SOVIET PHYSICS JETP VOLUME 21, NUMBER 6 DECEMBER, 1965

ON THE THEORY OF THE VIBRATIONAL STRUCTURE OF THE OPTICAL SPECTRA OF PARAMAGNETIC CRYSTALS

B. Z. MALKIN

Kazan' State University

Submitted to JETP editor December 9, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 1637-1645 (June, 1965)

Single-phonon electronic-vibrational transitions in ionic crystals containing impurity ions of transition-group elements are considered. The vibrational structure of the luminescence spectrum of the $CaF_2:Tu^{2+}$ crystal is calculated theoretically. Comparison with experiment confirms the presence of a vibrational structure in the lines due to quasi-local vibrations. The possibility of studying the dynamics of a crystal containing impurities by means of optical spectroscopy is discussed.

BESIDES the narrow lines of phononless transitions, one observes in the luminescence and absorption spectra of ionic crystals containing transition-group ions as impurities, a large number of comparatively narrow lines corresponding to electronic-vibrational transitions. The vibrational structure of the line spectra carries information both about the spectrum of the ion and about the spectrum of the crystal vibrations.[1]

This paper gives a theoretical calculation of the vibrational structure of the optical spectrum of a crystal with a small concentration of paramagnetic impurities. The problem is divided into two parts: it is necessary first of all to find the spectrum of vibrations of a crystal with an isolated impurity center by the method of I. Lifshitz,[2] and then, with the aid of the partial distribution of the energy of the crystalline lattice so obtained, to calculate the intensity of the electronic-vibrational transitions.

Narrow electronic-vibrational lines arise when the energy of the lattice vibrations is partially localized in a small frequency interval. In a regular crystal this localization of the energy can take place close to the limiting frequencies of the vibrational branches, where the density of the vibrational states is a maximum, and also if the dispersion curves have flat portions.[3,4] In the optical spectra of crystals with impurities, intense electronic-vibrational lines can be observed also as a result of the redistribution of the energy in the spectrum of the lattice vibrations occurring when the impurity ion is introduced. With a significant change in mass and force constants, vibrations are excited in narrow intervals of frequencies of the quasi-continuous spectrum (quasi-local vibrations), and local vibrations with discrete frequencies appear. We are principally interested in the question of the appearance of quasi-local and local vibrations[5] in the vibrational structure of the optical luminescence and absorption spectra of paramagnetic crystals containing as impurities, ions of the iron and rare-earth groups.

1. INTENSITY OF THE ELECTRONIC-VIBRATIONAL LINES

We shall treat the interaction of the impurity ion with the crystalline lattice in the harmonic approximation. The Hamiltonian of the ion + lattice system will be written in the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_i + \hat{\mathcal{H}}_l + \hat{\mathcal{H}}_{em} + \hat{\mathcal{H}}_{ev}, \qquad (1)$$

where $\hat{\mathcal{H}}_i$ is the Hamiltonian of the ion in the static crystal field, the eigenvalues $E(\Gamma)$ and eigenfunctions of which are assumed known, and $\hat{\mathcal{H}}_{em}$ is the Hamiltonian of the interaction of the ion with the electromagnetic field. The lattice Hamiltonian

$$\hat{\mathcal{H}}_l = \sum_f \frac{\hbar\omega(f)}{2}(a_f a_f^+ + a_f^+ a_f), \qquad (2)$$

where a_f^+ and a_f are respectively the creation and annihilation operators of phonons of frequency $\omega(f)$, the subscript f taking on the values from 1 to 3sN, if the crystal consists of N unit cells and has s atoms in each cell.

