High resolution infrared absorption spectra, crystal field, and relaxation processes in CsCdBr$_3$:Pr$^{3+}$.

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High resolution low-temperature absorption spectra of 0.2 % Pr$^{3+}$ doped CsCdBr$_3$ were measured in the spectral region 2000–7000 cm$^{-1}$. Positions and widths of the crystal field levels within the $^3H_5, ^3H_4, ^3F_2$, and $^3F_3$ multiplets of the Pr$^{3+}$ main center have been determined. Hyperfine structure of several spectral lines has been found. Crystal field calculations were carried out in the framework of the semiphenomenological exchange charge model (ECM). Parameters of the ECM were determined by fitting to the measured total splittings of the $^3H_4$ and $^3H_6$ multiplets and to the observed in this work hyperfine splittings of the crystal field levels. One- and two-phonon relaxation rates were calculated using the phonon Green’s functions of the perfect (CsCdBr$_3$) and locally perturbed (impurity dimer centers in CsCdBr$_3$:Pr$^{3+}$) crystal lattice. Comparison with the measured linewidths confirmed an essential redistribution of the phonon density of states in CsCdBr$_3$ crystals doped with rare-earth ions.

I. INTRODUCTION

Crystals of rare-earth (RE) doped quasi-one-dimensional double bromides CsCdBr$_3$ are widely studied, mainly, because of their property to incorporate RE$^{3+}$ ions in pairs, even at low RE concentrations. This makes them a promising material for up-conversion lasers. The structure of CsCdBr$_3$ belongs to the $D_{4h}$ space group and consists of linear chains of face-sharing [CdBr$_6$]$^{4-}$ octahedra along the c-axis. Positional symmetry for Cd$^{2+}$ is $D_{3d}$. RE$^{3+}$ ions substitute for Cd$^{2+}$ forming centers with different mechanisms of charge compensation. The main center consists of two RE$^{3+}$ ions placed in the chain on each side of an adjacent cadmium vacancy, [RE$^{3+}$–Cd$^{2+}$ vacancy–RE$^{3+}$]. Both RE$^{3+}$ ions in such a center are equivalent, their positional symmetry lowers from $D_{3d}$ to $C_{3v}$. Spectra of many other centers with different configurations were reported in EPR and optical studies of CsCdBr$_3$:RE crystals. In particular, positional symmetry for RE$^{3+}$ ions in minor axial centers which are supposed to appear at higher RE concentrations, namely, [RE$^{3+}$–RE$^{3+}$–Cd$^{2+}$ vacancy] or [RE$^{3+}$–Cd$^{2+}$ vacancy–Cd$^{2+}$–RE$^{3+}$], is again $C_{3v}$, but two RE$^{3+}$ positions are not equivalent, while in [RE$^{3+}$–Cs$^{+}$ vacancy] centers positional symmetry of RE$^{3+}$ ion is $C_s$.

Though the spectra of CsCdBr$_3$:Pr$^{3+}$ were intensively studied before, crystal field energies of the lowest excited multiplets were not investigated in absorption. The positions of crystal field levels for the main center, as reported by different authors, differ by 2–14 cm$^{-1}$. Typical spectral resolution used in the mentioned works was 0.8–2 cm$^{-1}$, while the only high resolution study (it concerned the $^3D_2$ level) revealed spectral lines as narrow as 0.1 cm$^{-1}$. Peculiar doublet line shape was observed for the $^3H_4(\Gamma_1) \rightarrow$
1 \textit{D}_2(\Gamma_3) \text{ transition and explained by the combined effect of unresolved hyperfine structure and non-axial crystal strains.}

The very first analysis of the crystal field energies of Pr\textsuperscript{3+} in CsCdBr\textsubscript{3} showed that the crystal field affecting the symmetric dimer centers consists of a strong cubic and a weak trigonal components and that the last one is determined mainly by the quadrupolar \((B_0^0)\) term. This conclusion was confirmed in the studies of the crystal field energies of Tm\textsuperscript{3+} and Ho\textsuperscript{3+} symmetric pair centers where data obtained from both optical and submillimeter EPR investigations were taken into account. The sets of crystal field parameters obtained in Refs. \[2,8\] from the fitting of the simulated energy level schemes to the measured \(40\) energy levels of Pr\textsuperscript{3+} are close to one another and provide small enough root-mean square deviations (22.4–11.1 \text{ cm}^{-1}) between calculated and observed energy level data. However, some of the crystal field parameters in CsCdBr\textsubscript{3}:RE\textsuperscript{3+} presented in the literature, in particular \(B_0^0\) and \(B_0^6\), vary nonmonotonically with the occupation number of the \(4f\) electron shell.

We have undertaken the low temperature high resolution infrared absorption study of CsCdBr\textsubscript{3}:Pr\textsuperscript{3+} with the aims (i) to determine directly positions of crystal field levels in the region between 2000 and 7000 \text{ cm}^{-1} and (ii) to study the line widths and shapes and thus to obtain information on relaxation processes and hyperfine interactions. We also performed crystal field calculations for the main center in the framework of the semiphenomenological exchange charge model (ECM), based on the analysis of the local lattice structure. Parameters of the ECM were corrected by fitting the calculated hyperfine splittings of crystal field levels to the experimental data from our measurements. The electron-phonon interaction effects, in particular, the low temperature relaxation of excited states of the \((\text{Pr}^{3+})_2\)-dimer due to one- and two-phonon transitions between the crystal field sublevels of the \(3\text{H}_5, 3\text{H}_6, 3\text{F}_2\) and \(3\text{F}_3\) multiplets, are studied in the framework of the recently derived rigid ion model of lattice dynamics of doped CsCdBr\textsubscript{3}:RE crystals.

**II. EXPERIMENT**

CsCdBr\textsubscript{3} crystals containing 0.2\% of Pr\textsuperscript{3+} were grown by the method described in Ref. \[12\]. Crystals easily cleave along the \(c\)-axis. We have prepared a 1.3 mm thick sample (sample A) with the \(c\)-axis parallel to the cleaved face. The sample was upheld at a controlled temperature of 5 K in a helium vapor cryostat. Unpolarized absorption spectra were measured with a BOMEM DA3.002 Fourier transform spectrometer in the spectral range between 2000 and 7000 \text{ cm}^{-1} with a resolution from 1.0 to 0.05 \text{ cm}^{-1}. In Fourier transform spectroscopy, the quantity \(\text{Res} = 1/L\), where \(L\) is the maximum optical path difference, is indicated as the resolution. The full width at half height (FWHH) of the instrumental function depends on a particular apodization function used. We used no apodization and, thus, worked with the narrowest possible instrumental function (FWHH= 0.6 \text{ Res}). It is easy to show that, in this case, the shape of a spectral line is essentially unchanged provided that FWHH \(\leq\) Res.

