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Nonradiative relaxation and inhomogeneous splitting of aggregated optical centers in the Nd^{3+}-doped CaF_2 and SrF_2 crystals (FLN and decay study)

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Abstract

Site-selective fluorescence and laser excitation spectroscopy for different types of optical centers in $SrF_2 : Nd^{3+}$ (0.3 – 1.0%) and $SrF_2 : La^{3+}$ (1.0%) : Nd^{3+} (0.2%) were performed at 4.2 K. The crystal-field levels of the $^4I_{9/2}$, $^4F_{3/2}$, and $^4G_{5/2}$ multiplets for different Nd^{3+} optical centers were determined in $SrF_2 : Nd^{3+}$ (0.3%). An attempt was made to identify some of the new optical centers on the basis of their fluorescence lifetimes and crystal-field splitting. Some models of these centers have been discussed. Two–six times reduction of the $^4F_{3/2}$ multiplet lifetime was observed in the pair M-center in comparison with the single optical centers due to energy cross-relaxation in the pair. A fine splitting of the levels at the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ crystal-field transition (1.5 cm^{-1}) similar to that in CaF_2 (2.4 cm^{-1}) was found for the Nd–Nd pair in SrF_2. The variation of the splitting from CaF_2 to SrF_2 nicely demonstrates the R^{-5} dependence of coherent quadrupole–quadrupole interaction.

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Keywords: Optical centers; Site-selective spectroscopy; Coherent and incoherent ion–ion interaction; Resonance splitting

1. Introduction

A fine resonance dynamical splitting at the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ (Z1 → D1) Stark–Stark transition in both the rhombic $(Nd_{Ca}–F_i)_2$ pair M-center and in the trigonal $(Nd_{Ca}–F_i)_4$ quartet N-center was previously found in the $CaF_2 : Nd^{3+}$ crystals in the spectral domain by absorption spectroscopy [1] and in the time domain by coherent beating of the accumulated photon echo (APE) [2] at $T = 10$ K and was confirmed by laser-induced site-selective time-resolved fluorescence spectroscopy at $T = 4.2$ K [3]. Strong coherent quadrupole–quadrupole interaction between the Nd^{3+} ions inside the M and the N complexes was proposed as the reason for this splitting [1]. In contrast to CaF_2 the aggregated Nd^{3+} centers in the SrF_2 crystal have not been reliably identified

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before. The purpose of this work is to identify such clusters and to determine the energy diagram of the Stark levels for the ground $^4I_{9/2}$ and the excited $^4F_{3/2}$ and $^4G_{5/2}$; $^2G_{7/2}$ states for different Nd^{3+} centers in the SrF_2 crystal. On the basis of these results we will try to compare the strength of coherent Nd^{3+}–Nd^{3+} interaction in the pair centers of $SrF_2:Nd^{3+}$ crystal with the known values for $CaF_2:Nd^{3+}$.

2. Experimental results and discussion

The experimental set-up used in this study is described in our previous paper of the similar study in the $CaF_2:Nd^{3+}$ crystals [3].

