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Abstract

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WIDTH OF LIGHT-ABSORPTION BANDS OF IMPURITY IONS WITH AN UNFILLED SHELL IN CRYSTALS

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In the absorption and luminescence spectra of light by ions with an unfilled d-shell in crystals (for example, $\mathrm{Cr}^{3+}(3d^3)$ in ruby), there are both broad bands (with half-width $\Delta\nu \sim 3000$–$5000\ \mathrm{cm}^{-1}$) and narrow ones (with $\Delta\nu \sim 0.1\ \mathrm{cm}^{-1}$) ($^{1-3}$). It is now very important to investigate the nature of the broadening of $d-d$, $f-f$, and $d-f$ transitions in impurity ions located in diamagnetic crystals, and to understand why some transitions give broad bands in crystals and others narrow ones.

The shape of the absorption and luminescence bands of impurity centers in crystals and solutions, as well as the vibrational "structure" of a broad band, are described by the Davydov-Pekar theory ($^{4-9}$). In this article, the possibility is taken into account that a band may be broadened owing to a change in the state of the ion during thermal vibrations of the ligands.

The magnitude of the broadening will be different for different transitions. If the energy difference of the levels $\mathcal{E}_i - \mathcal{E}_j$ is described by a function $f_{ij}(Dq, \alpha, \beta)$, where Dq is the strength of the cubic field, α is the set of parameters of fields of lower symmetry, and β are the parameters of the electrostatic repulsion of the electrons of the $d(f)$-shell from one another, then the change of the parameters by ΔDq, $\Delta\alpha$, and $\Delta\beta$, occurring in the process of thermal vibration, will cause a change in the transition energy by

$$\Delta(\mathcal{E}_i - \mathcal{E}_j) = f_{ij}(Dq + \Delta Dq,\ \alpha + \Delta\alpha,\ \beta + \Delta\beta) - f_{ij}(Dq, \alpha, \beta). \qquad (1)$$

In order to estimate $\Delta(\mathcal{E}_i - \mathcal{E}_j)$ quantitatively, one must know f_{ij}, Dq, α, β, ΔDq, $\Delta\alpha$, and $\Delta\beta$. Obviously, the larger $\frac{\partial f_{ij}}{\partial(Dq)}$, ΔDq (and also $\Delta\alpha$, $\frac{\partial\alpha}{\partial(Dq)}$, $\Delta\beta$, and $\frac{\partial\beta}{\partial(Dq)}$), the broader the band $i \leftrightarrow j$ must be. Strictly speaking, $\Delta(\mathcal{E}_i - \mathcal{E}_j)$ is determined by all the partial derivatives $\frac{\partial f_{ij}}{\partial R_n}$ and ΔR_n, where R_n is the radius vector of the n-th ion of the crystal lattice, and $|\Delta R_n|$ is the amplitude of its thermal vibrations; however, expressions for the widths of bands in terms of all R_n and ΔR_n are very cumbersome, and we shall not present them, all the more so because for numerical estimates it is more convenient to use directly the values Dq, α, β, ΔDq, $\Delta\alpha$, and $\Delta\beta$.

For a first rough estimate of $\Delta(\mathcal{E}_i - \mathcal{E}_j)$ by formula (1), Dq and ΔDq must be found.

In the mean-field approximation, the parameters β do not enter into f_{ij}, but instead the experimental values of the energies of the terms S, P, D, etc., of the free ion enter. The splittings of each term in a cubic field $O = 432 = {}^3/_4$ ($T_d = \bar{4}3m = {}^3/_4$, $O_h = m3m = {}^3/_4$) are most simply obtained by means of the method of equivalent operators (10).