Precision of the experimental line positions was 0.05–0.3 \text{ cm}^{-1}, depending on a particular line. Precise absolute wave number scale is an intrinsic property of Fourier transform spectroscopy. Line widths were determined from absorbance spectra calculated with a zero-line taken at a half of transmitted intensity. In such a way we tried to take into consideration the fact that the incident light is unpolarized but a majority of lines is 100\% polarized.

The lowest frequency region of the \(3\text{H}_4 \rightarrow 3\text{F}_3\) spectral transition has also been measured with the resolution of 0.005 \text{ cm}^{-1} using another sample, 3.1 mm thick and oriented approximately along the \(c\)-axis (sample B). It allowed almost pure \(k\parallel c\) geometry and, consequently, \(E, H \perp c\) polarization of the incident light.

**III. EXPERIMENTAL RESULTS**

Fig. 1 shows low temperature transmittance spectra of CsCdBr\textsubscript{3}:Pr\textsuperscript{3+} (0.2\%) corresponding to different infrared transitions. The first excited state of the ground multiplet \(3\text{H}_4\) lies at about 170 \text{ cm}^{-1} and is not populated at helium temperatures. So, low temperature absorption spectra display crystal field levels of the excited multiplets directly. They are listed in Table 1, together with data from other publications.
As the ground state is the $^3H_4(^1\Gamma_1)$ singlet, excited $\Gamma_1$ states manifest themselves in $\pi$-polarization but $\Gamma_3$ states — in $\sigma$-polarization, while $\Gamma_2$ states are silent in electric dipole approximation (see Table 2). Magnetic dipole transitions are usually very weak, with a possible exception for the $^3H_4 \rightarrow ^3H_5$ transition that is allowed for the free Pr$^{3+}$ ion.

The symmetries of the $^3F_3$ crystal field levels have been determined from a comparison between the spectra of the two differently oriented samples (samples A and B). The assignement of the 6483.3 cm$^{-1}$ level as a $\Gamma_3$ level is strongly supported by the well resolved hyperfine structure (hfs) observed in high resolution spectra (see inset 1 of Fig. 1d and Fig. 2a). The point is that while $\Gamma_3$ levels exhibit the magnetic hfs, $\Gamma_1$ and $\Gamma_2$ do not. The next $\Gamma_3$ level also shows the traces of unresolved hfs, namely, the 6503.5 cm$^{-1}$ line has a flat bottom (see inset 2 of Fig. 1d).

Expansion of the 6483.3 cm$^{-1}$ line into six components yields 0.040 cm$^{-1}$ wide Gaussians. The Gaussian shape of hfs components gives evidence that an inhomogeneous broadening due to random crystal fields exceeds a homogeneous broadening due to nonradiative transitions to the nearest $^1\Gamma_2$ level lying at about 10 cm$^{-1}$ lower (we did not observe $^3H_4(^1\Gamma_1) \rightarrow ^3F_3(^1\Gamma_2)$ transitions forbidden as electric dipole ones). The lineshapes of the 6496.5 cm$^{-1}$ ($\Gamma_1 \rightarrow \Gamma_1$) and 6503.5 cm$^{-1}$ ($\Gamma_1 \rightarrow \Gamma_3$) lines reveal homogeneous broadening of 0.17 and 0.31 cm$^{-1}$, respectively. Such a broadening comes, evidently, from electron-phonon interaction and implies a noticeable density of phonon states in the region between 20 and 30 cm$^{-1}$ corresponding to the distances from the considered levels to lower crystal field levels.

Other examples of level broadening due to electron-phonon interaction can be found in the $^3H_2$ multiplet which is situated in the region of about 2400 cm$^{-1}$ (see Fig. 1a). The lowest level of this multiplet lying at about 2234 cm$^{-1}$ was reported to be the $^1\Gamma_2$ level, from polarized fluorescence measurements [1]. In that case, a strong very narrow (with the width of 0.05 cm$^{-1}$) line observed at 2234.8 cm$^{-1}$ corresponds to the magnetic dipole transition $^3H_4(^1\Gamma_1) \rightarrow ^3H_5(^1\Gamma_2)$. As we have already mentioned, such a situation is possible just for the $^3H_4 \rightarrow ^3H_5$ spectral multiplet. The next level lies at 26 cm$^{-1}$ from the bottom of the multiplet and, though suffers from a phonon relaxation, exhibits hfs as it follows from the shape of 2261.4 cm$^{-1}$ line. This is in accordance with the previously made assignments of this level symmetry as $\Gamma_3$. Three closely spaced levels at 2316.6, 2331.9 and 2347.8 cm$^{-1}$ are broad. Their widths are 3.0, 3.3 and 3.7 cm$^{-1}$ respectively, and it is not possible to determine their symmetries. Calculations described below show that an overall hyperfine splittings of $\Gamma_3$ levels do not exceed 0.5 cm$^{-1}$. Consequently, the level widths of 3–4 cm$^{-1}$ are, mainly, due to rapid phonon-assisted decay to lower levels. In accordance with the crystal field calculations (see below), at least one of these three broad absorption lines is to be assigned to another center. The next level is more narrow again. According to the shape of the line at 2546.7 cm$^{-1}$ it contains unresolved hfs and thus corresponds to the $\Gamma_3$ level. The distances from this level to lower levels exceed the length of the phonon spectrum ($\sim 180$ cm$^{-1}$ [1]). Because of that, one-phonon relaxation is not possible.

The highest frequency line observed at 2572.1 cm$^{-1}$ could be attributed to the $^3H_4(^1\Gamma_1) \rightarrow ^3H_5(^2\Gamma_2)$ magnetic dipole transition. But the $^3H_5(^2\Gamma_2)$ level lying at 26 cm$^{-1}$ above the $^3H_5(^3\Gamma_3)$ level (2546 cm$^{-1}$) should be broadened due to one- and two-phonon transitions to the lower crystal field sublevels, and the width of the respective spectral line should be about 0.3–0.5 cm$^{-1}$ (see Table 3), not 0.05 cm$^{-1}$ as observed. Probably, this line belongs to some other Pr$^{3+}$ center. Weak narrow lines observed at 2153.6 and 2167.3 cm$^{-1}$ (see Fig. 1a) also have to be assigned to some other centers. If these levels belonged to the main center, the level at 2234.8 cm$^{-1}$ would be broadened by the nonradiative transitions to these levels. It is not the case experimentally.

We were able to find only two levels in the $^3F_2$ multiplet and the lowest sublevel in each of $^3F_4$ and $^3H_6$. The level at 5073 cm$^{-1}$ which lies far (250 cm$^{-1}$) from a lower level is, evidently, broadened by unresolved hfs and is thus a $\Gamma_3$ level. The measured hyperfine splittings and widths of hyperfine sublevels found from the experimental line shapes are presented in Table 3, to compare with the calculated hyperfine splittings and the estimated one-phonon decay rates (see the next section).

