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Spectroscopy and upconversion of $CsCdBr_3:Pr^{3+}$

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In $CsCdBr_3$ the trivalent Pr ions substitute the divalent Cd ions. Charge compensation leads to Pr vacancy centers. By selective excitation and fluorescence spectroscopy and by annealing the crystals, three different Pr centers could be identified. The first one is the well-known symmetric pair center Pr^{3+}–Cd^{2+} vacancy–Pr^{3+}, the second one is the asymmetric pseudopair center Pr^{3+}-Pr^{3+}-Cd^{2+} vacancy, and the third one finally is a Pr^{3+} single ion with a Cs^+ vacancy nearby. Energy-level schemes of all three centers were deduced from polarized site-selective spectra including the symmetries of the crystal-field states. Only the Pr^{3+}-Pr^{3+}-Cd^{2+} vacancy center showed upconversion emission from $^3P_0$ and $^3P_1$ under pulsed $^1D_2$ excitation.

I. INTRODUCTION

$CsCdBr_3$ is a very interesting host material for studying pair effects between rare-earth (RE) ions. It crystallizes in the hexagonal $CsNiCl_3$ structure[1,2] with chains of confacial $(CdBr_6)^{4-}$ octahedra arranged along the threefold crystallographic axis and separated by Cs^+ ions. The trivalent rare-earth (RE) ions easily substitute the divalent Cd ions. This fact requires charge compensation. In the quasilinear crystal structure of the Cd^{2+} chains the number of possible configurations for charge compensation is very limited. This leads to a restricted number of Pr^{3+} centers. We could identify the following three centers (Fig. 1):

(i) The *a* center: Pr^{3+}-Cs^+ vacancy.

The site symmetry of the Pr^{3+} ion is C_S with the mirror plane containing the threefold crystallographic axis. This center of low symmetry has been found by electron paramagnetic resonance (EPR) experiments, too.[3]

(ii) The *b* center: Pr^{3+}-Pr^{3+}-Cd^{2+} vacancy.

Since both Pr^{3+} sites are crystallographically not equivalent we have to deal with a pseudopair. The site symmetry of both Pr^{3+} ions is C_{3v}. This asymmetric or pseudopair center has already been proposed in the literature for other RE ions in $CsCdBr_3$ as for Nd^{3+},[4] Er^{3+},[5,6] and Ho^{3+}.[7] In all these cases the *b* center has been described as a minority center of little interest. In our experiments on Pr^{3+}-doped $CsCdBr_3$ it turned out to be the only center giving rise to upconversion emission. The excitation lines for upconversion have been found already by Ramaz *et al.*[8], but have been interpreted as belonging to the symmetric pair center Pr^{3+}-Cd^{2+} vacancy–Pr^{3+} called the *c* center by us. Upconversion by the asymmetric pair center has yet been identified only by us for Pr^{3+} (Ref. 9) and by Goldner and Pellé[6] for Er^{3+}, in the latter case by broad-band laser excitations covering the slightly different frequencies of the pair partners.

(iii) The *c* center: Pr^{3+}-Cd^{2+} vacancy–Pr^{3+}.

This is the "classical" RE center in $CsCdBr_3$ mostly discussed in the literature and identified by McPherson and Henling[1] by EPR experiments on Gd^{3+}. Many authors report that about 90% and more of the RE ions enter the crystal as pairs of this type.[8,10,11] Upconversion is usually reported from doubly excited states of these symmetric pairs, e.g., for Ho^{3+},[12] Tm^{3+},[13] and Er^{3+}.[5,6,14,15,16] The upconversion process has been explained by a phonon-assisted cross relaxation. In our case of Pr^{3+} for upconversion by cross relaxation, energy gaps of several thousands of wave numbers have to be bridged by the assisting phonons.[9,17] This is unrealistic keeping in mind that the highest phonon frequencies in $CsCdBr_3$ are of the order of 160 cm^{-1} (Ref. 18) or, maybe, 200 cm^{-1} because the crystal consists of heavy ions only. Doping with 1% Pr^{3+} did not change the known Raman spectra[18] as found experimentally.[19] Therefore we[9,17] proposed another process to be responsible for the upconversion: cooperative energy transfer

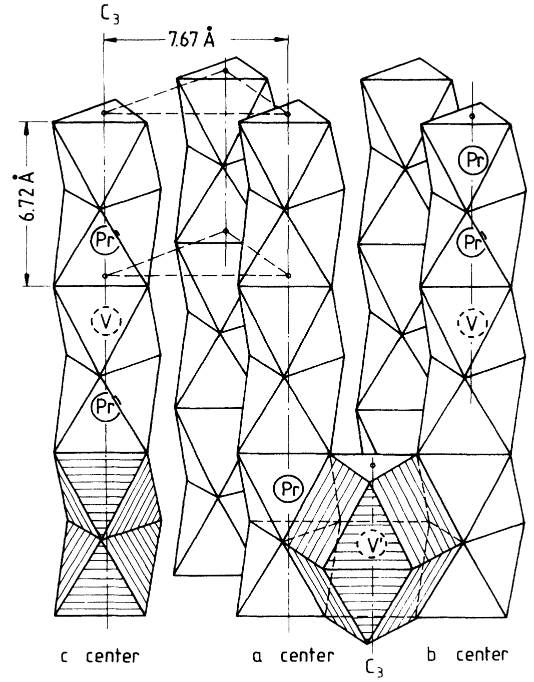

FIG. 1. Structure of $CsCdBr_3$, its unit cell, and the three Pr^{3+} centers. V = Cd^{2+} vacancy, V' = Cs^+ vacancy.

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from the two excited Pr^{3+} ions to electronic excitations of the lattice followed by a relaxation of these excitations and a back transfer of energy to one of the ions transferring it into a higher excited state. This cooperative energy transfer obviously works only for strong ion-ion interaction. Therefore it was found yet only for the asymmetric *b* center, where the Pr^{3+} ions sit on neighboring Cd^{2+} sites and coupling by direct superexchange via the Br^- ions can be expected.

The site symmetry of the single Pr^{3+} ions in the *c* center is C_{3v}, the total symmetry of the pair relative to its center is D_{3d}. As long as the Davydov or resonance splitting of the two ions is hidden in the linewidth, the spectra can be analyzed by the single-ion symmetry C_{3v} as done in this paper.

Section II of the paper describes the crystal growth, experimental procedure, and equipment. In Sec. III the three different centers are defined by means of their crystal-field spectra between the states $^3H_4$ and $^1D_2$. In Sec. IV the upconversion emission is discussed and it is shown that only the asymmetric *b* center is responsible for it. In Sec. V we give information about a number of other states such as $^3P_0$, $^3P_1$, and others.

