Covalent mechanism of cooperative optical transitions and energy transfer in systems with paired lanthanide ions

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A new covalent mechanism is developed for the interaction of excited lanthanide ions (Ln^{3+}) appearing in the composition of small-radius optically active pair centers, in which the two ions have shared bridging ligands. It is shown that there is a specific interaction between the excited ions, which is associated with virtual transitions of electrons between the Ln^{3+} ions through the bridging ligands and which can be regarded as a generalization of the magnetic superexchange interaction to optical effects. A general formalism of the covalent interaction is developed, within which the influence of the covalency and the bridging ligands on the intensity of two-ion cooperative optical transitions and the energy transfer rate between the excited ions is investigated. It is shown that the intensity of a cooperative $(00)\rightarrow(ij)$ optical transition from the ground state to a doubly excited state for a pair of Ln^{3+} ions is strongly dependent on the nature of the bridging ligands and the local geometry of the three-center Ln(A)–ligand–Ln(B) system and can increase by several orders of magnitude upon passage from ionic (fluorides and oxides) to covalent compounds (bromides and iodides). The possible influence of the covalent mechanism on the strong anti-Stokes luminescence and the up-conversion effects in $CsCdBr_3:Ln^{3+}$ crystals containing small-radius ion pairs are discussed.
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1. INTRODUCTION

The cooperative optical processes in insulating crystals activated by lanthanide ions (Ln^{3+}) have aroused heightened interest on the part of investigators working in the field of the spectroscopy of crystals and solid-state lasers.[1–3] As we know, when Ln^{3+} ions are sufficiently close to one another in a crystal or a multinuclear complex, such processes as energy transfer between excited ions, two-ion cooperative luminescence and absorption, up-conversion,[4–8] and many other processes begin to be displayed. These processes become possible owing to the interaction between the ions and depend strongly on its magnitude.

It has been traditionally assumed that Ln^{3+} ions in an insulating crystal interact directly with one another via an electric multipole, mainly a dipole–dipole, interaction.[7,8] Numerous investigations in this area have shown that the theoretical models based on these interactions faithfully describe the main experimental laws governing energy transfer between excited ions in most cases. Nevertheless, there is presently a large accumulation of experimental data indicating that the use of only multipole–multipole interactions is insufficient for systems with closely arranged Ln^{3+} ions. These systems include crystals of $Cs_3Ln_2X_9$ (X=Cl, Br, I) and $CsCdBr_3:Ln^{3+}$, as well as crystals with a high concentration of activator ions, whose investigation has been the subject of many publications in the last few years. There is interest in these crystals because they have some unusual luminescence properties, including strong up-conversion effects, which are important for creating new lasers operating in the visible and UV regions using diode-laser pumping in the near-IR range.[9,10]

It should be specially noted that the Ln^{3+} ions in small-radius pair centers are in a unique situation. This is because in all actually existing insulating crystals any two nearest-neighbor Ln^{3+} ions are bonded to one another not directly, but by means of one or more shared bridging ligands, which are usually anions with completely filled electronic shells, such as F^-, O^{2-}, Cl^-, etc. The optically active $4f$, $5d$, and $6s$ orbitals of one lanthanide ion overlap the ns and np valence orbitals of the bridging ligand, which, in turn, overlap the optically active orbitals of the other lanthanide ion. This means that the $4f$ electrons are no longer strictly localized near the Ln^{3+} ions, since, due to the overlapping, they can pass from one Ln^{3+} ion to the other through the bridging ligands, which serve as mediators of this interaction. These transitions are virtual processes and result in the appearance of a specific interaction between the Ln^{3+} ions, in which both the geometry of the system and the nature of the bridging ligands play important roles. Since covalency and overlap are intimately related to one another, this interaction mechanism can be called covalent. In most insulating crystals this interaction has a short-range character and is effective only for nearest-neighbor Ln^{3+} ions joined by shared bridging ligands.

The role of the virtual transitions of electrons between Ln^{3+} ions in pair centers becomes clearer if we recall that these processes are responsible for the magnetic interaction between Ln^{3+} ions in insulators. It is generally known that these transitions underlie the so-called superexchange mechanism.[11] The exchange parameters of the superexchange mechanism for typical insulating lanthanide compounds are of the order of several cm^{-1} (Ref. 12). In other words, the covalent mechanism can be regarded as a generalization of the superexchange mechanism to optical transitions, and the main difference between them is that the su-

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perexchange mechanism describes the exchange interaction between the ground-state Stark levels of the Ln^{3+} ions, while the covalent mechanism considered here describes a broader group of effects involving two excited Ln^{3+} ions, including two-ion cooperative optical transitions and energy transfer between excited Ln^{3+} ions.

Thus, there is sufficient reason to believe that the covalent mechanism should play an important role in cooperative optical processes in intimate pairs of Ln^{3+} ions and in concentrated systems, where it can be at least as important as the multipole–multipole mechanism.

The main purpose of this paper is to formulate a general microscopic model of the covalent mechanism and to examine its role in cooperative optical processes and energy transfer in real lanthanide compounds. The formalism of the model of the covalent mechanism is developed in Sec. 2, and in Sec. 3 we examine in detail the mechanisms of the virtual transitions of electrons between Ln^{3+} ions though bridging ligands for the purpose of quantitatively evaluating the corresponding transfer integrals. In Sec. 4 this model is used to evaluate the intensities of cooperative optical transitions in an ion pair in a crystal or in a binuclear complex, and quantitative evaluations of the intensity of two-ion cooperative optical transitions in ionic (fluoride) and covalent (bromide) host crystals are given. In the last section of this paper we consider the main features of the new mechanism and briefly discuss the principal experimental results pertaining to possible manifestations of this mechanism in compounds containing small-radius pairs of Ln^{3+} ions.

2. GENERAL MICROSCOPIC MODEL OF THE COVALENT MECHANISM FOR PAIRS OF Ln^{3+} IONS WITH SHARED BRIDGING LIGANDS

Let us consider a pair of Ln^{3+} ions A and B that are nearest neighbors in an insulating crystal or in a binuclear complex (we note at once that we restrict the treatment to Ln^{3+} ions only to be specific, since the mechanism described below is also generally applicable to transition-metal and actinide ions). We assume that these ions are joined to one another by means of one or more shared bridging ligands (F^-, O^{2-}, Cl^-, etc), which have a closed ns^2np^6 electronic shell. Hereinafter we shall denote the wave functions of the individual Stark levels of the $4f^{N_A}$ electronic configuration of ion A everywhere by Ψ_i, the one-electron functions of the optically active electrons ($4f$, $5d$, and $6s$) by ψ_α, and the corresponding functions of ion B by ϕ_β. Since the direct overlap between the one-electron orbitals of two Ln^{3+} ions is fairly small in real systems, we shall assume that the wave functions ψ_α and ϕ_β are orthogonal.

The complete electronic Hamiltonian of the combined system of the pair of ions has the form

$$H=H_A+H_B+V_{AB}+h_{AB}. \tag{1}$$

Let us consider its structure in greater detail.