Many of the observed levels coincide with those of Refs. [1]–[3] found from selectively excited fluorescence measurements. We did not observe any additional structure due to nonequivalence of Pr$^{3+}$ positions in asymmetric pair centers. Thus, our results support the conclusion of Refs. [1]–[3] that the main center in CsCdBr$_3$:Pr$^{3+}$ is a symmetric pair [Pr$^{3+}$–Cd$^{2+}$ vacancy–Pr$^{3+}$].

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IV. CRYSTAL FIELD CALCULATIONS

The energy level pattern of the $^{141}\text{Pr}^{3+}$ ion (the nuclear spin $I = 5/2$, 100% abundant, the $4f^2$ electron shell) in the trigonal crystal field can be represented by eigenvalues of the effective parametrized Hamiltonian

$$H = V_{ee} + H_{so} + \Delta E(L, S, J) + H_{cf} + H_{hf},$$

where $V_{ee}$ is the two-body Coulomb energy; $H_{so}$ corresponds to the spin-orbit interaction (we use in the present work $\zeta = 746.2 \text{ cm}^{-1}$ and Slater integrals $F_2 = 304.4; F_4 = 45.47; F_6 = 4.41 \text{ cm}^{-1}$ [13]), $H_{cf}$ is the crystal field Hamiltonian

$$H_{cf} = B_2^0 O_2^0 + B_4^1 O_4^1 + B_6^1 O_4^1 + B_6^3 O_6^0 + B_8^1 O_6^0 + B_8^3 O_6^0$$

where $(O_k^l)$ are the Stevens operators [15], the quantization axis $z$ coincides with the symmetry axis $C_3$ of the crystal lattice, and $H_{hf}$ is the nuclear energy responsible for the hyperfine structure of the optical spectra. Because we neglect many minor interactions (three-body terms, spin-other-orbit interaction, two-body correlations in the crystal field terms and etc.), shifts of the multiplet centers of gravity $\Delta E(L, S, J)$ are introduced to fit the calculated spectrum to the experimental data. Only projections of the electron-nuclear magnetic and quadrupolar interactions on multiplet manifolds with fixed orbital ($L$), spin ($S$) and total ($J$) angular momenta were considered:

$$H_{hf} = A(L, S, J) \mathbf{L} \mathbf{S} + \frac{e^2 Q (1 - \gamma)}{4I (2I - 1)} V_{zz} [3I_z^2 - I(I + 1)] -$$
$$- \frac{3e^2 Q (r^{-3}) \alpha_J}{4I (2I - 1)} \left[ \frac{1}{3} (3r^2 - J(J + 1)) (3I_z^2 - I(I + 1)) + \frac{1}{2} (J_z I_z + J_z I_z) (I_z I_z + I_z I_z) + \frac{1}{2} (J_z J_z + J_z J_z) (I_z I_z + I_z I_z) \right].$$

Here $A(L, S, J)$ is the magnetic dipole hyperfine constant (in the free ion $A(3H_4) = 1.093 \text{ GHz}$ [16], the corresponding hyperfine constants for other multiplets are obtained using this value and neglecting the core electron polarization contributions which do not exceed 1.5% of the $4f$ electron contributions [13]), $Q = -5.9 \times 10^{-30} \text{ m}^2$ [14] is the nuclear quadrupole moment, $\gamma = -70 \pm 10$ is the Sternheimer antishielding factor [16], $\alpha_J$ are reduced matrix elements of the second rank spherical operators, $(r^{-3})$ are moments of the radial wave function of the $4f$ electrons calculated in [17], and the electric field gradient at the Pr$^{3+}$ nucleus equals

$$eV_{zz} = \sum_i e q(i) \frac{3 \cos^2 \theta(i) - 1}{R(i)^3}$$

where $q(i)$ is the charge (in units of the proton charge $e$) of a lattice ion with spherical coordinates $R(i)$, $\theta(i)$ and $\varphi(i)$ in the system of coordinates having its origin at the Pr$^{3+}$ nucleus.

As we have already mentioned in the Introduction, the crystal field parameters obtained earlier from the fitting to the measured energy levels of Pr$^{3+}$ [25] and Nd$^{3+}$ [26] in CsCdBr$_3$, though providing small enough deviations between the calculated and observed energy levels, exhibit nonmonotonic variation within the RE$^{3+}$ family (see Table 4). Moreover, there are large discrepancies between the measured in this work hfs of the absorption lines and the hfs, calculated with the crystal field parameters from Ref. [8]. In particular, the 6483 cm$^{-1}$ line exhibits well resolved hfs of total width 0.21 cm$^{-1}$, while the calculated width is 0.11 cm$^{-1}$.

The formal fitting procedure employed in [25][26][27] evidently brings about overestimated 6-rank parameters of the trigonal crystal field component.

To clear up relations between the crystal field parameters and their origin, we estimated them in the framework of the exchange charge model [14]. The crystal field is represented as a sum $(B_p^k = B_{pq}^k + B_{ps}^k)$ of the electrostatic field of the lattice ions and the exchange charge field defined by the parameters

$$B_{pq}^k = -e^2 K_p^k (1 - \sigma_p) (r_p^{-3}) \sum_i q(i) \frac{O_p^k(\theta(i), \varphi(i))}{R(i)^{p+1}},$$

(5)
The energy of the interionic interaction is assumed to be a sum of Coulomb and non-Coulomb terms. The force constants, corresponding to interactions between the nearest neighbors, Pr\(^{3+}\)–Br\(^{-}\), Cd\(^{2+}\)–Br\(^{-}\), Cs\(^{+}\)–Br\(^{-}\), and Br\(^{-}\)–Br\(^{-}\), have been obtained from the study of the CsCdBr\(_3\) lattice dynamics \([11]\). According to results of simulating the relaxation energy minimum with respect to the ion displacements (see Table 5), the distance between the Pr\(^{3+}\) ions attracted by the Cd\(^{2+}\) vacancy diminishes from the value of the lattice constant \(c = 0.6722\) nm \([13]\) down to 0.5915 nm. This value is very close to the distance of 0.593 nm between the Gd\(^{3+}\) ions \([20]\) and 0.5943 nm between the Tm\(^{3+}\) ions \([23]\) in the symmetric pair centers in CsCdBr\(_3\), as determined from the EPR spectra. In the perfect lattice, the first coordination shell of a Cd\(^{2+}\) ion has the radius of 0.277 nm; in the symmetric dimer center six Br\(^{-}\) ions nearest to the Cd\(^{2+}\) vacancy are forced outwards, but the displacements of the Pr\(^{3+}\) ions along the dimer axis are so large that the corresponding Pr\(^{3+}\)–Br\(^{-}\) distance decreases down to 0.275 nm. On the contrary, the terminal triangles of the Br\(^{-}\) ions lag behind the impurity ions and the corresponding interionic distance increases up to 0.290 nm. These values agree with the distances (0.264 and 0.286 nm) between the Yb\(^{3+}\) and the nearest Br\(^{-}\) ions in the intrinsic dimer units in Cs\(_2\)Yb\(_2\)Br\(_9\) \([22]\).  