II. EXPERIMENTAL

The crystals were grown from the starting materials CsBr (suprapur, Merck, Germany), $CdBr_2$, and $PrBr_3$ (both 3*N*, Cerac, USA). The single crystals were grown by the Bridgeman technique in a quartz ampoule by lowering it in a furnace through a temperature gradient of about 15 °C/cm with a speed of about 1 mm/h. The crystals were not tempered. The distribution coefficient of the Pr^{3+} ions turned out to be greater than unity. So the Pr^{3+} concentration was higher in the lower part of the crystal as could easily be seen by its coloration. The concentration of Pr^{3+} in the starting material has been 1% of substituted Cd^{2+} ions. The crystals were of good optical quality. The crystal structure has been checked by x-ray diffraction. Powdered samples gave Debye-Scherrer photographs of good quality and verified the crystallographic data given by McPherson, McPherson, and Atwood.[2] Single crystals did not give satisfactory diffraction patterns, neither by the Laue nor by the Bragg method. This demonstrates that our doped crystals did not have a satisfactory long-range order. A high degree of disorder in $CsCdBr_3$ due to stacking faults has already been discussed by Wolfert and Blasse.[20] Furthermore, a quite strong statistical deviation of the Pr^{3+} pair axes from the macroscopic crystallographic axis by $\sigma_e \approx \pm 11°$ degrees was measured by hole-burning spectroscopy.[21] Another interesting feature of $CsCdBr_3$ is its high optical refractive index and its high birefringence[22] as shown in Fig. 2. The high refractive index has the consequence that in a crystal plate only $\frac{1}{6}$ of the full solid angle is available for direct escape of the fluorescence emission out of the crystal. The rest of the fluorescence has to leave the crystal in a more or less undefinite way after multiple internal reflections. This together with the high birefringence of the crystal may be the reason for the relatively poor degree of polarization of the fluorescence spectra. This idea is supported by the fact that the absorption spectra, where the total reflection of the light inside the crystal is of no importance, were well polarized. The excitation spectra showed an acceptable degree of polarization too.

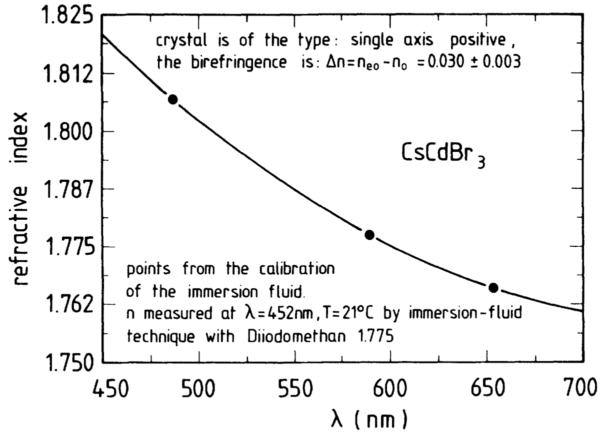

FIG. 2. Optical refractive index of $CsCdBr_3$ and its birefringence (Ref. 22).

The fluorescence of the crystals was excited by a tunable dye laser pumped by a N_2 laser.[23] The spectra were recorded with a 3m McPherson spectrometer. The fluorescence signal was detected by a cooled Hamamatsu R 943-05 photomultiplier in photon-counting regime. The crystal was immersed in liquid helium at 1.6 K or in helium gas at 4.2 K. In some cases the fluorescence was excited by a Spectra-Physics M 380 tunable dye-ring laser pumped by an argon laser.

III. $^3H_4 \longleftrightarrow {}^1D_2$ SPECTRA

Definition of the three centers

The three centers were identified by their spectra according to the following procedures. First an absorption spectrum was taken to find the strongest lines and the spectral region of the $^3H_4 \rightarrow {}^1D_2$ (Fig. 3) absorptions. To complete the absorption spectrum an excitation spectrum (Fig. 4) of the total fluorescence was taken giving the weaker absorptions, too. After that the dye laser was tuned on every excitation line and the resulting fluorescence spectra were recorded. Three basically different fluorescence spectra Figs. 5(a), 5(b), and (5c) were found. These fluorescence spectra were attributed to three different Pr^{3+} centers labeled *a*, *b*, and *c*. The structure of these centers was determined later on by group-theoretical methods and by annealing the crystal. Some of the fluorescence spectra turned out to be superpositions of two of the basic ones indicating overlapping absorption lines of two different centers.

To check the classification of the fluorescence spectra by the three centers, excitation spectra of all fluorescence lines were taken. As expected we found three basically different excitation spectra, one for each center.

Now, for every center the polarizations of the best excitation and fluorescence spectra were determined and a

C_{3v}

Crystal - field splittings of the free - ion states

J	Γ_1	Γ_2	Γ_3
0	1		
1		1	1
2	1		2
3	1	2	2
4	2	1	3
5	1	2	4
6	3	2	4

Selection rules for electric dipole radiation

C_{3v}	Γ_1	Γ_2	Γ_3
Γ_1	π	-	σ
Γ_2	-	π	σ
Γ_3	σ	σ	σ,π

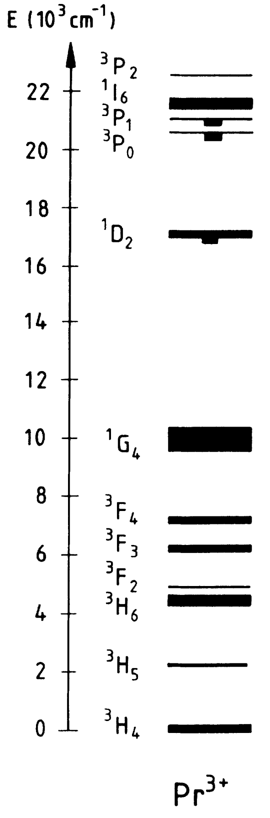

FIG. 3. The free-ion states of Pr^{3+}, their crystal-field splittings, and the selection rules for electric dipole transitions in C_{3v} symmetry.

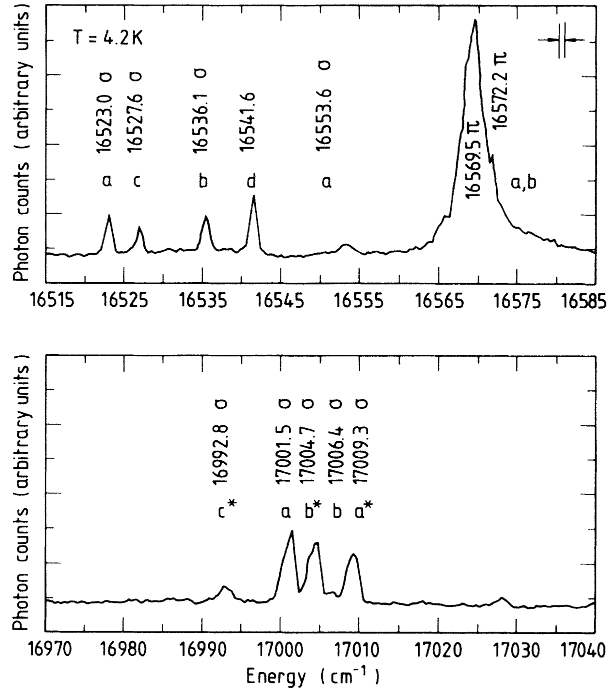

FIG. 4. Excitation spectra of the total $^1D_2$ fluorescence. Temperature of the crystal is 4.2 K. The spectral resolution is shown. The lines belonging to the three different centers are labeled *a*, *b*, and *c*. *d* stands for an excitation line which did not show a definite fluorescence spectrum. The lines with an asterisk are the lines used to excite the pure characteristic fluorescence spectra of the corresponding center. Polarizations are labeled by $\sigma(E \perp C_3)$ and $\pi(E \parallel C_3)$.

