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Hexamer clusters in MeF₂:Yb³⁺ (Me=Ca,Sr,Ba)

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Abstract. The electronic structure and g factors of simple impurity centers and hexamer ytterbium clusters in fluorites have been calculated in terms of the exchange charge model. Preliminarily, their local crystal structures have been calculated in the framework of the shell model with the inclusion of lattice distortions near the impurity. Crystal structure and g factors have been calculated of linear cluster Yb–F–Yb–F oriented along a trigonal axis in BaF₂.

1. Introduction

Fluorites MeF₂ (Me = Ca, Sr, Ba) doped with ytterbium Yb³⁺ have attracted attention of researchers for several decades due to their practical application as laser media, scintillation materials, and phosphors. For example, phosphors that emit white light under excitation by a diode laser owing to the up-conversion mechanism have been developed in recent years [1]. Moreover, fluorites have a high-symmetry cubic structure that is retained even after significant doping [1], which makes them convenient for investigations.

At low impurity concentrations (of the order of 0.1 at %), single centers in which Yb³⁺ substitutes for a Me²⁺ cation are formed in MeF₂. The compensation of the excess charge can be nonlocal (cubic center) or local, e.g., by an interstitial fluorine ion F⁻ located at the interstitial site of the fluorine sublattice on the C₃ or C₄ axis (trigonal or tetragonal centers). For impurity concentrations of the order of 1 at % and higher, clusters are formed from Yb³⁺ and F⁻ ions.

Spectra of single centers and clusters have been investigated by different methods, such as electron paramagnetic resonance, electron–nuclear double resonance [2–6], selective laser excitation [7], and optical detection of electron paramagnetic resonance [8, 9]; however, the Stark structure of even single Yb³⁺ impurity centers remains unknown in many respects. Only recently, the reliable interpretation of the spectra of the simplest (cubic) Yb³⁺ centers in CaF₂ and CdF₂ was proposed by Gerasimov and Falin [8]. Up to now, there are disagreements in the interpretation of spectra of tetragonal centers, e.g., in the classification of levels according to representations [7, 10].

In recent years, the optical spectra of CaF₂:Yb³⁺ have been studied experimentally for impurity concentrations of the order of 0.1 at % and higher (to a few percent) [7, 11, 12] when nanoclusters containing several Yb³⁺ ions can be formed. Only the main types of nanoclusters formed according to the fluorite motif, their symmetry, and the maximum number of the rare-earth ions forming a cluster were determined experimentally [13]. Therefore, in order to interpret the spectra at high impurity concentrations, it is necessary to perform consistent calculations of the crystal structure and the electronic spectrum of the cluster. This simulation and interpretation of the spectrum were carried out for hexamer clusters M₆F₃₆ (M is a trivalent rare-earth ion) in fluorites by Kazanskii, Nikiforov et al.
[14], who calculated the crystal structure in the framework of the shell model in the pair potential approximation. In this case, the relaxation of the crystal lattice near the cluster was taken into account. The parameters for Gd\(^{3+}\) located in the middle of the rare earth series were taken as parameters of the pair interactions between rare earth and crystal ions. These parameters were determined from the condition for the reproduction of distortions of the fluorine sublattice in the \(\text{MeF}_2:\text{Gd}^{3+}\) impurity centers investigated by electron–nuclear double resonance [15]. This approach allows one to adequately reproduce the crystal lattice distortions near the impurity that makes the main contribution to the parameters of the crystal field. In [14], the electronic spectrum was calculated in the framework of the exchange charge model developed by Malkin [16–18]. In the calculation of the crystal field parameters, the model accounts for the effects of covalence, overlapping, and the electron density transfer between the rare-earth ion and ligands. This model has been successfully used to describe the spectra of almost all single rare-earth ion centers in fluorites. In [14], the authors calculated the g factors and demonstrated that each rare-earth ion in the \(\text{M}_6\text{F}_{36}\) hexacluster is in the tetragonal crystal field with a large axial component induced by the antiprism of eight fluorine ions (Fig. 1).

All levels of the cubic centers \(\text{CaF}_2:\text{Yb}^{3+}\) and \(\text{CdF}_2:\text{Yb}^{3+}\) were classified according to their representations in [8]. This allows one to determine the parameters of the exchange charge model for Yb\(^{3+}\) and to use them in the calculations of the spectra of single centers and nanoclusters. In our earlier work [19], we calculated the crystal structure of \(\text{MeF}_2:\text{Yb}^{3+}\) (Me = Ca, Sr, Ba) impurity centers. In this case, the parameters of the Yb\(^{3+}\)-F pair interactions were determined from the condition for the reproduction of the distortions in the fluorine sublattice of these centers investigated by the electron–nuclear double resonance method.

