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REDUCED ABSORPTION OF THE Nd^{3+} *ION IN VARIOUS BASES*

Yu. K. VORON'KO, M. V. DMITRUK, G. V. MAKSIMOVA, V. V. OSIKO, M. I. TIMOSHECHKIN, and I. A. SHCHERBAKOV

P. N. Lebedev Physics Institute, U.S.S.R. Academy of Sciences

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The integral absorption of a single Nd^{3+} ion is investigated in various matrices and at various concentrations. Comparison of the experimental data and theory yield information on the statistics of the optical centers and their symmetry.

INTRODUCTION

INTEGRAL absorption of rare-earth ions introduced in a crystal base is not only an important characteristic influencing laser output parameters, but also a quantity capable of yielding important information regarding the processes occurring in activated crystals. It is well known qualitatively that the values of the integral absorption of equal concentrations of the same ion introduced into different hosts are essentially different. In addition, on the basis of the results of one of our earlier investigations,[1] we can expect the integral absorption per ion to depend in some cases on the activator concentration. In the present investigation we studied the relative absorption of the Nd^{3+} ion in a large number of hosts having different crystal structures and optical-center structures. In most hosts, the Nd^{3+} concentration was varied in a wide range.

INVESTIGATED CRYSTALS AND EXPERIMENTAL PROCEDURE

The table lists a summary of the investigated hosts in which the Nd^{3+} ion was introduced, and some of their characteristics.[1-3] All the crystals were grown in accordance with the procedures described in [4,5,10,11] The divalent fluorides were crystals of type I (see [12]). The investigated characteristic was chosen to be the relative absorption

$$J=\frac{1}{n_0}\int\limits_{\Delta\nu} k(\nu)\,d\nu, \qquad (1)$$

where n_0 is the number of Nd^{3+} ions per cm^3, $k(\nu)$ is the absorption coefficient of light of frequency ν (in cm^{-1}), and $\int_{\Delta} k(\nu)d\nu$ is (in the case of Nd^{3+}) the absorption due to the transitions, in the interval $\Delta\nu$, from the Stark components of the ground level $^4I_{9/2}$, populated at room temperature, to the Stark components of the excited levels $^4F_{3/2}$; $^4F_{5/2}$, $^2H_{9/2}$; $^4F_{7/2}$, $^4S_{3/2}$; $^2G_{7/2}$, $^4G_{5/2}$. The absorption was measured in these groups because these are precisely the transitions that make the main contribution to the integral absorption of laser crystals activated with Nd^{3+}.

Absorption spectra in the form $1 - I/I_0 = f(\lambda)$ (where I_0 is the intensity of the incident light and I the intensity of the transmitted light) were obtained at room temperature with an SF-8 spectrophotometer using a

Host	Nd^{3+} concentration, wt.%	Lattice structure* [2,4,5]	Lines in absorption spectra**	τ_{rad} of the Nd^{3+} ion level, msec [1,2,5,6,7]
CaF_2	0.1—5	cub, $O_h^5 - Fm3m$	L, $(M+N)$, P[6]	$L - 1.2$ $M+N - >0.1$
SrF_2	0.1—5	cub, $O_h^5 - Fm3m$	L, M, P [1]	$L - 1.2$ $P - 0.12$
BaF_2	0.3—10	cub, $O_h^5 - Fm3m$	L, M, P [1]	$L - 8$ $P - 0.26$
LaF_3	0.1—4	hex, $D_{6h}^3 - C6/mcm$	OTC [7]	0.7—0.08
CeF_3	0.3—4	hex, $D_{6h}^3 - C6/mcm$	OTC [5]	0.3—0.18
$CaF_2 - YF_3$(3 wt.%)	0.1—4	cub, $O_h^5 - Fm3m$	MC [8]	1—0.7
$CaF_2 - YF_3$(6 wt.%)	0.1—4	cub, $O_h^5 - Fm3m$	MC [8]	1—0.7
$CaF_2 - YF_3$(12 wt.%)	0.1—4	cub, $O_h^5 - Fm3m$	MC [8]	1—0.7
$CaF_2 - CeF_3$(3 wt.%)	0.3—1	cub, $O_h^5 - Fm3m$	MC [8]	0.7
$CaF_2 - CeF_3$(5 wt.%)	0.3—1	cub, $O_h^5 - Fm3m$	MC [8]	0.7
$BaF_2 - LaF_3$(30 wt.%)	1—8	cub, $O_h^5 - Fm3m$	MC [8]	0.8
$Y_3Al_5O_{12}$	0.3	cub, $O_h(10) - Ia3d$	STC [9]	0.2
Silicate glass	3.6	—	MC	0.4
$CaWO_4 - Nb$	0.05—1.5	tetr., $C_{4h}^6 - 14/a$	STC [9]	0.175
$CaWO_4 - Na$	0.05—1.5	tetr., $C_{4h}^6 - 14/a$	STC [9]	0.175