group-theoretical analysis was performed. The symmetries of the crystal-field components and the selection rules for electric dipole transition between them are given in Fig. 3 for C_{3v}. The spectra for the *b* and *c* centers could be analyzed by this symmetry. It is expected for Pr^{3+} ions substituting the Cd^{2+} ions and having the charge compensation by a Cd^{2+} vacancy on the C_3 axis (Fig. 1). The resulting energy-level diagrams for both centers are shown in Fig. 6. The decision which spectrum belongs to which pair could be done by optical bleaching and/or by annealing the crystal at 350 °C for 48 h. The asymmetric *b* center (Fig. 1) is obviously thermodynamically less stable than the symmetric *c* center. By annealing the crystal it should be possible to transform the *b* center into the *c* center. Indeed we could find a relative change of the intensity of the *b* and *c* spectra, whereas the spectra of the *a* center remained unchanged. The spectrum which decreased in intensity was attributed to the unstable *b* center, the other spectrum which increased in intensity to the stable *c* center. The same effect could be achieved by optical bleaching: tuning a strong laser beam on a *b* absorption line. The resulting phonon emission by radiationless transition obviously transforms the *b* center into the *c* center, too. This seems to be the physical effect behind the yet unexplained persistent spectra hole burning[24] of the *b* center transition at $\tilde{\nu}=17\,004\ \mathrm{cm}^{-1}$.

The spectra of the *a* center contain more lines than the spectra of the *b* and *c* centers. This means that this center has a lower symmetry than the other two. Symmetry reduction from C_{3v} offers only two possibilities: C_3 and C_S. In both cases the degeneracy of the free ion states is completely lifted and no decision between the two site symmetries can be made on this basis. But looking at the crystal structure a site of C_S symmetry is very plausibly made up by a single Pr^{3+} ion on a Cd^{2+} site with a Cs^+ vacancy in the next neighborhood for charge compensation (Fig. 1). Figure 7 gives the energy-level scheme of the *a* center based on C_S symmetry.

It is interesting to compare the energy-level diagrams of the three centers. The energy-level diagrams for the two pair centers *b* and *c* (Fig. 6) are very similar. Comparing them with Fig. 3 shows that not all components of the crystal-field splitting could be found. The energy-level diagram of the *a* center (Fig. 7) nicely demonstrates the level splitting by symmetry reduction: The doubly degenerate levels Γ_3 in C_{3v} symmetry split into a Γ_1 and a Γ_2 component in C_S. The similarity of the energy-level schemes of all three centers demonstrates that the crystal-field splitting is mainly due to the bromium octahedra around the Pr^{3+} ions and that the charge compensation in the second neighborhood does not change

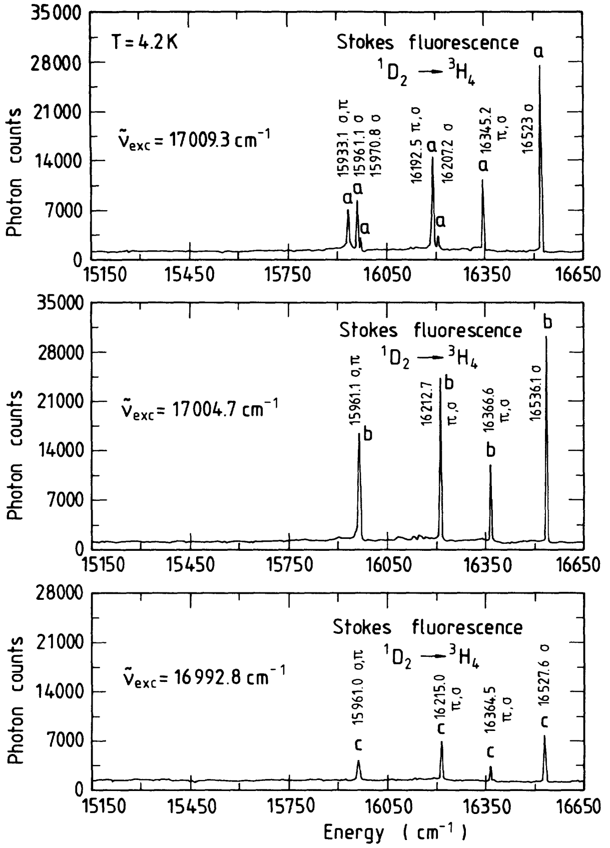

FIG. 5. Fluorescence spectra which define spectroscopically the three different centers *a*, *b*, and *c*. For a new crystal the ratio of the intensities of the spectra was about 1:1:0.2, respectively. For the excitation lines see Fig. 4. In case of mixed polarizations the first label means the dominant one in this and in all following figures.

the even part of the crystal field significantly. Interesting in this context is the fact that the crystal-field components of the Pr^{3+} ions in the asymmetric *b* center show a pronounced doublet structure for the $^1D_2$ state. It is obviously due to the two different sites in this pseudopair. Unfortunately, this doublet structure could not be resolved for the crystal-field components of $^3H_4$. The reason is that the spectrometer used for taking the fluorescence spectra had a lower spectral resolution than the tunable laser used for the excitation spectra.

IV. UPCONVERSION EMISSION

Upconversion fluorescence by $^1D_2$ excitation was found from the states $^3P_0$ and $^3P_1$. The population of $^3P_0$ takes place dominantly via the $^3P_1$ level by a strong radiationless relaxation as was shown by its fluorescence dynamics.[9,17] Because of its short lifetime of some μs the $^3P_1$ fluorescence is quite weak. The strongest upconversion emissions are due to the transitions $^3P_0 \rightarrow {}^3F_2$ and $^3P_0 \rightarrow {}^3H_6$. All transitions found in upconversion are listed in Table I. The most interesting transition is the one from $^3P_0{:}\Gamma_1 \rightarrow {}^3H_4{:}\Gamma_3$. Its final level has the energy of 575 cm^{-1} which corresponds to a crystal-field component of the *b* center. We could not find any upconversion emission which ended on a crystal-field component of the other centers. This fact suggests that only the *b* center shows upconversion. To verify this hypothesis the excitation spectrum of the upconversion fluorescence was taken and compared with the excitation spectra of the Stokes fluorescence of all three centers. The result is shown in Fig. 8. It clearly demonstrates that only the excitation spectrum of the Stokes fluorescence of the *b* center coincides with the excitation spectrum of the upconversion. This proves that only the *b* center shows upconversion and that all transitions and levels given in Table I belong to this center.

Another interesting question is the order of the upconversion process. It can be determined by the dependence of the intensity of the upconversion fluorescence on the power of the exciting radiation. This dependence is shown in Fig. 9. It is given for a crystal after three different treatments. The highest upconversion efficiency was achieved for the new crystal immediately after the growing procedure. After a number of experiments with laser irradiation into the upconverting lines the efficiency of upconversion decreased gradually. One example for this effect is shown in Fig. 9 by the curve with the second highest efficiency. The efficiency of the upconversion could be decreased further by annealing the crystal for 48 h at 350 °C. In all three cases the power dependence of the upconversion process is quadratic indicating a two-photon process. Because the order of the process did not change by the treatments of the crystal we conclude that the observed decrease in the upconversion efficiency is not due to a change in the physical process behind it but simply by a reduction of the number of active centers. This has been the fingerprint for the assumption that the thermodynamically less stable *b* center transforms into the *c* center under resonant laser irradiation and under annealing as discussed already above.