Taking into account the local lattice deformation, we obtained from Eqs. (4, 5, 6) the following crystal-field parameters (values are in cm\(^{-1}\)) for Pr\(^{3+}\) ion in the symmetric dimer center (the electrostatic contribution to the quadrupolar crystal field component \(B_{2q}^0 = -\varepsilon^2(1 - \sigma_2)\langle r^2 \rangle V_{zz}/4\) was computed exactly with the Ewald method):

\[
\begin{align*}
B_{2q}^0 &= -445.5(1 - \sigma_2) - 1.123 G_s - 2.828 G_p; \\
B_4^0 &= -42.7(1 - \sigma_4) - 4.52 G_s - 10.12 G_p; \\
B_2^0 &= 1184(1 - \sigma_4) + 156.84 G_s + 341.60 G_p; \\
B_6^0 &= 1.68(1 - \sigma_6) + 1.96 G_s + 0.4395 G_p; \\
B_3^0 &= 13.4(1 - \sigma_6) + 12.56 G_s + 13.56 G_p; \\
B_8^0 &= 24.9(1 - \sigma_6) + 27.61 G_s + 9.06 G_p.
\end{align*}
\]

Values of the model parameters \(G_s = 5.4; G_p = 6.1\) have been determined by comparing the calculated and measured total splittings of the ground state \(^3H_4\) and of the excited multiplet \(^3H_6\), the shielding factors have been fixed at \(\sigma_4 = \sigma_6 = 0, \sigma_2 = 0.89\) in accordance with the theoretical estimations \([16]\). Thus

and

\[
B_{pS}^k = \frac{2(2p + 1)}{7} e^2K_p^k \sum_i (G_s S_s(i)^2 + G_s S_s(i)^2 + \gamma_p G_s S_s(i)^2) \frac{O_k^p(\theta(i), \varphi(i))}{R(i)},
\]

respectively. Here \(K_p^k\) are numerical factors \([10]\), \(\sigma_p\) are the shielding factors, \(\gamma_2 = 3/2, \gamma_4 = 1/3, \gamma_6 = -3/2, G_s\) and \(G_p\) are dimensionless parameters of the model. The expression (6) involves the sum over only the nearest neighbors (six bromine ions) of the RE\(^{3+}\) ion. The overlap integrals \(S_s = \langle 4f, m = 0|4p, m = 0 \rangle\), \(S_\sigma = \langle 4f, m = 1|4p, m = 1 \rangle\) have been computed using the radial 4\(f\) wave function of the Pr\(^{3+}\) ion from Ref. \([17]\) and the 4\(s\), 4\(p\) wave functions of the Br\(^{-}\) ion given in \([18]\). Dependencies of the overlap integrals on the interionic distance \(R\) (in Angstroms) are approximated by the following expressions:

\[
\begin{align*}
S_s &= 0.09988 \exp(-0.20882 R^{2.17238}); \\
S_\sigma &= 0.04610 \exp(-0.03733 R^{1.0662}); \\
S_\pi &= 0.39635 \exp(-0.87514 R^{1.30253}).
\end{align*}
\]

Equations (3, 4, 5) present the crystal field parameters as explicit functions of relative positions of the impurity Pr\(^{3+}\) ion and the lattice ions. We analyzed distortions in the relaxed CsCdBr\(_3\) lattice containing the substitutional dimer \([\text{Pr}^{3+}–\text{Cd}^{2+} \text{ vacancy}–\text{Pr}^{3+}]\) in the framework of the same quasimolecular model as the one already used in \([6]\) to calculate the structure of symmetric Tm\(^{3+}\) dimers. Values of ion displacements from their equilibrium positions in the perfect lattice were obtained by minimizing the potential energy of the cluster which involved the nearest 50 ions around the symmetric dimer center. These ions belong to the first (12 Br\(^{-}\)), second (2 Cd\(^{2+}\)), third (12 Cs\(^{+}\)), and fourth (24 Br\(^{-}\)) coordination shells of the impurity Pr\(^{3+}\) ions (see Table 5).
obtained crystal field parameters (column \(a\) of Table 4) were used as starting values for the fitting procedure constrained by the additional conditions that the calculated hfs had to agree with the experimental data.

The final values of the crystal field parameters for the Pr\(^{3+}\) centers as compared with the corresponding parameters of Tm\(^{3+}\), Ho\(^{3+}\), and Nd\(^{3+}\) centers are given in column \(b\) of Table 4. Despite the large trigonal distortion of the nearest bromine octahedron, the main features of the crystal field splittings are determined by the cubic component of the crystal field. The \(B_6^0\) and \(B_6^6\) parameters involve the largest changes from the initial (calculated) to the final (fitted) values. These differences are most probably caused by the overestimated displacements of the six Br sites, the main features of the crystal field splittings are determined by the cubic component of the crystal field. The \(B_6^0\) and \(B_6^6\) parameters of Table 4 were obtained by diagonalizing the Hamiltonian (1) in the space of 516 states (terms \(^3H, ^3F, ^3P, ^1I, ^1G, ^1D\) were taken into account) with fitted barycenters of the free-ion multiplets. The measured splittings of the \(^3H_4, ^3H_5, ^3H_6, ^3F_2, ^3F_3, ^3F_4, ^3P_1, ^3P_2, ^1D_2\) multiplets of Pr\(^{3+}\) are satisfactorily described by our final set of crystal-field parameters (column \(b\) in Table 4).

The computed hfs of \(\Gamma_1\) and \(\Gamma_2\) crystal field singlets consists of three doublets with the total width \(\Delta E\) of no more than 0.02 cm\(^{-1}\), which can not be resolved in the optical spectra. The quadrupolar contributions to the hfs are very small (\(\sim 10^{-4}\) cm\(^{-1}\)), the calculated hfs of \(\Delta\) doublets is actually equidistant with intervals of no more than 0.1 cm\(^{-1}\). An example of the simulated envelope of the absorption line \(^3H_4(\Gamma_1) \rightarrow ^3F_3(\Gamma_3)\), where individual transitions between different electron-nuclear states are presented by Gaussians of 0.04 cm\(^{-1}\) width, is given in Fig. 2b. The observed irregular shape of the hfs of some absorption lines (see Fig. 2a and Ref. [5]) is most probably caused by crystal fields of low symmetry. We discussed this point in more details in another publication [23].