*Notation: cub. – cubic lattice, hex. – hexagonal lattice, tetr – tetragonal lattice.

**Notation: OTC – one type of center, MC – multiplicity of centers, STC – several types of centers.

two-beam scheme.[1] In the subsequent calculations, these spectra were reduced to the form $k = f(\nu)$ and the values of the integral were determined experimentally. Data on the densities of the investigated crystals, which were needed to determine the number of activator particles per cm^3 of the host, were taken from [2]. Densities of substances for which there are no published data were determined with the aid of a pycnometer. To perform our calculations it was necessary also to know the activator concentration. Fluoride crystals, both simple and mixed, were grown by such a procedure that the concentration of the active ions in the crystal corresponded to the concentration of the activator in the charge.[6] In oxygen-containing crystals, the Nd^{3+} concentration was determined by chemical analysis.

EXPERIMENTAL RESULTS

The investigated hosts were divided by us into three groups: 1) individual fluorides, 2) mixed fluorides, 3) oxygen-containing hosts.

Figure 1 shows the concentration dependences of the relative absorption for crystals of the first group (CaF_2, SrF_2, BaF_2, LaF_3, and CeF_3). It is seen from this figure that the value of J of LaF_3 and CeF_3 does not depend on the concentration C of the Nd^{3+} ions. A dependence of J on the concentration is observed in the case of CaF_2-Nd^{3+} and SrF_2-Nd^{3+}, and the dependence is similar for both crystals. The absolute value of J for CaF_2 is somewhat higher. Particular interest attaches to the concentration dependence of the relative absorption in the case of BaF_2. We call attention to the sharp increase of J at both small and large activator concentrations.

Figure 2 shows analogous relations for mixed-fluoride crystals. A maximum relative absorption, independent of the concentration, is possessed by Nd in the system BaF_2–LaF_3–Nd^{3+}. The value of J of the Nd^{3+} ion in CaF_2–YF_3 crystals is somewhat lower than in the case of BaF_2–LaF_3–Nd^{3+}, and is still lower in CaF_2–CeF_3–Nd^{3+}.

Figure 3 shows plots of J of the Nd^{3+} ions against their concentration in oxygen-containing hosts. The maximum value of J is possessed Nd^{3+} in the $CaWO_4$ lattice, and an increase of J is observed at large concentrations. In glass, the relative absorption of Nd^{3+} for two investigated concentrations turned out to be independent of the concentration. For yttrium-aluminum garnet crystals, the value of J was determined for one concentration, 0.3 wt.% of Nd^{3+}. At this concentration, the relative absorption of Nd^{3+} in the garnet is smaller than in the case of $CaWO_4$.

From a comparison of Figs. 1–3 it is seen that the relative absorption J depends strongly on the matrix into which the activator is introduced, and reaches the maximum values in the case of an activator introduced into oxygen-containing hosts. The difference in the values of J reaches one order of magnitude. In some hosts, a concentration dependence of J is also observed.

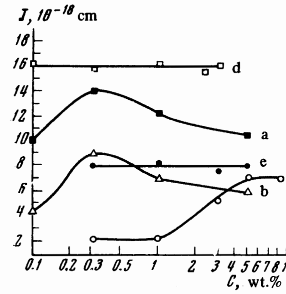

FIG. 1.