2.1. L-center with the single Nd^{3+} ion

In the tetragonal symmetry L-center where the lattice Ca^{2+} cation is replaced by the impurity Nd^{3+} ion the charge-compensating fluorine F_i^- ion is located at the nearest to the rare-earth ion available interstitial position. The tetragonal symmetry of this center in CaF_2 and SrF_2 was established by EPR [4]. Fig. 1 presents inter-multiplet absorption spectra at the $^4I_{9/2}(Z) \rightarrow {}^4F_{3/2}(R)$ transition for $SrF_2:Nd^{3+}$ (0.3%), $SrF_2:Nd^{3+}$(1.0%), $SrF_2:La^{3+}$ (1%)$:Nd^{3+}$ (0.2%), and $CaF_2:Nd^{3+}$(0.2%) at $T = 4.2$ K. One can see that along with the L-center there are many absorption lines of more complex centers. Comparison of the absorption spectra of $SrF_2:Nd^{3+}$ (0.3%) and $SrF_2:Nd^{3+}$ (1.0%) shows that the relative concentration of aggregated centers increases with increase in total neodymium concentration. At 1% of Nd^{3+} concentration the absorption line of the L-center in SrF_2 is considerably stronger than in CaF_2 due to the less-effective process of Nd^{3+} aggregation in the former one. The value of the Stark splitting of the $^4F_{3/2}$ multiplet is found to be 82 cm^{-1}, which is 1.4 times less than in CaF_2. The positions of the Stark levels of the $^4I_{9/2}$, $^4F_{3/2}$ and $^4G_{5/2}$ multiplets in the L-center in the crystals in this study measured by absorption (Fig. 2) and laser fluorescence excitation (Fig. 3A) technique are in agreement with those reported in the earlier works [5,6]. The fluorescence lifetime measured at the R1 → Z1 transition is 1.65 ms at $T = 4.2$ K which is close to 1.7 ms measured at $T = 10$ K [6].

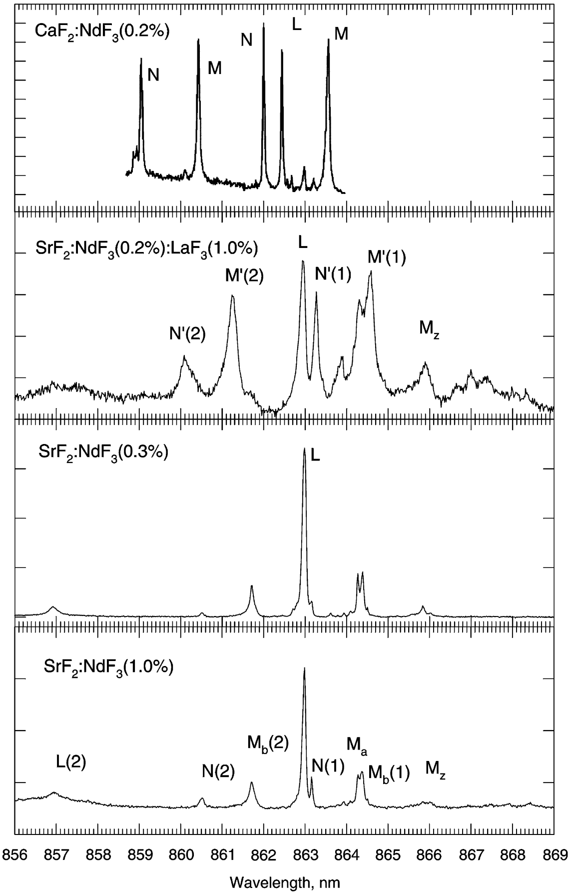

Fig. 1. Absorption spectra for CaF_2 and SrF_2 crystals for the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition of the Nd^{3+} ions at 4.2 K.

3. Other optical centers

Weak clusterization in SrF_2 did not allow earlier reliable identification of pair and other aggregated neodymium centers as was done in CaF_2. In doing so the absorption and fluorescence excitation spectra, as well as site- selective fluorescence kinetics decay were measured in $SrF_2:Nd^{3+}$ crystals. In addition, we compared the data obtained for the well-known aggregated centers in $CaF_2:Nd^{3+}$ (0.2%) and $SrF_2:Nd^{3+}$ (1%) with the results for