The S and P terms do not split;

$$\begin{aligned}
&D;\quad T_2^*,\ -4Dq;\quad E_0,\ 6Dq;\\
&F;\quad A_2,\ -12Dq;\quad T_2,\ -2Dq;\quad T_0,\ +6Dq;\\
&G;\quad A_0,\ -2Dq;\quad T_0,\ -Dq;\quad E_0,\ -\frac{2}{7}Dq;\quad T_2,\ \frac{13}{7}Dq.
\end{aligned} \tag{2}$$

* The designations of the terms correspond to the monograph of M. A. El'yashevich (11), with the exception of $T_0 = F_0$ and $T_2 = F_2$.

Allowance for mixing of terms will replace the linear dependences f_{ij} on Dq (2) by more complicated ones. The same is obtained also in the strong-field approximation (2). The transition $e^n t^{N-n} \to e^{n'} t^{N-n'}$, where $d = t + e$ and $d^N = e^n + t^{N-n}$, gives a broad band for $n' \neq n$ and a narrow band for $n' = n$, since the distance between the levels is equal to $10(n - n')Dq$. However, this criterion is not sufficient, since almost all terms are mixed. For the transitions

$$\begin{gathered}
{}^2T_2(t) \leftrightarrow {}^2E_0(e) \quad (\text{in ions Ti}^{3+},\ \text{V}^{4+},\ \text{Mn}^{6+},\ \text{Zr}^{3+},\ \text{Nb}^{4+},\ \text{Hf}^{3+}),\\
{}^2T_2(t^5e^4) \leftrightarrow {}^2E_0(t^6e^3) \quad (\text{Cu}^{2+},\ \text{Ag}^{2+},\ \text{Hg}^{3+}),\\
{}^5E_0(t^3e) \leftrightarrow {}^5T_2(t^2e^2) \quad (\text{Cr}^{2+},\ \text{Mn}^{3+},\ \text{Mo}^{2+},\ \text{Tc}^{3+},\ \text{W}^{2+},\ \text{Re}^{3+}),\\
{}^5T_2(t^4e^2) \leftrightarrow {}^5E_0(t^3e^3) \quad (\text{Fe}^{2+},\ \text{Co}^{3+},\ \text{Ru}^{2+},\ \text{Rh}^{3+},\ \text{Os}^{2+},\ \text{Ir}^{3+},\ \text{Pt}^{4+}),\\
{}^4A_2(t^3) \leftrightarrow {}^4T_2(t^2e) \quad (\text{Cr}^{3+},\ \text{V}^{2+},\ \text{Mn}^{4+},\ \text{Mo}^{3+},\ \text{Nb}^{2+},\ \text{Tc}^{4+},\ \text{W}^{3+},\ \text{Ta}^{2+},\ \text{Re}^{4+}),\\
{}^4A_2(t^3e^4) \leftrightarrow {}^4T_2(t^4e^3) \quad (\text{Co}^{2+},\ \text{Ni}^{3+},\ \text{Rh}^{2+},\ \text{Pd}^{3+},\ \text{Ir}^{2+},\ \text{Pt}^{3+}),\\
{}^3A_2(e^2) \leftrightarrow {}^3T_2(te) \quad (\text{V}^{3+},\ \text{Cr}^{4+},\ \text{Zr}^{2+},\ \text{Nb}^{3+},\ \text{Hf}^{2+},\ \text{Ta}^{3+},\ \text{W}^{4+}),\\
{}^3A_2(t^6e^2) \leftrightarrow {}^3T_2(t^5e^3) \quad (\text{Ni}^{2+},\ \text{Pd}^{2+},\ \text{Pt}^{2+}),\quad -f_{ij} = 10Dq,
\end{gathered} \tag{3}$$

since both term i and term j belong to the configuration $t^n e^{N-n}$ indicated in parentheses, not mixed with other configurations (the insignificant mixing of states with different nl can be neglected in calculating the energy spectra). The transitions (3) must give broad bands with oscillator strength $\sim 10^{-3}$—10^{-5}, as is observed experimentally ([1],[2]).