The excitation spectrum of the Stokes fluorescence of the *b* center shows an interesting doublet structure already mentioned. It does not show up in Fig. 8 for lack of resolution but it is indicated in the energy-level scheme in Fig. 6. This doublet is actually a pseudodoublet each level belonging to Pr^{3+} ions on two slightly different sites (Fig. 1). This statement is proved by the different fluorescence spectra resulting from selective excitation into the two doublet levels. The best example is the pseudodoublet $\Gamma_3{:}{}^1D_2$ at 17 004.7, 17 006.4 cm^{-1}. Excitation into the lower level results only in Stokes fluorescence as can be seen in Fig. 5. This fluorescence spectrum was used to define the *b* center spectroscopically. But excitation of the higher pseudodoublet level gives Stokes as well as upconversion fluorescence. Both emissions together are given in Fig. 10. Analogous behavior shows the lower $\Gamma_3{:}{}^1D_2$ pseudodoublet at 16 536.1, 16 537.3 cm^{-1}. Again excitation of the lower level gives Stokes fluorescence only and excitation of the higher level gives both Stokes and upconversion emission although the latter one is quite weak. Since this pseudodoublet is the lowest crystal-field component of $^1D_2$ this behavior is easy to understand on the basis of energy conservation. For upcon-

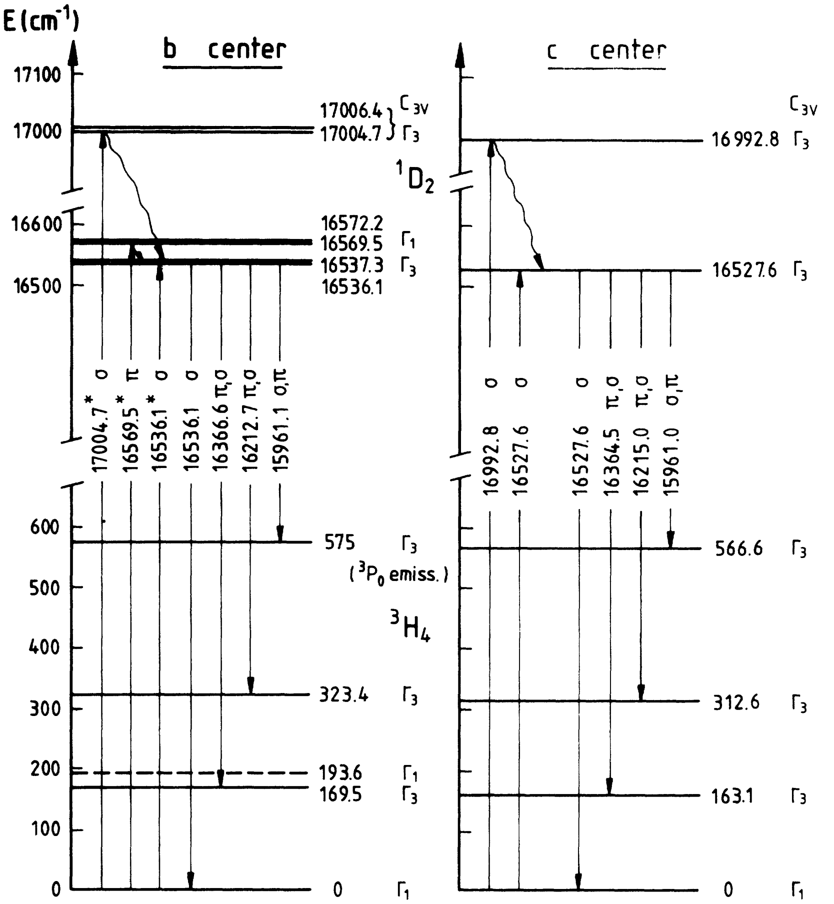

FIG. 6. Energy-level scheme of both of the pair spectra b and c from excitation and fluorescence spectra. For the pseudodoublets of the b center only the transition energy to the stronger component is shown. The level Γ_3:575 cm^{-1} was identified by $^3P_0$ emission, too. The asterisk indicates that this transition was also found in absorption. The broken line means a level found from upconversion fluorescence.

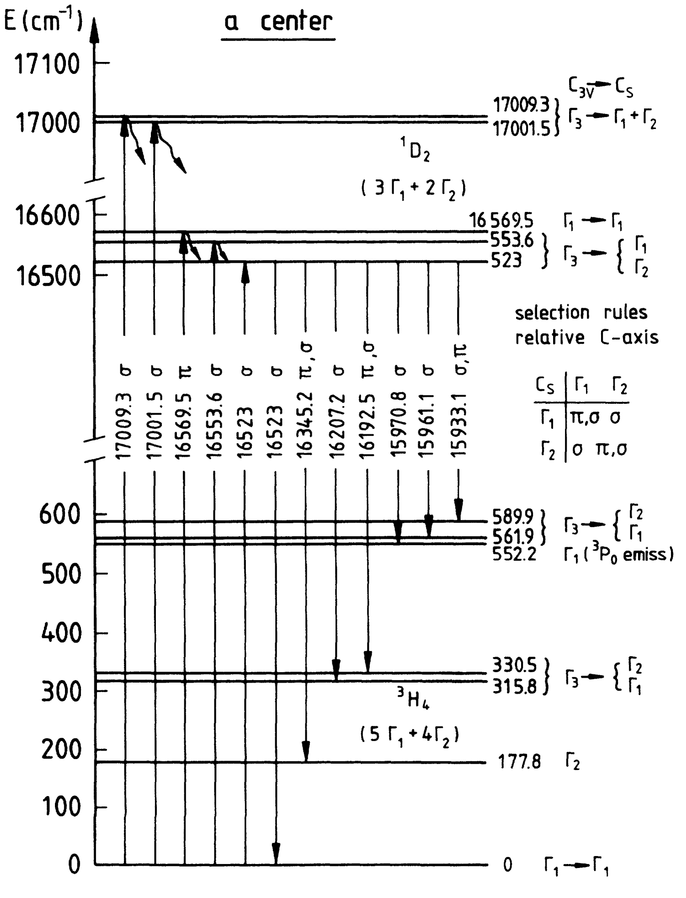

FIG. 7. Energy-level scheme of the single-ion a center from excitation and fluorescence spectra. Symmetry reduction $C_{3v} \rightarrow C_S$ gives $\Gamma_1,\Gamma_2 \rightarrow \Gamma_1$, $\Gamma_3 \rightarrow \Gamma_1+\Gamma_2$. The barycenters of the split Γ_3 levels coincide well with their positions for the b center. The symmetry of the Γ_1 level at 552.2 cm^{-1} was determined by $^3P_0$ emission, too.

TABLE I. Fluorescence transitions found in upconversion. The emitting levels are Γ_1:$^3P_0$ ($\tilde{\nu}=20\,388.3$ cm^{-1}) and $^3P_1$ ($\tilde{\nu}=20\,957$ cm^{-1}). w, s, ss mean weak, strong, and strongest emissions. All transitions belong to the *b* center. Accuracy is about ±2 cm^{-1}.