The Hamiltonian of the electronic-vibrational interaction is

$$\hat{\mathcal{H}}_{ev} = \sum_\lambda V_\lambda Q_\lambda,$$

where V_λ is a function of the coordinates of the electrons of the impurity ion, and Q_λ are the symmetrical vibrations of the complex containing the impurity ion, represented as linear orthogonal combinations of the displacements of the ions from their equilibrium positions:

$$Q_\lambda = \sum_\alpha a_{\lambda\alpha} u_\alpha .$$

The displacements u_α are expanded in the normal coordinates of the crystal

$$u_\alpha = M_\alpha^{-1/2} \sum_f \psi_\alpha(f) d(f),$$

$$d(f) = [\hbar / 2\omega(f)]^{1/2} (a_f^+ + a_f), \tag{3}$$

where M_α is the mass of the corresponding ion. We also write the symmetrical vibrations in the form of an expansion in the normal coordinates:

$$Q_\lambda = \sum_f \tau_\lambda(f) d(f), \tag{4}$$

$$\tau_\lambda(f) = \sum_\alpha a_{\lambda\alpha} M_\alpha^{-1/2} \psi_\alpha(f). \tag{5}$$

In the electronic-vibrational band we shall consider only the part due to single-phonon transitions. The intensity of the electronic-vibrational band is calculated by second-order perturbation theory,[6] the perturbation being $\hat{\mathcal{H}}_{\mathrm{em}} + \hat{\mathcal{H}}_{\mathrm{ev}}$.

The vibrational structure in luminescence and absorption spectra can be investigated in exactly the same way; hence, we consider only luminescence spectra. We shall mainly be interested in the frequencies of the narrow electronic-vibrational lines and their relative intensities. Experimentally, these quantities depend weakly on temperature, so that we limit the study to the vibrational structure at T = 0, when only transitions with the emission of phonons are excited.

The greatest contribution to the intensity of the electronic-vibrational band $I_{\mathrm{ev}}(\omega)$ comes from forced electric dipole transitions. Using an expression we derived earlier for $I_{\mathrm{ev}}(\omega)$,[6] we obtain for T = 0 for transitions between energy levels of the ion Γ and Γ', with degeneracies $g(\Gamma)$ and $g(\Gamma')$ and difference in energy $E(\Gamma) - E(\Gamma') = \hbar\omega_0$:

$$I_{\mathrm{ev}}(\omega) = \frac{4}{3\hbar c^3 g(\Gamma)} \sum_f \frac{\Delta\omega(f)}{2\pi} \times \frac{(\omega_0 - \omega(f))^3 A(f)}{[\omega - \omega_0 + \omega(f)]^2 + [\Delta\omega(f)/2]^2}, \tag{6}$$

$$A(f) = \sum_{\alpha=1}^{g(\Gamma)} \sum_{\beta=1}^{g(\Gamma')} \left| \sum_{\Gamma''\gamma} \left\{ \frac{\hat{\mathcal{H}}_{\mathrm{ev}}(\Gamma_\alpha, n_f; \Gamma_\gamma'', n_f + 1)\hat{\mu}(\Gamma_\gamma''; \Gamma_\beta')}{E(\Gamma) - E(\Gamma'') - \hbar\omega(f)} + \frac{\hat{\mu}(\Gamma_\alpha; \Gamma_\gamma'')\hat{\mathcal{H}}_{\mathrm{ev}}(\Gamma_\gamma'', n_f; \Gamma_\beta', n_f + 1)}{E(\Gamma') - E(\Gamma'') + \hbar\omega(f)} \right\} \right|^2, \tag{7}$$

where $\Delta\omega(f)$ is the total width of the levels Γ and Γ' the vibration of frequency $\omega(f)$, and μ is the electric dipole moment operator for the ion. The occupation number n_f is zero at T = 0.

We shall assume that the point group of the crystal symmetry at the impurity site includes the inversion operation. In considering transitions between ionic levels of the same parity belonging to the same electronic configuration, it is necessary to take into account in $\hat{\mathcal{H}}_{\mathrm{ev}}$ only those symmetrical vibrations that transform according to the odd irreducible representations of the point group of the crystal, since the electric dipole moment operator changes sign on inversion. The levels Γ'' must belong to another configuration, and the energy $E(\Gamma'')$ is then significantly greater than $E(\Gamma)$ and $E(\Gamma')$ and the phonon energies $\hbar\omega(f)$ in the denominators of Eq. (7) can be neglected.