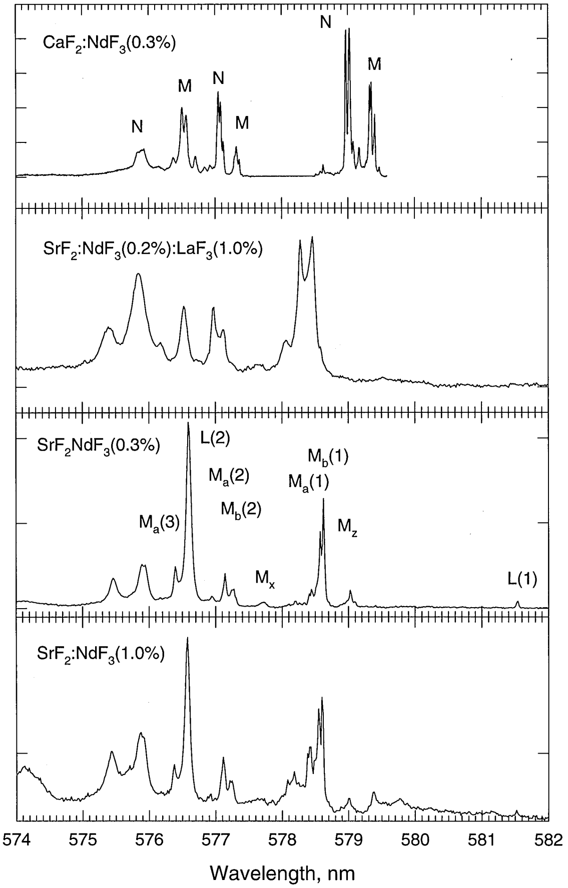

Fig. 2. Absorption spectra for CaF_2 and SrF_2 crystals for the $^4I_{9/2} \rightarrow {}^4G_{5/2}$; $^2G_{7/2}$ transition of the Nd^{3+} ions at 4.2 K.

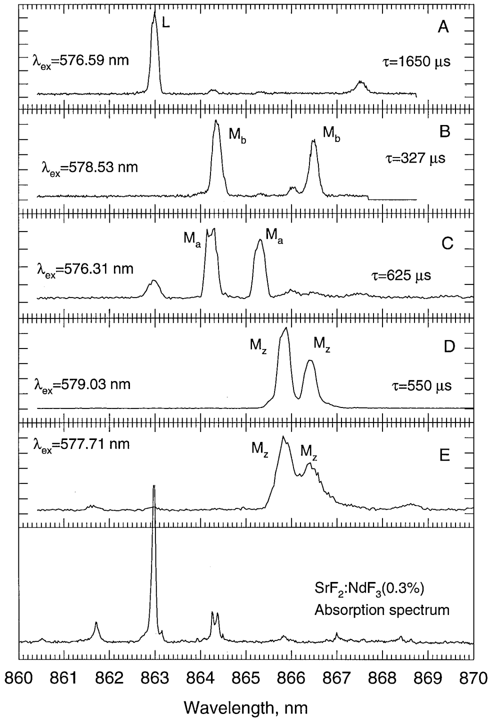

Fig. 3. Site-selective fluorescence spectra of the $SrF_2 : NdF_3$ (0.3%) crystal for the $^4F_{3/2}(1) \rightarrow {}^4I_{9/2}(1,2)$ Stark–Stark transitions along with the absorption at the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ (1, 2) ones.

the mixed $SrF_2 : Nd^{3+}$ (0.2%) : La^{3+} (1.0%) crystal. Fig. 1 shows the absorption spectra of these crystals at the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition. Co-doping of the Nd^{3+}-doped fluorite-type crystals, for example with La^{3+}, leads to the formation of the M′-centers where one Nd^{3+} ion in the pair is substituted for optically inactive La^{3+}. Analysis of Fig. 1 shows that the formation of La–Nd complexes (M′-centers) in SrF_2 is more effective than Nd–Nd (M-centers) ones. In addition, in $SrF_2 : Nd^{3+}$ (0.2%) : La^{3+} (1.0%) the relative intensity of the L-centers absorption is considerably less than in $SrF_2 : Nd^{3+}$ (1.0%) for approximately the same total concentration of rare-earth dopants. As it was shown for CaF_2 crystal [7] additional La^{3+} impurity leads to the increase in the total value of Stark splitting of the $^4F_{3/2}$ multiplet of the M′-center with shifting of the higher $^4F_{3/2}$ sublevel up and the lower one down. Using this fact and by comparing of $SrF_2 : Nd^{3+}$ and $SrF_2 : Nd^{3+} : La^{3+}$ absorption spectra we may identify N(1) and $M_b(1)$ peaks as low Stark levels and $M_b(2)$ and N(2) as a higher Stark levels of the $^4F_{3/2}$ multiplet belonging to different centers. The distance between $M_b(1)$ and $M_b(2)$ lines is 30 cm^{-1} which is 1.4 times less than for the M-center in CaF_2. This result is similar to that found for the L-center in CaF_2 and SrF_2 where this ratio is also 1.4. There is no energy shift of the M_z absorption bands in $SrF_2 : Nd^{3+}$ (0.2%) : LaF_3 (1.0%) and $SrF_2 : Nd^{3+}$ found. This allows to propose that this type of center is a single rare-earth impurity center which could differ from the L-center by the way of charge compensation (analog of Y-center in CaF_2 [7] when the extra charge of Nd^{3+} is compensated by two F_i^- in the first or in the second coordination sphere or by one F_i^- in the second sphere [8]).