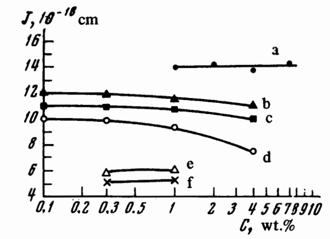

FIG. 2.

FIG. 1. Concentration dependence of the relative absorption of Nd^{3+} (T = 300°K) in different lattices: a – CaF_2, b – SrF_2, c – BaF_2, d – LaF_3, e – CeF_3 (C – concentration of NdF_3).

FIG. 2. Concentration dependence of the relative absorption of Nd^{3+} (T = 300°K) in the following lattices: a – BaF_2 – LaF_3 (30 wt.%), b – CaF_2 – YF_3 (3 wt.%), c – CaF_2 – YF_3 (6 wt.%), d – CaF_2 – YF_3 (12 wt.%), e – CaF_2 – CeF_3 (3 wt.%), f – CaF_2 – CeF_3 (5 wt.%) (C – NdF_3 concentrations).

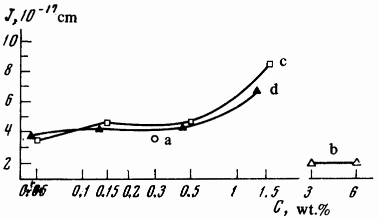

FIG. 3. Concentration dependence of relative absorption of Nd^{3+} (T = 300°K): a – in $Y_3Al_5O_{12}$ lattice, b – in glass, c – in $CaWO_4$ – Nb lattice, d – in $CaWO_4$ – Na lattice (C – Nd concentration).

DISCUSSION OF RESULTS

In activated laser crystals, the rare-earth ions, particularly Nd^{3+}, enter as constituents of several types of optical centers.[1,6,11] Therefore the quantity J determined by us is conveniently represented in the form

$$J = \frac{1}{n_0} \sum_p \sum_i \int k_{ip}(\nu)\, d\nu, \qquad (2)$$

where the sum over i denotes summation over all the Stark transitions of the p-th center, the sum over p denotes summation over the number of optical centers in the crystal, and $k_{ip}(\nu)$ is the coefficient absorption of the i-th transition of the p-th center.

As is well known, the absorption coefficient is connected with the absorption probability, which in turn is connected with the probability of the spontaneous transition. The probability of the spontaneous transition can in this case be written in the form

$$A = \frac{1}{n_0} \frac{8\pi\nu^2}{c^2} \int k(\nu)\, d\nu, \qquad (3)$$

where n_0 is the number of activator particles per cm^3, ν is the transition frequency, c is the speed of light, and $k(\nu)$ is the absorption coefficient. An estimate of the dipole-transition probability[13] yields the following value:

$$A_{\text{dip}} = \frac{64\pi^4 e^2}{3hc^3} \nu^3 r_0^2 \beta. \qquad (4)$$

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[1] In the case of LaF_3 and CeF_3 crystals, the principal optical axis made an angle of 90° with the observation direction. In the case of $CaWO_4$, the principal optical axis coincided with the observation direction.

This expression contains constant factors that depend only on the atomic constants, the frequency ν, the factor r_0 that is governed in the case of rare-earth ions by the dimensions of the 4f shell, and the coefficient β. The quantity β is connected with the degree of violation of the selection rules for induced dipole transitions, i.e., it is determined by the symmetry of the intracrystalline field, which depends both on the symmetry of the lattice into which the ion is introduced and on the local surroundings of the ion; in other words, it is determined by the eigenfunctions of the combining states.[13-15] Consequently, the difference between the experimentally determined quantity $n_0^{-1}\int k(\nu)d\nu$ for different transitions that do not differ greatly in frequency is due to the change of β:

$$\frac{1}{n_0}\int k(\nu)\,d\nu=\frac{8\pi^3e^2\nu r_0^2}{3hc}\beta. \tag{5}$$

The measured quantity J, which characterizes the multiplicity of the transitions, corresponds to a certain transition probability averaged over the different transitions of one center and over the transitions in different centers. Expression (3) for such an averaged probability takes the form

$$\bar{A}=\frac{8\pi}{c^2qm}\sum_p\sum_i\frac{1}{n_p}\alpha_{ip}\nu_{ip}^2\int k_{ip}(\nu)\,d\nu, \tag{6}$$

where q is the number of transitions in one center, m the number of optical centers, n_p the number of ions entering in the p-th center, and α_{ip} a coefficient that lifts the dependence of the integral on the populations of the excited Stark components of one level.

Introducing into this expression the quantity γ_{ip}, which takes into account the distribution of the activator over the different optical centers, as well as the coefficient g_{ip} by which a certain average frequency ν_{av} must be multiplied in order that each term of the sum correspond to the frequency of the given transition, expression (6) can be represented in the form

$$\bar{A}=\frac{8\pi}{c^2qm}\frac{1}{n_0}\nu_{av}^2\sum_p\sum_i g_{ip}^2\alpha_{ip}\gamma_{ip}\int k_{ip}(\nu)\,d\nu. \tag{7}$$

The averaged probability corresponds also to a certain averaged value of β:

$$\bar{A}=\frac{64\pi^4e^2}{3hc^3qm}r_0^2\nu_{av}^3\sum_p\sum_i\beta_{ip}g_{ir}^3. \tag{8}$$

Taking (5), (7), and (8) into account, we can represent J in the form

$$J=\frac{8\pi^3e^2r_0^2\nu_{av}}{3hc}\gamma(C;M)\varphi(C,M)\Phi(C;M)\sum_p\sum_i\beta_{ir}, \tag{9}$$

where γ(C, M) is a function that takes into account the distribution of the activator over the different optical centers; φ(C, M) is a function that takes into account the populations of the Stark components of the ground level at a fixed temperature; Φ(C, M) is a function by which the values of the averaged frequency ν_{av} must be multiplied to obtain the frequency of each possible transition. All these quantities depend on the matrix M, into which the Nd^{3+} ion is introduced, since the Stark splitting of the ground level may be different in different hosts. The dependence of J on the concentration is due to the fact that the relative concentration of the different Nd^{3+} centers depends on the total concentration of the activator.

The frequency shift of the center of gravity of the individual absorption groups, both on going from one matrix to the other and following concentration changes, is small. In the former case it does not exceed 200 cm^{-1}, and in the latter, owing to the appearance of new optical centers, it is of the order of ten reciprocal cm. The influence of the function Φ(C, M) on the relative values of J can therefore be neglected. Consequently, we can assess the dependence of the relative absorption on either the matrix in which the Nd^{3+} is introduced or its total concentration, with sufficiently good approximation, by assuming that J depends only on the intensity and symmetry of the intracrystalline field. In the presence of several types of centers, J may have a concentration dependence with a character determined by the statistics of the optical centers in the crystal. Let us consider the experimental results from this point of view.

Individual fluorides. It was shown in [4,5,7] that the optical spectra of the crystals LaF_3–Nd^{3+} and CeF_3–Nd^{3+} contain lines of a single system. This indicates that in these matrices the local surrounding of Nd^{3+} has very little influence on the symmetry of the intracrystalline field. Thus, it can be assumed that p = 1 and that β, and consequently also the transition probabilities, are averaged only over the transitions of the Nd^{3+} ion contained in one type of optical center. The functions γ(C, M) and φ(C, M) are likewise independent of the concentration. This explains why the relative absorption in the LaF_3–Nd^{3+} and CeF_3–Nd^{3+} systems, which reflect in this case the averaged probability of the transition (the crystal-splitting schemes of Nd^{3+} are practically the same in LaF_3 and CeF_3), does not depend on the Nd^{3+} concentration. In the case of LaF_3–Nd^{3+} this averaged transition probability is higher than in the case of CeF_3–Nd^{3+}, thus indicating a different character of the coupling between the Nd^{3+} ion and the ions surrounding it in these crystals (Figs. 1d, e).