Thus, we can perform consistent simulation of the Stark structure of Yb\(^{3+}\) in different centers: in the shell model, with the parameters of interionic interactions Yb\(^{3+}\)-F unique for all the fluorites \(\text{MeF}_2:\text{Yb}^{3+}\), we can calculate the crystal structure of the single impurity centers and also ytterbium nanoclusters and take into account the lattice relaxation near the impurity. Then, with the calculated structure, we can calculate the parameters of the exchange charge model from the interpreted cubic center spectra [8] and use them to calculate the electronic structure of the tetragonal impurity centers and nanoclusters.

![Figure 1. (a) Hexamer cluster and (b) local environment of a rare-earth ion.](image-url)
2. Calculation of the crystal structure
The expression for the crystal lattice energy, the parameters of the pair interionic potentials and methods of their calculations are given in [15, 19]. The lattice parameters of MeF₂ calculated with these parameters agree well with the experiment (table 1).

### Table 1. Lattice parameters of the crystals (pm)

| Crystal   | Experiment [20] | Calculation |
|-----------|-----------------|-------------|
| CaF₂      | 544.3           | 544.7       |
| SrF₂      | 578.0           | 579.3       |
| BaF₂      | 617.8           | 623.2       |

The calculations were carried out using the GULP program [21]. In this program, the crystal lattice structure near the impurity is calculated by the Mott–Littleton method, according to which a spherical region containing a defect and an adjacent spherical layer are considered. Ions in the region containing the defect can be shifted within the limits of its symmetry, and a polarization is allowed in the adjacent layer. The sizes of the region and the layer were chosen in such a way as to adequately describe the lattice distortion, i.e., the sizes were increased until the ion coordinate near the defect determined from the energy minimum become unchanged. For the purposes of verifying, we calculated the crystal field parameters. In the noncubic impurity centers and clusters, it is convenient to use the parameter B₂₀, to which only the distorted region of the lattice near the defect contributes. For example, in the tetragonal impurity centers CaF₂:Yb²⁺, the lattice relaxation (including the polarization layer) should be taken into account in the radius of 17 Å, which corresponds to 1500 ions. In the calculations of the structure of the hexamer cluster M₆F₃₆ (figure 1) which fits into the unit cell, the lattice relaxation was taken into account in the radius 25 Å, which corresponds to approximately 10⁴ ions. The relaxation in the same region was taken into account when calculating the structure of the M₆F₃₇ cluster that differs from the above M₆F₃₆ cluster only by the presence of the additional interstitial fluorine ion at the cluster center. We verified to what extent the inclusion of the lattice distortion near the cluster is substantial when calculating the crystal field parameters. For comparison, we calculated the crystal field parameters in the M₆F₃₆ cluster without inclusion of the relaxation, i.e., the ion coordinates near the cluster were taken equal to the coordinates of the pure lattice. The crystal field parameters calculated without inclusion of the relaxation are significantly different. For example, the crystal field parameters B₂₀, B₆₀, and B₆₄ have other sign and they are different in magnitude by a factor of three or four. Note here that the lattice distortions near the cluster decay very fast. In the Mott–Littleton method that allows ion displacements, the increase in the first region radius from 10 to 18 Å, i.e., from 328 to 1822 ions, respectively, does not practically influence the values of the crystal field parameters, e.g., as a result, the Stark levels are shifted by 5–7 cm⁻¹.

The ion coordinates in the M₆F₃₆ cluster are listed in tables 2 and 3; the origin of coordinates is in the cluster center. The cluster can be conveniently represented as three coordination spheres F(12), Yb(6), and F(24). Each of the spheres can be characterized by one ion (tables 2 and 3). First two spheres F(12) and Yb(6) are strongly displaced during the relaxation. After the relaxation, the F(12) atoms have practically such a radial distance as the Yb(6) atoms have; i.e., they lie at the same spherical surface (table 3). Twenty four fluorine atoms F(24) forming the outer part of the cluster are slightly displaced with respect to their positions in the pure crystal (table 3).