3.1. M_b-center

Absorption spectra of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$; $^2G_{7/2}$ transition for the crystals studied are shown in Fig. 2. Fluorescence spectra from the $^4F_{3/2}$ multiplet of Nd^{3+} optical centers with excitation into the $^4G_{5/2}$ multiplet are presented in Fig. 3. Three fluorescence spectral lines with maxima at 864.3, 866.4 (Fig. 3B) and 873.9 nm obtained under 578.53 nm excitation associated with transitions of the M_b-center from the lower lying Stark level of the $^4F_{3/2}$ multiplet to the first, second, and third Stark levels of the ground $^4I_{9/2}$ multiplet were registered. The measured Stark energy levels positions for this M_b-center (Table 1) are very close to the results of work [6]. The measured fluorescence lifetime (Table 2) was found to be four times larger at 4.2 K ($\tau = 327$ μs) in $SrF_2 : Nd^{3+}$ than for the pair (Nd–Nd) M-centers in CaF_2 ($\tau = 79$ μs). According to Han et al. [6] the fluorescence lifetime of the M_b-centers in $SrF_2 : Nd^{3+}$ at 10 K is 237 μs whereas at 77 K it was found even shorter at 105.6 μs [9]. Previously, the lifetime shortening with temperature was observed for the M-pair (Nd–Nd) center in CaF_2 [10]. Using the results of this work the quenching energy transfer rates from the $^4F_{3/2}$ multiplet in the Nd–Nd pair in CaF_2 could be determined at different temperatures. In the range of 4.2–10 K it was found to be constant ($W_0 = 8877\ s^{-1}$). Knowing the energy transfer rate in the pair we could determine the C_{DA} – micro-efficiency of energy transfer (as $C_{DA} = W_0 \times R_{\min}^6$) if we know the Nd–Nd distance in the pair. In [8] the positions of the La^{3+} ions and interstitial fluorine ions (F_i^-) in the La–La pair in CaF_2 and SrF_2 were determined theoretically in the configuration of minimum energy. As the ionic radii are very close for Nd^{3+} and La^{3+} we used these results for estimation of the distance in the Nd–Nd pair in these crystals. They were found to be 0.364 and 0.396 nm for CaF_2 and SrF_2 crystals, respectively. According to Basiev et al. [11] the dipole–dipole interaction is dominant in the nonradiative energy transfer if the squares of the reduced matrix elements $U^{(4)}$ and $U^{(6)}$ are much higher than the squares of $U^{(2)}$ for both the donor and acceptor transitions involved. This condition is fulfilled for the cross-relaxation from the $^4F_{3/2}$ state since the matrix elements $U^{(2)}$ for all electronic transitions participating in the process are equal or close to zero. With this in mind we estimated C_{DA} micro-parameters at different temperatures in the $CaF_2 : Nd^{3+}$ and $SrF_2 : Nd^{3+}$ crystals. The result of these calculations in the pair M-center in CaF_2 and SrF_2 are presented in Table 3. It is seen that the value of C_{DA} increases for both the crystals when the temperature rises. According to Voron'ko et al. [10] the fluorescence of the M-center in $CaF_2 : Nd^{3+}$ at $T = 77$ K is quenched completely. This is an indication of phonon-assisted resonance energy transfer and deals with the increase in temperature of the overlap integral of the donor (excited Nd^{3+} ion) fluorescence spectrum and absorption spectrum of acceptor (the second unexcited ion of the