A different picture is observed in divalent fluorides (Figs. 1a, b). It is demonstrated in [1,6] that at least three types of optical centers, greatly differing in their properties (L, N, and P), are present. The relative concentration of the L centers is large in the concentration region up to 0.3 wt.%, that of the M centers from 0.3 to 2 wt.%, and that of the P centers above 2 wt.%. The maxima in the J(C) curves for CaF_2 and SrF_2 indicate that the lowest symmetry is possessed by the M centers. At higher concentrations, where the P centers having the more complicated structure predominate, J decreases, the average transition probability is smaller, and consequently the symmetry is higher.

Let us compare the values of J with the radiative lifetime τ_{rad} of the $^4F_{3/2}$ levels. Such a comparison is meaningful only for L centers, since, as shown in [1,3], these are not quenched up to a neodymium concentration of 1 wt.% (the M centers are quenched in all three hosts). In the L centers of both CaF_2–Nd^{5+} and in SrF_2–Nd^{3+}, τ_{rad} of the excited state of $^4F_{3/2}$ amounts to 1.2 msec. The difference in J for these two crystals at low Nd^{3+} concentrations can be attributed to two circumstances.

1. In the case of CaF_2–Nd^{3+}, the M centers, which have larger transition probabilities than the L centers, appear at lower concentrations, and when the Nd^{3+} content is 0.1–0.3 wt.% their relative concentration is larger than in SrF_2–Nd^{3+} crystals (formally, the difference between the functions $\gamma(C, M)$, and consequently the contribution of these centers to the averaged probability, are also larger).

2. It is possible that the ratios of the probabilities of the transitions ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_j$ ($j = {}^{11}/_2, {}^{13}/_2, {}^{15}/_2$) in CaF_2 and SrF_2 are different (since τ_{rad} of the excited state ${}^4F_{3/2}$ is determined by the transitions ${}^4F_{3/2} \rightarrow {}^4I_j$ ($j = {}^{11}/_2, {}^{13}/_2, {}^{15}/_2$), and the quantity J characterizes the probability of the transition ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$). The influence of the function $\varphi(C, M)$ is in this case small, since the crystal-splitting schemes of Nd^{3+} in the L centers are similar in CaF_2 and SrF_2. The difference between the absolute values of the averaged transitions probabilities in the M and P centers in CaF_2 and SrF_2 is due to the difference between the lattice constants (5.46 Å for CaF_2 and 5.78 Å for SrF_2), and also to the different character of the coupling.

The concentration dependence of the relative absorption for Nd^{3+} in the BaF_2 lattice differs greatly from the analogous dependences for CaF_2–Nd^{3+} and SrF_2–Nd^{3+} (Fig. 1c). It is seen that the relative concentration of optical centers having small transition probabilities and consequently a high degree of symmetry is large in the concentration region up to 1 wt.% Nd^{3+} in the crystal. Starting with 1 wt.%, their relative concentration decreases and the concentration of the low-symmetry P centers, which have larger absorption cross sections, begins to increase. Let us compare τ_{rad} of the L and P centers in BaF_2–Nd^{3+}. It is shown in [1] that the L centers in BaF_2 are not subject to concentration quenching up to 1 wt.%, and the P centers up to 5 wt.% Nd^{3+}. It is seen from the table that τ_{rad} of the Nd^{3+} ion in BaF_2 differ by approximately 30 times for the L and P centers, whereas for the regions where the L and P centers predominates the values of J differ by approximately 5 times. Taking into account the character of the deactivation of the excited ${}^4F_{3/2}$ level (which was mentioned earlier), and also the fact that the measurements of τ_{rad} were made at T = 77°K and the measurements of J at room temperature, it can be stated that a redistribution of the probabilities of ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_j$ transitions takes place ($j = {}^{11}/_2, {}^{13}/_2, {}^{15}/_2$), depending on the temperature and on the local surrounding of the Nd^{3+} ion.