Making use of the inequality $\omega_0 \gg \omega(f)$ and the expansion (4), we find

$$A(f) = \sum_{\alpha=1}^{g(\Gamma)} \sum_{\beta=1}^{g(\Gamma')} \left| \sum_\lambda \sigma_\lambda^{\alpha\beta} \tau_\lambda(f) \right|^2 \frac{\hbar}{2\omega(f)}, \tag{8}$$

$$\sigma_\lambda^{\alpha\beta} = \sum_{\Gamma_\gamma''} \left\{ \frac{V_\lambda(\Gamma_\alpha; \Gamma_\gamma'')\hat{\mu}(\Gamma_\gamma''; \Gamma_\beta')}{E(\Gamma) - E(\Gamma'')} + \frac{\hat{\mu}(\Gamma_\alpha; \Gamma_\gamma'') V_\lambda(\Gamma_\gamma''; \Gamma_\beta')}{E(\Gamma') - E(\Gamma'')} \right\}. \tag{9}$$

In the case of the vibrations in the quasicontinuous spectrum, we can neglect the width of the vibrational levels; if we neglect also the width of the electronic levels, we obtain

$$I_{\mathrm{ev}}(\omega) = \frac{2\omega_0^3}{3c^3 g(\Gamma)} \times \sum_f \frac{\delta(\omega - \omega_0 + \omega(f))}{\omega(f)} \sum_{\alpha,\beta} \left| \sum_\lambda \sigma_\lambda^{\alpha\beta} \tau_\lambda(f) \right|^2. \tag{10}$$

It follows from Eq. (10) that the dependence of the intensity of the electronic-vibrational transitions on the frequency of the phonons is determined to a great extent by the quantities $\tau_\lambda(f)$, i.e., in accordance with Eq. (5), with the reduced amplitudes $\psi_\alpha(f)$. For vibrations of a regular crystal

$$\psi_\alpha(f) = N^{-1/2} W_\alpha(f) \exp(i\mathbf{k}_f \mathbf{R}_\alpha), \tag{11}$$

where $\mathbf{R}_\alpha$ is the radius vector of the corresponding lattice site, $W_\alpha(f)$ are the components of the polarization vector of the vibration f with wave vector $\mathbf{k}_f$, normalized over an elementary cell. In this case sharp maxima in the function $I_{\mathrm{ev}}(\omega)$ can arise only because of extrema in the distribution function for the vibrational states over the quasi-continuous spectrum. In a crystal containing impurities, new vibrations appear, and the reduced amplitudes of these vibrations are normalized by functions that have under certain conditions sharp maxima,[5] which leads to the appearance of additional lines in the vibrational structure.

The intensity distribution in the electronic-vibrational lines excited by local vibrations with discrete frequencies ω_D is given by the equation

$$I_{\mathrm{ev}}(\omega)=\frac{2\omega_0^3}{3c^3g(\Gamma)}\times\frac{\Delta\omega_D}{2\pi}\,\frac{\sum\limits_{\alpha,\beta}\Big|\sum\limits_{\lambda}\sigma_\lambda{}^{\alpha\beta}\tau_\lambda(\omega_D)\Big|^2}{\omega_D[(\omega-\omega_0+\omega_D)^2+(\Delta\omega_D/2)^2]},\qquad(12)$$

where $\Delta\omega_D$ is the width of the discrete vibrational energy level of the crystal.