Table 1
Energy levels positions (cm^{-1}) for different optical centers in the SrF_2 (0.3%) : Nd^{3+} crystal obtained from absorption, excitation and fluorescence spectra at 4.2 K

Center type		L	M_a	M_z	M_b
	Z1	0	0	0	0
$^4I_{9/2}$	Z2	57	13	7	28
	Z3	153	110		127
$^4F_{3/2}$	R1	11 584	11 569	11 550	11 567
	R2	11 667			11 597
$^4G_{5/2}$	D1	17 197	17 282	17 270	17 284
	D2	17 343	17 327	17 328	17 324

Table 2
Fluorescence lifetime of the $^4F_{3/2}$ multiplet for different optical centers in $SrF_2 : Nd^{3+}$

Center type	Life time, μs (TK)
L	1650 (4.2 K)[a]
	1700 (10 K) [6]
	325 (4.2 K)[a]
$M(M_6)$	237 (10 K) [6]
	105.6 (77 K) [9]
M_a	615 (4.2 K)[a]
M_z	550 (4.2 K)[a]

[a] Result of this paper.

Table 3
The $C_{DA}/10^{-41}$ (cm^6/s) — micro-parameter of the nonradiative energy transfer from the $^4F_{3/2}$ multiplet of the Nd^{3+} ion in the pair M-centers in the CaF_2 and SrF_2 crystals

T(K)	4.2	10	77
CaF_2	2.07 [10], 2.6 [3]	2.07 [10], 2.14 [5]	
SrF_2	0.523[a]	0.897 [5]	3.013 [9]

[a] Result of this paper.

Nd–Nd pair). The larger values of C_{DA} in CaF_2 in comparison with SrF_2 may be related to the larger overlap integrals of electronic resonances of donors and acceptors because of different values of Stark splitting. The larger lifetimes of the $^4F_{3/2}$ manifold of the pair M-center in SrF_2 in comparison with CaF_2 is caused by larger minimal distance (Nd–Nd) and the smaller values of the C_{DA} micro-parameters in SrF_2.

3.2. M_a- and M_z-centers

The fluorescence of the M_a-center is more pronounced when we excite the third Stark level of the $^4G_{5/2}$, $^2G_{7/2}$ multiplet at 576.31 nm (Fig. 3C).

The fluorescence of the M_z-center is more pronounced when we excite at 579.03 nm into the lowest Stark level of the $^4G_{5/2}$, $^2G_{7/2}$ multiplet (Fig. 3D). This center exhibits rather low value of Stark splitting of the ground $^4I_{9/2}$ multiplet suggesting low values of the even crystal-field parameters. The Stark energy level positions of the ground $^4I_{9/2}$ multiplet obtained for the M_a and the M_z centers after the fluorescence spectra analysis are presented in Table 1. The fluorescence lifetime of the M_z-center (550 μs) is quite close to that of the M_a-center (615 μs) (see Table 2). If our presumption that the M_z-center is the single center with the compensation of an extra charge of Nd^{3+} ion by two interstitial F_i^- ions spaced in the first or in the second coordination sphere (like Y- center in CaF_2) or by one F_i^- in the second sphere is correct; then its lifetime reduction can be connected with the increase in the radiative rate due to higher values of the odd crystal-field parameters in comparison with those for the L-center. The same can be true for the M_a-center. There is good indirect evidence of the discussed nature of these two centers. Theoretical calculations of work [8] show that the energy change in forming the La^{3+}–F_i^- complex from an isolated ion and interstitial fluorine ion in the second coordination sphere is larger in $SrF_2:La^{3+}$ than in $CaF_2:La^{3+}$. And vice versa, the energy change on forming the La^{3+}–F_i^- complex with an interstitial fluorine in the first coordination sphere is larger for $CaF_2:La^{3+}$ than for $SrF_2:La^{3+}$. This can prove the lack of the M_a and M_z complex centers in $CaF_2:Nd^{3+}$ and their existence in $SrF_2:Nd^{3+}$.

