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Broadening of the Lines Due to the $4f^n$–$4f^{n-1}5d$ Transitions of Ce³⁺, Pr³⁺, and Tb³⁺ Ions in the Absorption Spectra of CdF₂ Crystals

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Abstract—The structure of the absorption spectra of Ce³⁺, Pr³⁺, and Tb³⁺ ions in the vicinity of 4f–5d transitions has been investigated. At low temperatures the absorption spectra exhibit a weakly pronounced fine structure, in contrast to narrow-line spectra in crystals of Ca, Sr, and Ba fluorides. The spectra of Ce³⁺, Pr³⁺, and Tb³⁺ ions in CdF₂ can be considered as the absorption spectra of these ions in alkali-earth fluorides, broadened by 60–75 cm⁻¹. The broadening is related to the autoionization of electron from the local $5d(e_g)$ level to the energy-degenerate states of the conduction band of CdF₂ crystal.

INTRODUCTION

The optical spectra of f–d transitions of rare-earth ions in crystals remain rather poorly investigated. The 5d orbitals are much more diffuse than the 4f orbitals, and their interaction with the crystal lattice is much stronger. Due to this, the $4f^n$–$4f^{n-1}5d$ (denoted as 4f–5d below) absorption and excitation spectra consist of zero-phonon lines with a wide vibrational wing. A line structure is generally observed on the low-energy edge. The structure disappears with a shift to higher energies. This is explained by the line broadening, which is caused by the interaction of higher lying d states with the states of the same energy in the conduction band [1, 2]. The broadening of the $4f^n$–$4f^{n-1}5d$ lines of trivalent rare-earth ions in cadmium fluoride crystals has not been investigated.

EXPERIMENTAL

CdF₂ crystals were grown in vacuum in graphite crucibles by the Stockbarger method. Rare-earth trifluorides in concentrations of 0.01, 0.1, or 1 mol % were added to the charge [3].

Absorption spectra were measured on a Perkin-Elmer L950 spectrophotometer at a temperature of about 8 K using a Janis Research CCS-100/204N cryorefrigerator. The absorption spectra of CdF₂ crystals and alkali-earth fluorides with Ce³⁺, Pr³⁺, and Tb³⁺ impurity ions near the 4f–5d transitions were measured with a resolution of 0.1–0.05 nm at a temperature of about 8 K.

The fundamental absorption edge of pure CdF₂ crystals was observed at about 200 nm at room temper-

ature; it was shifted to 185 nm at liquid-nitrogen temperature (Fig. 1a). The absorption on allowed 4f–5d transitions was measured for only Ce³⁺, Pr³⁺, and Tb³⁺ ions. The 4f–5d absorption bands of other rare-earth ions (Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, and Yb³⁺) in CdF₂ fall in the wavelength range below 180 nm and could not be detected.

EXPERIMENTAL RESULTS

The room-temperature absorption spectra of CdF₂–0.1% CeF₃ contain a band peaking at 307 nm. Bands with a similar position were observed in the spectra of other alkali-earth fluorides. These bands are due to the transitions from the ground $4f^1$ level to the $5d(e_g)$ level in the Ce³⁺ ion. The band acquires a fine structure with a decrease in temperature (Fig. 1). The structure of the long-wavelength band of Ce³⁺ in CdF₂ is much less pronounced than in other alkali-earth fluorides. At low temperatures, an absorption band near 195 nm manifests itself due to the blue shift of the fundamental absorption edge. As in the case of other alkali-earth fluorides [4–7], this band is due to the $4f$–$5d(t_{2g})$ transitions in Ce³⁺.