The most essential difference between results of our calculations and fitting procedures performed in [3] is connected with assignments of symmetry types of some crystal field energy levels. In particular, symmetries of the third \(2\Gamma_3\) and fourth \(\Gamma_1\) sublevels of the \(^3H_2\) multiplet and of the second \(1\Gamma_3\) and third \(\Gamma_2\) sublevels of the ground \(^3H_4\) multiplet are inverted in [3] (it should be noted that our scheme of crystal field energies of the ground state agrees with the assignment of Ref. [3]). Additional measurements of polarized spectra are to be carried out to check our predictions.

V. RELAXATION BROADENING OF THE CRYSTAL FIELD LEVELS

Even at the liquid helium temperature the hfs of the most of excited crystal field sublevels is masked by the spontaneous relaxation broadening. Strong electron-phonon interaction effects in CsCdBr\(_3\);RE\(^{3+}\) crystals originate from the specific density of phonon states which has large maxima in the low frequency region (20–40 cm\(^{-1}\)) in the perfect crystal lattice (see Fig. 3 and Ref. [11]). The Hamiltonian of the electron-phonon interaction, expanded in a power series in ion displacements from their equilibrium positions, can be written as follows

\[
H_{el-ph} = \sum_{s\alpha} V_\alpha(s)[u_\alpha(s) - u_\alpha(RE)] + \sum_{s\alpha\beta} \frac{1}{2} V_{\alpha\beta}(s)[u_\alpha(s) - u_\alpha(RE)][u_\beta(s) - u_\beta(RE)]...;
\]

\[
V_\alpha(s) = \sum_{pk} B^k_{p,\alpha}(s)O^k_p, V_{\alpha\beta}(s) = \sum_{pk} B^k_{p,\alpha\beta}(s)O^k_p,
\]

where \([u(s) - u(RE)]\) is the difference between dynamic displacements of the ligand ion \(s\) and the RE ion, and \(B^k_{p,\alpha}(s), B^k_{p,\alpha\beta}(s)\) are the coupling constants. The probability of the one-phonon transition between the initial \((i)\) and final \((f)\) states of the RE ion with the energy gap \(\hbar\omega_{if} > 0\) can be represented as

\[
W_{if} = \frac{2}{\hbar} \sum_{s\alpha s'\beta} \langle f|V_\alpha(s)|i\rangle \text{Im} g_{\alpha\beta}(ss'|\omega_{if})\langle i|V_{\beta}(s')|f\rangle(1 + n(\omega_{if})),
\]

where \(n(\omega)\) is the phonon occupation number, and \(g_{\alpha\beta}(ss'|\omega)\) are spectral representations of the Green’s functions for differences between the ion displacements [24]. We performed a calculation of the relaxation
rates for all the crystal field sublevels within the manifolds of $^3H_5$, $^3F_2$ and $^3F_3$ multiplets using the phonon Green’s functions of the perfect (CsCdBr$_3$) and locally perturbed (impurity dimer centers in CsCdBr$_3$:Pr$^{3+}$) crystal lattices obtained in [1]. The formation of a dimer leads to a strong perturbation of the crystal lattice (mass defects in the three adjacent Cd$^{2+}$ sites and large changes of force constants). As it has been shown in [1], the local spectral density of phonon states essentially redistributes and several localized modes corresponding to different representations of the dimer point symmetry group $D_{3d}$ appear near the boundary of the continuous phonon spectrum of the unperturbed lattice. As an example of changes in the phonon spectrum, we present in Fig. 3 spectral densities $D_{aa}(\omega)$ of displacement-displacement autocorrelation functions

$$
\langle u_w^2(R) \rangle = \int D_{aa}(\omega) d\omega,
$$

(10)
in the perfect ($R = \text{Cd}^{2+}$) and perturbed ($R = \text{Pr}^{3+}$) lattices at zero temperature. The contributions to $D_{aa}(\omega)$ from the localized modes of $\Gamma_{3g}$ (196.5 cm$^{-1}$) and $\Gamma_{3u}$ (190 cm$^{-1}$) symmetry, and to $D_{zz}(\omega)$ from the localized modes of $\Gamma_{1g}$ (191.7 cm$^{-1}$) and $\Gamma_{2u}$ (191.2 cm$^{-1}$) symmetry are presented by Lorentzians with the proper weights and the full width of 2 cm$^{-1}$.

We took into account interactions of Pr$^{3+}$ ion with its nearest neighbors (six Br$^-$ ions) only. Values of coupling constants were computed in the framework of the ECM with the same parameters as those used in the crystal field calculations (explicit expressions of the $B_{p,\alpha}(s)$, $B_{p,a\beta}(s)$ are given in [10,24]). Matrix elements of electron operators $V_{\alpha}(s)$ were calculated with the eigenfunctions of the Hamiltonian (1). Calculated inverse lifetimes $1/\tau_i = W_i = \sum_j W_{ij}$ (the sum is over states $f$ which belong to the same multiplet as the crystal field level $i$ does, with lower energies) are given in Table 3. It is seen that despite many simplifying approximations there is a good correlation between the measured linewidths and the relaxation rates obtained with the perturbed Green’s functions. Calculations with Green’s functions of the perfect lattice gave overestimated (up to an order of magnitude higher) values of relaxation rates. Thus, we conclude that the increased Pr$^{3+}$-ligand elastic interaction, as compared to the Cd$^{2+}$-Br$^-$ interaction, and corresponding enhancement of correlations between displacements of the impurity RE$^{3+}$ ion and its neighbors strongly suppresses the electron-phonon coupling.

It should be noted that the measured width of the doublet $^3\Gamma_5(^3H_5)$ is five times larger than the estimated total linewidth, though the one-phonon relaxation broadening of this level is not possible at low temperatures. We suppose that this level, and two upper levels $^4\Gamma_4(^3H_5)$, $^4\Gamma_3(^3H_5)$ are essentially broadened due to the two-phonon relaxation. The probability of the spontaneous emission of two phonons contains three terms which correspond to the first order contribution from the nonlinear electron-phonon interaction:

$$
W_{ij}^{(2a)} = \frac{1}{\pi} \sum_{\alpha\beta\gamma\delta} \langle f|V_{\alpha\beta}(s)|i\rangle \langle i|V_{\gamma\delta}(s')|f\rangle \times 
\int \int \text{Im}g_{\alpha\gamma}(ss'|\omega_1)\text{Im}g_{\beta\delta}(ss'|\omega_2)\delta(\omega_{if} - \omega_1 - \omega_2)d\omega_1d\omega_2,
$$

(11)
to the second order contribution from the linear electron-phonon interaction:

$$
W_{ij}^{(2b)} = \frac{2}{\pi\hbar^2} \sum_{jl} \int \int \left( \frac{M_{ij}^{fj}(\omega_1)M_{ii}^{il}(\omega_2)}{\omega_{ij} - \omega_1} \right) \delta(\omega_{if} - \omega_1 - \omega_2)d\omega_1d\omega_2,
$$