Fluorescence of the M_z-center (Fig. 3E) was observed also using 577.71 nm excitation into the M_x absorption band (Fig. 2). However, the pronounced build-up of the M_z-center fluorescence decay with this excitation shows that the M_x absorption band belongs to another optical center. An effective nonradiative energy transfer to the M_z-center could be proposed as a reason for this build-up.

4. Fine levels splitting of pair centers

The maximum value of a fine dynamical splitting up to 2.4 cm^{-1} for the Z1 → D1 crystal field Stark–Stark transition of the pair M-center of Nd^{3+} in CaF_2 was found in Refs. [1–3,12] using time resolved site-selective fluorescence spectroscopy, photon echo and selective laser-saturation spectroscopy. It was shown theoretically in Ref. [1] that the fine dynamical splitting is caused by resonance electric quadrupole–quadrupole interaction between Nd^{3+} ions in the pair. For this interaction the fine splitting is proportional to $\Delta = e^2\langle r^2\rangle^2/R_{\min}^5|(J||U^{(2)}||J')|^2$, where $\langle r^2\rangle$ is the square of the 4f electronic radius averaged over the 4f-wave function. This type of interaction is maximal for the $^4G_{5/2}$ multiplet as the reduced matrix element $(^4I_{9/2}||U^2||^4G_{5/2}) = 0.897$ [13] is extremely large compared to those from the ground state to other excited multiplets $((^4I_{9/2}||U^2||^{2S+1}L_J) < 0.1)$. The theoretical analysis gives the value of the splitting equal to 1–7 cm^{-1} which is close to the experimental data. For the determination of the fine splitting of the pair center in SrF_2 we studied the excitation spectra of the M_b-centers with

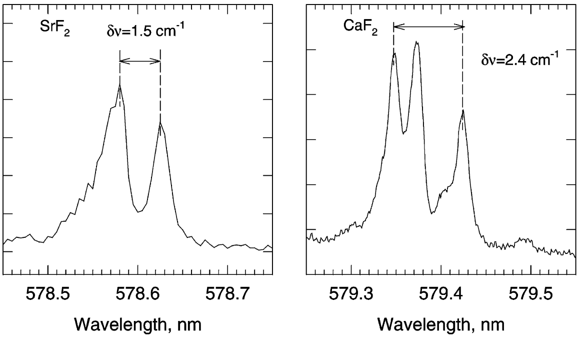

Fig. 4. Dynamical fine-splitting of the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ Stark–Stark transition due to quadrupole–quadrupole interaction in the Nd–Nd pair M-center in CaF$_2$ and SrF$_2$ crystals.

fluorescence registration at 866.4 nm (R1 → Z2 transition). The result (Fig. 4) demonstrates a fine splitting of R1 → D1 crystal-field transition of the M_b-center with the value of 1.5 cm^{-1}. The reason for this expected reduction in the value of the dynamical splitting from CaF$_2$ to SrF$_2$ is the increase in the lattice parameters in SrF$_2$ in comparison with CaF$_2$. The following ratios confirm the R^{-5} dependence of the measured values of the fine splitting, which is indicative of coherent quadrupole–quadrupole interaction in the Nd–Nd pair:

$$\frac{\Delta(\mathrm{CaF_2})}{\Delta(\mathrm{SrF_2})} = \frac{2.4\ \mathrm{cm}^{-1}}{1.5\ \mathrm{cm}^{-1}} = 1.60,$$

$$\frac{R^5_{\min}(\mathrm{SrF_2})}{R^5_{\min}(\mathrm{CaF_2})} = \frac{(0.396\ \mathrm{nm})^5}{(0.364\ \mathrm{nm})^5} = 1.52,$$

where $R_{\min}(\mathrm{SrF_2})$ and $R_{\min}(\mathrm{CaF_2})$ is the minimum distance between the Nd ions in the pair.