### Table 2. Ion coordinates in the M₆F₃₆ cluster (Å)

| Ion   | Before relaxation | After relaxation |
|-------|-------------------|------------------|
|       | x     | y     | z     | x     | y     | z     |
| F(12) | 0.0000 | −1.3619 | −1.3619 | 0.0000 | −2.0090 | −2.0090 |
| Yb(6) | 2.7238 | 0.0000 | 0.0000 | 3.0673 | 0.0000 | 0.0000 |
| F(24) | −1.3619 | −1.3619 | 4.0858 | −1.4038 | −1.4038 | 4.2843 |
3. Exchange charge model

In the exchange charge model [16, 17], the crystal field parameters are written as the sum of the electrostatic and exchange contributions

\[
B^q_p = B^q_p + B^q_{PS} 
\]

The electrostatic contribution is

\[
B^q_p = K_p \cdot \left(1 - \sigma_p \right) \cdot e^2 \cdot \left\langle r^p \right\rangle \cdot \sum_{i=1}^{N} (-Z_i) P^q_p (x_i, y_i, z_i, r_i) \cdot r_i^{-(2p+1)}
\]

where \((x_i, y_i, z_i, r_i)\) are polynomials [22], are numerical factors [23], \(\left\langle r^p \right\rangle\) is the average value of \(r^p\) of ⁴f electron [24], \(\sigma_p\) is the screening parameter of the ⁴f shell with external ⁵s and ⁵p shells [25], \(x_i, y_i, z_i\) are the ion coordinates; \(r_i\) is the distance from the origin of the coordinates to an ion. Relationship (2) is written in the Hartree unit system. When summing, the index \(i\) runs over all the lattice ions and, since an ion is represented in the shell model as the sum of two point charges, namely, the core and the shell, the summation is performed over both the cores and the shells; thus, the contribution of the lattice polarization is taken into account. The exchange contribution is

\[
B^q_{PS} = K_p \cdot \frac{2 \cdot (2p + 1)}{(2 \cdot l + 1)} \cdot e^2 \cdot \sum_{i=1}^{M} S_p (r_i) \cdot r_i^{-(p+1)} \cdot P^q_p (x_i, y_i, z_i, r_i)
\]

Here, when summing, the index \(i\) runs only over the ligand cores, \(l\) is the orbital moment, \(S_p\) is a combination of the squared overlapping integrals of Yb ⁴f functions with the ⁵s and ⁵p functions of fluorine

\[
S_p = G_s \cdot S^2_s + G_{\sigma} \cdot S^2_{\sigma} + G_{\pi} \cdot k_p \cdot S^2_{\pi}
\]

The numerical coefficients \(k_p\) were obtained when general relationship (4) was deduced in [16]

\[
k_2 = -k_6 = \frac{3}{2}, \quad k_4 = \frac{1}{3}.
\]

The overlapping integrals \(S_s\), \(S_\sigma\), and \(S_\pi\) were calculated by formulas presented in [26] on the wave functions [26, 27]. The dependence of the overlapping integrals on the rare-earth ion–ligand distance was approximated by an exponential function

\[
S_s (r) = 0.2373 \cdot \exp (-0.9286 \cdot r^{1.6183}),
\]

\[
S_\sigma (r) = 0.1317 \cdot \exp (-0.6699 \cdot r^{1.593}),
\]

\[
S_\pi (r) = 2.0152 \cdot \exp (-2.7567 \cdot r^{0.8927}).
\]
Here, $r$ is expressed in angstroms, the approximation range 1.8–3.2 Å corresponds to the Yb–F distance in the impurity centers and the clusters. In relationship (4), $G_s$, $G_\sigma$, and $G_\pi$ are dimensionless parameters of the model, i.e., exchange charges. In this case, they are determined from the condition of the best reproduction of the spectrum of the cubic centers CaF$_2$:Yb$^{3+}$ and CdF$_2$:Yb$^{3+}$ [8]. The electronic structure of Yb$^{3+}$ for the known crystal field parameters was calculated using the Reid program obtained from its author (Dr M.F. Reid, University of Canterbury). This program takes into account the $J$–$J$ mixing and uses the effective Hamiltonian for 4f electrons of rare earths [28]. The parameters for Yb$^{3+}$ were taken from [29].

