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SPECTROSCOPY OF ION PAIRS IN BINUCLEAR COMPOUNDS; CsCdBr₃:Pr³⁺

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The spectroscopy of pairs of rare-earth ions is demonstrated for Pr³⁺:CsCdBr₃. For reasons of charge compensation only two definite types of Pr³⁺ pairs are formed independent of concentration. Only the pair with the Pr³⁺ ions as direct neighbors shows upconversion. The dynamics of this upconversion process is studied by time-resolved spectroscopy and discussed in the energy level schemes of the single ions, and the pair.

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Coupled pairs of 3*d* and 4*f* ions offer a number of new physical effects as compared to the single ions which are of interest for basic research as well as for applications. We are mainly interested in optical effects of coupled ions in incoherent as well as in coherent radiation fields. In incoherent fields the following effects have been found:

1. Cooperative absorption and emission of photons [1]. This effect means that two ions can absorb or emit a photon of the sum energy

$$h\nu = h\nu_A + h\nu_B, \quad (1)$$

where $h\nu_A$ and $h\nu_B$ are energy differences on the ions *A* and *B*, respectively. The cooperative absorption or emission are caused by the ion-ion coupling, and in terms of perturbation theory they end on or originate from a virtual level.

2. Upconversion by cross relaxation [2]. In this case two excited ions accumulate their excitation energies on one of them transferring it to a higher excited state, whereas the other ion relaxes down to a lower state. In this case we get the emission of a photon

$$h\nu \leq h\nu_A + h\nu_B \quad (2)$$

from a real level.

For ion pairs in coherent radiation fields no experimental results exist yet. Theoretical calculations [3] predict that the resonance splitting Δ of the coupled ion pair depends on the inversion n of the ions

$$\Delta \propto \rho_{\text{exc}} - \rho_{\text{gr}} = n. \quad (3)$$

This means that the resonance frequency of the ion pair becomes inversion dependent, and an intrinsic optical bistability can be expected [3]. The physical explanation for the inversion dependent resonance splitting Δ is that the coupling of the coherent radiation field to the ions overrides the coherent ion-ion coupling resulting in $\Delta = 0$ for full inversion $n = 0$.

The last two pair effects discussed can be used in applications for upconversion lasers, i.e. for lasers with oscillation frequencies higher than the pump frequencies, and for bistable optical components in photonics, i.e. in signal processing with photons. For studying the dynamics of pair effects and for applications statistically formed pairs in doped crystals mostly used so far are not very useful: there are too many pairs of different coupling and orientation, and their spectra overlap one with another and with the single ion spectrum. Therefore, it is necessary to look for binuclear compounds, i.e. compounds in which the optical active ions enter as definite pairs. There are generally two different choices:

1. Stoichiometric compounds, as $\text{Cs}_3\text{RE}_2\text{I}_9$ or $\text{Cs}_3\text{RE}_2\text{Br}_9$ with the $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ structure [4]. The rare-earth (RE) ions enter these compounds as confacial double octahedra. The disadvantage of these compounds is that crystals are complicated to grow, and that they are hygroscopic.

2. Doped compounds as $\text{CsCdBr}_3\cdot\text{RE}$. This compound has the CsNiCl_3 -structure forming confacial chains of CdO_6 octahedra which are separated by the Cs ions [5]. The RE^{3+} ions enter the Cd^{2+} sites. Charge compensation gives rise to the following centers as found by us:

1. Center *c*: $-\text{Cd}^{2+}-\text{Pr}^{3+}-(\text{Cd vacancy})-\text{Pr}^{3+}-\text{Cd}^{2+}-$. This is the classical center by charge compensation in the linear chain discussed already in ESR experiments by McPherson in 1977 [5]. For this center we could not find any pair effects: no resonance splitting of the spectral lines, and no upconversion effects. The optical spectra could be analyzed in the C_{3v} symmetry of the single ions.
2. Center *b*: $-\text{Cd}^{2+}-\text{Pr}^{3+}-\text{Pr}^{3+}-(\text{Cd vacancy})-\text{Cd}^{2+}-$. This is not a real pair system, because the positions of the two Pr^{3+} ions are not identical, but only similar. Indeed, small splittings of the energy levels due to the slightly different crystal fields could be found. Only for this center upconversion ${}^1D_2 \rightarrow {}^3P_1, {}^3P_0$ could be found, and its dynamics has been studied in more detail by time-resolved spectroscopy. The spectrum of this center could be analyzed by the C_{3v} symmetry of the single Pr^{3+} ions, too. In contrast to the center *c* this center is thermodynamically unstable and transforms into the center *c*, at room temperature over weeks and months, at higher temperatures (350°C) within days. This has been the basis for its identification.
3. Center *a*: $-\text{Cd}^{2+}-\text{Pr}^{3+}-\text{Cd}^{2+}-(\text{Cs vacancy})-$. It is an "asymmetric" single ion center of reduced symmetry. Its spectrum could be analyzed by C_s symmetry.

The selectively excited 1D_2 -fluorescence of the centers *a* and *c* decays almost identically with a decay time of $137 \mu\text{s}$. The 1D_2 fluorescence of the *b* center is different: it shows a steep decay with a time constant of $2.3 \mu\text{s}$ over the first one or two decades, and then it decays the same way as the other two centers. This already shows the influence of the upconversion process on this center. The strongest upconversion fluorescence was found for the transition $^3P_0 \rightarrow ^3H_4$, and a weaker one for $^3P_1 \rightarrow ^3H_5$. The strongest upconversion fluorescence was found for "new" crystals. It decreased with age or after annealing according to the already mentioned conversion of the *b* to *c* centers. The fact that the upconversion fluorescence is created by the *b* centers is best verified by excitation spectroscopy. The excitation spectrum of the upconverted fluorescence is identical with the excitation spectrum of the 1D_2 Stokes fluorescence of the *b* centers only.

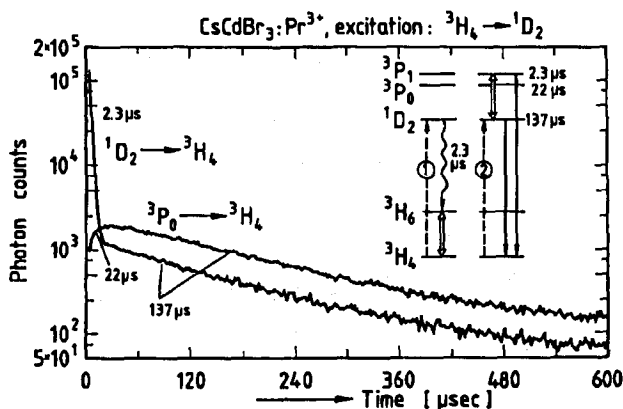


Fig. 1. Time dependence of the Stokes fluorescence $^1D_2 \rightarrow ^3H_4$ and the upconverted fluorescence $^3P_0 \rightarrow ^3H_4$ after pulse excitation $^3H_4 \rightarrow ^1D_2$. $T = 4.2 \text{ K}$.

Figure 1 shows the dynamics of the upconversion process after pulse excitation ($\approx 5 \text{ ns}$) into the 1D_2 level. The 1D_2 fluorescence shows the typical double decay mentioned above. The 3P_1 fluorescence was too weak to measure its time dependence accurately. The 3P_0 fluorescence is obviously fed via the 3P_1 level, because there is no energy resonance for a cross relaxation to populate the 3P_0 level directly. Its fluorescence rises with its intrinsic lifetime, and decays with the time constant of $137 \mu\text{s}$ common to all long-term decays. This means that all the long-term decays are fed from the same electronic energy reservoir with this lifetime. The insert gives an explanation of the dynamics in the usually used single-ion picture. For upconversion both ions have to be excited into the 1D_2 level. Then ion one relaxes down to the 3H_6 level in about $2.3 \mu\text{s}$, the time constant of the short time decay of the 1D_2 fluorescence. Now the cross relaxation process responsible for the upconversion becomes active: $^3H_6 \rightarrow ^3H_4$ for ion one, $^1D_2 \rightarrow ^3P_1$ for ion two. The levels 3H_6 and 1D_2 are the feeding levels of the upconversion process, and their common lifetime determines the long-term decay of all upconverted as well as the Stokes fluorescences. The common lifetime of the feeding levels is mainly

