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Fine level splitting of aggregate neodymium centers in CaF_2 crystals

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Abstract

A fine spectral structure of pair and quartet centers of Nd ions in CaF_2 crystals was investigated by the selective laser absorption saturation and time resolved pump/probe technique at 8–30 K. The spectral hole–antihole pairs were observed under laser excitation of the pair Nd ions. It was shown that the main absorption lines reflect a splitting of the lowest Stark level of the $^4G_{5/2}$ state caused by a strong coherent interaction between Nd ions in cluster with total splitting values 2.4 and 3.3 cm^{-1} for pair and quartet centers, respectively. Energy diagram, including singly and doubly excited states, was built for a strongly coherent interacting pair. The study of dynamics of the absorption saturation for different time delay between probe and pump pulses allowed us to estimate relaxation time (~8 ns) among ground and excited state sub-levels. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, a large number of papers have been devoted to investigations of pair optical centers of rare-earth (RE) ions in crystals. Spectroscopic investigations of these ion pairs with very small inter-ionic distance open a direct way for the study of interesting optical phenomena like fast delocalization of the excitation, energy transfer, cooperative effects, excited state absorption and coherent ion–ion interaction [1–6]. Along with spectral hole burning and photon echo techniques, the method of double frequency excitation was developed to investigate fine level splittings of different RE ions in solids [7]. The fine splitting of the Stark levels of Nd^{3+} pair centers in LaF_3 crystals were studied by this technique [7]. For these crystals, an analysis is complicated due to the spectral overlap of weak absorption bands of the different type of pair centers and strong single ion absorption bands. In contrast to this, the absorption bands of the single and pair Nd^{3+} centers in CaF_2 crystals are not overlapped [8,9]. Besides, due to heterovalent substitution of Ca^{2+} by Nd^{3+}, the latter ions are easily clusterized even at small

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(~0.1%) Nd^{3+} concentrations [8]. Thus, CaF_2 crystals are good candidates for the spectroscopic study of the pair ions.

The structure of Nd^{3+} pair centers in CaF_2 crystals was studied by spectroscopic [8,9] and EPR [10,11] technique. In Refs. [10,11], the ~0.2 cm^{-1} splittings of the lowest Stark level of the ground $^4I_{9/2}$ state of Nd^{3+} ions were revealed and explained in frame of the magnetic dipole–dipole and exchange interactions within pair Nd^{3+} clusters. In Ref. [12], using accumulated photon echo technique, we confirmed singlet–triplet splitting. Also much larger (~2 cm^{-1}) level dynamical splittings of the excited $^4G_{5/2}$ Stark level were observed [12,13].

In this paper, we study the structure of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd^{3+} ions in Nd^{3+} pair and quartet optical centers and dynamics of the excitation energy transfer among sub-levels, using time-resolved hole-burning technique. Our results enable us to establish the nature of the fine level structure of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition in these optical centers.

2. Experimental technique

CaF_2 crystals containing 0.3 wt.% of NdF_3 were grown in a fluorine atmosphere by the Bridgman method. During the growth, divalent Ca^{2+} ions are replaced by trivalent Nd^{3+} ions. The crystal is saturated by interstitial fluorine ions (F_i^-) to maintain electroneutrality. In CaF_2 crystals, Nd^{3+} ions can be distributed among different types of centers with different absorption spectra. At low doping concentrations, the CaF_2:Nd^{3+} absorption spectra are assigned to the L center in which the charge compensating F_i^- ion is in the nearest interstitial position to a single Nd^{3+} ion (Nd^{3+}–F_i^-). As the impurity concentration increases, the attraction of the (Nd^{3+}–F_i^-) dipoles leads to the formation of a pair cluster $(Nd^{3+}–F_i^-)_2$ called M center and more complex N centers. Thus, the M center involves two Nd^{3+} ions in the nearest cation positions associated with two interstitial F_i^- ions. A rhombic symmetry of the M center was established by EPR technique [10,11]. A structural model for the N center involving four neodymium ions and four interstitial F^- $(Nd^{3+}–F_i^-)_4$ has been proposed [14]. Absorption spectra of the studied crystals CaF_2:Nd^{3+} (0.3 wt.%) consist of absorption bands being assigned mainly to M and N clusters.