4. Electronic structure of Yb$^{3+}$ in single impurity centers and nanoclusters

The parameters of the exchange charges ($G_s = 11$, $G_\sigma = 30$, and $G_\pi = 38$) were determined from the condition of the best reproduction of the levels and the $g$ factors of the cubic Yb$^{3+}$ centers in CaF$_2$ and CdF$_2$.

| J | Irrep | CaF$_2$ calculation | experiment [8] | CdF$_2$ calculation | experiment [8] |
|---|------|---------------------|----------------|---------------------|----------------|
| 5/2 | $^2\Gamma_8$ | 10867 | 10840 | 10880 | 10867 |
| | $^2\Gamma_7$ | 10384 | 10381 | 10389 | 10392 |
| | $^1\Gamma_6$ | 717 | 778 | 731 | 755 |
| | $^1\Gamma_8$ | 660 | 644 | 671 | 676 |
| 7/2 | $^1\Gamma_7$ | 0 | 0 | 0 | 0 |
| | $^2\Gamma_7$ | g=-1.41 | g=-1.41 | g=-1.41 | g=-1.411 |
| | $^1\Gamma_7$ | g=3.37 | g=3.438 | g=3.37 | g=3.429 |

Table 4. Energy levels (cm$^{-1}$) and $g$ factors of the cubic Yb$^{3+}$ centers in CaF$_2$ and CdF$_2$

| J | Irrep | SrF$_2$ calculation | experiment [30] | BaF$_2$ calculation | experiment [30] |
|---|------|---------------------|----------------|---------------------|----------------|
| 5/2 | $^2\Gamma_8$ | 10785 | 10783 | 10715 | 10739 |
| | $^2\Gamma_7$ | 10356 | 10358 | 10333 | 10339 |
| | $^1\Gamma_6$ | 629 | 600 | 556 | 542 |
| | $^1\Gamma_8$ | 581 | 586 | 514 | 535 |
| 7/2 | $^1\Gamma_7$ | 0 | 0 | 0 | 0 |
| | $^2\Gamma_7$ | g=-1.41 | - | g=-1.41 | - |
| | $^1\Gamma_7$ | g=3.47 | g=3.441 | g=3.47 | g=3.422 |

Table 5. Energy levels (cm$^{-1}$) and $g$ factors of the cubic Yb$^{3+}$ centers in SrF$_2$ and BaF$_2$

The agreement with the experiment is good (table 4). Thus, to determine the three empiric parameters, more than ten experimental quantities were used. For purposes of additional verification of the $G_i$ parameters, they were used in calculations of the cubic Yb$^{3+}$ centers in SrF$_2$ and BaF$_2$. We also obtained good agreement with the experiment [30] (table 5) in the values of the energy levels and in their representation classification. The spectrum of the tetragonal Yb$^{3+}$ center in CaF$_2$ was calculated as well (table 6). In the representation classification of the levels, the calculated results agree with the data of [7]. Thus, using the three parameters $G_s$, $G_\sigma$, and $G_\pi$, we succeeded in describing the electronic levels and the $g$ factors of the cubic and tetragonal centers, in the aggregate about 30 experimental
quantities. This allows us to use them in what follows in calculations of the spectra of the nanoclusters.

Table 6. Energy levels (cm$^{-1}$) and g factors of the tetragonal Yb$^{3+}$ centers in CaF$_2$

| J   | Irrep | Calculation | Experiment [7] |
|-----|-------|-------------|----------------|
| 5/2 | $\Gamma_7$ | 10725 | 10766 |
| 5/2 | $\Gamma_6$ | 10472 | 10410 |
| 5/2 | $\Gamma_7$ | 10308 | 10322 |
| 7/2 | $\Gamma_7$ | 510 | 588 |
| 7/2 | $\Gamma_6$ | 498 | 520 |
| 7/2 | $\Gamma_6$ | 240 | 456 |
| 7/2 | $\Gamma_7$ | 0 | 0 |
| 7/2 | $\Gamma_7$ | $g_\parallel=2.29$ | $g_\perp=2.414$ |
| 7/2 | $\Gamma_7$ | $g_\parallel=3.81$ | $g_\perp=3.801$ |

The energy spectrum of a cluster is formed by the crystal field, exchange and resonance interactions [31]. In the case of a rare-earth ion, the spin–orbital interaction and the crystal field of one ion are much more than the exchange, magnetic dipole-dipole, and resonance interactions; because of this, we can consider the Stark levels in one rare earth ion.