For the transitions:

$$\begin{gathered}
{}^5T_2(t^4e^2) \leftrightarrow a^3E_0,\ a^1E_0; \\
{}^5E_0(t^3e) \leftrightarrow a^3E_0,\ a^3T_0,\ a^3T_2,\ a^3A_2,\ a^1A_2,\ a^1T_0; \\
{}^3T_0(t^2) \leftrightarrow a^1T_2,\ a^1E_0,\ a^1A_0; \\
{}^3A_2(t^6e^2) \leftrightarrow a^1E_0,\ a^1A_0; \\
{}^4A_2(t^3) \leftrightarrow a^2E_0,\ a^2T_0,\ a^2T_2; \\
{}^4T_0(t^5e^2) \leftrightarrow a^2T_0,\ a^2T_2; \\
{}^6A_0(t^3e^2) \leftrightarrow {}^4A_0(t^3e^2),\ 2^4E_0(t^3e^2),\ a^2A_0,\ {}^4A_2(t^3e^2)
\end{gathered} \tag{4}$$

and a number of transitions between excited levels, $\dfrac{\partial f_{ij}}{\partial(Dq)} \simeq 0$, and they must give narrow bands. We do not give the expressions f_{ij} for transitions (4), since almost all of them are very cumbersome, and for most transitions they cannot be obtained in general form.

Let us estimate the magnitude of the broadening for bands (3) and (4). For divalent ions $Dq \sim 1000$ cm^{-1}, for trivalent ions ~ 1500—2000 cm^{-1}, and for tetravalent ions ~ 2000 cm^{-1} ([2]).

Let us relate ΔDq to the amplitude of thermal vibrations of the ligands ΔR. For a charge q, located at the center of an octahedron (O), a tetrahedron (T_d), and a cube (O_h), at a distance R from point charges q_ℓ located at the vertices of the polyhedra ([10]),

$$Dq = \frac{35qq_\ell\langle r^4\rangle}{16\sqrt{21\pi}\,R^5}(O), \quad Dq = -\frac{35qq_\ell\langle r^4\rangle}{36\sqrt{21\pi}\,R^5}(T_d), \quad Dq = -\frac{35qq_\ell\langle r^4\rangle}{18\sqrt{21\pi}\,R^5}(O_h). \tag{5}$$

Since $\Delta R \ll R$, differentiating (5) with respect to R under the assumption that

$$\frac{\partial\langle r^4\rangle}{\partial R} \simeq 0$$

(the change of $\langle r^4\rangle$ with R can be taken into account by the method of Petrashen ([12])), we obtain

$$\Delta Dq \simeq -10Dq\,\frac{\Delta R}{R}. \tag{6}$$

Calculations using more exact formulas for Dq, taking into account the long-range order, lead to the same order of magnitude of ΔDq.

From formulas (1), (6), for the broad bands (3) we obtain

$$\Delta(\mathcal{E}_i - \mathcal{E}_j) \simeq 100 Dq \frac{\Delta R}{R}. \tag{7}$$

The dependence of ΔR on T will give the variation of this effect with temperature. The smaller the mass of the ligands, the larger $\Delta(\mathcal{E}_i - \mathcal{E}_j)$, since $\Delta R \simeq \Delta R_0 \sqrt{m_0/m}$, where m (m_0) is the mass of the ligands. The greatest effect of band broadening is produced by water of crystallization, especially if the protons are in the immediate vicinity of the impurity ion. If, however, the ligands are O^{2-} ions, then $\Delta(\mathcal{E}_i - \mathcal{E}_j)$ will be 4 times smaller than for protons. For bands (3), calculations by (7) give $\Delta(\mathcal{E}_i - \mathcal{E}_j) \sim 900$–$2000$ cm^{-1} (at $T = 0$°K).

Numerical estimates of f_{ij} for bands (4) give, at $T = 0$°K, $\Delta(\mathcal{E}_i - \mathcal{E}_j) \lesssim 1$ cm^{-1}.

The true width of the transitions due to excitation of phonons, exchange, and other effects will always be greater than the numbers given.

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Note: Figure translations are in progress. See original paper for figures.

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