For time-resolved absorption measurement, we used the radiation of two identical tunable dye lasers with 5 ns pulse duration, a bandwidth of 0.07 cm^{-1}, and a repetition rate of 50 Hz. The focused radiation of the first laser (pump beam) with a pulse energy up to 0.2 mJ was used to saturate the Nd^{3+} ion absorption at the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. The tunable radiation of the second dye laser (probe beam) was used for the measurement of the absorption spectrum. For a better signal to noise ratio, the transmitted probe signal was normalized by the probe intensity. The signal and reference pulses were detected by photodiodes and acquired by two boxcar integrators and divided shot by shot by a PC. To avoid saturation by the probe beam, the probe laser energy was kept 100 times weaker than the pump energy. The probe pulses were delayed relative to the pump pulses from 0 to 22 ns by using an optical delay line. The samples were cooled by a closed cycle helium cryostat down to 8 K.

3. Experimental results and discussion

Fig. 1 (curve a) shows the absorption spectrum of the transition between the lowest Stark levels of the ground ($^4I_{9/2}$) and excited ($^4G_{5/2}$) states of Nd^{3+}, measured at $T = 8$ K by the probe beam in absence of the pump beam. Each of the M and N bands consists of at least four absorption bands with 0.9 cm^{-1} (1.8 cm^{-1}) splitting between the main M1, M2 (N1, N2) absorption bands. Line widths of 0.57–0.53 cm^{-1} (0.81–0.96 cm^{-1}) reflect inhomogeneous broadening or unresolved internal structure for the M (N) centers, which is larger for the more complex N centers. The lower traces in Fig. 1 show absorption spectra measured under the excitation into the N1 band (578.99 nm, curve b) and the M2 band (579.37 nm, curve c) with a pump/probe delay time of $\tau_d = 2$ ns. It can be seen that a hole is burnt in the absorption spectra at the pumping wavelength (arrows directed upward).

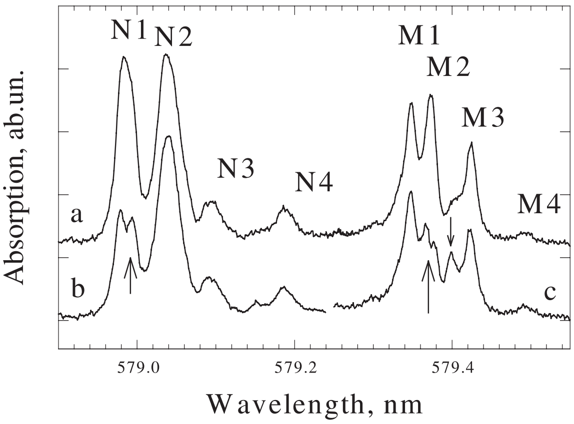

Fig. 1. Absorption spectra of the M and N centers at $T = 8$ K: a. without pumping, b. under laser pumping into band N1, and c. under laser pumping into band M2.

Additionally, a new absorption peak (antihole) appears in the M-center absorption spectrum (arrows directed down). The observed hole widths are determined by the instrumental line width (the homogeneous line width for this transition at 8 K is less than 0.1 GHz [12]). In order to determine the nature of the fine level structure, we measured absorption spectra under pumping into the main absorption bands of the M and N bands. Fig. 2 shows changes in the absorption spectrum of M and N centers (the difference ΔK between the initial absorption spectrum and the spectrum under selective laser saturation) under different pumping wavelengths with a pump/probe delay time of $\tau_\mathrm{d} = 2$ ns. In this figure, spectral holes and antiholes look like positive and negative peaks, respectively. The traces d–f in Fig. 2 show that the antihole position (arrows directed down) depends on pumping frequency. However, the sum of hole frequency and antihole frequency remains constant ($\omega_\mathrm{ah} + \omega_\mathrm{h} = \mathrm{const}$). By varying the pulse energies and the repetition rate, we ensured that laser heating effects were negligible. Transformations of the N center absorption while pumping M center transitions and vice versa were not observed.