We shall examine further the shape of the electronic-vibrational bands and the question of the emergence of narrow electronic-vibrational lines in the example of $CaF_2{:}Tu^{2+}$, for which there exists the possibility of comparing the results of the theoretical calculation with experiment.[7]

2. THE VIBRATIONAL STRUCTURE OF THE OPTICAL SPECTRA OF DIVALENT RARE-EARTH IONS IN FLUORITE

Impurity divalent rare-earth ions replace the Ca^{2+} ion in the fluorite lattice. The mass at the lattice site is greatly changed (by about a factor of four); the change in the force constants can thereby be left out of account, since the valency is conserved. The change in the force constants can be neglected only for transitions within the limits of the internal 4f shell, which interacts weakly with the crystal field. In reality the force constants are different in different states even of the same ion. This means that the Stokes and anti-Stokes components of the vibrational structure of the same phononless line have different frequencies: in luminescence the frequencies of the absorbed phonons pertain to the upper level of the transition, the frequencies of the emitted phonons, to the lower level of the transition.

In the vibrational structure of the luminescence spectrum of a crystal of $CaF_2{:}Tu^{2+}$ the frequencies of corresponding Stokes and anti-Stokes components differ on the average by about 10 cm^{-1}. This approximation, which takes into account only the change in mass, limits the accuracy of the calculation by this amount. But mainly the accuracy of the calculation is determined by how well the vibrational spectrum of a regular crystal is known, in particular the limiting values of the frequencies of the vibrational branches.

The unit cell of fluorite consists of one Ca^{2+} ion and two nonequivalent F^- ions and is represented by a rhombohedron with edge r_0 = 2.745 Å (point group O_h). The quasi-continuous spectrum of the lattice vibrations consists of nine partially overlapping bands (see Table I). The optically active frequencies of the vibrations were measured by Kaiser et al.[8]; the dispersion curves were calculated theoretically by Ganesan and Srinivasan.[9] Using the data of these authors, we were able to make an approximate calculation of the spectrum of vibrations of CaF_2 crystal with a heavy impurity center. We neglected the anisotropy of the crystal and approximated the dispersion curves by straight lines, while maintaining the values of the frequencies at the band limits. In the calculations we did not take into account the dependence of the polarization factors $W_\alpha^j(k)$ on wave vector; their values for k = 0 were used.

Table I. Limits of the vibrational branches in the CaF_2 crystal

j	Type of vibration	$\omega_j(\mathbf{k})$, in cm^{-1}	
		$\mathbf{k}=0$	$\mathbf{k}=\mathbf{k}_{max}$
1	acoustical longitudinal	0	318
2,3	acoustical transverse	0	175
4	optical longitudinal	463	327
5	optical transverse	257	190
6	optical transverse	257	314
7	Raman longitudinal	321.5	152
8	Raman transverse	321.5	212
9	Raman transverse	321.5	346

Notes. j is the number of the branch, and $k_{max} = (6\pi^2/v_0)^{1/3}$, where $v_0 = 2r_0^3$ is the volume of a unit cell

When one Ca^{2+} ion is replaced by a Tu^{2+} ion, a three-fold degenerate normal vibration splits off from each vibrational level of the regular crystal with degeneracy θ = 48 (the number of operations in the O_h group); this vibration has a frequency $\omega(r)$ falling in the interval between two neighboring values of the frequencies of the regular crystal.[10] The frequencies $\omega(r)$ satisfy the equation

$$1+\frac{\Delta M}{M_{\mathrm{Ca}}}\omega^2(r)N^{-1}\sum_{\mathbf{k},j}\frac{|W_{x\mathrm{Ca}}^{j}(\mathbf{k})|^2}{\omega_j^2(\mathbf{k})-\omega^2(r)}=0,\qquad(13)$$

where $\Delta M = M_{Ca} - M_{Tu}$.

In our approximation the Ca^{2+} ions do not participate in Raman vibrations; hence in the interval 318—327 cm^{-1} a local vibration appears with frequency 326 cm^{-1}. The reduced amplitudes of the vibrations of the impurity ion with frequencies of the quasi-continuous spectrum are normalized by the condition[5]

$$\sum_{\alpha=x,y,z}|\psi_{\alpha\mathrm{Tu}}(r)|^2=\frac{M_{\mathrm{Ca}}}{\Delta M\omega^2(r)}F_r\times\left[\pi^2F^2(\omega^2(r))+\left(1+\int\frac{F(\mu)\,d\mu}{\mu-\omega^2(r)}\right)^2\right]^{-1},\qquad(14)$$

$$F(\omega^2)=\frac{v_0}{(2\pi)^3}\frac{\Delta M}{M_{\mathrm{Ca}}}\omega^2\sum_j\int\limits_{\omega_j^2(\mathbf{k})=\omega^2}\frac{|W_{x\mathrm{Ca}}(\mathbf{k})|^2}{|d\omega_j^2(\mathbf{k})/d\mathbf{k}|}dS. \qquad (15)$$