5. Conclusion

Site-selective fluorescence and laser excitation study of the $\mathrm{SrF_2:Nd^{3+}}$ (0.3–1.0%) and $\mathrm{SrF_2:La^{3+}}$ (1.0%)$:\mathrm{Nd^{3+}}$ (0.2%) crystals at 4.2 K has identified Stark-level energy positions of different optical centers. Two–six times reduction of the $^4F_{3/2}$ multiplet lifetime was observed in the pair M-center in comparison with the single optical centers due to dipole–dipole quenched energy transfer in the Nd–Nd pair. Slower energy transfer rate from the $^4F_{3/2}$ multiplet of the M-center in SrF$_2$ in comparison with CaF$_2$ is caused by larger minimal distance (Nd–Nd) and by the smaller values of the C_{DA} micro-parameter in SrF$_2$.

A fine splitting for the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ Stark–Stark transition of the Nd^{3+} pair center was found to be $\Delta = 1.5\ \mathrm{cm}^{-1}$ in SrF$_2$ similar to the dynamical splitting for the Nd^{3+} pairs in CaF$_2$ ($\Delta = 2.4\ \mathrm{cm}^{-1}$). The reduction in the value of fine splitting from CaF$_2$ to SrF$_2$ demonstrates the R^{-5} dependence predicted for coherent quadrupole–quadrupole interaction and proves the dynamical character of this splitting.

Acknowledgements

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References

[1] T.T. Basiev, V.V. Fedorov, A.Ya. Karasik, K.K. Pukhov, J. Lumin. 81 (1999) 189.
[2] T.T. Basiev, Ya.A. Karasik, V.V. Fedorov, K.W. Ver Steeg, JETP 86 (1) (1998) 156.
[3] Y.V. Orlovskii, T.T. Basiev, V.V. Osiko, H. Gross, J. Heber, J. Lumin. 82 (1999) 251.
[4] N.E. Kask, L.S. Kornienko, M. Fakir, Fiz. Tverd. Tela (USSR) 6 (1964) 549.
[5] Yu.K. Voron'ko, A.A. Kaminskii, V.V. Osiko, Sov. Phys. JETP 22 (1966) 295.
[6] T.P.J. Han, G.D. Jones, R.W.G. Syme, Phys. Rev. B 47 (1993) 14706.
[7] Yu.K. Voron'ko, V.V. Osiko, A.M. Prokhorov, I.A. Shcherbakov, Proc. Lebedev's Phys. Inst. 60 (1972) 3.
[8] J. Corish, C.R.A. Catlow, P.W.M. Jacobs, S.H.O. Ong, Phys. Rev. B 25 (1982) 6425.
[9] Yu.V. Orlovskii, T.T. Basiev, I.N. Vorob'ev, V.V. Osiko, A.G. Papashvili, Laser Phys. Int. J 6 (1996) 448.
[10] K.K. Voron'ko, V.V. Osiko, A.M. Prokhorov, I.A. Shcherbakov JETP 60 (1971) 943.
[11] T.T. Basiev, Yu.V. Orlovskii, Yu.S. Privis, J. Lumin. 69 (1996) 187.
[12] W. Beck, V.V. Fedorov, T.T. Basiev, C. Flytzanis, A.Ya. Karasik, D. Richard, Technical digest of International Conference ICONO'98, Moscow, 1998.
[13] W.T. Carnall, P.R. Fields, K. Raynak, J. Chem. Phys. 49 (1968) 4424.