(12)
where

$$
M_{ii}^{fj}(\omega_n) = \sum_{ss'} \langle f|V_{\alpha}(s)|j\rangle \text{Im}g_{\alpha\beta}(ss'|\omega_n) \langle j|V_{\beta}(s')|m\rangle,
$$

(13)
and to the combined action of the first and second order transition amplitudes:

$$
W_{ij}^{(2c)} = \frac{2}{\pi\hbar} \sum_{ss''\gamma\delta} \sum_{\alpha\beta\gamma\delta} \langle \langle f|V_{\alpha\beta}(s)|i\rangle \langle i|V_{\gamma\delta}(s'')|j\rangle \langle j|V_{\beta}(s')|f\rangle + c.c. \rangle \times 
\int \int \text{Im}g_{\alpha\gamma}(ss'|\omega_1)\text{Im}g_{\beta\delta}(ss'|\omega_2) \frac{1}{\omega_{ij} - \omega_1} \delta(\omega_{if} - \omega_1 - \omega_2)d\omega_1d\omega_2.
$$

(14)
The calculated sum of two-phonon relaxation rates \( \sum f_i W_i^{(2a)} \) corresponding to spontaneous transitions from the doublet \( ^3\Gamma_3(3H_5) \) to all lower sublevels of the \( ^3H_5 \) multiplet, induced by the nonlinear terms in Eqn. (8) equals \( 1.8 \times 10^{10} \text{ s}^{-1} \) and is almost exactly cancelled by the contribution \(-1.7 \times 10^{10} \text{ s}^{-1}\) from "crossed" terms of Eqn. (4). We have obtained the remarkably larger contribution to the inverse lifetime of this doublet \( (7.1 \times 10^{10} \text{ s}^{-1}) \), that agrees satisfactorily with its measured linewidth, from the second order terms given in Eqn. (13). It should be noted that relaxation processes that involve excitations of localized modes of \( \Gamma_{3u} \) and \( \Gamma_{3g} \) symmetry dominate yielding more than a half of the total relaxation rate.

VI. CONCLUSION

High resolution (1–0.005 cm\(^{-1}\)) infrared (2000–7000 cm\(^{-1}\)) absorption spectra of CsCdBr\(_3\):Pr\(^{3+}\) (0.2 %) were taken at low temperatures. Crystal field levels of the \( ^3H_5, ^3H_6, ^3F_2, \) and \( ^3F_3 \) multiplets for the symmetric pair center \([\text{Pr}^{3+}-\text{Cd}^{2+} \text{vacancy}–\text{Pr}^{3+}]\) were found directly in absorption. Hyperfine structure, inhomogeneous and relaxation-induced widths of several crystal field levels were measured.

We performed crystal field calculations in the framework of the semiphenomenological exchange charge model and took into account local lattice deformation around an impurity center. Only two parameters of the model had to be determined by a comparison of calculated and experimental energy levels. Thus obtained crystal field parameters were corrected by fitting the calculated hyperfine structure to the measured one. It follows from our results that despite a large trigonal distortion of the bromine octahedra in the nearest surroundings of impurity Pr\(^{3+}\) ions, crystal field splittings are determined, mainly, by the cubic component of the crystal field.

Using the results of the crystal field calculations and of the lattice dynamics analysis we were able, for the first time, to calculate exactly (without any additional fitting parameters) one- and two-phonon spontaneous relaxation rates. The calculated total relaxation rates reveal the linewidths which are in reasonable agreement with the measured ones. The obtained information on relative efficiency of linear and nonlinear terms in the Hamiltonian of the electron-phonon interaction in stimulation of the phonon emission is important for the thorough derivation of the theory of multiphonon relaxation in rare-earth compounds.

The peculiarities of the electron-phonon interaction effects in CsCdBr\(_3\):Pr\(^{3+}\) crystals originate from the specific density of phonon states that extends by only \( \sim 180 \text{ cm}^{-1} \) in the perfect CsCdBr\(_3\) lattice, and from the localized modes induced by the impurity dimer centers. Another important feature and, probably, the most interesting result of this study, is a strong suppression of the effective electron-phonon coupling due to a local increase of elastic forces in the activated crystal and the corresponding enhancement of correlations between displacements of the impurity RE ion and its neighbors.

ACKNOWLEDGEMENTS

An encouraging interest of G. N. Zhizhin is acknowledged. This work was supported in part by the RFBR (Grant N 99–02 16881) and the Russian Ministry of Science (Grant N 08.02.28 of the Program "Fundamental Spectroscopy").

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FIGURES

Wave number (cm$^{-1}$)

