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in Tetrahedral Yttrium Clusters in Cadmium Fluoride**

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## Models of $Gd^{3+}$ Paramagnetic Centers in Tetrahedral Yttrium Clusters in Cadmium Fluoride

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Zero-field splitting parameters of  $Gd^{3+}$  ions localized in three types of tetrahedral clusters were estimated using the superposition approximation. The cluster structures were determined from the minimum condition of the energy of a lattice with a rare earth cluster. The monoclinic centers with  $b_{20} = -345$  MHz and  $b_{20} = -600$  MHz were related to  $[CdY_2GdF_{26}]$  and  $[Cd_2YGdF_{26}]$  clusters, respectively.

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1. Electron paramagnetic resonance spectra contain unique data about the structure of the impurity ion nearest environment in crystals which can be obtained from values of Zeeman and zero field splittings (ZFS). The amount of this information enlarges with the increase of the spin of paramagnetic defect. The corresponding analysis (construction of the spin-Hamiltonian) allows to determine a symmetry class of the paramagnetic ion position and its symmetry group.

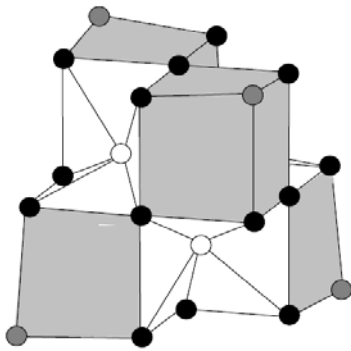
**Table 1.** Spin-Hamiltonian parameters for monoclinic and trigonal  $Gd^{3+}$  centers in  $Y_xGd_yCd_{1-x-y}F_{2+x+y}$ . [1, 2] (the standard deviation  $f$  and parameters  $b_{nm}$  are given in MHz).  $T = 300$  K.

	$C_s$	$C_{3v}$	$C_s$
$g_x$	1.988(6)	1.992(5)	1.992
$g_y$	1.991(6)	1.992(5)	1.992
$g_z$	1.991(3)	1.992(5)	1.992
$b_{20}$	-345(4)	-200(6)	-600
$b_{21}$	287(24)		
$b_{22}$	87(14)		
$b_{40}$	25(2)	80(3)	
$b_{41}$	3(12)		
$b_{42}$	17(10)		
$b_{43}$	-554(40)	2300(60)	
$b_{44}$	-30(15)		
$b_{60}$	-2.4(15)	-17(3)	
$b_{61}$	-7(14)		
$b_{62}$	-4(14)		
$b_{63}$	1(30)	-270(50)	
$b_{64}$	-5(20)		
$b_{65}$	-60(80)		
$b_{66}$	7(25)	490(50)	
$f$	12	25	

The EPR spectra of  $Y_xGd_yCd_{1-x-y}F_{2+x+y}$  ( $x = 0.03, y \leq 0.001$ ) single crystals were studied in works [1-2]. Besides already known cubic center, trigonal and two monoclinic centers of  $Gd^{3+}$  ions were found. Spin-Hamiltonian parameters are listed in table 1 ( $z \parallel C_3, y \parallel C_2$ ).

It is necessary to note that under rotation of the coordinate system around the  $y$  axis, the value of  $(b_{21}^2 + b_{22}^2)$  of the intensive monoclinic center has a minimum near the orientation defined by Euler's angles  $\alpha = 0, \beta = -7.17^\circ, \gamma = 0$  ( $b_{21}$  changes a sign), whereas  $|b_{20}|$  shows a maximum. These facts: maximization of the parameter  $b_{20}$  while  $b_{21}$  tends to zero, determine orientation of the pseudo-symmetry axis of the fine structure second-rank tensor. The nearness of this axis to  $C_3$  means that observable monoclinic center most likely originates due to distortions of the  $C_{3v}$  symmetry center.