1) H_A and H_B are the electronic Hamiltonians of the individual Ln^{3+} ions A and B, which include both all the intraionic interactions of the electrons and the local crystal fields acting on these ions. We assume that the Hamiltonian H_A describes the complete crystal-field spectrum of ion A not only for the ground electronic configuration $4f^{N_A}$, but also for excited configurations of the type $4f^{N_A-1}n'f'$, such as $4f^{N_A-1}5d$:

$$\begin{aligned} &4f^{N_A}: && H_A\Psi_n=E_n(A)\Psi_n, \\ &4f^{N_A-1}5d: && H_A\Psi_n(fd)=E_n(A,fd)\Psi_n(fd), \end{aligned} \tag{2}$$

where Ψ_n, $\Psi_n(fd)$, $E_n(A)$, and $E_n(A,fd)$ are the wave functions of the crystal-field levels of ion A for the ground-state ($4f^{N_A}$) and excited ($4f^{N_A-1}$) $5d$ configurations. In addition, we shall assume that the Hamiltonian H_A also describes the complete energy spectrum of ion A for different configurations with N_A+1 and N_A-1 electrons, which differ from the ground-state $4f^{N_A}$ configuration by no more than one one-electron state:

$$\begin{aligned} &4f^{N_A+1}: && H_A\Psi_n^-=E_n^-(A)\Psi_n^-, \\ &4f^{N_A-1}: && H_A\Psi_n^+=E_n^+(A)\Psi_n^+, \\ &4f^{N_A}5d: && H_A\Psi_n^-(fd)=E_n^-(A,fd)\Psi_n^-(fd), \end{aligned} \tag{3}$$

where the wave functions Ψ and the self-energies E with plus and minus signs refer to the corresponding configurations with N_A-1 and N_A+1 electrons. Similar relations also hold for ion B.

2) The term V_{AB} in (1) refers to the Hamiltonian of the Coulomb interaction between the electrons of ion A and the electrons of ion B:

$$V_{AB}=\sum_{r_i\in A}\sum_{r_j\in B}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{4}$$

which is responsible for the multipole–multipole interaction between the $4f$ electrons of the Ln^{3+} ions. Since the role of these interactions has previously been discussed in detail in the literature,[7,8] we shall not examine it in this paper.

3) The last term h_{AB} in (1) is the "kinetic energy" operator:

$$h_{AB}=\sum_{\alpha\beta}(t_{\alpha\beta}a_\alpha^+(A)\alpha_\beta(B)+t_{\alpha\beta}^*a_\beta^+(B)\alpha_\alpha(A)). \tag{5}$$

This Hamiltonian describes the virtual transitions of electrons between ions A and B: $AB\rightarrow A^+B^-$ and A^-B^+. The symbols $a_\alpha^+(A)$, $\alpha_\alpha(A)$, $a_\beta^+(B)$, and $\alpha_\beta(B)$ denote the Fermi creation and annihilation operators of an electron in the $4f$ and $5d$ atomic orbitals (with the wave functions ψ_α and ϕ_β) of ion A or B, and $t_{\alpha\beta}$ is the corresponding transfer integral, whose microscopic origin will be discussed below. We shall show that the Hamiltonian (5) plays a key role in the covalent mechanism of cooperative optical effects.

The wave functions of an unperturbed pair of ions (i.e., a pair in which the interaction $U_{AB}=V_{AB}+h_{AB}$ equals zero) are described by antisymmetrized products of the corresponding single-ion wave functions:

$$\Psi_i\Phi_j=[\Psi_i(x_1,\ldots,x_{N_A})\Phi_j(x_{N_A+1},\ldots,x_{N_A+N_B})]_{as}, \tag{6}$$

where $[\ldots]_{as}$ denotes the operation of antisymmetrization with respect to all the electronic variables. When U_{AB} is nonzero, the wave function $\Psi_i\Phi_j$ of a pair state mixes with the wave functions $\Psi_k\Phi_l$ of other pair states:

$$\Psi_i\Phi_j-\sum_{k\neq i}\sum_{l\neq j}\frac{\langle\Psi_i\Phi_j|U_{\mathrm{AB}}|\Psi_k\Phi_l\rangle}{E_k(\mathrm{A})+E_l(\mathrm{B})-E_i(\mathrm{A})-E_j(\mathrm{B})}\Psi_k\Phi_l\,, \tag{7}$$

[where $E_i(\mathrm{A})$ and $E_j(\mathrm{B})$ are the energies of the corresponding states of ions A and B]. This means, in particular, that the ground-state wave function $\Psi_0\Phi_0$ of the ion pair AB mixes with the wave functions of excited pair states, including the states with opposite parity $\Psi_k\Phi_l(fd)$, which correspond to the two-ion $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}-1}5d$ configuration:

$$\Psi_0\Phi_0-\sum_{k\neq 0}\sum_{l\neq 0}\frac{\langle\Psi_0\Phi_0|U_{\mathrm{AB}}|\Psi_k\Phi_l\rangle}{E_k(\mathrm{A})+E_l(\mathrm{B})}\Psi_k\Phi_l$$
$$-\sum_{k\neq 0}\sum_{l\neq 0}\frac{\langle\Psi_0\Phi_0|U_{\mathrm{AB}}|\Psi_k\Phi_l(fd)\rangle}{E_k(\mathrm{A})+E_l^{fd}(\mathrm{B})}\Psi_k\Phi_l(fd), \tag{8}$$

where Ψ_0 and Φ_0 are the ground-state wave functions of ions A and B, whose energies are taken as a reference point: $E_0(\mathrm{A})=E_0(\mathrm{B})=0$.

Since the covalent effects of the interaction associated with the kinetic Hamiltonian h_{AB} are considered below in this paper, we must set $V_{\mathrm{AB}}=0$ and $U_{\mathrm{AB}}=h_{\mathrm{AB}}$. In this case, however, Eqs. (7) and (8) cannot be used directly, since the two-ion matrix elements $\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|\Psi_k\Phi_l\rangle$ vanish. Therefore, the kinetic operator h_{AB} must be replaced by a certain effective covalent Hamiltonian $V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})$, which acts in the space of the two-ion wave functions $\Psi_i\Phi_j$ without electron transfer. This Hamiltonian is obtained by projecting the kinetic Hamiltonian h_{AB} onto the space of the functions $\Psi_i\Phi_j$ without electron transfer. This requires construction of the two-ion wave functions $Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})$ and $Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})$, which correspond to excited states with electron transfer, from the corresponding single-ion functions with $N_\mathrm{A}\pm 1$ electrons on ion A and $N_\mathrm{B}\mp 1$ electrons on ion B:

$$Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})=\Psi_m^+\Phi_n^-=[\Psi_m^+(x_1,\ldots,x_{N_\mathrm{A}-1})$$
$$\times\Phi_n^-(x_{N_\mathrm{A}},x_{N_\mathrm{A}+1},\ldots,x_{N_\mathrm{A}+N_\mathrm{B}})]_{\mathrm{as}}, \tag{9}$$
$$Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})=\Psi_m^-\Phi_n^+=[\Psi_m^-(x_1,\ldots,x_{N_\mathrm{A}},x_{N_\mathrm{A}+1})$$
$$\times\Phi_n^+(x_{N_\mathrm{A}+2},\ldots,x_{N_\mathrm{A}+N_\mathrm{B}})]_{\mathrm{as}},$$

where the double subscript mn reflects the parentage of the two-ion functions with electron transfer. We also note that the states $Q_{mn}(\mathrm{A}\leftrightarrow\mathrm{B})$ corresponding to a two-ion $4f^{N_\mathrm{A}-1}$–$4f^{N_\mathrm{B}}5d$ configuration, which form from the original $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}}$ configuration as a result of a $4f(\mathrm{A})\rightarrow 5d(\mathrm{B})$ electron-transfer process, and $Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})=\Psi_m^+\Phi_n^-(fd)$ are also possible.