determined by the lifetime of the 1D_2 level, the lifetime of 3H_6 is expected to be much longer. This explanation suffers from the physically unrealistic assumption that the lifetimes of the 1D_2 levels of the two ions are drastically different, $2.3 \mu\text{s}$ and $137 \mu\text{s}$, respectively. Furthermore, a fast radiationless relaxation $^1D_2 \rightarrow ^3H_6$ is unrealistic, too because of the large energy gaps between the electronic levels as compared with the maximum phonon energies of the crystal of about 150 cm^{-1} .

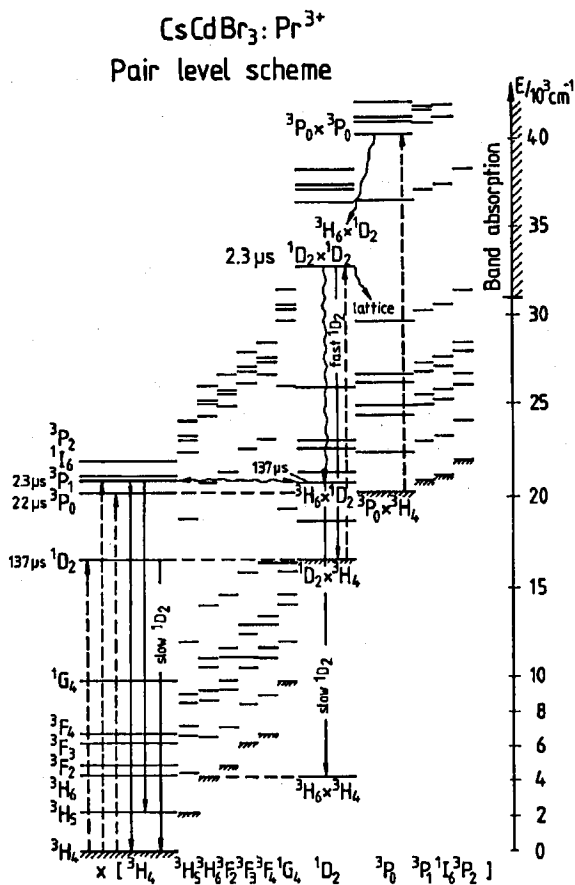


Fig. 2. Ion-pair energy level diagram for two coupled Pr^{3+} ions with the transitions relevant for the upconversion dynamics.

A more realistic explanation of the upconversion process can be given in an ion-pair energy level diagram as given in Fig. 2. This energy level diagram is suggested by the fact that upconversion needs strong ion-ion coupling because it was found only for the direct neighbors in the b center. In this energy level diagram it is obvious that the doubly excited state $^1D_2 \times ^1D_2$ can have another lifetime than the lower states $^1D_2 \times ^3H_6$ and $^1D_2 \times ^3H_4$. First of all, it is in resonance with a band absorption of the lattice [6], and furthermore the electronic energy gaps below it

are much smaller in the pair scheme than in the single-ion one. The feeding state for the upconversion is now the state ${}^3H_6 \times {}^1D_2$ which is in resonance with the ${}^3P_1 \times {}^4H_4$ state responsible for the upconversion fluorescence. The use of the pair energy level diagram implies that the ion-ion coupling is stronger than the other dynamical interactions of the ions, the interactions with the phonons and with the radiation field.