Mixed fluorides. The generation and spectroscopic investigations of mixed systems have been the subject of several papers.[8, 16, 18] It is concluded in [8] that these bases contain a large number of optical TR^{3+} centers. The concentration dependences of the relative absorption of Nd^{3+} in the mixed systems BaF_2–LaF_3, CaF_2–YF_3, and CaF_2–CaF_3 are shown in Fig. 2. It is seen that the largest value of J is possessed by Nd^{3+} introduced in BaF_2–LaF_3 (Fig. 2a), and J does not depend on the Nd^{3+} concentration. This fact indicates that in the investigated concentration region the redistribution of the relative concentrations of most optical centers does not influence the relative absorption J and the average transition probability.

An increase of the total content of Nd^{3+} in CaF_2–YF_3 crystals leads to the redistribution of the relative concentrations of optical centers having different symmetry in a direction of increasing relative number of centers with higher symmetry (Figs. 2b–d). In other words, just as in the case of $CaF_2:Nd^{3+}$ and $SrF_2:Nd^{3+}$, a tendency appears towards formation of centers of more complicated in structure but higher symmetry when the total Nd^{3+} concentration increases.

The increase of the YF_3 concentration also leads to a certain decrease of the average transition probability. A similar action is exerted also on the relative absorption by an increase in the CeF_3 content of cerofluorite crystals. There is practically no concentration dependence in this case (Figs. 2e, f). The difference in the behavior of J for BaF_2–LaF_3–Nd^{3+} and CaF_2–YF_3–Nd^{3+} is due to the fact that BaF_2–LaF_2 contains 30 wt.% LaF_3, i.e., the disorder of the crystal structure is maximal in this system.

Recognizing that the lifetimes of the excited state of Nd^{3+} in mixed systems (see the table) have been measured at room temperature and are approximately equal to each other, the difference between the average probabilities of the transitions indicates a different degree of luminescence quenching of Nd^{3+} in these matrices, or else is connected with the different ratio of the probabilities of the transitions ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_j$ ($j = {}^{11}/_2, {}^{13}/_2, {}^{15}/_2$).

Oxygen-containing hosts. It is seen from Fig. 3b that the relative absorption of Nd^{3+} in glass does not depend on the Nd^{3+} concentration at the two investigated concentrations, and that the value of J in garnet, at equal concentration, is smaller than in $CaWO_4$ (Figs. 3a, c, d). The presence of several types of Nd^{3+} centers in $CaWO_4$ is evidenced by data obtained in several investigations.[9, 11, 19–21] At low Nd^{3+} concentrations, the relative absorption is practically independent of whether the compensator is Na or Nb. At Nd^{3+} concentrations higher than 1 wt.% in the case of niobium compensation, centers of lower symmetry appear, having larger transition probabilities, as is reflected in our results (Fig. 3c). In the case of sodium compensation, this effect is somewhat weaker (Fig. 3d).

CONCLUSION

As already noted, in different hosts the Nd^{3+} may be in fields of different intensity and structure, and this explains the strong difference between the relative absorption of Nd^{3+} in different hosts. The situation is more complicated with the concentration dependences of J. Let us turn to formula (9). In LaF_3 and CeF_3 crystals it can be assumed that p = 1. In this case the quantity β is averaged only over transitions of Nd^{3+} belonging to practically one type of center. Since the probability of each individual transition (and also the functions γ and φ when p = 1) does not depend on the activator concentration, it follows also that J does not depend on the concentration. Let us examine another extreme case, that of large p and consequently of small concentrations of individual centers. In this case, as shown by the experiment, the functions γ and φ are likewise independent of the concentration and averaging of β over transitions in different centers does not lead to a noticeable concentration dependence of J. Such a situation is realized in glasses and in mixed systems at compositions corresponding to maximum disorder of the crystal structure (BaF_2-LaF_3). Only in the intermediate case, when the number of centers is small and their structure is greatly different, can the redistribution of the relative concentrations of these centers result in a noticeable concentration dependence of J, as is indeed observed experimentally for the systems CaF_2-Nd^{3+}, SrF_2-Nd^{3+}, BaF_2-Nd^{3+}, and $CaWO_4-Nd^{3+}$. The character of these dependences yields information on the statistics of optical centers of different structure.