The matrix elements $\langle\Psi_i\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_k\Phi_l\rangle$ of the effective covalent operator acting on the space of the two-ion functions of the $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}}$ configuration are defined by second-order perturbation theory formulas with respect to the kinetic operator h_{AB}:

$$\langle\Psi_i\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_k\Phi_l\rangle$$
$$=\sum_{Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})}\frac{\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})\rangle\langle Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})|h_{\mathrm{AB}}|\Psi_k\Phi_l\rangle}{\Delta E_{mn}(\mathrm{A}\rightarrow\mathrm{B})}$$
$$-\sum_{Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})}\frac{\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})\rangle\langle Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})|h_{\mathrm{AB}}|\Psi_k\Phi_l\rangle}{\Delta E_{mn}(\mathrm{B}\rightarrow\mathrm{A})}, \tag{10}$$

where the summation is carried out over all the virtual electron-transfer states $Q_{mn}(\mathrm{A}\leftrightarrow\mathrm{B})$ and the $\Delta E_{mn}(\mathrm{A}\leftrightarrow\mathrm{B})$ in the denominators correspond to the energies of these states. The matrix elements of the effective covalent Hamiltonian for the two-ion $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}-1}5d$ configurations are defined in a similar manner:

$$\langle\Psi_i\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_k\Phi_l(fd)\rangle$$
$$=-\sum_{Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})}\frac{\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})\rangle\langle Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})|h_{\mathrm{AB}}|\Psi_k\Phi_l(fd)\rangle}{\Delta E_{mn}(\mathrm{A}\rightarrow\mathrm{B})}$$
$$-\sum_{Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})}\frac{\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})\rangle\langle Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})|h_{\mathrm{AB}}|\Psi_k\Phi_l(fd)\rangle}{\Delta E_{mn}(\mathrm{B}\rightarrow\mathrm{A})}, \tag{11}$$

The matrix elements $\langle\Psi_i\Phi_j|V_{\mathrm{AB}}|Q_{mn}(\mathrm{B}\rightarrow\mathrm{A})\rangle$ can be expressed in terms of the transfer integrals $t_{\alpha\beta}$ appearing in the kinetic operator h_{AB} (5). For this purpose the two-ion wave functions $\Psi_m\Phi_n$ and $Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})$ must be written in terms of the Slater determinants $\mathrm{Det}(\mathbf{p})$ and $\mathrm{Det}(\mathbf{q})$ composed of the $4f$ and $5d$ orbitals of ions A and B:

$$\Psi_i\Phi_j=\sum_{\mathbf{p}}C(\mathbf{p})\mathrm{Det}(\mathbf{p}), \tag{12}$$

$$Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})=\sum_{\mathbf{q}}C(\mathbf{q})\mathrm{Det}(\mathbf{q}),$$

where the vectors $\mathbf{p}$ and $\mathbf{q}$ denote the sets of atomic orbitals comprising Det(**p**) and Det(**q**) (the appearance of one $5d$ orbital is also possible in the latter determinant):

$$\mathbf{p}=(4f_{k_1}(\mathrm{A}),\ldots,4f_{k_{N_A}}(\mathrm{A}),4f_{k_A+1}(\mathrm{B}),\ldots,4f_{k_A+N_B}(\mathrm{B})),\tag{13}$$

$$\mathbf{q}=(4f_{k_1}(\mathrm{A}),\ldots,4f_{k_{N_A-1}}(\mathrm{A}),$$

$$\times 4f_{k_{N_A}}(\mathrm{B}),\ldots,4f_{k_{N_A+N_B-1}}(\mathrm{B}),n'l'_{k_{N_A+N_B}}),$$

where $n'l'=4f$ or $5d$. As a result we have

$$\langle\Psi_i\Phi_j|h_{\mathrm{AB}}|Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})\rangle=\sum_{\mathbf{p}}\sum_{\mathbf{q}}C^{+}(\mathbf{p})C(\mathbf{q})$$

$$\times\langle\,\mathrm{Det}(\mathbf{p})|h_{\mathrm{AB}}|\mathrm{Det}(\mathbf{q})\rangle.\tag{14}$$

The double sum in (14) is easily calculated, since the matrix element $\langle\mathrm{Det}(\mathbf{p})|h_{\mathrm{AB}}|\mathrm{Det}(\mathbf{q})\rangle$ is nonzero only if the determinants Det(**p**) and Det(**q**) differ with respect to no more than one pair of orbitals, viz., $4f_\alpha(\mathrm{A})$ and $n'l'_\beta(\mathrm{B})$:

$$\langle\mathrm{Det}(\mathbf{p})|h_{\mathrm{AB}}|\mathrm{Det}(\mathbf{q})\rangle=\langle 4f_\alpha(\mathrm{A})|h_{\mathrm{AB}}|n'l'_\beta(\mathrm{B})\rangle$$

$$=t_{\alpha\beta}(4f,n'l').\tag{15}$$

Equations (10)–(15) permit a quantitative evaluation of the magnitude of the covalent interaction in the system AB of two Ln^{3+} ions, between which there is virtual $\mathrm{AB}\rightarrow\mathrm{A}^{+}\mathrm{B}^{-}$, $\mathrm{A}^{-}\mathrm{B}^{+}$ electron exchange through the shared bridging ligands (whose mechanisms are considered below). For example, the two-ion matrix elements $\langle\Psi_i\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_k\Phi_l\rangle$ (10) specify the probability amplitude of a transition between the two pair states $\Psi_i\Phi_j$ and $\Psi_k\Phi_l$, while the matrix elements $\langle\Psi_i\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_k\Phi_l(fd)\rangle$ (11) specify the degree of mixing of the wave functions of opposite parity with the wave function of the ground configuration and, consequently, the intensities of the pair optical transitions, which will be discussed below.

3. TRANSFER INTEGRALS IN PAIRS OF LANTHANIDE IONS WITH BRIDGING LIGANDS

The transfer integrals have heretofore been treated as empirical parameters. They are actually closely related both to the electronic structure of the bridging ligands and to the local geometry of the ion pair. In this section we examine the mechanisms of the virtual transitions of electrons between Ln^{3+} ions via shared bridging ligands in detail in order to express the corresponding transfer integrals $t_{\alpha\beta}$ in terms of such quantum-chemical quantities as overlap integrals and orbital energies.

As we know, for two atoms in direct contact the transfer integrals $t_{\alpha\beta}$ between the orbitals ψ_α and ϕ_β of these atoms coincide with the corresponding resonance integrals

$$\epsilon_{\alpha\beta}=\int\psi_\alpha^{*}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{r})\right)\phi_\beta d\mathbf{r},\tag{16}$$

where $\mathbf{p}^2/2m$ is the kinetic energy operator and $V(\mathbf{r})$ is an effective one-particle potential. Resonance integrals are widely used in quantum-chemical calculations, and there are many well developed methods for calculating them. In particular, the most frequently employed method is the Wolfsberg–Helmholtz approximation

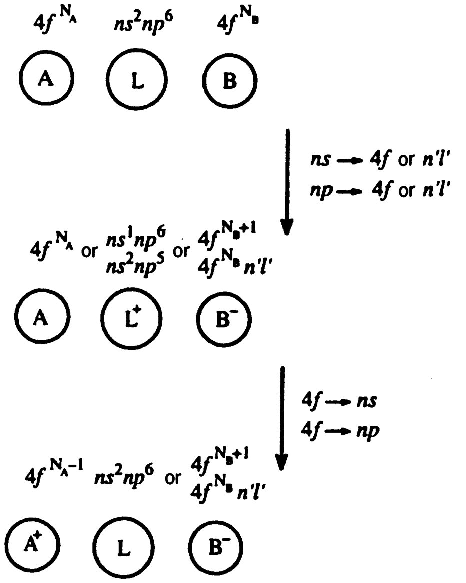

FIG. 1. General scheme of virtual transitions of an electron between Ln^{3+} ions in a three-center $\mathrm{Ln}^{3+}(\mathrm{A})$–ligand–$\mathrm{Ln}^{3+}(\mathrm{B})$ system.

$$\epsilon_{\alpha\beta}=\frac{K}{2}(E_\alpha+E_\beta)S_{\alpha\beta},\tag{17}$$

where E_α and E_β are the energies of the corresponding atomic orbitals ψ_α and ϕ_β, $S_{\alpha\beta}$ are the overlap integrals between these orbitals, and K is an empirical constant, which equals 2 or 1.75 (Ref. 13).