Transition	Wave number (cm^{-1})	Polarization	Final level (cm^{-1})	
$^3P_0\rightarrow{}^3H_4$	20 388.3	π	0	Γ_1
w	20 194.7	π	193.6	Γ_1
	19 812.9	σ	575.4	Γ_3
$^3P_1\rightarrow{}^3H_5$	18 723.0	π	2233.8	
w	18 695.0	σ	2261.3	Γ_3
	18 409.5	σ	2547.5	Γ_3
$^3P_0\rightarrow{}^3H_6$	16 027.1	σ	4361.2	Γ_3
s	16 014.3	π	4374.0	Γ_1
	15 687.6	σ	4700.7	Γ_3
	15 663.0	π	4725.3	Γ_1
$^3P_0\rightarrow{}^3F_2$	15 315.0	σ	5073.2	Γ_3
ss	15 242.7	σ	5145.6	Γ_3
	15 235.7	π	5152.6	Γ_1

version both ions of the pseudopair have to be excited but the laser frequency is only resonant with one of them. So the only way to get both ions excited is to excite the first one by the laser, to wait for a radiationless energy transfer to the second one, and to reexcite the first one by a second laser photon. If the ion with the higher energy level is excited directly it can transfer its excitation energy to the other one by ion-ion interaction and by emission of a phonon although this process has quite a low probability in the standard picture of phonon-assisted energy transfer:[25] The electronic matrix elements as well as the phonon phase factors cancel almost completely for nearly identical electronic states and low phonon frequencies, respectively.

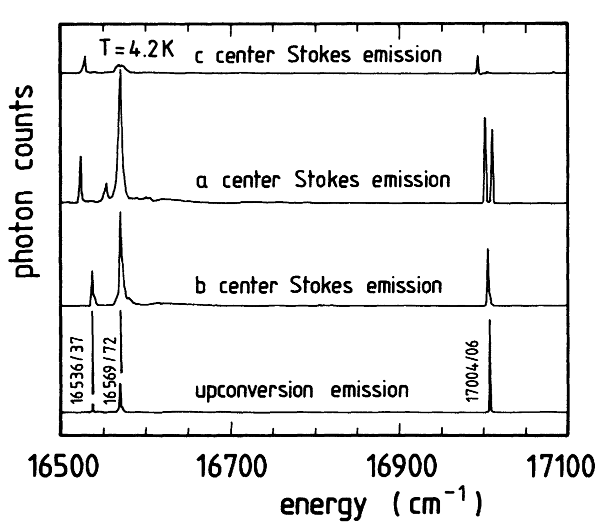

FIG. 8. Excitation spectra of the Stokes fluorescence from $^1D_2$ of all three centers in comparison with the excitation spectrum of the upconversion emission from $^3P_0$.

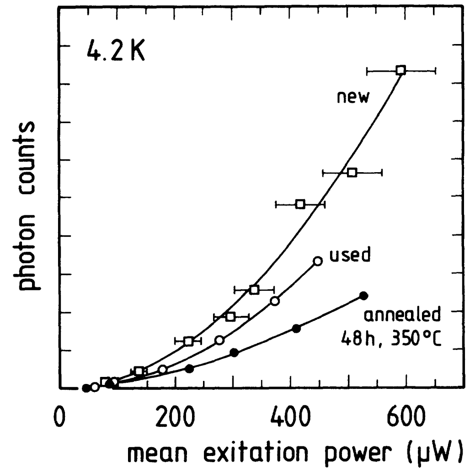

FIG. 9. Dependence of the intensity of the upconversion fluorescence on the excitation power. The lines are fitted quadratic parabolas. The curves are given for a new crystal, the same crystal after performing a number of upconversion experiments, and after annealing it. The pulse width of the exciting laser was 4 ns and its repetition frequency 35 Hz.

If the ion with the lower energy level is excited there is no chance for energy transfer to the other ion at low temperature because there are no phonons available to conserve the overall energy. So the second ion cannot be excited and the first one has to emit its energy by Stokes fluorescence only, as observed.

Having in mind this explanation and coming back to the higher Γ_3 pseudodoublet at 17 004.7, 17 006.4 cm^{-1} discussed above, one comes to the conclusion that the fast radiationless relaxation between the higher and the lower Γ_3 components of $^1D_2$ must be an isolated process on each ion, i.e., there is no energy transfer between the ions of the pair during this relaxation. Otherwise selective excitation of both pseudodoublet levels of the higher Γ_3 state should result in more or less identical Stokes and anti-Stokes fluorescence spectra. This explanation is physically plausible: radiationless relaxation with energy

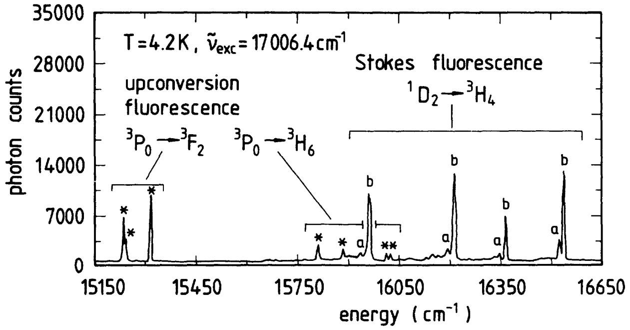

FIG. 10. Upconversion and Stokes fluorescence by excitation of the upper level of the pseudodoublet $\tilde{\nu}=14\,004.7$, 14 006.4 cm^{-1}. The asterisks denote the upconversion lines. The weak lines of the *a* center are due to spectral overlap.

transfer between the ions is a process of one order higher in perturbation theory than the direct relaxation within the same ion because it needs ion-ion interaction in addition to the ion-phonon coupling.

High-resolution excitation spectra of the Stokes and upconversion emissions for both Γ_3:$^1D_2$ pseudodoublets are shown in Figs. 11 and 12. In contrast to the other figures shown in this paper they were taken with the tunable dye-ring laser having a cw power of about 300 mW and with crystals of low concentration (0.2%). Both figures show nicely the described difference in the excitation properties of the pseudodoublet lines: The lines of higher energy (16 537.3, 17 006.4 cm^{-1}) show up only in the excitation spectrum of the upconversion emission whereas in the excitation spectrum of the Stokes fluorescence both pseudodoublet lines are present. But, the excitation lines of the pseudodoublet Γ_1:$^1D_2$ at 16 569.5, 16 571.7 cm^{-1} behave quite differently. They both appear in the excitation spectrum of the upconversion as well as of the Stokes fluorescence with comparable intensities. The reason for this different behavior is not yet clear to us. In contrast to the other two doublet transitions this one seems to have a stronger ion-phonon coupling: Its linewidth is relatively wide and the quite strong vibronic sideband belongs to this transition probably, too. Whether this really is the reason for the different behavior of this pseudodoublet still remains an open question.

The vibronic sideband shows a further interesting feature. It appears much stronger in the excitation spectrum of the upconversion than in that of the Stokes emission compared to the electronic transitions. The reason is obviously that the vibronic sideband originates from both ions of the pseudopair. Due to the broad linewidth of the sidebands the laser cannot differentiate between the two ions and excites both of them. So in contrast to the electronic excitation lines no energy transfer is necessary to get both ions excited. This results in the observed higher efficiency of upconversion in the vibronic sideband as compared to the electronic lines.