At low temperatures, the weak absorption band at about 247 nm becomes more pronounced (Fig. 1a). The absorption band of Ce³⁺ in this region in the spectra of alkali-earth fluorides increases in the series from BaF₂ to CaF₂; its intensity significantly increases with an increase in the cerium concentration [8]. When cerium is introduced jointly with an alkaline metal impurity (NaF, KF), the excess charge of Ce³⁺ ions is compensated for by the alkaline metal ion, spaced by
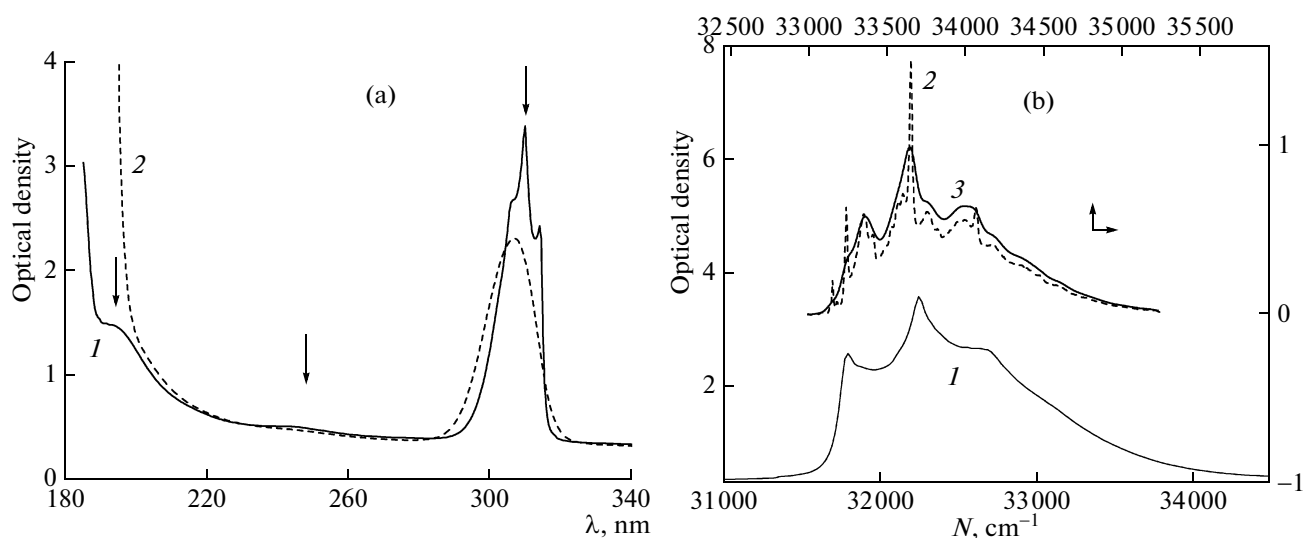
Fig. 1. Absorption spectra of $CdF_2-0.1\%$ CeF_3 crystals at 7.7 K (panels a, b; curves *1*) and 270 K (a, curve *2*) and $SrF_2-0.1\%$ CeF_3, NaF crystals at 13 K (b, curves *2, 3*). Curve *3* (b) was obtained by broadening spectrum *2* (b) using a Gaussian filter with a half-width of 75 cm^{-1}. The peaks are shifted along the abscissa axis to show the curve similarity.
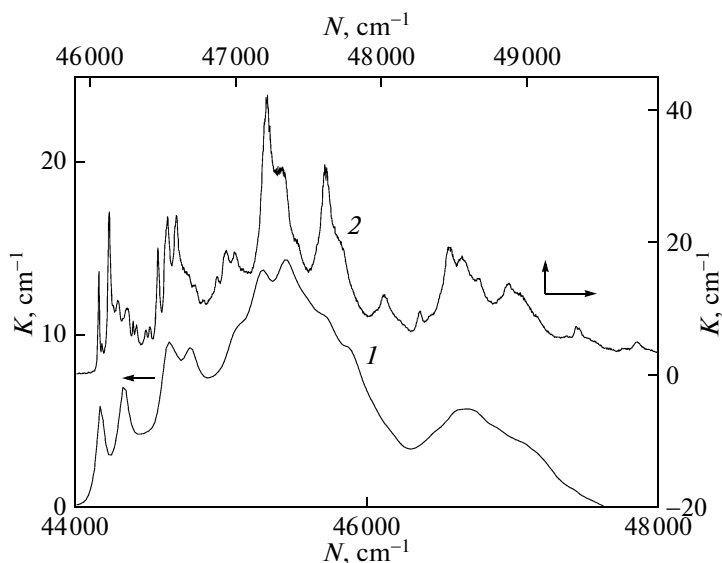

Fig. 2. Absorption spectra of (*1*) $CdF_2-0.01\%$ PrF_3 crystals at 7.5 K and (*2*) $BaF_2-0.01\%$ PrF_3 crystal at 6.5 K. The spectrum of BaF_2 crystal is shifted along the abscissa axis for convenience of comparison.

a rather large distance; this leads to the formation of cubically coordinated Ce ions and the absence of a band near 250 nm in the spectra of CaF_2 [7] and SrF_2 [9].