Transmittance

$^3H_4 \rightarrow ^3H_5$

2200 2300 2400 2500 2600

0.5

2234 2235

2259 2262

2544 2547

2571 2572

(a)
FIG. 1. Transmittance spectra of CsCdBr₃:Pr³⁺ at 5 K corresponding to the optical transitions from the ground state \(^3\)H₄(¹T₁) to the excited (a) \(^3\)H₅, (b) \(^3\)H₆, (c) \(^3\)F₂, and (d) \(^3\)F₃ crystal field multiplets. Spectral resolution is 0.055, 0.3, 0.3, and 0.05 cm\(^{-1}\) for (a), (b), (c), and (d), respectively, and 0.005 cm\(^{-1}\) for insert 1 of Fig. 1(d). Very sharp lines in the spectral region 2300–2400 cm\(^{-1}\) are due to residual CO₂ in the spectrometer.
FIG. 2. (a) Measured with resolution 0.005 cm$^{-1}$ and (b) calculated hyperfine structure of the $^3H_4(^1\Gamma_1) \rightarrow ^3F_3(^1\Gamma_3)$ transition of CsCdBr$_3$:Pr$^{3+}$. 
FIG. 3. Simulated spectral densities of displacement-displacement autocorrelation functions for Cd$^{2+}$ in CsCdBr$_3$ (dotted curves) and for Pr$^{3+}$ in the impurity dimer centers (solid curves).
| Multiplet | Measured | This work | Literature data [1-4] | Calculated |
|-----------|----------|-----------|-----------------------|------------|
| $^3H_4$   | 0        | 0         | $^1\Gamma_1$          | $^3\Gamma_1$ |
|           |          | 166–170   | $^1\Gamma_2$, $^1\Gamma_3$? | 168        |
|           |          | 194–196   | $^2\Gamma_3$, $^2\Gamma_2$? | 188        |
|           |          | 323–328   | $^1\Gamma_3$           | 293        |
|           |          | 551–555   | $^1\Gamma_3$           | 545        |
|           |          | 574–580   | $^1\Gamma_3$           | 564        |
| $^3H_5$   | 2234.8 (0.05) | $^1\Gamma_1$, $^1\Gamma_2$? | 2230–2236   | $^1\Gamma_2$ |
|           | 2261.4 (0.64) | $^1\Gamma_3$           | 2256–2264   | 2251        |
|           | 2316.5 (3.0) | $^1\Gamma_3$, $^1\Gamma_2$? | 2309–2318   | 2330        |
|           | 2331.9 (3.3) | $^1\Gamma_3$, $^1\Gamma_2$? | 2327–2334   | 2334        |
|           | 2348.4 (3.7) | $^1\Gamma_3$           | 2347        | 2620        |
|           | 2546.7 (0.7) | $^2\Gamma_3$           | 2533–2547   | 2540        |
|           |          | 2654–2595 | $^2\Gamma_2$           | 2593        |
|           |          |          |                       | 2620        |
| $^3H_6$   | 4362.8 (0.19) | $^1\Gamma_3$           | 4362–4364   | 4363        |
|           |          | 4374–4378 | $^1\Gamma_3$           | 4390        |
|           |          | 4413–4415 | $^1\Gamma_3$           | 4414        |
|           |          | 4494      | $^1\Gamma_3$, $^1\Gamma_2$ | 4539        |
|           |          | 4700–4704 | $^1\Gamma_3$, $^1\Gamma_2$ | 4710        |
|           |          | 4725–4730 | $^1\Gamma_3$, $^1\Gamma_2$ | 4733        |
|           |          | 4761      | $^1\Gamma_3$, $^1\Gamma_2$ | 4765        |
|           |          | 4781–4808 | $^1\Gamma_3$, $^1\Gamma_2$ | 4804        |
|           |          | 4808–4843 | $^1\Gamma_3$, $^1\Gamma_2$ | 4815        |
| $^3F_2$   | 5073.0 (0.11) | $^1\Gamma_3$           | 5070–5076   | 5073        |
|           |          | 5145–5153 | $^1\Gamma_3$, $^1\Gamma_2$ | 5128        |
| $^3F_3$   | 5153.5 (2.8) | $^1\Gamma_3$           | 5152–5158   | 5136        |
|           |          | 6473–6479 | $^1\Gamma_3$           | 6473        |
|           |          | 6480–6488 | $^1\Gamma_3$           | 6483        |
|           |          | 6499–6500 | $^1\Gamma_3$           | 6485        |
|           |          | 6500–6510 | $^1\Gamma_3$           | 6495        |
|           |          | 6526–6535 | $^1\Gamma_3$, $^1\Gamma_2$ | 6533        |
| $^3F_4$   | 6858.0 (<1) | $^1\Gamma_3$           | 6858–6860   | 6858        |
|           |          | 6894      | $^1\Gamma_3$, $^1\Gamma_2$ | 6907        |
|           |          | 6903–6908 | $^1\Gamma_3$, $^1\Gamma_2$ | 6902        |
|           |          | 6914      | $^1\Gamma_3$, $^1\Gamma_2$ | 6930        |
|           |          | 7103–7104 | $^1\Gamma_3$, $^1\Gamma_2$ | 7115        |
|           |          | 7111–7117 | $^1\Gamma_3$, $^1\Gamma_2$ | 7108        |
| $^1G_4$   | 9777      | 9777      | $^1\Gamma_1$           | 9860        |
|           |          | 9889      | $^1\Gamma_1$, $^1\Gamma_3$ | 9899        |
|           |          | 9955      | $^1\Gamma_1$, $^1\Gamma_3$ | 10427       |
|           |          | 10453     | $^1\Gamma_1$, $^1\Gamma_3$ | 10453       |
| $^1D_2$   | 16536–16540 | $^1\Gamma_3$           | 16536       | $^1\Gamma_3$ |
|           | 16567–16570 | $^1\Gamma_3$           | 16588       | $^1\Gamma_3$ |
|           | 17004–17011 | $^1\Gamma_3$           | 17001       | $^1\Gamma_3$ |
| $^3P_0$   | 20386–20393 | $^1\Gamma_3$           | 20386       | $^1\Gamma_3$ |
| $^3P_1$   | 20956–20964 | $^1\Gamma_3$           | 20964       | $^1\Gamma_3$ |
| $^3P_2$   | 21011–21047 | $^1\Gamma_3$           | 21011       | $^1\Gamma_3$ |
|           | 22163–22177 | $^1\Gamma_3$           | 22165       | $^1\Gamma_3$ |
|           | 22216–22229 | $^1\Gamma_3$           | 22223       | $^1\Gamma_3$ |
TABLE II. Selection rules for electric dipole (d) and magnetic dipole (µ) transitions in C\textsubscript{3v} point group.

| C\textsubscript{3v} | \( \Gamma_1 \) | \( \Gamma_2 \) | \( \Gamma_3 \) |
|---------------------|----------------|----------------|----------------|
| \( \Gamma_1 \)     | \( d_z \)     | \( \mu_z \)    | \( d_x, d_y; \mu_x, \mu_y \) |
| \( \Gamma_2 \)     | \( \mu_z \)    | \( d_z \)      | \( d_x, d_y; \mu_x, \mu_y \) |
| \( \Gamma_3 \)     | \( d_x, d_y; \mu_x, \mu_y \) | \( d_x, d_y; \mu_x, \mu_y \) | \( d_z; d_x, d_y; \mu_x, \mu_y \) |

TABLE III. The calculated and measured total hyperfine structure widths \( \Delta E/\hbar \), the one-phonon relaxation rates \( W \) and the widths \( \Delta \omega \) (10\(^{10}\) s\(^{-1}\)) of the crystal field sublevels at the temperature of 5 K.

| 2S+1\( \text{L}_J \) | Crystal field energy (cm\(^{-1}\)) | \( \Delta E/\hbar \) | W\((a)\) | \( \Delta \omega \) |
|---------------------|-------------------------------|-----------------|--------|----------------|
| \( 3^2\text{H}_6 \) | \( ^1\Gamma_2 \ 0 \ (2235) \) | 0.05             | <0.94  | 0               | 0.94\((b)\) |
|                     | \( ^1\Gamma_3 \ 26 \)        | 6.68             | 6.41   | 15.5 [113]      | 5.65      |
|                     | \( ^2\Gamma_3 \ 82 \)        | 5.43             | 255 [573] | 56.6      |
|                     | \( ^1\Gamma_1 \ 97 \)        | 0.16             | 157 [745] | 62.2      |
|                     | \( ^3\Gamma_3 \ 312 \)       | 2.65             | 7.2\((c)\) | 13.2      |
|                     | \( ^2\Gamma_2 \ 358 \)       | 0                | 52 [59] |
|                     | \( ^4\Gamma_3 \ 385 \)       | 9.03             | 59 [311] |