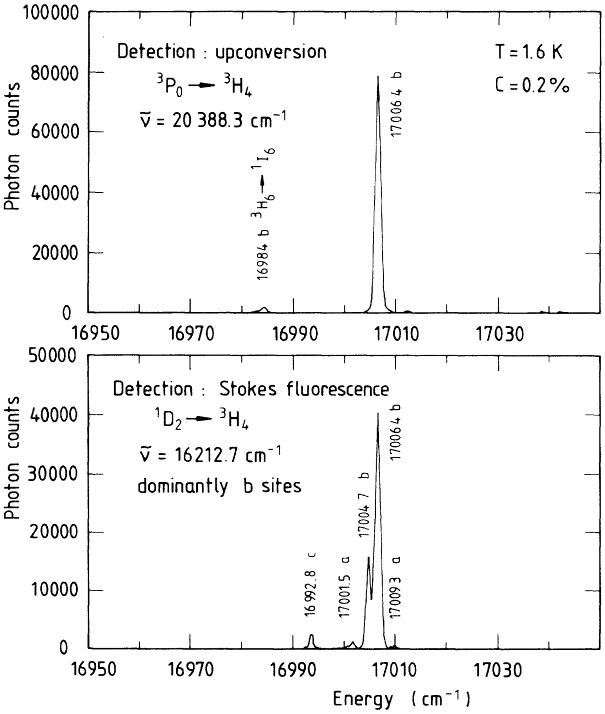

FIG. 11. Excitation spectra of the Stokes and upconversion emissions of the b center with high resolution in the absorption region of the upper Γ_3:$^1D_2$ pseudodoublet; cw excitation with ~300 mW. The small a and c lines are due to spectral overlap.

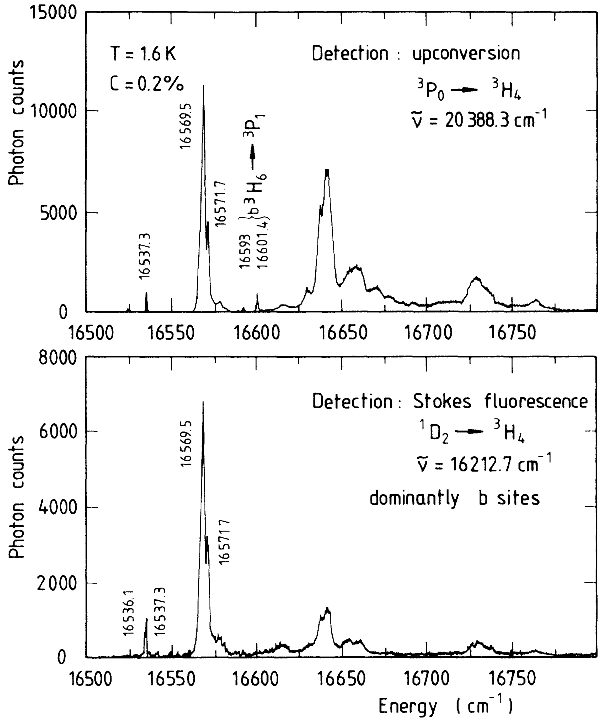

FIG. 12. The same as Fig. 11, but in the absorption regions of the lower Γ_3:$^1D_2$ and of the Γ_1:$^1D_2$ pseudodoublets.

There are two other interesting features in the excitation spectra of the upconversion fluorescence, the absorption lines at 16 593 cm^{-1} and 16 601.4 cm^{-1} in Fig. 12 and at 16 984 cm^{-1} in fig. 11. These transitions are not resonant with any transition originating from the ground state $^3H_4$, but they originate from the excited state $^3H_6$ and end up in the states $^3P_1$ and $^1I_6$, respectively. So they are not due to upconversion by resonant excitation from the ground state but they are due to excited-state absorption. The $^3H_6 \rightarrow {}^3P_1$ absorptions can be explained in the following way (Fig. 13): Weak absorptions in the vibronic sideband of the $^3H_4 \rightarrow {}^1D_2$ transition (Fig. 12) at 16 593 and 16 601.4 cm^{-1} give rise to a small $^1D_2$ population, and by successive relaxations $^1D_2 \rightarrow {}^3H_6$ a weak population of the $^3H_6$ level can be built up. From this level we get initial electronic absorptions from $^3H_6$ to $^3P_1$. The $^3P_1$ level can now decay in two ways:

(i) By radiationless relaxation to $^3P_0$: The emission from this level is identical with the upconversion emission, and therefore the $^3H_6 \rightarrow {}^3P_1$ absorptions show up in the excitation spectrum of the upconversion.

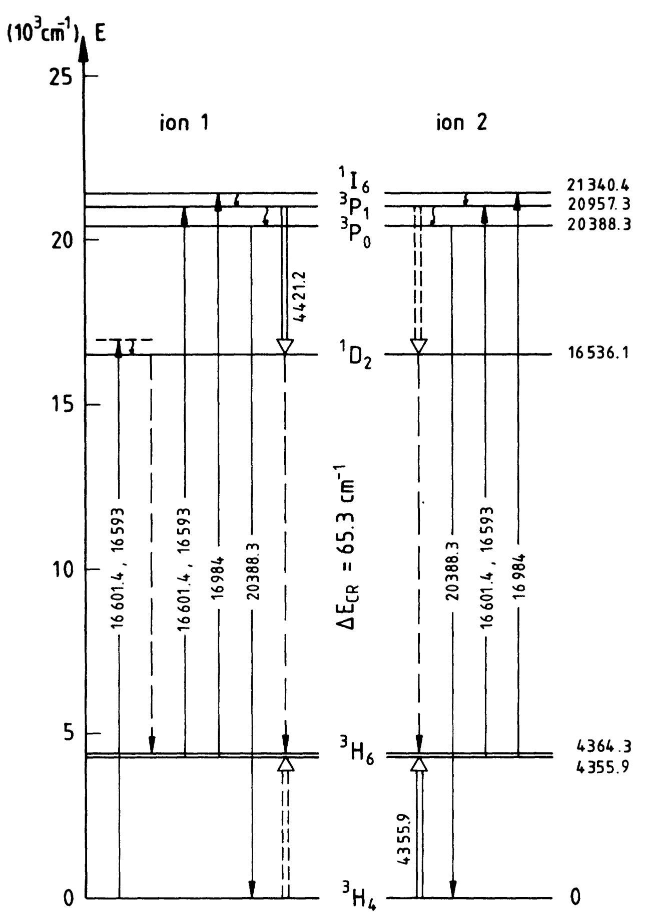

FIG. 13. Relevant energy levels and transitions involved in the photon avalanche process leading to absorptions from the excited $^3H_6$ level. The double arrows indicate the cross relaxations and the wavy lines radiationless transitions. The broken line symbolizes all possible direct and indirect transitions $^1D_2 \rightarrow {}^3H_6$.

(ii) By strong cross relaxation with the second ion of the pseudopair:

$$^3P_1 \times {}^3H_4 \rightarrow {}^1D_2 \times {}^3H_6 + \hbar\omega_{ph} \ . \qquad (1)$$

By this cross relaxation and by the $^1D_2 \rightarrow {}^3H_6$ relaxations mentioned above, the level $^3H_6$ becomes repopulated by two decay channels. This way the overall repopulation probability of $^3H_6$ can be greater than one giving rise to a self-sustaining excited-state absorption called a photon avalanche process.[26]

The build up of the initial population for the $^3H_6 \rightarrow {}^1I_6$ absorption at 16 984 cm^{-1} (Fig. 11) is harder to explain than for the $^3H_6 \rightarrow {}^3P_1$ absorptions discussed above because no vibronic absorptions are present at this frequency. Whatever the origin of the initial $^3H_6$ population is, the resulting $^3H_6 \rightarrow {}^1I_6$ absorption leads to a population of the $^3P_1$ state by successive radiationless transitions from $^1I_6$ to $^3P_1$. From this state the feedback process to repopulate the starting $^3H_6$ state is just the same as already given above.