The problem of quantitatively evaluating transfer integrals is greatly complicated when we pass from a two-center system to a three-center system, such as $\mathrm{Ln}^{3+}(\mathrm{A})$–ligand–$\mathrm{Ln}^{3+}(\mathrm{B})$. In this case the optically active $4f$, $5d$, and $6s$ atomic orbitals overlap the valence orbitals of the bridging ligands, while their direct overlap is usually negligibly small. For this reason an electron cannot pass directly from ion A to ion B without entering the ligand. Since typical ligands (such as F^{-}, O^{2-}, Cl^{-}, etc.) have a closed ns^2np^6 electronic shell, the direct transfer of an electron from a Ln^{3+} ion to the ligand is impossible, and the $\mathrm{Ln}^{3+}(\mathrm{A})\rightarrow\mathrm{ligand}\rightarrow\mathrm{Ln}^{3+}(\mathrm{B})$ electron-transfer process takes place in two steps. The overall scheme of this process is presented in Fig. 1. In the first step an electron passes from the ligand L to Ln^{3+} ion B with the formation of an intermediate ionized ns^1np^6 or ns^2np^5 configuration in the ligand, and in the second step another electron passes from Ln^{3+} ion A to the ligand, restoring its closed ns^2np^6 electronic configuration. Since the energies $\Delta E_{ik}(\mathrm{L}\rightarrow\mathrm{Ln}^{3+})$ for electron transfer from a ligand to a metal ion are usually considerably greater than the corresponding resonance integrals $\epsilon_{\alpha\beta}(\mathrm{L}\rightarrow\mathrm{A})$ or $\epsilon_{\alpha\beta}(\mathrm{L}\rightarrow\mathrm{B})$, the total transfer integral $t_{\alpha\beta}$ can be obtained in second-order perturbation theory:

$$t_{\alpha\beta}=\sum_{\gamma\in ns,np}\frac{\epsilon_{\alpha\gamma}(\mathrm{L}\rightarrow\mathrm{B})\epsilon_{\gamma\beta}(\mathrm{A}\rightarrow\mathrm{L})}{\Delta E_{\alpha\gamma}(\mathrm{L}\rightarrow\mathrm{Ln}^{3+})}. \tag{18}$$

It should be noted that this approximation can be considered perfectly correct for lanthanide systems, where the overlap of the highly localized $4f$ orbitals with the environment is sufficiently small. When there are several bridging ligands $\mathrm{L}_1, \ldots, \mathrm{L}_q$ between ions A and B, the expression (18) is easily generalized by the formula

$$t_{\alpha\beta}=\sum_{\mathbf{q}}^{\text{ligands}}\sum_{\gamma\in ns,np}\frac{\epsilon_{\alpha\gamma}(\mathrm{L}_q\rightarrow\mathrm{B})\epsilon_{\gamma\beta}(\mathrm{A}\rightarrow\mathrm{L}_q)}{\Delta E_{\alpha\gamma}(\mathrm{L}_q\rightarrow\mathrm{Ln}^{3+})}. \tag{19}$$

As follows from (19), the resultant transfer integral $t_{\alpha\beta}$ is additive with respect to the different bridging ligands L_q and intermediate valence orbitals. It must, however, be noted that in real systems a large number of different channels of $\mathrm{Ln}^{3+}(\mathrm{A}) \rightarrow$ ligand $\rightarrow \mathrm{Ln}^{3+}$ (B) electron transfer, which appear as a result of different combinations of the initial, intermediate, and final orbitals $\alpha \in \mathrm{Ln}^{3+}(\mathrm{A})$, $\gamma \in \mathrm{L}_q$, $\beta \in \mathrm{Ln}^{3+}(\mathrm{B})$, are possible. Since the contributions from the individual channels can differ in both magnitude and sign, considerable interference effects between different electron-transfer channels and strong sensitivity to the local geometry of the system are possible in the mechanism under consideration. Equation (19) can be used for realistic evaluations of transfer integrals in real systems.

4. COVALENT MECHANISM AND INTENSITIES OF PAIR OPTICAL TRANSITIONS

In this section we consider the mechanisms of two-ion cooperative optical transitions in a pair of Ln^{3+} ions associated with the covalent interaction mechanism.

The general expression for the matrix element $M(00\rightarrow ij)$ of the electric-dipole transition from the ground state $\Psi_0\Phi_0$ of a pair to the doubly excited state $\Psi_i\Phi_j$ was derived by Dexter[8] for the case of a Coulomb interaction V_{AB} between the ions. The analogous expression for the covalent interaction mechanism is easily obtained by simply replacing the matrix elements of the Coulomb Hamiltonian by the matrix elements of the effective covalent Hamiltonian defined by Eqs. (10) and (11):

$$\begin{aligned}M(00\rightarrow ij)=&-\sum_k\frac{\langle\Psi_i|\mathbf{e}\cdot\mathbf{R}_\mathrm{A}|\Psi_k(fd)\rangle\langle\Psi_k(fd)\Phi_j|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_0\Phi_0\rangle}{E_j(\mathrm{B})+E_k(\mathrm{A},fd)}-\sum_k\frac{\langle\Phi_j|\mathbf{e}\cdot\mathbf{R}_\mathrm{B}|\Phi_k(fd)\rangle\langle\Psi_i\Phi_k(fd)|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_0\Phi_0\rangle}{E_i(\mathrm{A})+E_k(\mathrm{B},fd)}\\&-\sum_k\frac{\langle\Psi_0|\mathbf{e}\cdot\mathbf{R}_\mathrm{A}|\Psi_k(fd)\rangle\langle\Psi_k(fd)\Phi_0|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle}{E_k(\mathrm{A},fd)-E_i(\mathrm{A})-E_j(\mathrm{B})}-\sum_k\frac{\langle\Phi_0|\mathbf{e}\cdot\mathbf{R}_\mathrm{B}|\Phi_k(fd)\rangle\langle\Psi_0\Phi_k(fd)|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle}{E_k(\mathrm{B},fd)-E_i(\mathrm{A})-E_j(\mathrm{B})},\end{aligned} \tag{20}$$

where

$$\mathbf{e}\cdot\mathbf{R}_\mathrm{A}=e\sum_{p=1}^{N_A}r_p,\quad \mathbf{e}\cdot\mathbf{R}_\mathrm{B}=e\sum_{p=N_A+1}^{N_A+N_B}r_p \tag{21}$$

are the electric-dipole moment operators of ions A and B.