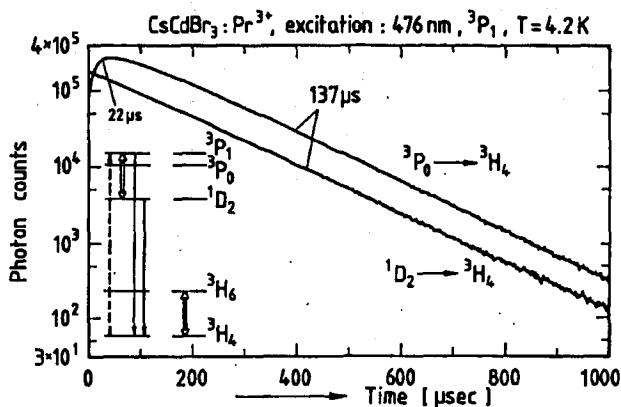


Fig. 3. Fluorescence decay of the levels 3P_0 and 1D_2 after 3P_1 excitation.

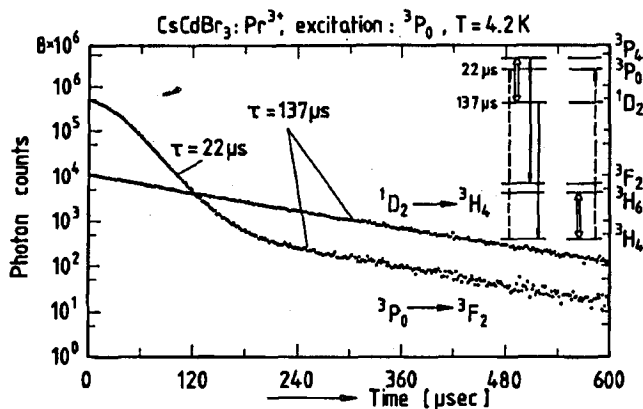


Fig. 4. Fluorescence decay of the levels 3P_0 and 1D_2 after 3P_0 excitation.

Figure 3 shows the fluorescence decays of the levels 3P_0 and 1D_2 after excitation into the level 3P_1 . 3P_1 - 3H_5 fluorescence could be found, too. It was quite weak and had a lifetime of $\approx 2.3 \mu\text{s}$. Within the errors of the experiment it is the same value as for the lifetime of the doubly excited state ${}^1D_2 \times {}^1D_2$. It is not clear to us yet if this is only an accidental coincidence, or if it has some physical mean-

ing. Both fluorescences from 3P_0 and 1D_2 show again the same long-term decay of $137 \mu\text{s}$. This fact, and the fact that the exponential 1D_2 decay starts immediately after the excitation pulse mean that the 3P_1 excitation results simultaneously in an excitation of the resonant ${}^3H_6 \times {}^1D_2$ level. This level is responsible for the slow 1D_2 fluorescence observed, and it is the feeding reservoir for the long-term 3P_0 fluorescence.

Figure 4 shows finally the fluorescence decay of the levels 3P_0 and 1D_2 after 3P_0 excitation. The long-term decay is again the same as before. For short times the 3P_0 decays with its intrinsic lifetime of $22 \mu\text{s}$. The undelayed fluorescence of the 1D_2 level, and the common long-term decay of both levels 3P_0 and 1D_2 indicate that the pair level ${}^3H_6 \times {}^1D_2$ has been excited either directly or via the doubly excited state ${}^3P_0 \times {}^3P_0$ followed by a fast relaxation (Fig. 2). It is obvious that these fluorescence decays hardly can be explained in the single-ion energy level diagrams.

Conclusions

1. The experiments have shown that in $\text{CsCdBr}_3:\text{Pr}^{3+}$ exist at least three types of Pr^{3+} centers.
2. Only the *b* center with the Pr^{3+} ions as direct neighbors show upconversion fluorescence.
3. The energy level diagram for the coupled ion pair has to be used to explain the dynamics of the upconversion process.

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