The energy of the phonon emitted in the cross-relaxation process described by Eq. (1) is $\hbar\omega \leq 65.3$ cm^{-1}. It is equal to 65.3 cm^{-1} if the cross relaxation ends on the lowest crystal-field component of $^3H_6$, and it is smaller if higher crystal-field components of $^3H_6$ are involved. The magnitude of this phonon means that at low temperatures the cross-relaxation process as given in Eq. (1) is a one-way downconversion process. Only at higher temperatures, where $kT \geq 65$ cm^{-1} ($T \geq 90$ K), the reverse cross relaxation, i.e., upconversion by cross relaxation, can be expected. This fact demonstrates once more that at low temperatures upconversion in Pr^{3+}:$CsCdBr_3$ cannot be explained by a cross-relaxation process as already stated.[9,17]

V. OTHER EXCITED STATES

There are two states higher in energy than $^1D_2$ which show fluorescence and are of further interest: $^3P_0$ and $^3P_1$ (Fig. 3). Both states could be found in absorption and in excitation spectra. The excitation spectra give more details because they show weak absorptions more pronounced. Figure 14 shows the excitation spectrum of the total fluorescence in the spectral region of the $^3P_0$ absorption. The most prominent line has a doublet structure. The energies are 20 386.7 and 20 388.3 cm^{-1}. The line at 20 388.3 cm^{-1} was found in upconversion as a fluorescence line, too. From this we can conclude that it belongs to the *b* center which is responsible for the upconversion. The origin of the other line could not be identified in detail. Selectively excited fluorescence spectra from both lines could not really be taken because their separation is almost identical with the linewidth of our laser. Changing the excitation frequency within the doublet gave almost identical fluorescence spectra. Identical fluorescence spectra were found too by tuning the laser on all the other small absorption lines shown in Fig. 14. The origin of the narrow lines, probably electronic ones, is not yet clear to us. The broader lines obviously are vibronic sidebands belonging to the strong doublet. They show up much stronger relative to the electronic transition in the Na^+-Pr^{3+}(10:1) co-doped sample, where in addition to some specific Na-Pr lines only transitions belonging to the *b* center could be found. The vibronic line

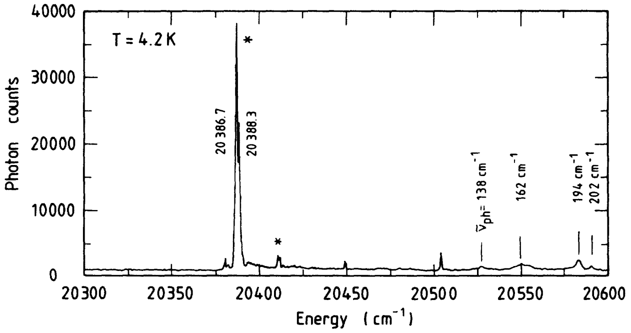

FIG. 14. Excitation spectrum of the total fluorescence in the spectral region of the $^3H_4 \rightarrow {}^3P_0$ absorption. The lines with an asterisk were found in absorption, too. The spectrum is π polarized only. $\bar{\nu}_{ph}$ denotes the phonon frequencies of the vibronic sidebands.

at $\tilde{\nu}_{\mathrm{ph}}=162\ \mathrm{cm}^{-1}$ is due to the A_{1g} lattice mode, the strongest line found in Raman scattering.[19] The vibronic line at $\tilde{\nu}_{\mathrm{ph}}=202\ \mathrm{cm}^{-1}$ demonstrates that the phonon spectrum in CsCdBr_3 obviously extends up to this energy possibly due to polar modes which are not Raman active.

The symmetry of the $^3P_0$ state and of the lowest crystal-field component of the ground state $^3H_4$ of all three centers is Γ_1. So the π polarization of the absorption doublet is consistent with a $\Gamma_1 \rightarrow \Gamma_1$ electric dipole transition for all centers. Exciting the $^3P_0$ level in the doublet absorption lines fluorescence was found from the $^3P_0$ and $^1D_2$ levels. The $^3P_0 \rightarrow {}^3H_4$ fluorescence showed transitions to known crystal-field components of the ground state of all three centers. This way it is proved that the absorption doublet at 20 386.7, 20 388.3 cm^{-1} belongs to the $^3H_4 \rightarrow {}^3P_0$ transition of all of them. From this fact it must be expected generally that the $^3P_0$ fluorescence due to direct $^3P_0$ excitation is a superposition of transitions of all three centers.

The situation is different for the $^1D_2$ emissions by $^3P_0$ excitation. Only weak $^1D_2 \rightarrow {}^3H_4$ emission was found, the final levels belonging all to the *b* sites only. This finding can be explained by the fact that the energy difference between $^3P_0$ and $^1D_2$ is about 4000 cm^{-1}, too much for an effective radiationless relaxation $^3P_0 \rightarrow {}^1D_2$ by phonons with a maximum energy of about 200 cm^{-1}. Furthermore there is no resonance for a cross relaxation with phonon emission either. Because of these arguments no $^1D_2$ fluorescence should show up at all. But if we assume that a doubly excited $^3P_0 \times {}^3P_0$ state of the *b* center can show upconversion like a doubly excited $^1D_2 \times {}^1D_2$ state by cooperative energy transfer to a lattice excitation as discussed above, $^1D_2$ emission can be expected by a succeeding $^3P_1 \times {}^3H_4 \rightarrow {}^1D_2 \times {}^3H_6$ cross relaxation. In this case a weak $^1D_2$ emission can be expected for the *b* sites only, as found experimentally.

The state $^3P_1$ is expected to split in a crystal field of C_{3v} symmetry into a nondegenerate Γ_2 and into a doubly degenerate Γ_3 component. This concerns the ions of the *b* and *c* centers. The *a* center is expected to show additionally a small splitting of the degenerate component due to symmetry reduction (according to the results in Sec. III). According to the selection rules we have to expect the following electric dipole transitions: (i) *a* center: three transitions $^3H_4{:}\Gamma_1 \rightarrow {}^3P_1{:}2\Gamma_1+\Gamma_2$, (ii) *b* center: one σ transition $^3H_4{:}\Gamma_1 \rightarrow {}^3P_1{:}\Gamma_3$, (iii) *c* center: one σ transition $^3H_4{:}\Gamma_1 \rightarrow {}^3P_1{:}\Gamma_3$. But the excitation spectrum of the total fluorescence in the spectral region of the $^3P_1$ absorption shows only one strong electronic line in π polarization at 21 046.3 cm^{-1} found in absorption, too. In the excitation spectrum we found additionally two much weaker narrow π transitions as in Fig. 14. They yielded the same fluorescence spectrum as the strong one. They are probably due to distorted sites and will not be discussed further.