Similar to the spectra of cerium in alkali-earth fluorides, the 247- and 195-nm bands of CdF_2 exhibit no fine structure. The band near 190 nm in the spectra of CaF_2, SrF_2, and BaF_2 crystals consists of three subbands, two of which are due to the spin–orbit interaction (two different orientations of electron spin with respect to the orbital momentum). The nature of the third subband remains unclear [4, 8]. This splitting was

not observed for CdF_2 crystals (Fig. 1a), obviously, due to the proximity of the fundamental absorption edge.

The fine structure of the long-wavelength absorption band of Ce^{3+} ions in CdF_2 is shown in Fig. 1b along with the spectrum of cubic Ce^{3+} centers in SrF_2. Three subbands spaced by about 450 cm^{-1} can clearly be seen in the CdF_2 spectrum. Narrow zero-phonon lines of cubic Ce^{3+} centers were measured previously in CaF_2 (at a distance of 430 cm^{-1}) [8], SrF_2 (410 cm^{-1} [9]), and BaF_2 (396 cm^{-1}). The repetition of the zero-phonon line is explained in terms of the formation of

local modes, which cover the central cerium ion and its eight nearest neighbors [7]. This explanation is consistent with the decrease in frequency in the series of CdF_2, CaF_2, SrF_2, and BaF_2 compounds, which was observed experimentally. Indeed, the distance between the central cerium ion and its nearest neighbors increases in this series (because the lattice constant increases); correspondingly, the local vibrational frequencies of the CeF_8 fragment should decrease. At the same time, the observed order cannot be explained in terms of perturbation of lattice phonons by the impurity ion, because the decrease in the frequencies of longitudinal optical phonons is of another order of magnitude. The frequencies of longitudinal optical vibrations at 300 K in CaF_2, CdF_2, SrF_2, and BaF_2 are, respectively, 474, 404, 382, and 330 cm^{-1} [10].

An application of a Gaussian filter with a half-width of 75 cm^{-1} makes the absorption spectrum of SrF_2–Ce similar to that of the CdF_2–Ce spectrum (Fig. 1b).

The spectra of CdF_2–0.01% PrF_3 crystals contain a series of absorption bands, among which three double lines with a distance of about 160 cm^{-1} can be selected (Fig. 2). The absorption spectrum is fairly complicated: however, the main details of the absorption spectra of CdF_2–Pr and BaF_2–Pr are similar. The absorption spectrum of BaF_2–Pr contains a number of narrow lines. The lines in the absorption spectrum of CdF_2–Pr are much wider (Fig. 2). The shape of the absorption spectrum of CdF_2–Pr for PrF_3 concentrations of 0.01 and 0.1 mol % is the same, which indicates the absence of a tendency toward aggregation of praseodymium ions in CdF_2. The half-width of the first two (most pronounced) lines in the absorption spectrum of CdF_2–Pr is about 70 cm^{-1}.

The absorption spectra of Tb^{3+} ions in crystals of alkali-earth fluorides presented in Fig. 2 exhibit a pronounced line structure in the case of CaF_2 crystals and a less pronounced structure for SrF_2 and BaF_2 crystals.

The absorption spectrum of Tb^{3+} ions in CdF_2 is shown in Fig. 3. This spectrum contains at least three absorption bands, spaced by approximately 450 cm^{-1} from each other. The shape of the absorption spectrum of Tb^{3+} ions is very similar to that of Ce^{3+} ions in CdF_2 (Figs. 3 and 1). Therefore, the local vibration frequencies of TbF_8 and CeF_8 clusters in CdF_2 are identical. The line broadening in the absorption spectrum of BaF_2–0.01% TbF_3 crystals makes it similar to that of CdF_2–Tb crystals (Fig. 4).