| \( 3^2\text{F}_2 \) | \( ^1\Gamma_3 \ 0 \ (4363) \) | 2.00             | 2.26   | 0               | 1.30\((b)\) |
|                     | \( ^1\Gamma_3 \ 0 \ (5073) \) | 1.15             | 1.32   | 0               | 0.94\((b)\) |
|                     | \( ^2\Gamma_3 \ 75 \)        | 2.09             | 14 [31] |
|                     | \( ^1\Gamma_1 \ 80 \)        | 0.03             | 32 [57] | 52.8      |
|                     | \( ^1\Gamma_2 \ 0 \ (6473) \) | 0.03             | 0      |
|                     | \( ^1\Gamma_3 \ 10 \)        | 3.71             | 3.96   | 0.52 [9.0]     | 0.75\((b)\) |
|                     | \( ^1\Gamma_1 \ 23 \)        | 0                | 4.5 [26] | 3.20      |
|                     | \( ^2\Gamma_3 \ 30 \)        | 1.53             | 1.69   | 15.8 [95]     | 5.85      |
|                     | \( ^2\Gamma_2 \ 53 \)        | 0                | 63 [98] |

\(a\) - numbers in square brackets were obtained with the phonon spectrum of the unperturbed crystal lattice,

\(b\) - the inhomogeneous width,

\(c\) - two-phonon relaxation rate.

TABLE IV. Crystal field parameters B\textsubscript{p} (cm\(^{-1}\)) of symmetric dimer centers in CsCdBr\textsubscript{3}:RE\textsuperscript{3+} crystals.

| p | k | Tm (4\textit{f}\textsuperscript{12}) [6] | Ho (4\textit{f}\textsuperscript{10}) [7] | Nd (4\textit{f}\textsuperscript{3}) [9] | Pr (4\textit{f}\textsuperscript{2}) [8] | this work a | b |
|---|---|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|-------------|---|
| 2 | 0 | -81.4                                  | -75.6                                  | -102                                   | -79                                    | -72.3       | -70 |
| 4 | 0 | -82.0                                  | -94.3                                  | -121                                   | -149                                   | -128.8      | -140.6 |
| 4 | 3 | 2362                                   | 2841                                   | 3698                                   | 4044                                   | 4115        | 4191 |
| 6 | 0 | 11.26                                  | 12.75                                  | 14.06                                  | 22.62                                  | 14.95       | 15.1 |
| 6 | 3 | 153                                    | 216                                    | 342                                    | 347                                    | 164         | 279 |
| 6 | 6 | 106                                    | 150                                    | 187                                    | 37                                     | 229         | 101 |
TABLE V. Structure of the symmetric dimer Pr$^{3+}$-Cd$^{2+}$ vacancy-Pr$^{3+}$ (lattice constants $a = 0.7675$ nm; $c = 0.6722$ nm; $\nu = 0.1656$).

| Ion | Coordinates | \begin{align*} \text{Ion} & \quad \text{coordinates} \\
\text{Pr}^{3+})_{1,2} & \quad 0 & 0 & \pm [0.5 - 0.06003] \\
(\text{Br}^-)_{1,4} & \quad \pm \sqrt{3}[\nu - 0.01032] & 0 & \pm [0.75 - 0.01400] \\
(\text{Br}^-)_{2,5} & \quad \pm \sqrt{3}[\nu + 0.01032] / 2 & \pm \sqrt{3}[\nu - 0.01032] / 2 & \pm [0.75 - 0.01400] \\
(\text{Br}^-)_{3,6} & \quad \pm \sqrt{3}[\nu + 0.01032] / 2 & \pm \sqrt{3}[\nu - 0.01032] / 2 & \pm [0.75 - 0.01400] \\
(\text{Br}^-)_{7,10} & \quad \pm \sqrt{3}[\nu - 0.03022] & 0 & \pm [0.25 - 0.00152] \\
(\text{Br}^-)_{8,11} & \quad \pm \sqrt{3}[\nu + 0.03022] / 2 & \pm \sqrt{3}[\nu - 0.03022] / 2 & \pm [0.25 - 0.00152] \\
(\text{Br}^-)_{9,12} & \quad \pm \sqrt{3}[\nu + 0.03022] / 2 & \pm \sqrt{3}[\nu + 0.03022] / 2 & \pm [0.25 - 0.00152] \\
(\text{Cs}^+)_{1,4} & \quad \pm 1 / \sqrt{3} - 0.02051 & 0 & \pm [0.75 + 0.00469] \\
(\text{Cs}^+)_{2,5} & \quad \pm 1 / \sqrt{3} + 0.02051 / 2 & \pm 1 / \sqrt{3} - 0.02051 / 2 & \pm [0.75 + 0.00469] \\
(\text{Cs}^+)_{3,6} & \quad \pm 1 / \sqrt{3} + 0.02051 / 2 & \pm 1 / \sqrt{3} + 0.02051 / 2 & \pm [0.75 + 0.00469] \\
(\text{Cs}^+)_{7,10} & \quad \pm 1 / \sqrt{3} - 0.00602 & 0 & \pm [0.25 - 0.01938] \\
(\text{Cs}^+)_{8,11} & \quad \pm 1 / \sqrt{3} + 0.00602 / 2 & \pm 1 / \sqrt{3} - 0.00602 / 2 & \pm [0.25 - 0.01938] \\
(\text{Cs}^+)_{9,12} & \quad \pm 1 / \sqrt{3} + 0.00602 / 2 & \pm 1 / \sqrt{3} + 0.00602 / 2 & \pm [0.25 - 0.01938] \\
(\text{Cd}^{2+})_{1,2} & \quad 0 & 0 & \pm [1 - 0.00290] \\
(\text{Br}^-)_{13-16} & \quad \pm \sqrt{3}[\nu - 0.5] + 0.00404 & \pm [0.5 + 0.00532] & \pm [0.25 + 0.00231] \\
(\text{Br}^-)_{17-20} & \quad \pm 0.5 / \sqrt{3} + 0.00258 & \pm [1.5 - 1.00616] & \pm [0.25 + 0.00231] \\
(\text{Br}^-)_{21-24} & \quad \pm 0.5 / \sqrt{3} + 0.00258 & \pm [1.5 - 0.00084] & \pm [0.25 + 0.00231] \\
(\text{Br}^-)_{25-28} & \quad \pm \sqrt{3}[\nu - 0.5] + 0.00151 & \pm [0.5 - 0.00288] & \pm [0.75 + 0.00058] \\
(\text{Br}^-)_{29-32} & \quad \pm 0.5 / \sqrt{3} + 0.00174 & \pm [1.5 - 1.00275] & \pm [0.75 + 0.00058] \\
(\text{Br}^-)_{33-36} & \quad \pm 0.5 / \sqrt{3}[1 - \nu] - 0.00325 & \pm [1.5 - 0.5 - 0.00013] & \pm [0.75 + 0.00058] \\
\end{align*}