The integral in (15) is taken over the surface $\omega_j^2(\mathbf{k}) = \omega^2$ in k space; the function F_r is defined by the equation

$$\sum_r \varphi(\omega^2(r))F_r = 3\int\varphi(\mu)F(\mu)\,d\mu, \qquad (16)$$

where $\sum_r$ signifies a sum over all vibrations with shifted frequencies.

The displacements of the Tu^{2+} ion from its equilibrium position are expanded only in the new normal coordinates with the split-off frequencies. The rest of the ions can vibrate both with the old frequencies and with the new in accordance with the equation[5]

$$\psi_\alpha(r)=-\frac{\Delta M}{M_{\mathrm{Ca}}}\omega^2(r)\sum_{\beta=x,y,z}g_{\alpha\beta}(\omega(r))\psi_{\beta\mathrm{Tu}}(r), \qquad (17)$$

where $g_{\alpha\beta}(\omega)$ is the Green's function of the equations of motion of the crystal lattice and equals

$$g_{\alpha\beta}(\omega)=\sum_{\mathbf{k},j}\frac{\psi_\alpha^j(\mathbf{k})\psi_\beta^{j*}(\mathbf{k})}{\omega_j^2(\mathbf{k})-\omega^2}. \qquad (18)$$

The reduced amplitudes of the vibrations with frequencies of the regular crystal $\omega_j(\mathbf{k})$ will be linear combinations of $\psi_\alpha^j(\mathbf{k})$ [see Eq. (11)], which go to zero at the impurity ion.[10]

The induced electrical dipole transitions between the Stark sublevels of the terms $^2F_{5/2}$ and $^2F_{7/2}$ of the Tu^{2+} ion are excited by the symmetrical vibrations of the cube of F^- ions surrounding the paramagnetic ion, which transform according to the odd irreducible representations of the group O_h: Γ_{2u}, Γ_{3u}, Γ_{4u}^{I}, Γ_{4u}^{II}, Γ_{5u} (we do not consider translation of the complex as a whole). In $\mathcal{H}_{ev}$ we leave only those terms that include the symmetrical vibrations $Q_\lambda(\Gamma_{4u}^{I})$ and $Q_\lambda(\Gamma_{4u}^{II})$, which are expanded in the normal coordinates of the crystal with the split-off frequencies $\omega(r)$. This permits the study of the characteristics of the vibrational structure that arise as a result of the redistribution of vibrational energy when a heavy impurity ion is introduced into a crystal, without going through a detailed calculation of the quantities $\sigma_\lambda^{\alpha\beta}$ from Eq. (9).

The symmetrical vibrations $Q_\lambda(\Gamma_{4u}^{I})$ were chosen as the following:

$$Q_\lambda(\Gamma_{4u}{}^{\mathrm{I}})=-\frac{4}{3\sqrt{2}}u_{\lambda\mathrm{Tu}}+\frac{1}{6\sqrt{2}}\sum_{i=1}^{8}u_{\lambda F_i}\quad(\lambda=x,y,z). \qquad (19)$$