The general microscopic mechanism of a cooperative transition can be illustrated by the scheme presented in Fig. 2. The system AB of two Ln^{3+} ions passes from its ground state $\Psi_0\Phi_0$ as a result of a $4f(\mathrm{A})\rightarrow 5d(\mathrm{B})$ electron-transfer act (due to the action of the kinetic operator h_{AB}) into the charge-transfer state $Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})=\Psi_m^+\Phi_n^-(fd)$, from which it passes after a second $4f(\mathrm{B})\rightarrow 4f(\mathrm{A})$ electron-transfer act into the state $\Psi_i\Phi_k(fd)$, which is assigned to the two-ion $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}-1}5d$ configuration. Finally, a dipole-allowed $4f^{N_\mathrm{B}-1}5d\rightarrow 4f^{N_\mathrm{B}}$ transition takes place in ion B under the action of a quantum of light, and, as a result, the system AB reaches the final doubly degenerate state $\Psi_i\Phi_j$, which is assigned to the ground-state $4f^{N_\mathrm{A}}$–$4f^{N_\mathrm{B}}$ configuration.

This scheme can be extended directly to the case of a $\Psi_i\Phi_j\rightarrow\Psi_k\Phi_l$ transition for an arbitrary pair of doubly excited states.

Due to the complexity of the electronic structure of the Ln^{3+} ions, a detailed quantitative calculation of the intensities of pair transitions of the type $\Psi_0\Phi_0\rightarrow\Psi_i\Phi_j$ for real lanthanide systems is impossible without using numerical methods. Nevertheless, after making several simplifying assumptions, we can attempt to obtain some approximate estimates for the purpose of establishing the relationship between the intensities of cooperative transitions and the nature of the bridging ligands, as well as for drawing some general conclusions regarding the effectiveness of the covalent mechanism. Using (20) for this purpose, we represent $-M_{ij}(00\rightarrow ij)$ in the form

$$-M_{ij}(00\rightarrow ij)\approx T\langle 4f|er|5d\rangle. \tag{22}$$

Here $\langle 4f|er|5d\rangle$ is the matrix element of the parity-allowed $4f$–$5d$ transition, and T is the reduction factor, whose characteristic value is given by the ratio

$$T\approx\frac{\langle\Psi_0\Phi_l(fd)|V_{\mathrm{AB}}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle}{E(4f-5d)}, \tag{23}$$

where $E(4f-5d)$ is a certain averaged energy of the $4f^{N_\mathrm{A}-1}5d\rightarrow 4f^{N_\mathrm{A}}$ transition, which does not depend on the subscripts of the single-ion wave functions Φ_l, Ψ_i, and Φ_j. The square of this factor specifies the ratio between the oscillator strengths of the $(00)\rightarrow(ij)$ pair transition and the one-ion dipole-allowed $4f$–$5d$ transition: $T^2=P_{\mathrm{coop}}^{ed}/P_{fd}^{ed}$.

The next approximation involves replacement of the matrix elements of the type $\langle\Psi_i\Phi_j|V_{\mathrm{AB}}|Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})\rangle$ by the

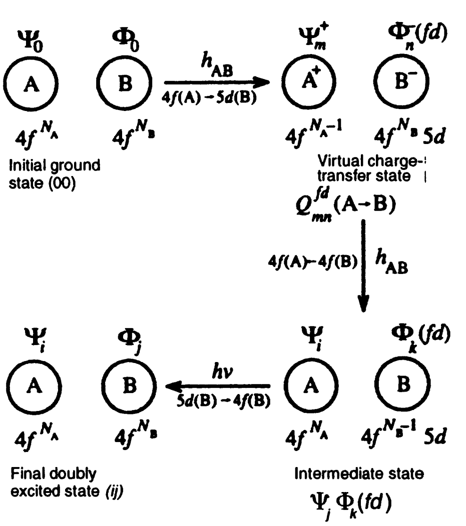

FIG. 2. Schematic representation of the microscopic process underlying a cooperative optical transition from the ground state (00) of a pair of Ln^{3+} ions AB to the doubly excited state (ij) under the covalent mechanism.

averaged transition integrals $t(4f-4f)$ and $t(4f-5d)$, which correspond, respectively, to $4f(A)\to 4f(B)$ and $4f(A)\to 5d(B)$ electron-transfer acts:

$$\begin{aligned}&\langle\Psi_i\Phi_j|V_{AB}|Q_{mn}(A\to B)\rangle\approx t(4f-4f),\\&\langle Q_{mn}(A\to B)|V_{AB}|\Psi_i\Phi_j(fd)\rangle\approx t(4f-5d).\end{aligned}\tag{24}$$

Of course, this approximation is fairly rough, since it ignores the angular dependence of the matrix elements associated with anisotropy of the overlap of the $4f$ and $5d$ orbitals with the ligand orbitals, but its use makes it possible to greatly simplify evaluation of the intensities.

Next, it must be taken into account that the coupling of the $4f$ and $5d$ electrons in the excited $4f^{N_B}5d$ and $4f^{N_B-1}5d$ configurations is mediated by the intra-atomic Coulomb and exchange interactions, each of which is described by three Slater parameters $[F^{2k}(5d,4f)$ and $G^{2k+1}(5d,4f)$, $k=0, 1, 2]$. It can be shown that in the expression (11) for the two-ion matrix elements $\langle\Psi_k(fd)\Phi_0|V_{AB}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle$ the products of matrix elements of the type $\langle\Psi_i\Phi_j|h_{AB}|Q_{mn}(B\to A)\rangle\times\langle Q_{mn}(B\to A)|h_{AB}|\Psi_k\Phi_l(fd)\rangle$ in the numerators will have different signs for the corresponding "high-spin" and "low-spin" states of the $4f^N5d$ configuration and that their energy dominators will differ by the magnitude of the energy of the intra-atomic exchange interaction between the $4f$ and $5d$ electrons $[\Delta E(A\to B)$ for the "low-spin" states and $\Delta E(A\to B)-J_{fd}$ for the "high-spin" states, respectively, where $\Delta E(A\to B)$ is the mean energy of the $4f^{N_A}$–$4f^{N_B}\to 4f^{N_A-1}$–$4f^{N_B}5d$ transition and $J_{fd}\approx G^1(5d,4f)]$. As a result, the energy denominator $1/\Delta E(A\to B)$ should be replaced by the expression $1/(\Delta E(A\to B)-J_{fd})-1/\Delta E(A\to B)\approx J_{fd}/\Delta E^2(A\to B)$, and the matrix element $\langle\Psi_k(fd)\Phi_0|V_{AB}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle$ is estimated by the expression

$$\langle\Psi_k(fd)\Phi_0|V_{AB}^{\mathrm{cov}}(\mathrm{eff})|\Psi_i\Phi_j\rangle=C\frac{t(4f-4f)t(4f-5d)J_{fd}}{\Delta E^2(A\to B)},\tag{25}$$

where C is a certain numerical factor, whose preliminary estimation for the simple $4f^1$-$4f^1$ system gives $C\approx 0.1$. Thus, we ultimately obtain

$$T\approx C\frac{t(4f-4f)t(4f-5d)J_{fd}}{\Delta E^2(A\to B)E(4f-5d)}.\tag{26}$$

It can be concluded from (26) that the intensity of a two-ion cooperative optical transition depends mainly on the transfer integrals, since $\Delta E(A\to B)$, $E(4f-5d)$, and J_{fd} are properties of the Ln^{3+} ions and vary comparatively little upon passage from one system to another.

4.1. Numerical evaluations of the intensity

Let us now numerically evaluate the oscillator strengths of the two-ion optical transitions associated with the covalent interaction mechanism. To reveal the dependence of the intensity of a transition on the nature of the ligand, we shall perform comparative calculations for hosts with a maximum ionic character of the chemical bonds (fluorides) and for more covalent hosts (bromides). Our purpose is to evaluate the reduction factor T for these hosts.