In conclusion, the authors are grateful to Z. M. Bruk for the chemical analytic determination of the neodymium in the oxygen containing crystals, and also to A. A. Sobol' and L. S. Gaĭgerova for taking part in a discussion of the results and for critical remarks.

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[1] Yu. K. Voron'ko, V. V. Osiko, and I. A. Shcherbakov, Zh. Eksp. Teor. Fiz. **55**, 1598 (1968) [Sov. Phys.-JETP **28**, 838 (1969)].

[2] A. A. Kaminskiĭ and V. V. Osiko, Neorganicheskie (Inorganic Materials) **3**, 417 (1967).

[3] Yu. K. Voron'ko and V. V. Osiko, ZhETF Pis. Red. **5**, 357 (1967) [JETP Lett. **5**, 295 (1967)].

[4] M. V. Dmitruk and A. A. Kaminskiĭ, Zh. Eksp. Teor. Fiz. **53**, 874 (1967) [Sov. Phys.-JETP **26**, 531 (1968)].

[5] M. V. Dmitruk, A. A. Kaminskiĭ, and I. A. Shcherbakov, Zh. Eksp. Teor. Fiz. **54**, 1680 (1968) [Sov. Phys.-JETP **27**, 900 (1968)].

[6] Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Zh. Eksp. Teor. Fiz. **49**, 420 (1965) [Sov. Phys.-JETP **22**, 295 (1966)].

[7] Yu. K. Voron'ko, M. V. Dmitruk, A. A. Kaminskiĭ, V. V. Osiko, and V. N. Shpakov, Zh. Eksp. Teor. Fiz. **54**, 751 (1968) [Sov. Phys.-JETP **27**, 400 (1968)].

[8] Yu. K. Voron'ko, A. A. Kaminskiĭ, V. V. Osiko, and A. M. Prokhorov, Neorganicheskie materialy **2**, 1161 (1966).

[9] Yu. K. Voron'ko and V. V. Osiko, Neorganicheskie materialy **3**, 413 (1967).

[10] Yu. K. Voron'ko, V. V. Osiko, V. T. Udovenchik, and M. M. Fursikov, Fiz. Tverd. Tela **7**, 267 (1965) [Sov. Phys.-Solid State **7**, 204 (1965)].

[11] V. I. Aleksandrov, Yu. K. Voron'ko, G. V. Maksimova, and V. V. Osiko, Neorganicheskie materialy **3**, 368 (1967).

[12] V. V. Osiko, Rost kristallov (Crystal Growth) **5**, 373 (1965).

[13] M. A. El'yashevich, Spektry redkikh zemel' (Rare Earth Spectra), Gostekhizdat, 1953.

[14] R. R. Judd, Phys. Rev. **127**, 750 (1962).

[15] W. F. Krupke, Phys. Rev. **145**, A325 (1966).

[16] Kh. S. Bagdasarov, Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Neorganicheskie materialy **1**, 2088 (1965).

[17] Kh. S. Bagdasarov, Yu. K. Voron'ko, A. A. Kaminskiĭ, V. V. Osiko, and A. M. Prokhorov, Kristallogr. **10**, 746 (1965) [Sov. Phys.-Crystallogr. **10**, 626 (1966)].

[18] Yu. K. Voron'ko, A. A. Kaminskiĭ, V. V. Osiko, and M. M. Fursikov, Kristallogr. **11**, 936 (1966) [Sov. Phys.-Crystallogr. **11**, 793 (1967)].

[19] V. Ranon, Phys. Lett. **8**, 154 (1964).

[20] R. W. Kidrie and M. Kestigian, Appl. Phys. Lett. **3**, 86 (1963).

[21] K. C. Chu and C. Kikuchi, J. Chem. Phys. **46**, 368 (1967).

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