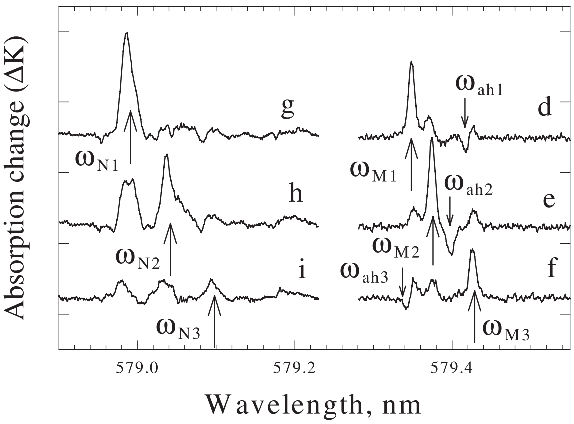

Fig. 2. Absorption change of the CaF_2:Nd^{3+} crystal under laser pumping into the bands N1 (g), N2 (h), N3 (i), M1 (d), M2 (e), and M3 (f).

These features of the absorption spectra of M centers can be explained in the frame of coherent Nd–Nd interaction in pair centers. As it was shown theoretically [13], coherent electric quadrupole–quadrupole ion interactions can lead to splittings of the $^4G_{5/2}$ level with an energy gap of several wave numbers. For the pair center energy levels, it is convenient to use a notation as $|\alpha,\beta\rangle$, where α and β are the individual states of the first and second ion in the pair [7]. In this notation, the ground state of a pair center, when the both ions are in the lowest Stark sub-levels, is written as $|^4I_{9/2},{}^4I_{9/2}\rangle$. Similarly $|^4I_{9/2},{}^4G_{5/2}\rangle$, $|^4G_{5/2},{}^4G_{5/2}\rangle$ correspond to one and two ions in the pair excited to the $^4G_{5/2}$ state. The absorption spectrum of the pair center shown in Fig. 1 (curve a) corresponds to the transition of one of the pair ions to the excited state: $|^4I_{9/2},{}^4I_{9/2}\rangle \rightarrow |^4I_{9/2},{}^4G_{5/2}\rangle$. The absorption, starting from the excited state refers to the excitation of the second ion in the pair and is written as $|^4I_{9/2},{}^4G_{5/2}\rangle \rightarrow |^4G_{5/2},{}^4G_{5/2}\rangle$. In this case, an antihole arises as a result of the laser induced excited state absorption. Using the wavelengths of the maximum absorption from the ground state (Fig. 1) and the antihole positions (Fig. 2, curves d–f), and taking into account that the sum of frequencies of the hole and antihole positions is constant, we can derive an energy diagram for the M center (Fig. 3). The scheme of the triplet splittings for the ground $^4I_{9/2}$ state was obtained from EPR measurements [9,10]. In the diagram (Fig. 3), we indicate only three split sublevels which correspond only to the three strongest

