ,which has the weak influence on the splittings of the terms of Nd^{3+} both in GaSe and GaS). We can explain this result as follows. The nearest-neighbours of Nd^{3+} in the centre of the GaSe (or GaS) layer are six ions of Se (or S), which are formed the triangular prism, it being known that three ions of Se (or S) are situated above, and three ions under the mirror plane. The distance of Nd-S in GaS:Nd^{3+} is 0,311nm, but the distance of Nd-Se in GaSe:Nd^3 is 0,323nm. Under identical other conditions the crystalline electric field at the Nd^{3+} site decreases with increasing of the distance between Nd^{3+} and nearest-neighbouring ions and the values of b_{n0} in GaSe:Nd^{3+} are smaller than those in GaS:Nd^{3+}.

The comparison of the experimental [8] and calculated crystal-field energy levels, which are obtained with the values of crystal-field parameters listed in (5) is shown in Table. In this table the crystal-field energy levels are characterized with the quantum number J_z (the projection of total angular momentum). But in reality we have taken into account that the nondiagonal (in J_z) matrix elements of potential (the term with b_{66} in (1)) admixes to given Stark state J_z the small part of the other Stark states, for which $J_z'=J_z \pm 6$.

Table. Comparison of the calculated energy levels for Nd^{3+} in GaSe with the experimental values (in cm^{-1}).

Term	J_z	Experimental	Calculation	Δ
$^4I_{9/2}$	7/2	0	3	3
	9/2	45	42	-3
	5/2	215	223	8
	1/2	235	240	5
	3/2	290	277	-13
$^4I_{11/2}$	11/2	1860	1881	21
	9/2	1910	1895	-15
	7/2	1995	1988	-7
	5/2	2055	2067	12
	3/2	2105	2104	-1
	1/2	2125	2115	-10
$^4I_{13/2}$	11/2	3810	3853	43
	13/2	3930	3878	-52
	9/2	3995	3945	-50
	7/2	4010	4032	22
	5/2	4065	4093	28
	3/2	4095	4106	11
	1/2	4110	4107	-3
$^4F_{3/2}$	1/2	11105	11087	-18
	3/2	11285	11303	18
$^4F_{5/2}$	1/2	-	12066	-
	3/2	12140	12153	13
	5/2	12265	12252	-13

The satisfactory agreement between the theoretical and experimental results shows that the luminescence of GaSe:Nd^{3+} obtaining in the works [2,8] is connected with Nd^{3+}, which is situated in the centre of GaSe layer.

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GaSe KRİSTALINDA Nd^{3+} İONUNUN ENERJİ SƏVİYYƏLƏRİNİN KRİSTALLİK SAHƏNİN TƏ'SİRİ İLƏ PARÇALANMASININ TƏDQİQİ

GaSe laylı yarımkeçiricilərində kristallik sahənin tə'siri ilə üçvalentli neodim ionlarının $4f^3$ enerji səviyyələrinin parçalanması tədqiq edilmişdir. GaSe:Nd^{3+} sistemi üçün kristallik sahənin parametrləri tə'yin olunmuşdur. Nəzəri hesablanmış enerji səviyyələrinin təcrübi nəticələrlə müqayisəsi aparılmışdır.

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РАСЩЕПЛЕНИЕ ЭНЕРГЕТИЧЕСКИХУРОВНЕЙ ИОНА Nd^{3+}ПОД ВЛИЯНИЕМ КРИСТАЛЛИЧЕСКОГО ПОЛЯ В КРИСТАЛЛЕ GaSe

Исследовано расщепление энергетических уровней $4f^3$ трехвалентного иона неодима под влиянием кристаллического поля в слоистых полупроводниках GaSe. Определены параметры кристаллического поля для системы GaSe:Nd^{3+}. Проведено сравнение рассчитанных энергетических уровней с экспериментальными результатами.

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