We first consider the atomic parameters needed to evaluate the transfer integrals $t(4f-4f)$ and $t(4f-5d)$ from Eq. (22). The resonance integrals appearing in this equation are calculated using the approximation (20), and the overlap integrals $S(4f-2s)$, $S(4f-2p)$, $S(5d-2s)$, and $S(5d-2p)$ are calculated using the radial double-zeta Slater functions for Ln^{3+} ions,[14] as well as the $2s$ and $2p$ atomic orbitals for F and the $4s$ and $4p$ atomic orbitals for Br (Ref. 15) with averaged Ln–F and Ln–Br distances typical of fluoride and bromide compounds of lanthanides. The energies of the following atomic orbitals were used in the calculations:

$$E_{\mathrm{Ln}}(4f)=-7\mathrm{eV},\quad E_{\mathrm{Ln}}(5d)=-5\mathrm{eV},$$

$$E_{\mathrm{F}}(2s)=-30\mathrm{eV},\quad E_{\mathrm{F}}(2p)=-20\mathrm{eV},$$

$$E_{\mathrm{Br}}(4s)=-25\mathrm{eV},\quad E_{\mathrm{Br}}(4p)=-12\mathrm{eV}.$$

The energies for electron transfer from a ligand to a lanthanide ion were approximated by the energy difference between the respective orbitals. To evaluate the energy of a $4f^{N_A}$–$4f^{N_B}\to 4f^{N_A-1}$–$4f^{N_B}5d$ transition, we used the value of the interatomic Coulomb repulsion between the $4f$ and $5d$ electrons $\Delta E(A\to B)=F^0(5d,4f)\approx 5$ eV (Ref. 16) and the value $J_{fd}\approx G^1(5d,4f)\approx 1$ eV (Ref. 17). In addition, we took the values $E(4f-5d)=5$ eV and $C=0.1$.

4.2. Fluoride crystals

The values of the overlap integrals for the fluorides are $S_\sigma(4f-2s)\approx S_\sigma(4f-2p)=0.02$ and $S_\sigma(5d-2s)\approx S_\sigma(5d-2p)=0.1$–$0.15$. Using them, from Eq. (19) we obtain the following estimates for the transfer integrals:

$$\begin{aligned}&t(4f-4f)\approx 0.02\mathrm{eV},\\&t(4f-5d)\approx 0.1\mathrm{eV}.\end{aligned}\tag{27}$$

Substituting these values into (22), for the reduction factor we obtain $T \approx 2 \times 10^{-6}$. Since the oscillator strengths P_{fd}^{ed} for dipole-allowed $4f$–$5d$ transitions usually fall in the range from 1 to 10^{-2}, we obtain

$$P_{\text{coop}}^{ed} = P_{fd}^{ed} T^2 \approx 10^{-14} - 4 \times 10^{-12}. \tag{28}$$

Therefore, in fluoride crystals the covalent mechanism produces very low intensities for the pair cooperative transitions, which are approximately six orders of magnitude smaller than the intensities of the single-ion $4f$–$4f$ electric-dipole transitions: $P_{4f-4f}^{ed} \approx 10^{-6}$.

4.3. Bromide crystals

The role of the covalent effects in compounds of lanthanides and transition metals increases significantly when we pass from fluoride compounds, which have the most ionic type of chemical bonding, to compounds with the less electronegative heavy halogens.[18] Owing to the greater diffuseness of the bromine $4s$ and $4p$ orbitals in comparison with the fluorine valence orbitals, the overlap integrals increase somewhat, i.e., $S_\sigma(4f-4s) \approx S_\sigma(4f-4p) = 0.03$ and $S_\sigma(5d-4s) \approx S_\pi(5d-4p) = 0.3$, while the energies for electron transfer from a ligand to a Ln^{3+} ion decrease. All this results in a significant increase in the overlap integrals:

$$t(4f-4f) \approx 0.1 \ \text{eV}, \tag{29}$$

$$t(4f-5d) \approx 0.6 \ \text{to} \ 0.8 \ \text{eV}.$$

Using (26), we obtain the value for the reduction factor $T \approx 3 \times 10^{-5}$, and, accordingly, for the oscillator strength we have

$$P_{\text{coop}}^{ed} \approx 10^{-11} \ \text{to} \ 10^{-9}. \tag{30}$$

Thus, the effectiveness of the covalent mechanism of pair optical transitions is greatly dependent on the nature of the bridging ligands and can increase by several orders of magnitude when we pass from fluoride crystals to bromide crystals.

4.4. Radius of action of the covalent mechanism and covalency of the host

The above estimates of the intensity of cooperative transitions, as well as the values of the two-ion matrix elements $\langle \Psi_i \Phi_j | H_{AB}^{\text{cov}}(\text{eff}) | \Psi_k \Phi_l \rangle$ of the effective Hamiltonian of the covalent interaction, refer to a pair of two nearest-neighbor ions separated only by shared bridging ligands. Now we shall discuss the question of the character of the variation of the covalent interaction as the distance between the ions increases.

As follows from Eqs. (10)–(15), all other conditions being equal, the matrix elements of the Hamiltonian $H_{AB}^{\text{cov}}(\text{eff})$ are proportional to the squares of the corresponding transfer integrals $t_{\alpha\beta}$, which are given by Eq. (19) for nearest-neighbor ions. Therefore, to analyze the law governing the variation of the covalent potential with the distance, the $AB \to A^+B^-$, A^-B^+ electron-transfer processes considered in Sec. 3 (see Fig. 1) must be generalized to the case of nonnearest-neighbor ions A and B in order to evaluate the transfer integrals.

It should, first of all, be noted that unlike a pair of nearest-neighbor ions, where it is sufficient to restrict ourselves to consideration of only the localized electronic states of the shared bridging ligands, for an arbitrary pair of lanthanide ions we must consider the band states of the crystal. In fact, in analogy to the scheme in Fig. 1, the $AB \to A^+B^-$ charge-transfer process for such a pair can be regarded as the capture of an electron by ion B from the completely filled valence band of the crystal followed by migration of a virtual hole through the crystal to ion A. The character of such migration and the probability of this process as a whole depend strongly on the width of the valence band of the crystal and differ significantly for crystals with ionic and covalent types of chemical bonding, which should be considered separately.

Typical ionic crystals are characterized by a narrow valence band, and the migration of a hole in them has a hopping character. In other words, on the way from ion B to ion A, a hole undergoes a definite number of hops between cations and anions (ligands), which increases with increasing distance between the ions. Each such hop is accompanied by a decrease in the total quantum amplitude of the $AB \to A^+B^-$ transition by a certain factor, which coincides in order of magnitude with the ion–ligand or ligand–ligand overlap integral S, and the resultant transfer integral is, therefore, proportional to S^n, where n is the minimum number of hops needed for the transition. Since the number n is proportional to the distance R_{AB} between the ions, taking into account (10)–(15), we find that the covalent potential for an ionic crystal decreases exponentially:

$$\langle \Psi_i \Phi_j | H_{AB}^{\text{cov}}(\text{eff}) | \Psi_k \Phi_l \rangle \propto \exp(-R_{AB}/R_0),$$

where the effective radius R_0 is proportional to S^2. As was shown above, the overlap integrals are fairly small ($S \leqslant 0.1$); therefore, the covalent potential for strongly ionic crystals (fluorides and most oxides) decreases very rapidly with the distance and is actually nonzero only for nearest neighbors. In moderately ionic crystals (bromides, iodides, and some sulfides) the exponential law is maintained, but due to the large values of the overlap integrals the effective radius R_0 increases, and the covalent interaction can play a more appreciable role for the next-nearest and more distant neighbors. These conclusions are in full agreement with numerous experimental data on exchange interactions between rare-earth or transition-metal ions in ionic crystals, according to which the constants of the exchange interaction (associated with the superexchange mechanism, which is similar to the covalent interaction mechanism) between nearest-neighbor ions with shared bridging ligands are considerably greater than the exchange constants for more distant ions.[19]

In crystals with a predominantly covalent type of chemical bonding (for example, in semiconductor chalcogenide and pnictide crystals) the hole-migration process is far more effective owing to the great width of the valence band, and it is mediated by the delocalized Bloch states of the crystals. Consequently, the covalent mechanism becomes effective even for fairly distant ions in this case. In these crystals the exponential dependence of the decrease in the covalent potential with distance is probably replaced by a different, more gently sloping dependence.