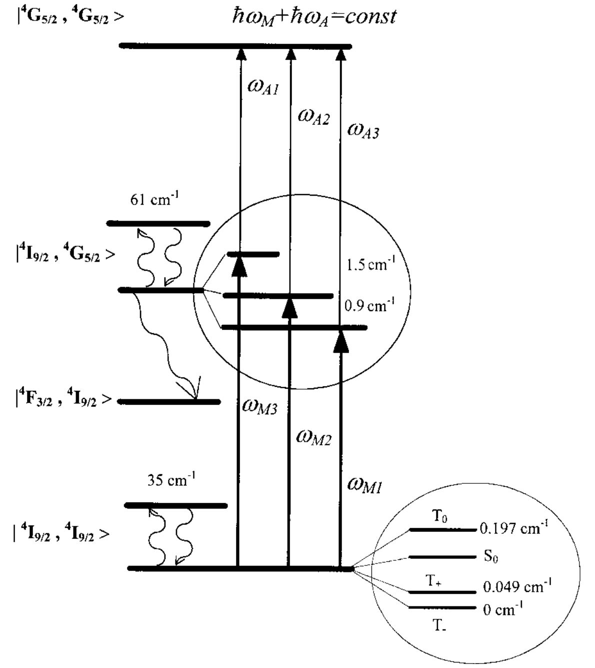

Fig. 3. Diagram of energy levels of strongly coupled Nd^{3+}–Nd^{3+} ions in the pair center.

bands (M1–M3), although some additional features are observed in the spectra in Figs. 1 and 2. The excitation of the M4 band does not change the absorption of the M1–M3 bands. This means, that the M1–M3 bands belong to one type of center (M center), while M4 should be attributed to another type. It should be noted that we failed to find the splitting of the upper state $|^4G_{5/2}, ^4G_{5/2}\rangle$ for the doubly excited ions within our best laser resolution ~ 0.07 cm^{-1}. This agrees with the results of [7] for Nd^{3+} pair ions in LaF_3 crystal, where a splitting was observed for the energy level corresponding to a pair with a single excited ion, and no splitting was observed for double excited ions.

For a study of the energy transfer between M sub-levels, we measured the dynamics of the absorption change by varying the optical time delay between the pump and probe pulses. Changes of the absorption coefficient (ΔK) induced by the pump into the most intensive absorption bands M1 and M2 at different pump/probe delay time are shown in Fig. 4A and B, respectively. At zero delay time, only one hole–antihole pair is observed.

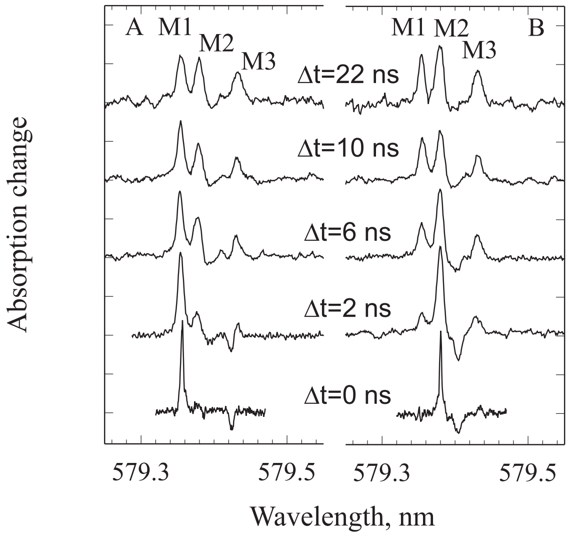

Fig. 4. Absorption change of the M center spectrum under pumping into the M1 (A) and M2 (B) bands for different pump/probe delay times.

As delay time increases, non-resonant holes arise and at $\tau_d = 22$ ns, the relation between peaks in the spectra of the absorption changes is close to the relation of the band intensities in the absorption spectrum of M center without pump radiation (Fig. 1). We also observe a rapid disappearance of the antiholes as τ_d increases. Note that the $^4G_{5/2}$ excited state lifetime of the M center is ~ 5 ns [16]. After multi-phonon relaxation, this neodymium center relaxes to the $^4F_{3/2}$ metastable level. The lifetime of the metastable level of the M center (95 μs [9]) exceeds considerably dephasing and population relaxation times on ground $^4I_{9/2}$ and excited $^4G_{5/2}$ states.