The vibrations $Q_\lambda(\Gamma_{4u}^{II})$ are orthogonal to $Q_\lambda(\Gamma_{4u}^{I})$. The expansions (4), with account taken of (17), take the form

$$Q_\lambda(\Gamma_{4u}{}^{\mathrm{I}})=-\frac{4}{3\sqrt{2}}\sum_r\left[\omega^2(r)\frac{\Delta M a(\omega(r))}{\sqrt{M_{\mathrm{Ca}}M_{\mathrm{F}}}}+1\right]$$

$$\times\frac{\psi_{\lambda\mathrm{Tu}}(r)}{\sqrt{M_{\mathrm{Ca}}}}d(r), \qquad (20)$$

$$Q_\lambda(\Gamma_{4u}{}^{\mathrm{II}})=-4\sum_r\omega^2(r)\frac{\Delta M b(\omega(r))}{\sqrt{M_{\mathrm{Ca}}M_{\mathrm{F}}}}\frac{\psi_{\lambda\mathrm{Tu}}(r)}{\sqrt{M_{\mathrm{Ca}}}}d(r), \qquad (21)$$

where

$$a(\omega)$$
$$=N^{-1}\sum_{\mathbf{k},j}\frac{W_{x\mathrm{Ca}}^{j}(\mathbf{k})W_{x\mathrm{F}}^{j*}(\mathbf{k})}{\omega_j^2(\mathbf{k})-\omega^2}\exp\left[i\frac{r_0}{2}(k_x+k_y+k_z)\right], \qquad (22)$$

$$b(\omega)$$
$$=N^{-1}\sum_{\mathbf{k},j}\frac{W_{x\mathrm{Ca}}^{j}(\mathbf{k})W_{y\mathrm{F}}^{j*}(\mathbf{k})}{\omega_j^2(\mathbf{k})-\omega^2}\exp\left[i\frac{r_0}{2}(k_x+k_y+k_z)\right]. \qquad (23)$$

We find, in accordance with (10), that the contribution to the intensity of the electronic-vibrational band within the limits of the quasi-continuous spectrum due to vibrations with new frequencies is proportional to

$$I_{\mathrm{ev}}(\bar\omega)\backsim\frac{\dfrac{16}{3}\left|\sigma(\Gamma_{4u}{}^{\mathrm{I}})\left[\bar\omega^2\dfrac{\Delta M a(\bar\omega)}{\sqrt{M_{\mathrm{Ca}}M_{\mathrm{F}}}}+1\right]+3\sqrt{2}\,\sigma(\Gamma_{4u}{}^{\mathrm{II}})\bar\omega^2\dfrac{\Delta M b(\bar\omega)}{\sqrt{M_{\mathrm{Ca}}M_{\mathrm{F}}}}\right|^2}{\Delta M\bar\omega^2\left[\pi^2F^2(\bar\omega^2)+\left(1+\displaystyle{-}\!\!\!\!\!\!\int\frac{F(\mu)\,d\mu}{\mu-\bar\omega^2}\right)^2\right]}F(\bar\omega^2),$$

$$0\leqslant\bar\omega=\omega_0-\omega\leqslant 463\ \mathrm{cm}^{-1}. \qquad (24)$$

The quantities $a(\omega)$ and $b(\omega)$ are calculated from the formulas

$$\sum_{\mathbf{k},j}\frac{\varphi^j(\mathbf{k})}{\omega_j^2(\mathbf{k})-\omega^2}$$
$$={-}\!\!\!\!\!\!\int\frac{\varphi(\mu)\,d\mu}{\mu-\omega^2}-\frac{\varphi(\omega^2)}{F(\omega^2)}\left(1+{-}\!\!\!\!\!\!\int\frac{F(\mu)\,d\mu}{\mu-\omega^2}\right), \qquad (25)$$

where

$$\varphi(\omega^2)=\frac{v_0}{(2\pi)^3}N\sum_j\int\limits_{\omega_j^2(\mathbf{k})=\omega^2}\frac{\varphi^j(\mathbf{k})\,dS}{|d\omega_j^2(\mathbf{k})/d\mathbf{k}|}. \qquad (26)$$

As a consequence of the orthogonality of the symmetrical vibrations Q_λ, the contribution to