In works [3-4],  $CdF_2 - RF_3$  ( $R = Sm - Lu, Y$ ) solid solutions with high contents ( $\sim 10\%$ ) of the rare-earth (RE) trifluorides were studied by the X-ray diffraction method. It was found out that tetrahedral RE (or yttrium) clusters (see Fig.1) exist in these solid solutions. There is a possibility of the incomplete replacement of the matrix cations by RE or yttrium ions in clusters, so for a part of clusters the problem of the extra charge compensation is solved. On the basis of these data, a conclusion has been made, that the observed paramagnetic centres correspond to  $Gd^{3+}$  ions in tetrahedral clusters:  $[Y_3GdF_{26}]^{1+}$  ( $C_{3v}$ ),  $[CdY_2GdF_{26}]^0$  ( $C_s$ ),  $[Cd_2YGdF_{26}]^{1-}$  ( $C_s$ ). The symmetry group of the  $Gd^{3+}$  ion is presented in round brackets. The superscripts specify difference between a charge of the defective cluster and a fragment of a lattice replaced by it. So, it is possible to correlate the observed  $Gd^{3+}$  trigonal centre with the  $[Y_3GdF_{26}]$  cluster, but it is not possible to establish a correspondence between the remaining cluster types and two monoclinic centers without calculations of the fine structure parameters. In other words, an application of a microscopic model is necessary to reveal the relation between the structure of the defect environment and the values of its ZFS parameters.



**Fig.1.** The structure of the tetrahedral rare earth cluster.

2. To solve this problem, the superposition model of the ground state ZFS under the approximations made in work [5] was used. The Spin-Hamiltonian parameters are presented in the following form

$$b_{2m} = \sum_d K_{2m}(\theta_d, \varphi_d) \cdot \bar{b}_2(R_d) \quad (1)$$

$$\bar{b}_2(R_d) = Z_d \cdot b_{2p}(R_0) \left(\frac{R_0}{R_d}\right)^3 + b_{2s}(R_0) \left(\frac{R_0}{R_d}\right)^{10}$$

The first and second terms in Eq. (1) are the contributions of the electrostatic field of the ligand point charge  $Z_d$  and the short-range metal-ligand interaction, respectively.  $K_{2m}(\theta_d, \varphi_d)$  is the angular structure factor and  $R_d, \theta_d,$  and  $\varphi_d$  are the spherical coordinates of the ligand.  $R_0 = 2.37 \text{ \AA}$  is the sum of the ionic radii of the impurity ion and the ligand. The values of the intrinsic parameters  $\bar{b}_{2p} = -\chi_p \bar{A}_{2p}, \bar{b}_{2s} = \chi_s \bar{A}_{2s}, \chi_p = -2.14, \chi_s = -2.70$  can be found in [5, 6]. The values  $\bar{A}_{2p,2s}$  according to [5] determine parameters

of the crystal field:

$$A_{2m} = \sum_d K_{2m}(\theta_d, \varphi_d) \left[ \bar{A}_{2p}(R_0) \left(\frac{R_0}{R_d}\right)^3 + \bar{A}_{2s}(R_0) \left(\frac{R_0}{R_d}\right)^{10} \right]. \quad (2)$$

The information about coordinates of the environment of the paramagnetic ion is necessary to calculate the parameters in the expression (1). The structure of the tetrameric clusters in cadmium fluoride was obtained by Chernyshev as a result of minimization of the lattice energy with a RE-ion cluster. The calculations were carried out in

the framework of the pair-potential approximation [7] using the shell model which allowed to take into account lattice polarization that plays significant role in the case of the charged impurity defects.

**Table 2.** Calculated with intrinsic parameters from work [5]  $b_{20}$  parameters for  $Gd^{3+}$  ions in clusters (in MHz)

Cluster	$b_{20}$ (point charges, 11 anions)	$b_{20}$ ( point charges and dipoles, 11 anions)	$b_{20}$ ( point charges and dipoles, 11 anions and 12 cations)
$GdY_3F_{26}$ ( $C_{3v}$ )	820	-3191	-93
$GdY_2CdF_{26}$ ( $C_s$ )	1086	-2732	-120
$GdYCd_2F_{26}$ ( $C_s$ )	1328	-2236	-121

**Table 3.** Experimental and calculated ZFS parameters of  $Gd^{3+}$ -F centres with superposition model parameters  $\bar{b}_{2p} = 13670$  MHz,  $\bar{b}_{2s} = 5670$  MHz.

	$b_{20}$ (expt.) MHz	$b_{20}$ (cal.), MHz
$CaF_2$ , $C_{4v}$	-4452(3) [8]	-4500
$SrF_2$ , $C_{4v}$	-3367(25) [9]	-3200
$SrF_2$ , $C_{3v}$	-406(2) [10]	-280
$BaF_2$ , $C_{3v}$	-407(3) [11]	-470