This experimental result is very surprising. Instead of two σ transitions, one for the *b* and one for the *c* center, and instead of three other transitions for the *a* center, we find only one strong transition in π polarization. The same result was found by Ramaz *et al.*,[27,8] too. They explained it by a magnetic $\Gamma_1 \rightarrow \Gamma_2$ dipole transition of the *c* center. This explanation seems to us quite unreasonable because of the selection rule $\Delta J=0,\pm 1$ for magnetic dipole transitions. This rule is neither obeyed by the directly involved states $^3H_4$ and $^3P_1$ nor is there any chance for a strong magnetic dipole transition due to *J*-*J* mixing by the crystal field as one can easily prove by inspecting the energy-level diagram of Pr^{3+} in Fig. 3.

The $^3P_1$ component at 21 046.3 cm^{-1} found in absorption does not show any fluorescence emission at low temperatures. So the other crystal-field component of $^3P_1$ is expected to be the one lower in energy from which the $^3P_1$ fluorescence starts. Its position could be determined to be at 20 957.3 cm^{-1} by coincidence of final crystal-field levels of $^3P_1 \rightarrow {}^3H_5, {}^3F_3$ emissions with already known final levels of $^3P_0$ emissions to the same states.

Excitation into the $^3P_1$ state results in fluorescence emissions from $^3P_1$, $^3P_0$, and $^1D_2$. The emissions from the $^3P_1$ state are generally quite weak because of strong nonradiative transitions $^3P_1 \rightarrow {}^3P_0$ for all three centers and a strong cross relaxation $^3P_1 \times {}^3H_4 \rightarrow {}^1D_2 \times {}^3H_6$ for the *b* center only. So most of the excitation energy leads to $^3P_0$ and $^1D_2$ emissions. The $^3P_0$ fluorescence spectrum by $^3P_1$ excitation turned out to be identical with the spectrum found by direct $^3P_0$ excitation, i.e., it contains lines from all centers. So we have again the situation as for $^3P_0$ that the excitation line seems to be common to all three centers within the linewidth of about 2 cm^{-1}. For the $^3P_0$ state which does not split in the crystal field, such a common line can be expected but not for the $^3P_1$ state.

So we have two strange results for the $^3P_1$ state: Its crystal-field splitting seems to be insensitive to the different crystal fields of the *a*, *b*, and *c* centers and, as discussed above, the $^3H_4{:}\Gamma_1 \rightarrow {}^3P_1$ transition at 21 046.3 cm^{-1} does not obey the crystal-field selection rules. The reason for this is not yet understood. Crystal-field theory obviously cannot explain the results. One possible explanation could be that the coupling of the $^3P_1$ state to the lattice excitations, probably excitons, responsible for the upconversion is strong enough with respect to the crystal field to break the symmetry selection rules for optical transitions and to quench the differences of the crystal-field splittings of the three centers. Thus it looks like the upconversion process and the breakdown of the selection rules have the same roots. This problem needs further investigation.

The fluorescence spectrum from $^1D_2$ by $^3P_1$ excitation is different. The $^1D_2 \rightarrow {}^3H_4$ fluorescence contains definitely only transitions belonging to the *b* center. From this we can conclude that the other $^1D_2$ emissions are *b* transitions, too. The absence of $^1D_2$ emission by exciting $^3P_1$ for the other two centers can be explained in the following way:

(i) The *a* center is a single ion center. The level $^1D_2$ can be populated only by a radiationless transition $^3P_1 \rightarrow {}^3P_0 \rightarrow {}^1D_2$ but the latter one is unreasonable by the arguments given above (radiative $^3P_1 \rightarrow {}^1D_2$ transitions can obviously be neglected).

(ii) The *c* center as a pair center could show in addition a cross relaxation of the form $^3P_1 \times {}^3H_4 \rightarrow {}^1D_2 \times {}^3H_6$

TABLE II. Summary of the energy levels found in $CsCdBr_3$:Pr^{3+}. Most of the levels were found from center-selective excited fluorescence spectra, upconversion included, by excitation into the $^1D_2$ state. The unidentified levels were found from $^3P_0$ emissions excited directly or via the $^3P_1$ state. Since the corresponding absorption lines have the same energy for all three centers, no selective excitation was possible, and the emissions could not be attributed to a specific center. Accuracy is about ±2 cm^{-1}. AV denotes the value found from the photon avalanche process.

State	*a*-center energy (cm^{-1})		*b*-center energy (cm^{-1})		*c*-center energy (cm^{-1})		Unidentified levels energy (cm^{-1})
$^3H_4$	0	Γ_1	0	Γ_1	0	Γ_1	
	177.8	Γ_2	169.5	Γ_3	163.1	Γ_3	
	315.8	Γ_1	193.6	Γ_1	312.6	Γ_3	
	330.5	Γ_2	323.4	Γ_3	566.6	Γ_3	
	552.2	Γ_1	575.0	Γ_3			
	561.9	Γ_1					
	589.9	Γ_2					
$^3H_5$	2105		2105		2113		2205
	2233		2118		2230		2366
	2253		2234		2257		
	2538		2262	Γ_3	2539		
	2549		2478				
			2545	Γ_3			
$^3H_6$	4355		4356	AV	4359		4502
	4365		4362	Γ_3	4368		4577
	4373		4374	Γ_1			
	4680		4415				
	4816		4701	Γ_3			
			4725	Γ_1			
			4808				
$^3F_2$	5065		5070	Γ_3	5062		5082
	5072		5145	Γ_3	5135		5090
	5135		5152	Γ_1	5143		
	5151						
$^3F_3$	6504						6483
	6511						6503
	6525						6530
	6532						
$^3F_4$	6890						6857
	6934						6911
	6941						7099
	6948						7110
	7148						
$^1D_2$	16 523	Γ_2	16 536.1 37.3	Γ_3	16 527.6	Γ_3	
	16 553.6	Γ_1					
	16 569.5	Γ_1	16 569.5 72.2	Γ_1			
	17 001.5	Γ_1,Γ_2	17 004.7 06.4	Γ_3	16 992.8	Γ_3	
	17 009.3	Γ_1,Γ_2					
$^3P_0$	20 386.7 88.3		Γ_1		all centers		
$^3P_1$	20 957.3 21 046.3				all centers		

as the *b* center does. But in the *c* center obviously, the lifetime of the $^3P_1$ level is too short and the interaction between the Pr^{3+} ions is too weak to result in a sufficient probability for cross relaxation. Since the cross relaxation is quite efficient for the *b* centers and since all other parameters of the phonon-assisted cross-relaxation process (like electron-phonon coupling and the phonon spectrum of the host crystal) are identical, one must conclude that the ion-ion coupling in the *c* center is reduced quite drastically as opposed to the *b* center by the vacancy between the Pr^{3+} ions. Based on the experimental results it is reduced at least by two orders of magnitude or even more.

All energy levels found in our selective absorption and emission experiments are summarized in Table II. A number of weaker transitions which could be due to disturbed sites or vibronics are omitted. If it was possible the levels were attributed to one of the three centers and their symmetries were given.

Our spectroscopic results have to be compared with the results of Ramaz *et al.*[27,8] Most of the levels given by them were found by us, too. But their interpretation is basically different from the one given by us. They "did not see any evidence" for other centers than the Pr^{3+}-Cd^{2+} vacancy-Pr^{3+} center that we call the *c* center and attributed all transitions and energy levels to this center only. Of course, their interpretation of the upconversion process is different, too.

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