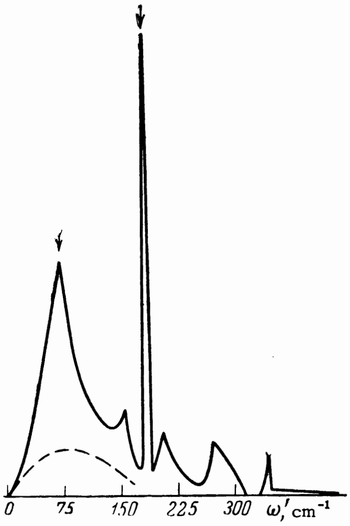

FIG. 1

$I_{ev}(\omega)$ from vibrations of the regular crystal can be represented in the form

$$I_{\text{ev}}(\omega) \infty \sigma^2(\Gamma_{4u}^{\text{I}})\theta_{\text{I}}(\bar{\omega}) + \sigma^2(\Gamma_{4u}^{\text{II}})\theta_{\text{II}}(\bar{\omega}). \qquad (27)$$

The functions $\theta_I(\bar{\omega})$ and $\theta_{II}(\bar{\omega})$ were calculated in accordance with Eq. (10).

Figures 1 and 2 show the electronic-vibrational bands calculated by Eqs. (24) and (27) for the values

$$\sigma(\Gamma_{4u}^{\text{II}}) / \sigma(\Gamma_{4u}^{\text{I}}) = 0, \quad \sigma(\Gamma_{4u}^{\text{II}}) / \sigma(\Gamma_{4u}^{\text{I}}) = -1 / \sqrt{3},$$

respectively.

From the shape of the curves shown in the figures, it follows that for different phononless lines the number and relative intensities of the electronic-vibrational satellites depend essentially on the relations between the corresponding matrix elements. The arrows in the figures point out lines due to quasi-local vibrations; the broken lines show the shape of the electron-vibrational band without any account taken of the distortion of the vibrational spectrum when an impurity is introduced.

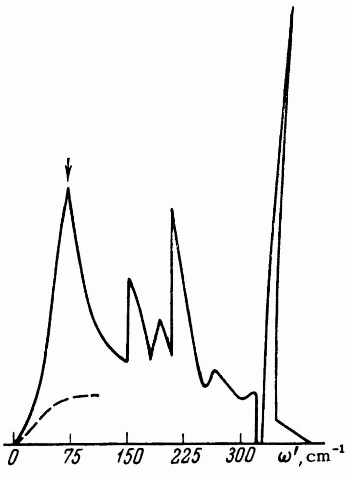

FIG. 2

Table II. Frequencies of the electronic-vibrational lines (in cm^{-1}) in the luminescence spectrum of a crystal of $CaF_2 : Tu^{2+}$ at 4.2°K

$\omega_0 = 8969.5\ \text{cm}^{-1}$ $\Delta\omega = 0.41\ \text{cm}^{-1}$		$\omega_0 = 8410.4\ \text{cm}^{-1}$ $\Delta\omega = 12\ \text{cm}^{-1}$	
Experiment [7]	Theory	Experiment [7]	Theory
97*	85*	95*	85*
180	156	173	152
221*	185*	—	—
257	205	253	212
348	346	339*	346*

*The asterisks denote the most intense lines

Two intense phononless lines accompanied by vibrational structure are observed in the luminescence spectrum of the Tu^{2+} ion in CaF_2. We present in Table II the experimental and theoretical values of the frequencies of the electronic-vibrational lines that correspond to the sharp maxima of the functions (24) and (27).[7] The expressions we have obtained for the intensity of the electron-vibrational band accurately determine the number of the most intense lines in the vibrational structure. The theoretical values of the frequencies agree rather well with the experimental data, in spite of the crude approximation to the spectrum of vibrations of the regular crystal. Taking into account the finite width of the electronic levels $\Delta\omega$ the form of the observed electronic-vibrational band should, in accordance with (6), be described by the integral from functions (24) and (27) with weight