For the description of the energy transfer dynamics between the M1 and M2 levels, we will use a parameter $\delta_i = \Delta K_i / K_i$, where K_i is the absorption peak value and ΔK_i is the absorption change. This parameter exhibits the relative absorption change and does not depend on the transition cross-section and is proportional to the relative population change. At delay time $\tau_d = 0$, it differs from zero only for the transition in resonance with pumping wavelength. Fig. 5 demonstrates the dependence of the ratio of δ_{nr} (non-resonant transition) to δ_p (pumped transition), as a function of τ_d,

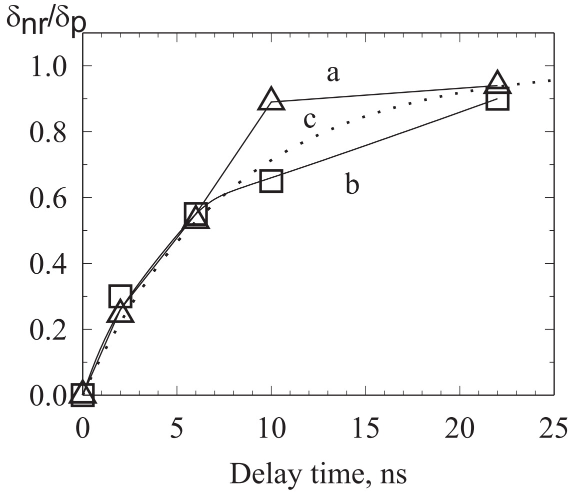

Fig. 5. The ratio of the relative absorption change δ_{nr} (non-resonant transition) to δ_p (pumped transition) versus the delay time under pumping of the M1 (curve a) and M2 (curve b) bands at 8 K. Dotted line shows an exponential relaxation fitting curve with relaxation time of 8 ns.

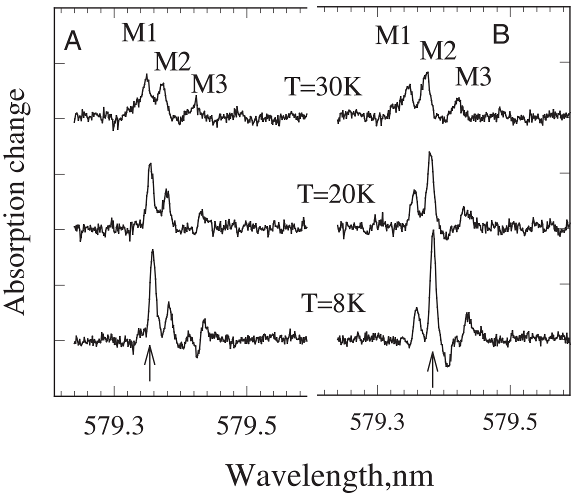

Fig. 6. Absorption change of the M center spectrum under pumping into the M1 (A) and M2 (B) bands for different temperatures.

when the M1 (curve a) and the M2 (curve b) bands were pumped at 8 K. At $\tau_d = 22$ ns, both dependencies approach 1. This corresponds to an equal population change of the studied transitions. The dotted curve demonstrates an exponential increase of the δ_n/δ_p ratio versus τ_d with an estimated energy redistribution time of about 8 ns between the M1 and M2 bands.

This time of the energy redistribution has a strong dependence on the temperature. In Fig. 6, one can see the absorption changes for laser excitation into the M1 (A) and M2 (B) for the temperatures 8, 20, and 30 K and a pump/probe delay of 2 ns. At 8 K, the resonant absorption change significantly exceeds the non-resonant absorption changes. However, already at 30 K, the pump/probe spectrum is similar to the non-saturated absorption spectrum (Fig. 1, curve a). This means that the population redistribution at 30 K is significantly faster than the time resolution of the experiment. We thus estimate, that the rise of the temperature from 10 to 30 K leads to a reduction of the energy redistribution time from ~8 ns to less than 2 ns.