DISCUSSION

The fundamental difference between the measured $4f$–$5d$ absorption spectra of rare-earth ions in CdF_2 and alkali-earth fluorides is that the CdF_2 spectra do not contain narrow lines. The absorption spectra of
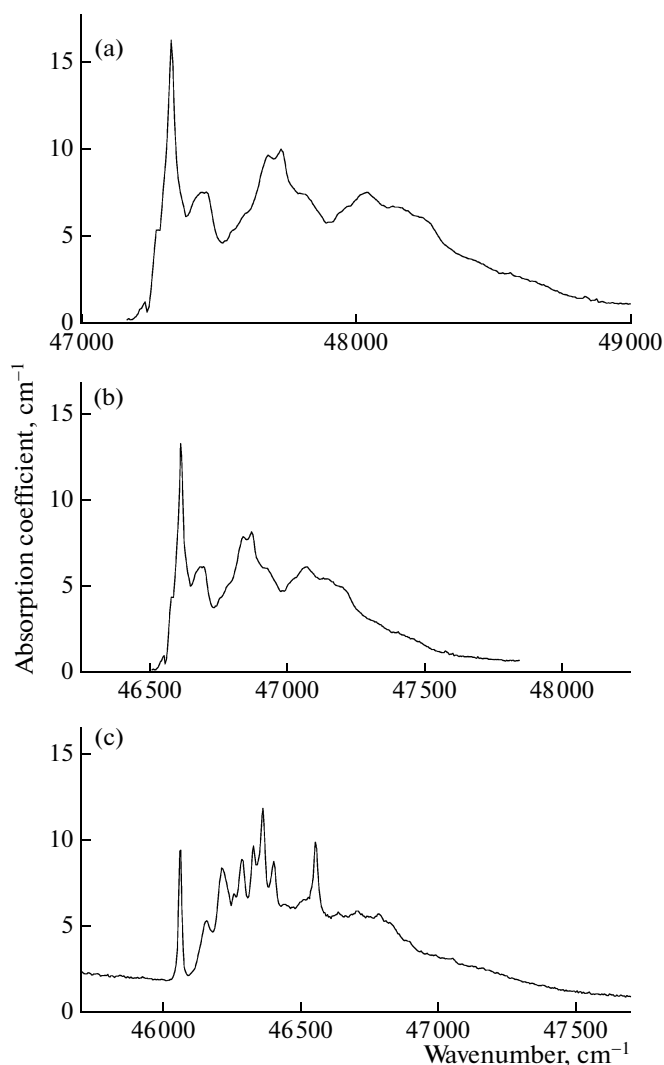

Fig. 3. Absorption spectra of Tb^{3+} ions in crystals of alkali-earth fluorides: (a) BaF_2–0.01% TbF_3, 8.1 K; (b) SrF_2–0.01% TbF_3, 7.9 K; and (c) CaF_2–0.01% TbF_3, 8.1 K.

Ce^{3+} and Pr^{3+} ions in crystals of alkali-earth fluorides consist of a set of narrow lines in the long-wavelength edge. The spectra of CdF_2 become similar to those of alkali-earth fluorides with Ce^{3+}, Pr^{3+}, and Tb^{3+} impurity ions when the spectral lines of the latter compounds are broadened by a Gaussian filter with a bandwidth of 60–75 cm^{-1}. Pure broadening of absorption lines does not prove that the level to which transition occurs lies in the conduction band. Broadening also arises due to the inhomogeneity of crystal, caused, for example, by introduction of impurities. Moreover, autoionization to the conduction band may occur only when the interaction between local excited states and the continuum of the conduction band is sufficiently strong.