$$[(\omega - \omega_0 + \bar{\omega})^2 + (\Delta\omega / 2)^2]^{-1}.$$

In this case the narrow maxima are lowered considerably more than the wide ones, and, as can be seen from the figures, the most significant line in the vibrational structure turns out to be the one with frequency 85 cm^{-1}, due to quasi-local vibrations, in complete agreement with experiment. Our calculations show that there could be a line at 326 cm^{-1} excited by local vibration. The intensity of this line is determined by the width $\Delta\omega_D$ of the discrete vibrational level, which depends on the decay time of this level and the concentration of impurity ions. It is very probable in the example we are considering that the width $\Delta\omega_D$ is large (the vibration frequency is close to the boundaries of the quasi-continuous spectrum), and the corresponding line is not observed.

The relative difference of the masses of rare-earth ions is not great, and our results for Tu^{2+} should describe the vibrational structure of the optical spectra of fluorite containing other rare-earth ions as impurities. Wood and Kaiser[11] describe the vibrational structure of the luminescence spectrum of Sm^{2+} in CaF_2. The luminescence is observed as a result of transitions between energy levels of the Sm^{2+} ion that belong to different electronic configurations (4f5d → 4f); hence there should not be any lines in the vibrational spectrum that are due to quasi-local vibrations with frequency $\sim 90\ \text{cm}^{-1}$ (single-phonon electric dipole transitions between levels of different parity are excited only by even symmetrical vibrations). Actually, the lowest frequency of the observed electronic-vibrational lines is $184\ \text{cm}^{-1}$, possibly because of two-phonon processes.

CONCLUSION

Our results refute the ideas of Axe and Sorokin[12] about the nature of the vibrational structure. They suggested that the narrow electronic-vibrational lines are excited by vibrations of the complex containing the impurity ion. The vibrational structure of the optical spectra of paramagnetic ionic crystals are always due to vibrations of the entire crystal as a whole, so that the change in the vibrational spectrum upon the introduction of impurities is very substantial. The vibrational spectra of crystals containing impurity centers have recently been studied intensively by means of the Mössbauer effect and neutron scattering. It should be noted that no less valuable information can also be obtained by means of more simple optical investigations, in particular by the study of the concentration dependence of the width of the local vibrations, the distribution of the energy of the crystal over the quasi-continuous spectrum, and the determination of the frequencies of the local and quasi-local vibrations.[13] The investigation of vibrational structure opens up the possibility of studying not only the motion of the impurity atom itself, as in the Mössbauer effect, but also the vibrations of its immediate surroundings, which modulate the Stark splitting of the energy levels in the crystalline field.

In conclusion the author expresses his deep gratitude to Prof. S. A. Al'tshuler for his interest in the work, valuable advice, and a discussion of the results.

---

[1] D. E. McCumber, Phys. Rev. **134**, A299 (1964).

[2] I. M. Lifshitz, Nuovo Cimento **3**, Suppl., 716 (1956).

[3] C. B. Pierce, Phys. Rev. **135**, A83 (1964).

[4] Richman, Satten, and Wong, J. Chem. Phys. **39**, 1833 (1963); I. Richman, Phys. Rev. **133**, A1364 (1964).

[5] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[6] B. Z. Malkin, FTT **5**, 3088 (1963), Soviet Phys.—Solid State **5**, 2262 (1964).

[7] Z. Kiss, Phys. Rev. **127**, 718 (1962).

[8] Kaiser, Spitzer, Kaiser, and Howarth, Phys. Rev. **127**, 1950 (1962).

[9] S. Ganesan and R. Srinivasan, Can. J. Phys. **40**, 74 (1962).

[10] Yu. Kagan and Ya. Iosilevskiĭ, JETP **44**, 1375 (1963), Soviet Phys. JETP **17**, 927 (1963).

[11] D. L. Wood and W. Kaiser, Phys. Rev. **126**, 2079 (1962).

[12] J. D. Axe and P. P. Sorokin, Phys. Rev. **130**, 945 (1963).

[13] R. H. Silsbee and D. B. Fitchen, Revs. Modern Phys. **36**, 432 (1964).

Translated by L. M. Matarrese
236