Table 7. Energy levels (cm$^{-1}$) and g factors of the hexamer Yb$^{3+}$ clusters in CaF$_2$

| J   | Irrep | Calculation | Experiment |
|-----|-------|-------------|------------|
| 5/2 | $\Gamma_6$ | 10865 | 10916 | 10870 | 10887 |
| 5/2 | $\Gamma_7$ | 10399 | 10653 | 10384 | 10400 |
| 5/2 | $\Gamma_7$ | 10261 | 10183 | 10204 | 10209 |
| 7/2 | $\Gamma_6$ | 677 | 766 | 675 | 686 |
| 7/2 | $\Gamma_7$ | 495 | 643 | 518 | 531 |
| 7/2 | $\Gamma_6$ | 108 | 172 | 103 | 110 |
| 7/2 | $\Gamma_7$ | 0 | 0 | 0 | 0 |
| 7/2 | $\Gamma_7$ | $g_\parallel=5.7$ | $g_\perp=7.63$ | $g_\parallel=6.8$ |
| 7/2 | $\Gamma_7$ | $g_\parallel=0$ | $g_\perp=0$ | $g_\parallel=0$ [14] |

Thus, after we had calculated the crystal structure, we calculated as well the crystal field at a single Yb$^{3+}$ ion located on axis $C_4$. In this case, the same parameters $G_i$ of exchange charges were used which
were used also in the single centers. The electronic structure of the levels and the g factors were calculated for the hexamer \( \text{Yb}_6\text{F}_{36} \) and \( \text{Yb}_6\text{F}_{37} \) clusters.

Table 7 lists the calculated data in comparison with the experimental data. The experimental g factors were taken from [14]. The nearest environment of the \( \text{Yb}^{3+} \) ion in the hexacluster is a distorted antiprism [32].

The experimental energy levels agree well with the calculated levels of the hexacluster \( \text{Yb}_6\text{F}_{36} \) and agree significantly worse with the levels of \( \text{Yb}_6\text{F}_{37} \). A comparison of the calculated levels with other experiment [12], where the spectrum of \( \text{CaF}_2: \text{Yb}^{3+} \) has been also measured at significant impurity concentrations (to 30 at %), as in the preceding case, gives a good agreement for the cluster \( \text{Yb}_6\text{F}_{36} \).

\( \text{Yb}^{3+} \) ion in the hexacluster forms a distorted antiprism [32]. The experimental energy levels agree well with the calculated levels of the hexacluster \( \text{Yb}_6\text{F}_{36} \) and agree significantly worse with the levels of \( \text{Yb}_6\text{F}_{37} \). A comparison of the calculated levels with other experiment [12], where the spectrum of \( \text{CaF}_2: \text{Yb}^{3+} \) was also measured at significant impurity concentrations (to 30 at %), as in the preceding case, gives a good agreement for the cluster \( \text{Yb}_6\text{F}_{36} \).

5. **Linear cluster \( \text{Yb–F–Yb–F} \) in \( \text{BaF}_2 \)**

The linear cluster \( \text{Yb–F–Yb–F} \) oriented along a trigonal axis in \( \text{BaF}_2 \) have been investigated by EPR methods [33, 34]. Ytterbium ions substitute \( \text{Ba}^{2+} \) ions and interstitial fluorines occupy the empty cubes in fluorine sublattice along the \( \text{C}_3 \) axis (Fig. 2).

Crystal structure of the cluster has been calculated. The calculations predicted that fluorine cubes around \( \text{Yb} \) are compressed on 1-2% whereas cubes around \( \text{F} \) extended on 1-2%. The values of g-factors have been calculated for one ytterbium that lie between interstitial fluorines. The calculated values are \( g_\parallel = 2.12 \) and \( g_\perp = 3.87 \). The experimental [33,34] values are \( g_\parallel = 2.25 \) and \( g_\perp = 4.02 \).

6. **Conclusions**

The parameters of the exchange charge model \( G_e, G_o, \) and \( G_c \) determined from the optical spectra of the cubic \( \text{Yb}^{3+} \) centers in \( \text{CaF}_2 \) and \( \text{CdF}_2 \) allow a successful description of the spectra of other single ytterbium centers. The calculations show that the spectrum of \( \text{CaF}_2: \text{Yb}^{3+} \), at the impurity concentrations of an order of 1 at % and higher, is due to the \( \text{Yb}_6\text{F}_{36} \) hexamer clusters.

The inclusion of the crystal lattice relaxation during formation of the hexamer cluster shows that the lattice inside the cluster is strongly distorted, and the \( \text{Yb}^{3+}(6) \) and \( \text{F}(12) \) ions lie practically on one sphere. However, the distortions quickly damp, and the \( \text{F}(24) \) fluorine atoms forming the external part of the cluster are displaced by only 0.2 Å. Thus, the cluster external sizes (9.4 Å) are slightly different from the corresponding distance between the ions in the pure lattice (9 Å).

The calculations of crystal structure and g-factors for \( \text{Yb–F–Yb–F} \) cluster in \( \text{BaF}_2 \) are in agreement with the experiment. This points to linear cluster formation in \( \text{BaF}_2 \).

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