Parameters of the model (except the ones for the short-range interaction) corresponding to electrostatic fields of point charges of the nearest  $F^-$  ions, were presented in work [5]:  $\bar{b}_{2p} = 6210$  MHz,  $\bar{b}_{2s} = 4273$  MHz at  $R_0 = 2.37$  Å. Fine structure parameters  $b_{20}$  for  $Gd^{3+}$  ions localized in clusters of three types calculated according to formulae (1), intrinsic parameters taken from work [5] and corresponding anion and cation coordinates are presented in Table 2. The contribution from dipole fields was taken into account by the summation of the charges of the cores and the shells of the ions. Nondiagonal parameters of the spin-Hamiltonian (values of these parameters depend on azimuthal coordinates of the ligands) were not calculated. Generally

speaking, it is improper to use the superposition parameters [6], obtained in the framework of the rigid ion model (the nearest  $F^-$  ions only) for the description of the system with polarized anion and cation environment. However, data of Table 2 very clearly show a ratio of the contributions from the point charges, dipole fields and cation environment. At the same time, pay attention to the essential influence of the contribution from the polarized anion environment on the results of the calculations.

The experimental ZFS data of the well known tetragonal and trigonal  $Gd^{3+}$  centers which appear in calcium, strontium and barium fluorides due to a charge compensation of the  $Gd^{3+}$  extra charge by the fluorine ion in the nearest neighbour or next nearest neighbour interstitial sites, were used for the extraction of the more appropriate empirical parameters (taking into account charged cation defects and polarization of the ions). The structure of these centers was calculated by Chernyshev V.A. in the same manner as for the ion coordinates of tetrahedral clusters.

The  $b_{20}$  parameters were expressed explicitly through intrinsic parameters according to formulae (1) and (2), accounting for short-range interactions, electrostatic interactions with the 11 polarized  $F^-$  ions and the contributions from cores and shells of 12 cations. The solution of the set of equations for intrinsic parameters ( $\bar{b}_{2p} = 13670$  MHz,  $\bar{b}_{2s} = 5670$  MHz) was obtained using the least-squares method. The accuracy of the theoretical description of the experimental data [8-11] using these parameters is seen from Table 3. The calculated  $b_{20}$  parameters of the  $Gd^{3+}$  ions, localized in three types of the tetrahedral clusters, are given in Table 4. For comparison and estimation of different contributions, values of the parameters calculated without taking into account the cation environment and dipole fields are also presented in Table 4.

**Table 4.** Calculated  $b_{20}$  parameters (in MHz) of  $Gd^{3+}$  ions in tetrahedral clusters ( $\bar{b}_{2p} = 13670$  MHz,  $\bar{b}_{2s} = 5670$  MHz)

Cluster	$b_{20}$ (point charges, 11 anions)	$b_{20}$ (point charges and dipoles, 11 anions)	$b_{20}$ ( point charges and dipoles, 11 anions and 12 cations)
$GdY_3F_{26}$ ( $C_{3v}$ )	483	-8342	-1525
$GdY_2CdF_{26}$ ( $C_s$ )	950	-7450	-1704
$GdYCd_2F_{26}$ ( $C_s$ )	1450	-6393	-1740

3. The sets of the computed  $b_{20}$  parameters for  $Gd^{3+}$  ions in the clusters of three types presented in the Tables 2 and 4 demonstrate a small range of absolute values and the constancy of signs. According to these results, we assigned the negative sign to  $b_{20}$  parameters (Table 1) of weakly-intensive  $Gd^{3+}$  centers with undetermined energy level order.

It is clear that  $b_{20}$  parameters from Table 4 with absolute values exceeding by several times the values from Table 1 disagree with the experimental data. However, it is possible to assume that errors in the considered models lead to large common shift of calculated parameter values but the tendency of the changes along series of clusters remains valid. If this is the case the comparison of the behaviour of the calculated and experimental  $b_{20}$  values allows to assign intensive monoclinic  $Gd^{3+}$  center with  $b_{20} = -345$  MHz to  $[CdY_2GdF_{26}]$  cluster with charge equal to the substituted fluorite structure fragment, and less intensive monoclinic centre can be related to  $[Cd_2YGdF_{26}]$  cluster.

In work [1] it has been shown that is possible to explain the existence of the cubic  $Gd^{3+}$  center in  $Y_xGd_yCd_{1-x-y}F_{2+x+y}$  crystals ( $x = 0.03$ ,  $y \leq 0.001$ ) only under the assumption of the formation of large enough cluster associations. In this case EPR spectrum belonging to the gadolinium ions in clusters which have in the nearest environment other clusters will be detected. It is not trivial simple to account for the influence of the neighbouring clusters, while modelling the tetrahedral cluster structure, because it is necessary to propose a model of the cluster association and to solve the computation problems. In the present work these problems were not solved, and apparently it was the main reason of the disagreement between the theory and experiment.

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