The redistribution rate between M1 and M2 levels ($\tau = 8$ ns at $T = 8$ K) is close to the rate of the direct relaxation process between the lowest and the second Stark levels in the $^4I_{9/2}$ ground (35 cm^{-1} gap) and the $^4G_{5/2}$ excited (61 cm^{-1} gap) states. The latter time was measured in EPR and photon-echo studies [11,12]. Due to the coincidence of these times, we suggest that the energy redistribution time between M sub-levels is determined by the non-radiative rates of the inter-Stark transitions of the ground and excited states. It should be noted that the rate of the direct phonon relaxation process is proportional to the phonon density of states and to the cube of the phonon frequency. From the above, we can neglect the direct transitions within the fine splitting levels with $\Delta E \approx 2$–$3\ \mathrm{cm}^{-1}$ in comparison with phonon relaxation process between Stark levels with $\Delta E \approx 35$–$61\ \mathrm{cm}^{-1}$ [11,12]. The observed increase of the relaxation rate on heating from 10 to 30 K is also in a good agreement with the temperature dependence of the rate of the direct relaxation process [12]. These rates of relaxation processes strongly exceed the energy transfer rates between different neodymium centers [15]. All these clearly demonstrate that the fine level structure is the result of level splitting due to intra-pair interactions.

As one can see from the Fig. 4, at delay time $\tau_d = 0$, holes are observed only at the pumping wavelength. This means that the absorption into the M1–M3 bands occurs from different sub-levels of the ground state. This was verified in Ref. [13], where the matrix elements of the transitions between triplet–singlet sub-levels of the ground state and the fine level structure of the exited state were calculated. In particular, it was shown that transitions from triplet and singlet sub-levels occur to different sub-levels of the fine structure of the excited state. The population relaxation among sub-levels of the ground and exited states leads to holes at non-resonant transitions.

Fig. 7 shows the dynamics of the N center absorption changes under pumping of the N_1 (Fig. 7A) and N_2 (Fig. 7B) bands. The $^4G_{5/2}$ excited state lifetime of N center is 3.4 ns [16], that is shorter than that of the M center (5.3 ns) and than the duration of the excitation. Such a short lifetime and large splitting and also the broadening of the N center bands do not allow us to observe the excited state absorption of the N center. Spectra A and B are considerably different at $\tau_d = 2$ ns. The saturation of the N1 band only slightly affects the absorption of the non-resonant N2 band. However, the pumping of the N2 band leads also to a large absorption decrease for the N1 band. At a delay time of $\tau_d = 22$ ns, spectra A and B become similar, however, unlike the M center, they are different from the initial absorption spectra in the absence of the laser saturation (Fig. 1). As one can see at a delay time of $\tau_d = 22$ ns, the absorption change in the N1 band is more than it is in the N2 band for pumping of either of the two bands. We attribute this fact to the influence of the excited Nd^{3+} ion on the absorption spectra of the other ions in the cluster. After the excitation of one of the four Nd ions to the $^4G_{5/2}$ state $\left(|4(^4I_{9/2})\rangle \rightarrow |3(^4I_{9/2}), ^4G_{5/2}\rangle\right)$ it relaxes fast to the metastable level $|3(^4I_{9/2}), ^4G_{5/2}\rangle \rightarrow |3(^4I_{9/2}), ^4F_{3/2}\rangle$. The N center lifetime of the metastable level is 35 μs [9]. As this exceeds considerably all time intervals of the measurements, the relaxation from metastable level can be neglected. Thus, the absorption changes at $\tau_d = 22$ ns can be caused by both decreasing absorption of the $|4(^4I_{9/2})\rangle \rightarrow |3(^4I_{9/2}), ^4G_{5/2}\rangle$ transition and increasing absorption of the $|3(^4I_{9/2}), ^4F_{3/2}\rangle \rightarrow |2(^4I_{9/2}), ^4F_{3/2}, ^4G_{5/2}\rangle$ transition. The fast spectral redistribution among the N1–N3 bands (< 10 ns) shows that the N1–N3 bands belong to one center type (N center). Excitation of the N4 band does not change the absorption of the other bands, and should be attributed to another center type.