In summation, it can be concluded that the radius of action of the covalent mechanism is greatly dependent on the "conducting" properties of the host with respect to the migration of a virtual hole from one metal ion to another. This conclusion is consistent with the known experimental data for molecular exchange systems,[19] according to which a significant exchange interaction can be maintained between magnetic metal ions joined by means of long molecular bridging groups with good "conducting" properties even at large distances (up to 10 Å).

4.5. Comparison of the effectiveness of the Coulomb and covalent mechanisms of pair optical transitions

The Coulomb mechanism of cooperative optical transitions was considered by Dexter in Ref. 8. In this context it would be interesting to compare the relative effectiveness of the Coulomb and covalent mechanisms for different types of crystals.

In the Coulomb model the intensity of a pair optical transition is determined by the mixing of the wave functions of the $4f$ and $5d$ states on one of the ions owing to the electric-quadrupole potential of a $4f$ electron of another ion. Consequently, the intensities of these transitions are considerably smaller than the intensities of single-ion $4f$–$4f$ transitions, where $4f$–$5d$ mixing occurs under the action of the odd part of the crystal-field potential of the nearby ligands. The electric-quadrupole potential of the second Ln^{3+} ion is smaller than the crystal-field potential by a factor of approximately $(r_{\rm AB}/R_{\rm AB})^2$, where $r_{\rm AB}$ is the effective radius of the $4f$ subshell. Therefore, since $(r_{\rm AB}/R_{\rm AB})\approx 0.1$ for nearest-neighbor ions, the intensity of a pair transition should amount to $(r_{\rm AB}/R_{\rm AB})^4\approx 10^{-4}$ of the intensity of a single-ion transition. In fact, for several reasons this factor should be decreased additionally by at least tenfold, which gives a final estimate for the intensity of a pair transition $P^{ed}_{\rm coop}=10^{-11}$–$10^{-13}$, this estimate being weakly dependent on the nature of the insulating host.

Thus, the covalent and Coulomb mechanisms are comparable in effectiveness for ionic crystals (fluorides and oxides), but in "covalent" crystals (i.e., in moderately ionic crystals, such as bromides, iodides, and possibly sulfides) the covalent mechanism is probably more effective. It should, however, be recalled that the estimates presented for the intensities of pair optical transitions are approximate and most probably reflect the maximum magnitude of the effect.

It is also noteworthy that, as in the case of the Coulomb potential, the effective covalent potential can be expanded in a series in spherical harmonics, in which each term can be treated formally as the corresponding multipole–multipole interaction. Therefore, from the phenomenological standpoint the difference between the Coulomb and covalent mechanisms is manifested in the law governing the variation of the potential with the distance between the ions, which was discussed above.

5. DISCUSSION

In describing the microscopic model, we endeavored primarily to portray the essential points of the covalent mechanism. It is important, however, to stress that since the microscopic mechanism formulated does not employ any artificial model approximations and essentially contains no empirical fitting parameters, it can serve as a basis for quantitative evaluations of the intensities of cooperative optical transitions and the absolute rates of energy transfer between excited lanthanide ions in nearest-neighbor pairs. It should be noted here that the quantitative analysis of the covalent mechanism for real systems involving many-electron Ln^{3+} ions is very difficult, mainly due to the large number of the virtual electron-transfer states $Q_{mn}(\mathrm{A}\rightarrow\mathrm{B})$. For example, the number of these states for a Nd^{3+}–Nd^{3+} pair is estimated by the product of the total number of electronic levels in the $4f^2$ and $4f^3 5d$ configurations, i.e., $91\cdot 3640\approx 300\,000$, and for pairs of ions from the middle of the lanthanide series this number can be as high as several million. Therefore, this problem is not subject to analytic solution and requires the use of numerical methods and computer calculations for specific systems.

Let us now discuss the experimental results for several real systems, in which the observed cooperative optical effects can be attributed to the covalent mechanism.

Crystals of CsCdBr$_3$ activated by Ln^{3+} ions have been the subject of extensive experimental research in the recent years.[9,10] They have numerous unusual optical properties, including strong anti-Stokes luminescence[20] and anomalously fast energy transfer between ions,[9] which are attributed to the presence of pair centers with closely arranged Ln^{3+} ions in these crystals.

The quasi-one-dimensional structure of crystalline CsCdBr$_3$ consists of infinite chains parallel to the c axis, which are formed by face-sharing CdBr$_6^{4-}$ octahedrons.[21] The introduction of impurity Ln^{3+} ions into this structure is accompanied by the formation of pair centers, in which three Cd^{2+} ions are replaced by two Ln^{3+} ions and one V^0(Cd^{2+}) cation vacancy. It has been established that two types of centers form in CsCdBr$_3$:Ln^{3+}: symmetric Ln^{3+}–V^0–Ln^{3+} centers (I) and less stable asymmetric Ln^{3+}–Ln^{3+}–V^0 centers (II). The asymmetric centers can be classified as small-radius centers, since the two Ln^{3+} ions in them are bonded to one another by means of three shared bridging ligands and are at the minimum possible distance ($R\approx 4$ Å), while in the symmetric centers the Ln^{3+} ions are not nearest neighbors ($R\approx 6$ Å).

This circumstance leads to a significant difference between the optical properties of these pairs. For example, the measured rate $W_{\rm AB}$ of the resonant $(^4G_{9/2},{}^4I_{9/2})\rightarrow(^4I_{9/2},{}^4G_{9/2})$ transition between Nd^{3+} ions in CsCdBr$_3$:Nd^{3+} is equal to 1.4×10^7 s^{-1} for the asymmetric pairs and only 10^5 s^{-1} for the symmetric pairs.[20] As we know, the rate $W_{\rm AB}$ of the resonant $\Psi_i\rightarrow\Phi_j$ transition is given by the expression

$$W_{\rm AB}=\frac{2\pi}{\hbar}|\langle\Psi_0\Phi_i|V_{\rm AB}|\Psi_i\Phi_0\rangle|^2\int g_{\rm A}(E)g_{\rm B}(E)dE, \tag{31}$$

where $g_A(E)$ and $g_B(E)$ are the line shapes of the absorption bands corresponding to the intraionic $\Psi_0 \rightarrow \Psi_i$ and $\Phi_0 \rightarrow \Phi_i$ transitions.[12] Since the asymmetric centers have a certain energy difference between the Stark levels for the identical $^4I_{9/2}$ and $^4G_{9/2}$ multiplets due to the inequivalence of the neodymium ions, the overlap of the absorption bands should decrease, and we can presume that the difference between the squares of matrix elements of the type $|\langle \Psi_0 \Phi_i | V_{AB} | \Psi_i \Phi_0 \rangle|^2$ for the asymmetric and symmetric centers should be even greater than the difference between the energy transfer rates W_{AB}, i.e., more than two orders of magnitude.