For example, the $4f$–$4f$ transitions in Eu^{2+}, which fall in the BaF_2 conduction band, do not undergo broadening [2]. The Fano resonance is observed for
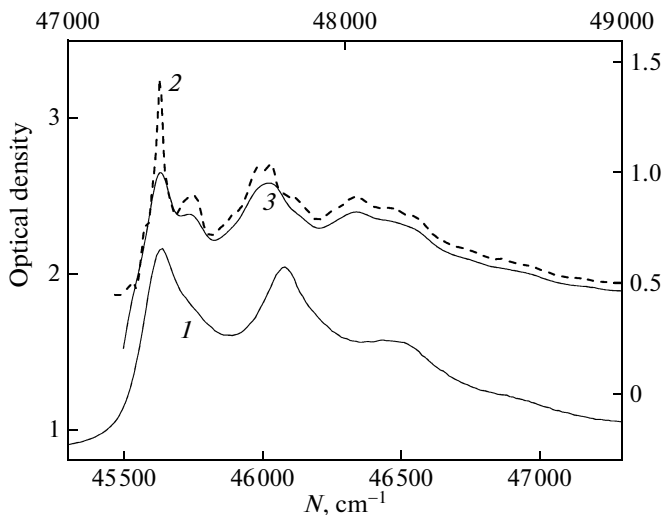
Fig. 4. Absorption spectra of (*1*) $CdF_2 - 0.01\%$ TbF_3 at 8.4 K and (*2*) $BaF_2 - 0.01\%$ TbF_3 at 8.1 K. Curve *3* is spectrum *2* broadened by a 60-cm^{-1} Gaussian filter.

the *d* states of rare-earth ions that fall in the conduction band; however, since the probability of the transition to local states significantly exceeds the probability of transition to the continuous states in the conduction band, one observes only a symmetric Lorentzian broadening instead of the well-known asymmetric Fano profile, which is observed for transitions with comparable probabilities [2]. The autoionization-induced level broadening for Eu^{2+} and Sm^{2+} ions in BaF_2 with respect to the line spectrum in SrF_2 was estimated to be 200–210 [2, 11] and 130 cm^{-1} [1], respectively. The line spectrum of Eu^{2+} in CaF_2, with a broadening of 75 cm^{-1} (a value close to those we obtained for Ce^{3+}, Pr^{3+}, and Tb^{3+} ions in fluoride cadmium crystals), makes it similar to the CdF_2 absorption spectrum [12].

The absorption lines of Tb^{3+} ions are significantly broadened in the $CaF_2 - SrF_2 - BaF_2$ series. Therefore, the distance between the $5d(e_g)$ level of Tb^{3+} ion and the bottom of the conduction band in SrF_2 and BaF_2 crystals becomes very small. At the same time, according to estimates, the $5d(e_g)$ level of Tb^{3+} ions in CaF_2 and BaF_2 should be below the bottom of the conduction band by 2.1 [13] and 1.2 eV [14], respectively. This difference is caused by the fact that the simple model [13, 14] does not take into account the exchange interaction. Recently, this effect was taken into account in [15] when estimating the positions of the levels of rare-earth ions in LaF_3 and La_2O_3. The exchange interaction leads to the following: rare-earth ions with numbers of electrons larger than 7 in the excited $4f^{n-1}5d$ state can be in the lowest (in energy) configuration with a high spin (HS) and in the configuration with a low spin (LS). The difference in the energies of these

states decreases almost linearly from 1 eV for Tb^{3+} to 0.3 eV for Lu^{3+} [15]. Since the ground state $4f^n$ is a low-spin one, the $4f^n - 4f^{n-1}5d$(LS) transitions are allowed. With regard to the correction of about 1 eV, it is clear that the $4f^7 5d$(LS) state of Tb^{3+} ion in the BaF_2 and SrF_2 lattices within the model [13–15] is close to the bottom of the conduction band and the transitions to this state are broadened, which is precisely the effect that we observed (Fig. 3).

CONCLUSIONS

Based on the experimental results of this study, we can suggest the following.

The $5d(e_g)$ level of Ce^{3+}, Pr^{3+}, and Tb^{3+} ions in CdF_2 is located far above the bottom of the conduction band, and the observed broadening of the $4f^n - 4f^{n-1}5d(e_g)$ absorption lines is caused by electron autoionization from the $5d(e_g)$ level to the energy-degenerate states of the conduction band of cadmium fluoride crystal.

The observed broadening of the lines due to the $4f^8 - 4f^7 5d$ transitions in Tb^{3+} ions in the $CaF_2 - SrF_2 - BaF_2$ series is caused by the approach of the $5d(e_g)$(LS) level to the bottom of the conduction band, which leads to electron autoionization.

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