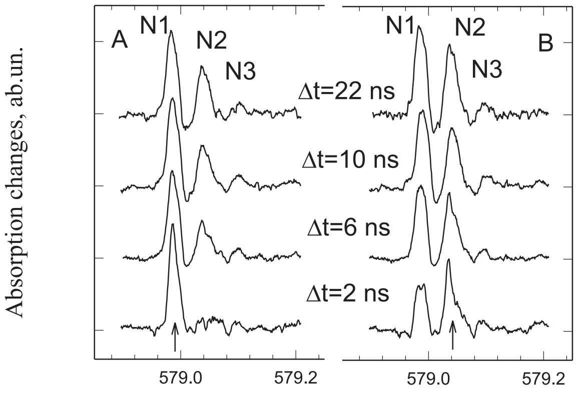

Fig. 7. Absorption change of the N center spectrum under pumping into the N1 (A) and N2 (B) bands for different pump/probe delay times.

In this paper, an attempt was made to observe cooperative luminescence where one photon is emitted by the doubly excited aggregate center. The emitted photon frequency is then equal to the sum of the two or more frequencies corresponding to the $|^4G_{5/2}, ^4G_{5/2}\rangle \rightarrow |^4I_{9/2}, ^4I_{9/2}\rangle$ ($\lambda = 289$ nm) and $|^4F_{3/2}, ^4F_{3/2}\rangle \rightarrow |^4I_{9/2}, ^4I_{9/2}\rangle$ ($\lambda = 432$ nm) transitions. For this purpose, the radiation of the two lasers with a high pulse energy up to 0.2 mJ was focused on the sample. The first laser radiation was adjusted to one of the M (or N) center absorption bands, corresponding to the excitation of one ion; the second laser radiation wavelength was tuned around this band. Under this excitation, we observed an anti-Stokes luminescence corresponding to the single ion transition $^4D_{3/2} \rightarrow {}^4I_{9/2}$ with a wavelength as short as 354 nm. The luminescence decay was about 100 and 50 ns for M and N centers, respectively. However cooperative luminescence could not be observed with a lowest detection limit of 10^{-4} of the $^4D_{3/2}$–$^4I_{9/2}$ upconversion fluorescence intensity.

4. Conclusion

The absorption transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ of Nd^{3+} ions in M (N) pair (quartet) optical centers in CaF_2 crystals were investigated by the time-resolved spectral hole burning technique. The spectral hole–antihole pairs were observed under the pair Nd ion excitation. Time-resolved absorption spectra transformations were studied at 8–30 K. It was shown that the structure of the excited level splittings is caused by strong coherent Nd–Nd ion interactions. The strong coherent ion–ion interaction leads to total 2.3 (3.3 cm^{-1}) splittings of the Stark levels of the $^4G_{5/2}$ excited state. In the pair (M) centers, it was shown that antihole corresponds to an excitation from a singly to a doubly excited ion pair ($|^4I_{9/2}, {}^4G_{5/2}\rangle \rightarrow |^4G_{5/2}, {}^4G_{5/2}\rangle$). An electronic energy level diagram, including singly and doubly excited states, was deducted for a strongly interacting pair. The study of the excitation transfer dynamics between M1 and M3 sublevels suggests that the estimated time (~8 ns) corresponds to one phonon non-radiative relaxation transitions between Stark levels in the ground and excited states.

In the N centers, a complicated dynamics of the N2 band absorption saturation is observed, which is explained by significant absorption of singly excited centers from a metastable level ($|3(^4I_{9/2}), {}^4F_{3/2}\rangle \rightarrow |2(^4I_{9/2}), {}^2G_{5/2}, {}^4F_{3/2}\rangle$).

Acknowledgements

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