It is difficult to explain such a sizable difference between the energy transfer rates for the symmetric and asymmetric centers within the multipole–multipole mechanism. In fact, since the distance between the Nd^{3+} ions in a symmetric center is approximately 1.5 times greater than that in an asymmetric center. The expected relative increase in the energy transfer rate upon passage from a symmetric center to an asymmetric center equals $(1.5)^6 \approx 11$ for the dipole-dipole mechanism and $(1.5)^{10} \approx 58$ for the quadrupole–quadrupole mechanism, which are considerably smaller than the experimental value. Although many details of these effects are still unclear, we can still conclude that the fast energy transfer between the Ln^{3+} ions in an asymmetric center in a $CsCdBr_3{:}Ln^{3+}$ crystal is due to the covalent mechanism considered above. It is noteworthy that when the typical value of the two-ion matrix element for Ln^{3+} ions $\langle \Psi_i \Phi_j | V_{AB} | \Psi_j \Phi_i \rangle \approx 1\ \mathrm{cm}^{-1}$ (see above) and an energy of the optical transition equal to 2 eV are used, Eq. (31) gives the estimate $W_{AB} = 7 \times 10^7\ \mathrm{s}^{-1}$, which, with consideration of the presence of band overlap, is in reasonable agreement with the experimental value $W_{AB} = 1.4 \times 10^7\ \mathrm{s}^{-1}$.

The fast energy transfer between excited Ln^{3+} ions leads to strong anti-Stokes luminescence in $CsCdBr_3{:}Ln^{3+}$ crystals. For example, in $CsCdBr_3{:}Ho^{3+}$ (with 0.3% Ho) the intensity of the anti-Stokes luminescence amounts to about a third of the intensity of the ordinary luminescence.[10,22] We assume that the covalent mechanism for the interaction of excited Ln^{3+} ions can play an important role in these highly efficient up-conversion optical materials and deserves intent study.

Cooperative luminescence was recently observed in Ref. 23 for Ln^{3+} ions in experiments with $Cs_3Yb_2Br_9$ crystals, whose structure contains dimeric $Ln_2X_9^{3-}$ complexes, which are structurally similar to the asymmetric centers in $CsCdBr_3{:}Ln^{3+}$. The oscillator strength of the pair cooperative $(^2F_{5/2}, ^2F_{5/2}) \rightarrow (^2F_{7/2}, ^2F_{7/2})$ transition for a Yb^{3+}–Yb^{3+} ion pair was evaluated in that study and found to be equal to $P = 4 \times 10^{-12}$, which is fairly close to the lower limit of the estimate that we obtained $P = 10^{-9}$–10^{-11}.

Greater intensities of the two-ion cooperative transitions in systems involving f ions should be expected for actinide systems. Uranium pentachloride UCl_5 can serve as an example of such compounds. The structure of this compound contains U_2Cl_{10} dimers, which consist of two distorted edge-sharing UCl_6^- octahedrons.[24] The two U^{5+} ions are joined to one another by means of two bridging ligands, and the distance between them is about 4 Å. Each U^{5+} ion has a simple $5f^1$ electronic configuration, and the upper edge of its crystal-field spectrum is near 12 000 cm^{-1} (Ref. 25). Since the less localized uranium $5f$ orbitals overlap the valence $3p$ and $3s$ orbitals of the bridging chloride ligands to a considerably greater extent than the $4f$ orbitals of Ln^{3+} ions overlap the ligand environment, the covalent effects play a significant role in the crystal-field splitting in the octahedral hexahalo complexes of pentavalent uranium UX_6^- (X = Cl, Br, and I).[26] Preliminary calculations of the intensities of the two-ion cooperative transitions give the estimate $P = 10^{-7}$–10^{-9}, which is commensurate with the intensities of ordinary single-ion transitions. Therefore, the situation in dimers of actinide ions should be more similar to the situation in dimers of transition-metal ions, for which intense pair cooperative optical transitions have been observed for many compounds.[27] In this context it is noteworthy that despite the simple electronic configuration of the U^{5+} ion, the quantitative interpretation of the spectrum of the electronic levels of UCl_5 runs into difficulties.[28] In particular, the calculated spin-orbit coupling constant ($\zeta_{5f} = 1196\ \mathrm{cm}^{-1}$) turned out to be considerably lower than the value characteristic of other compounds of pentavalent uranium ($\zeta_{5f} = 1900\ \mathrm{cm}^{-1}$) (Ref. 29). The probable reason for this may be related to the display of lines of pair electronic transitions in the electronic absorption spectra of this compound. This can be verified by further spectroscopic investigations of UCl_5, especially with the use of site-selective methods and with a time dependence of the fluorescence decay.

There are many more examples of lanthanide compounds containing nearest-neighbor ion pairs (including numerous inorganic and organometallic polynuclear complexes), in which the display of the covalent interaction mechanism between excited Ln^{3+} ions is likely. A detailed discussion of these data is beyond the scope of this paper. We note only that the compounds in which heavy halogens and chalcogenides (Br^-, I^-, S^{2-}, etc.) serve as the bridging ligands are most promising from the standpoint of the display of the covalent mechanism, since the valance orbitals of these ligands overlap the optically active atomic orbitals of the Ln^{3+} ions to a greater extent, producing greater values for the transfer integrals and, as a consequence, a stronger covalent interaction between the ions.

The covalent mechanism considered above can be applied after some modifications to the analysis of two-ion optical transitions in exchange-coupled pairs of transition-metal ions. Since the d orbitals overlap the valence orbitals of the bridging ligands to a considerably greater extent than do the $4f$ orbitals of Ln^{3+} ions, the covalent mechanism should lead to very high intensities for pair transitions. This is, in fact, observed in the electronic absorption and luminescence spectra for numerous pair centers and binuclear complexes of transition metals,[27] where the intensities of the pair and single-ion d–d transitions are comparable in magnitude.

6. CONCLUSIONS

We have shown that covalency effects and bridging ligands play an important role in the cooperative optical processes occurring in dimers with closely arranged Ln^{3+} ions and lead to a specific interaction between excited ions, which we have termed the covalent interaction. This interaction can be regarded as a generalization of the magnetic superexchange interaction between ions to pair cooperative optical processes. In this paper we have considered the general conception of this interaction and developed the corresponding microscopic model, which can serve as a basis for the further development of numerical methods using computer calculations for the purpose of a quantitative theoretical analysis of the optical and luminescence properties of two-ion Ln^{3+} centers. It follows from the model that the magnitude of the covalent interaction is greatly dependent on the nature of the bridging ligands and, in particular, that the intensity of the pair optical transitions increases strongly upon passage from electronegative "ionic" ligands (fluorine and oxygen) to more "covalent" ligands (bromine and iodine). This is attributed to the increase in the degree of overlap of the $4f$ and $5d$ orbitals of the lanthanides with the valance orbitals of the bridging ligands and to the decrease in the energies of electron transfer from a ligand to a Ln^{3+} ion. On the other hand, the covalent mechanism should lead to high rates of resonant energy transfer between excited ions in nearest-neighbor pairs, such as the asymmetric dimeric Ln^{3+}–Ln^{3+}– V^0 (Cd^{2+}) center in CsCdBr$_3$:Ln^{3+} crystals and, consequently, to a high efficiency for the energy-summation processes of two simultaneously excited Ln^{3+} ions in one of the ions and strong anti-Stokes luminescence.

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